Magnetic resonance analysis of Rh complexes in AgCl and NaCl

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Promotor : Prof. Dr. P. Matthys
Copromotor : Prof. Dr. F. Callens
### Table of physical constants [OHAN89]

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Chapter 1 : Introduction to the problem

1.1 The study of point defects in solids

Every deviation from the perfect crystal structure of a solid is called a defect. As defects seriously influence and in many cases determine the mechanical, electrical, optical and magnetic properties of solids, they have many technological applications. Defects in solids have been and still are intensively studied with various techniques depending on the type of solid, the type of defect and the type of information one wants to gather concerning the defect.

It is customary to classify solids by means of their electronic structure, related to their electronic conductivity, into three categories [HOOK91]: metals, semiconductors and insulators. Metals have a partially filled conduction band and, hence, high conductivity. At 0 K, semiconductors and insulators have a completely filled valence band, separated by a band gap from an empty conduction band. The difference between both is merely quantitative: semiconductors have a relatively narrow band gap, as a result of which they obtain an appreciable electronic conductivity at T > 0 K, whereas insulators have a very wide band gap and their electronic conductivity remains negligible at T > 0 K. Solids may also be classified according to the main force between their atomic or molecular constituents [KITT96]. For ionic solids, the main inter-atomic force is the Coulomb interaction between the cations (M⁺) and the anions (X⁻). Typical examples are the alkali halides, AX, with A⁺ = Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺ and X⁻ = F⁻, Cl⁻, Br⁻, I⁻. In covalent solids, the main interaction is the covalent binding between the atoms. The group IV semiconductors Si and Ge are examples of covalent solids. The main cohesive force in metallic solids is the interaction between the negative "free" electron sea and the positive metal ion lattice. Metals, e.g. iron, have such structure. The main cohesive force in a solid may also be an interaction of the Van der Waals type between neutral closed-shell atoms or molecules. This is the case for most organic solids.

According to their size, three types of defects in solids are usually defined [KITT96]. Point defects have dimension zero, which means that all spatial dimensions of the defect are very small compared to the dimensions of the crystal. Typical examples of point defects are vacancies or impurity atoms. Defects with one dimension comparable to the dimensions of the crystal lattice (with dimension one), are called linear defects. Examples of this kind of defects are edge and screw dislocations. Planar defects, with dimension two, may also occur in solids. The surface of the crystal is the most prominent defect of this type. Other examples are grain boundaries and stacking faults. Furthermore a distinction is made between intrinsic defects, which occur in chemically pure solids, and extrinsic defects, which are related to chemical impurities or dopants.

According to the type of information the researcher wants to gather, the distinction may be made between applied and fundamental research of defects in solids. The main concern of applied research is the relation between the type and the concentration of defects on the one hand, and the macroscopic material properties on the other. It usually involves a method for the detection of the defects and a measurement of the material property, which is examined. Statistical methods may be used in order to find the relation between the defect concentration and the material properties. The
ultimate goal of this applied research is finding a way to control the material properties by introducing or eliminating defects in the crystalline solid. Fundamental research, on the other hand, is more concerned with the structure of the defects themselves. Its ultimate goal is explaining the macroscopic material properties from the microscopic structure of individual defects. Fundamental research usually involves microscopic and/or spectroscopic techniques in order to obtain experimental data on the structure of defects. The importance of \textit{ab initio} quantum chemical calculations of defect structures is also increasing. Theoretical models of the defects and the solid may then be applied in order to explain the relation between the microscopic structure of the defect and its macroscopic influence on the solid.

The objective of this work is to determine the microscopic structure of rhodium (Rh) complexes in silver chloride (AgCl) and sodium chloride (NaCl). Rh is a transition metal: it has a partially filled 4d shell. Its ground state atomic configuration is (Kr)4d\(^{6}\)5s. AgCl and NaCl are ionic wide band gap semiconductors (or insulators) with the rock salt structure. In this structure, all cations (Ag\(^{+}\) or Na\(^{+}\)) are coordinated by a regular octahedron of six anions (Cl\(^{-}\)) and vice versa. According to the definitions given above, the subject may be described as fundamental research of extrinsic point defects in ionic wide band gap semiconductors. Although fundamental by nature, the subject attracts the attention of photographic industry, as Rh ions are widely applied as intentional impurities in photographic emulsions.

Whereas the structure of the larger one and two-dimensional defects in solids may be directly addressed using microscopic techniques (optical or electron microscopy), the structure of point defects, especially within the bulk of solids, can only be observed indirectly through spectroscopic techniques \cite{HEND72}. The determination of defect structures using these techniques is based on the observation of absorption or emission bands in the electromagnetic spectrum, characteristic for the defect in the solid. Well-known spectroscopic techniques are optical spectroscopy, operating in the ultraviolet (UV) and visible spectrum (10\(^{14}\)-10\(^{16}\) Hz), vibrational spectroscopy (IR, Raman), operating in the infrared (IR) (10\(^{11}\)-10\(^{14}\) Hz) and magnetic resonance spectroscopy (EPR, ENDOR, NMR), operating in the microwave (MW) (10\(^8\)-10\(^{11}\) Hz) and radio frequency (RF) (10\(^5\)-10\(^8\) Hz) spectrum. A certain spectroscopic technique will only then give structural information concerning a defect in a solid, if the solid is transparent and the defect has characteristic absorption and/or emission bands in the applied frequency region of the electromagnetic spectrum.

Among the spectroscopic techniques, the electron magnetic resonance techniques, electron paramagnetic resonance (EPR) and electron nuclear double resonance (ENDOR), are especially suited to study the microscopic structure of point defects in solids on the atomic scale. They are, however, restricted to the study of paramagnetic (with unpaired electrons) defects (showing characteristic absorption bands in the microwave frequency region) in solids, which are transparent for microwaves. The latter restriction prohibits the study of defects in magnetic, highly conducting (e.g., metals) and dipolar media (e.g., water). As AgCl and NaCl are diamagnetic (transparent for microwaves) and transition metals, e.g., Rh, may be introduced in these crystals in several different valence states, many of which are paramagnetic, the electron magnetic resonance techniques appear to meet all requirements for the purposes of this study.
1.2 Prominent point defects in AgCl and NaCl

The cubic rock salt crystal structure is shown in Figure 1.1a. It consists of a cationic and an anionic sublattice, which are both face-centred cubic. They are transformed into one another by a translation over a distance $a$ (nearest neighbour distance) along a $\{100\}$ direction. There are two types of substitutional sites in these crystals: the cation and the anion site. The first few shells of neighbours around, e.g., the cation site are given in Table 1.1. The two most obvious interstitial sites in this type of lattice are the body-centred site, which is the centre of a cube cornered by four cations and four anions and has tetrahedral symmetry, and the face-centred site, with two cation and two anion nearest neighbours and orthorhombic symmetry [STON75]. These two sites are indicated in Figure 1.1b.

![Figure 1.1: (a) unit cell of the rock salt lattice structure. (b) interstitial sites in the rock salt lattice: the body-centred site (light-grey) and the face-centred site (dark-grey). Large open circles represent anions, small filled circles represent cations.](image)

**Table 1.1**: The first few shells of neighbours around a cation site in the rock salt type lattices. $C$ represents cation and $A$ anion [STON75].

<table>
<thead>
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<th>Shell number</th>
<th>Typical member</th>
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<td>6</td>
<td>A</td>
</tr>
<tr>
<td>2</td>
<td>$(1,1,0)$</td>
<td>12</td>
<td>C</td>
</tr>
<tr>
<td>3</td>
<td>$(1,1,1)$</td>
<td>8</td>
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</tr>
<tr>
<td>4</td>
<td>$(2,0,0)$</td>
<td>6</td>
<td>C</td>
</tr>
<tr>
<td>5</td>
<td>$(2,1,0)$</td>
<td>24</td>
<td>A</td>
</tr>
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Several intrinsic point defects may occur in this type of crystals. The simplest defect imaginable is a vacancy, which occurs when in one of the lattice sites, an ion is missing. Vacancies introduce charges in ionic crystals. If the ions are monovalent, as is the case for NaCl and AgCl, a cation vacancy represents an effective negative charge (-e) and an anion vacancy an effective positive charge (+e).
The charge compensation for the presence of a vacancy in one of the sublattices may be preserved by a vacancy in the other sublattice. This type of defect is called a Schottky pair.

Another intrinsic way of compensating the charge of an anion or cation vacancy is the presence of an ion of the same type in an interstitial position of the lattice. The latter type of defect is called a Frenkel pair. Both types of defects are shown in figure 1.2. In alkali halides (e.g. NaCl) Schottky type defects are dominant, whereas in silver halides (e.g. AgCl) Frenkel defects in the cation sublattice prevail [HEND72]. Although at room temperature both vacancies and self-interstitials are mobile in AgX and AX crystals, they may be immobilised at lower temperature. The temperatures below which cation vacancies are immobilised in NaCl and AgCl are approximately 220 K [YANG85] and 150 K [HAY68], respectively. Ag⁺ interstitials, on the other hand, are still highly mobile at 150 K in AgCl crystals.

Figure 1.2: Intrinsic point defects in rock salt type lattices: the Schottky pair (in dashed ellipse) and the Frenkel pair (in dotted ellipse).

Figure 1.3: Radiation-induced intrinsic point defects in
(a) NaCl: the trapped-hole centre $V_K$ (dashed circle) and the trapped-electron centre $F$ (dotted circle).
(b) AgCl: the trapped-hole centre $Ag^{2+}$ (dashed circle) and the trapped-electron centre $Ag_e^+$ (dotted circle).

Both NaCl and AgCl have a completely filled valence band and an empty conduction band. The gap between both ($E_g$) is 3.245 eV for AgCl [HAMI88] and 8.75 eV for NaCl [WATT77]. If these crystals are irradiated with electromagnetic waves with a frequency $\nu \geq E_g/\hbar$, electron-hole pairs are created in
these crystals. The defect consisting of an electron and a hole bound to one another is called an exciton. The binding energy of this pair is, however, not high, which makes it possible for the electrons and the holes to become separated. An important class of intrinsic point defects in NaCl and AgCl is formed when these "free" electrons and holes are trapped at lattice sites.

The most prominent radiation-induced intrinsic centres in NaCl [HEND72] are the $F$ centre, which consists of an electron trapped at an anion vacancy, and the $V_{\kappa}$ centre, consisting of a hole trapped by a pair of nearest neighbour anions ($\text{Cl}_2^-$). The latter centre is, however, not stable at room temperature: at approximately 150 K holes become mobile in NaCl [YANG85]. In pure AgCl crystals, a shallowly trapped electron centre is produced upon supra band gap irradiation at low temperature. It is believed to be $\text{Ag}_{2}^+$ at a substitutional cation site [BENN95]. Also a self-trapped hole centre, $\text{Ag}^{2+}$ at a cation site, is produced in the same conditions [HOHN88]. These centres are only stable at very low temperature (e.g. at $T < 50$ K for the self-trapped hole centre in AgCl). These intrinsic trapped-hole and trapped-electron centres are represented in figure 1.3.

Next to the intrinsic point defects, a variety of extrinsic point defects may occur in rock salt type crystals doped with impurities. These may be cationic, anionic or neutral. If an impurity replaces a lattice ion in the crystal, it is called a substitutional impurity. If it resides in an interstitial position it will be referred to as an interstitial impurity. Substitutional impurities with the same valence state as the ions, which they are replacing, or interstitial atoms introduce no extra charges in the lattice. Substitutional ions with a different valence state and ions in interstitial positions, on the other hand, do introduce charges in the lattice, which need to be compensated. Charge compensation is usually accomplished by means of cation or anion vacancies, which may either be bound to the impurity and hence be in its close neighbourhood, or be at a large distance of the charged impurity. In the former case the charge compensation is called local, in the latter it is non-local (see figure 1.4).

The transition metal ions are an important and extensively studied class of impurities in alkali and silver halide crystals. These metal ions all have a partially filled $d$ shell and may occur in many different valence states. Their incorporation in AX or AgX crystals usually introduces localised states in the band gap, as a result of which they act as trapping centres for electrons and/or holes, produced upon irradiation. Transition metal ions are usually incorporated on substitutional cation positions and

![Figure 1.4: Substitutional divalent cation impurities (grey circles) in NaCl and AgCl may either be locally charge compensated (dashed ellipse) or non-locally charge compensated (dotted circle).](image-url)
strongly interact with the nearest anion neighbours, thus forming MX₆ complexes (M = transition metal). Depending on the valence state of the central transition metal ion, these complexes may be accompanied by one or several cation vacancies. The presence of transition metal ions in AX and AgX crystals is usually reflected in the optical absorption spectrum of the host crystal. Optical absorption measurements in the UV and visible spectrum thus provide a way of studying the structure of these point defects. Also vibrational spectroscopy may be applied to unravel their structure. As transition metal ions may either be incorporated in the crystals in a paramagnetic state, or may become paramagnetic upon electron or hole trapping after irradiation of the crystal, they can also be studied with electron magnetic resonance techniques, which will provide the most detailed information about their lattice surroundings. It should, however, be kept in mind that electron or hole trapping changes the valence state of the transition metal ion, and thus, in most cases, also the equilibrium configuration of charge compensating defects, e.g. cation vacancies, around the MX₆ complex. The study of paramagnetic trapped electron or trapped hole centres is only relevant in determining the structure of the diamagnetic precursor centre if the surrounding charge compensating defects are immobilised.

1.3 Justification of the study: relevance to photographic industry

A photographic film consists of a large number of fine and well-designed silver halide microcrystals, randomly arranged in thin gelatine layers [TANI95]. The sensitivity of this system is based on the formation of a developable silver cluster on the surface of the silver halide grains, the so-called latent image, upon exposure to light. In the subsequent development step, the silver halide grains on which a latent image was formed are completely reduced to metallic silver. According to recent theories, the smallest latent image clusters consist of three to five silver atoms [TANI95, HAMI88, MARC92]. They are formed by successions of electronic (capture of an electron) and ionic (capture of an interstitial silver ion, Ag⁺) steps at a partially positively charged surface site (the positive kink site) of the AgX grains, according to the scheme:

\[
\begin{align*}
(kink)^{\text{V2}} + e^{-} & \leftrightarrow (kink)^{\text{V2}} \\
(kink)^{\text{V2}} + AG_{i}^{+} & \leftrightarrow (kink \cdot AG)^{\text{V2}} \\
(kink \cdot AG)^{\text{V2}} + e^{-} & \leftrightarrow (kink \cdot AG)^{\text{V2}} \\
(kink \cdot AG)^{\text{V2}} + AG_{i}^{+} & \leftrightarrow (kink \cdot AG_{i})^{\text{V2}} \\
& \vdots \\
(kink \cdot Ag_{i-1})^{\text{V2}} + e^{-} & \leftrightarrow (kink \cdot Ag_{i-1})^{\text{V2}} \\
(kink \cdot Ag_{i-1})^{\text{V2}} + AG_{i}^{+} & \leftrightarrow (kink \cdot Ag_{i})^{\text{V2}}
\end{align*}
\]  

(1.1)

Interstitial Ag⁺ ions are abundantly present in AgX microcrystals through the Frenkel disorder. At the surface of the grains or at dislocations, they may even be produced independently from cation vacancies. The electrons needed for the latent image formation are produced by illumination, which creates electron-hole pairs in the silver halide microcrystals. As the intrinsic absorption of silver halides only covers the blue to UV part of the spectrum, spectral sensitisers are added to make the grains also sensitive to the red and the green components of light. In the most sensitive AgX grains all photoelectrons would be used for latent image formation. Photoelectrons may, however, also
recombine with photoholes and be lost for latent image formation. Moreover, photoholes may attack the latent (pre/sub) image Agₙ clusters, through the reaction:

\[ \text{Ag}_n + h^+ \rightarrow \text{Ag}_n^+ \rightarrow \text{Ag}_{n-1} + \text{Ag}^+ \]  \hspace{1cm} (1.2)

In order to control the processes in the formation and the destruction of the latent image, silver halide grains are doped in their core or at their surface with impurities, which interact with the photoelectrons and/or holes. Allovalent transition metal ion complexes usually act as electron trapping centres in AgX crystals. They are classified in the following way, according to the time during which the electron remains trapped \( (\tau_T) \), relative to the time needed for latent image formation \( (T_L) \):

- shallow traps: \( \tau_T << T_L \)
- undeep traps: \( \tau_T = T_L \)
- deep traps: \( \tau_T >> T_L \)

Shallow and undeep electron traps may be used to enhance the effective lifetime of the electron, preventing it from recombining with photoholes until these are immobilised. Deep electron traps immobilise photoelectrons, preventing them from taking part in the latent image formation.

Rh³⁺ ions are widely used as dopants in commercial photographic emulsions for the graphic arts industry [MARC92]. Applied research has demonstrated that adding these ions in small concentrations to AgX crystals results in a drastic decrease in the sensitivity and increase in the contrast of photographic films. This has been explained by assuming that the Rh³⁺ ion acts as a very efficient deep electron trap. The trapping efficiency is indeed such that Rh³⁺ doping can be used to control the sensitivity and the contrast of AgX films. The exact trap depth and trapping efficiency is strongly dependent on the direct lattice environment of the Rh³⁺ ions. For a detailed understanding of these properties, accurate structural models of the Rh impurity-related centres are indispensable. A complete structural model consists of the chemical nature and the valence state of the central ion, the chemical nature of its nearest, and preferably also its next-nearest neighbours and the way in which the charge of the ion is compensated in the AgX lattice. For paramagnetic Rh²⁺ centres, this information can be gathered by an electron magnetic resonance study. Although the Rh³⁺ ion is diamagnetic in a rock salt type crystalline environment, relevant information about its structure may be obtained from studying the trapped electron Rh²⁺ centres after supra band gap illumination of the crystals at temperatures at which charge compensating neighbouring defects are immobilised. A complication arises because of the sizes of the AgX emulsion microcrystals to be investigated.

The dimensions of AgX emulsion grains are typically of the order of μm, making them unsuitable for single crystal studies at low and intermediate microwave frequencies (< 100 GHz). The dependence of the electron magnetic resonance spectra on the orientation of the defect relative to the orientation of the external magnetic field provides information on the position of the ions in the complex. Therefore, only single crystal studies may be expected to provide the data, necessary to reconstruct the complete microscopic model of the complex. For randomly oriented microcrystals, a part of the angular dependent data may be recovered, but a lot of it is lost. Hence, the electron magnetic resonance study of rhodium complexes in AgCl emulsion grains alone may provide too little information for reconstructing a complete model. The study of similar rhodium complexes in large single crystal model systems for the AgX emulsion grains and \textit{ab initio} quantum chemical calculations of optimised
structures for these complexes supply indispensable additional information. In this work we have restricted ourselves to the former. In this respect, the choice of a good model system is vitally important. Moreover, one should always bear in mind that results obtained from the study of the model system may not apply to the industrially relevant AgX microcrystals. Figure 1.5 schematically represents the systems in which Rh complexes have been investigated at our laboratories. The main differences between these systems are indicated.

Figure 1.5: host crystals in which Rh impurities acting as electron traps are investigated. The AgCl emulsion microcrystals are the photographically relevant system. All other hosts are model systems. Large AgCl single crystals grown from aqueous solution are not available.

Silver halide emulsion microcrystals are prepared as a result of the reaction between a water-soluble silver salt (e.g. AgNO₃) and a water soluble halide salt (e.g. KCl) to form a water-insoluble silver halide salt (AgCl) in an aqueous gelatine solution. In the double jet precipitation method both salts are simultaneously poured into an agitated gelatine reaction solution. The Rh³⁺ containing dopant salt (e.g. Na₃RhCl₆·12H₂O) is dissolved in an aqueous NaCl solution, which is added as a separate flow to the gelatine solution during precipitation. Rh³⁺ ions may be coordinated by solvent molecules [ENDO90] in the dopant flow and the resulting [RhCl₆(H₂O)₆-n]³⁻ complexes may be incorporated in the AgCl microcrystals intactly.

Due to their insolubility in water, no large AgX single crystals can be grown from aqueous solution. The study of large AgX single crystals is therefore restricted to crystals grown from the melt. These may differ from the emulsion microcrystals due to two effects. There may first of all be a size effect. Several authors already pointed to important differences between large AgX crystals and AgX microcrystals (see e.g. [TANI95] and references herein), e.g. with respect to the generation and
equilibrium concentration of interstitial Ag⁺ and cation vacancies. A second difference is related to the crystal growth method. In melt-grown single crystals, e.g., the influence of the incorporation of solvent molecules, which is believed to be important in solution-grown crystals, cannot be studied. Crystal size effects can be studied by observing the differences between large melt-grown single crystals and similarly grown ground single crystals. In order to study the effect of the crystal growth method, model host crystals, which are structurally very similar to silver halides and can be grown both from aqueous solutions and from the melt, should be used. For the study of Rh³⁺ complexes in AgCl, NaCl has been chosen as a model system. AgCl and NaCl are structurally very similar: they have the same crystal structure and have nearly equal anion-cation nearest neighbour distances (a_{NaCl} = 0.282 nm and a_{AgCl} = 0.279 nm, at room temperature). There are, however, also important differences between these crystals. The ones most relevant to this work are:

1. The difference in the dominant type of intrinsic defects. In section 1.2 it was pointed out that Schottky disorder is dominant in NaCl, whereas Frenkel disorder prevails in AgCl. In addition to cation vacancies, interstitial Ag⁺ may also have an influence on the charge compensation of alicovalent transition metal complexes in AgCl. Interstitial Ag⁺ is extremely mobile in AgCl crystals, down to very low temperatures. No similar effects are present in NaCl.

2. The difference in width of the band gap. As NaCl has a much wider band gap than AgCl, more different valence states of transition metal ions may be stable in the former crystals.

3. The difference in dielectric constant. Due to its higher dielectric constant AgCl is more fit to accommodate electric fields, e.g. produced by the extra charges of alicovalent transition metal ions in the crystal, than NaCl.

In spite of these differences, the study of Rh complexes in NaCl provides interesting information on their general properties in rock salt type crystals.

From the fundamental point of view the study of paramagnetic Rh complexes in solution and melt-grown AgCl and NaCl is also important. In solution-grown crystals, complexes with mixed ligand structures (Cl⁻ and H₂O or OH⁻ ligands) may be investigated and in both types of crystals the influence of cation vacancies on the stability and electron trapping properties of Rh cations can be studied. The way in which nearby cation vacancies influence the electron magnetic resonance spectra of paramagnetic Rh complexes may be studied, with the aim of finding a direct method for vacancy detection. The electron magnetic resonance study of Rh complexes in NaCl and AgCl crystals thus appears to be justified, as well from the purely scientific viewpoint as because of the technological applications of these complexes in photographic industry.

1.4 Outline of the work

In chapter 2, an introduction to the experimental electron magnetic resonance techniques, which we have used in this work, will be given. In chapter 3, some general aspects of Rh²⁺ complexes in NaCl and AgCl will be discussed, based on literature data for these complexes. Chapters 4 - 6 will survey our personal achievements in the study of Rh complexes in these crystals. Chapter 4 mainly deals with a Rh⁺ centre identified in NaCl, for which no counterpart has been found in AgCl. Also some results for a Rh²⁺ complex, possibly related with a solvent molecule, in solution-grown NaCl will be
presented. Due to their low concentration, a complete analysis for the latter complexes was impossible. Chapter 5 is dedicated to the detection of charge compensating vacancies near [RhCl₆]⁴⁻ complexes in NaCl and AgCl single crystals. Finally, in chapter 6 the study of Rh²⁺ complexes in AgCl emulsion microcrystals is presented. Chapter 7 summarises the conclusions of the study of Rh complexes in AgCl and NaCl.
Chapter 2 : Introduction to electron magnetic resonance spectroscopy

No attempt will be made to give a general introduction to the electron paramagnetic resonance (EPR) and the various related double resonance techniques. Their description will be limited to what is necessary for a good understanding of the experimental part of this work. It will thus be focused on the study of paramagnetic transition metal ion complexes in solids. Moreover, only continuous wave (CW) electron magnetic resonance techniques will be discussed, as no pulsed techniques were used in this work.

2.1 Paramagnetic transition metal ions in a crystalline environment: quantum mechanical description

A rigorous description of paramagnetic transition metal ions in a crystalline environment involves finding the eigenvalues and eigenstates of the stationary Schrödinger equation

$$\hat{H}\psi = E\psi$$  (2.1)

in which $\psi$ is the wave function for all ions in the crystal and the Hamiltonian contains contributions of the kinetic and the potential energy of all electrons and nuclei in the crystal. Even in *ab initio* calculations this problem is approximated by assuming that this wave function can be factorised as follows

$$\psi = \psi_{\text{cluster}} \otimes \psi_{\text{lattice}}$$  (2.2)

in which $\psi_{\text{cluster}}$ is the wave function of the central transition metal ion and its first few shells of neighbours, the number of which is dependent on the required accuracy of the description, and $\psi_{\text{lattice}}$ is the wave function of the rest of the crystal lattice [LUAN91]. The problem is then reduced to finding eigenvalues and eigenstates of the restricted Schrödinger equation

$$\left(\hat{H}_{\text{cluster}} + \hat{V}_{\text{lattice}}\right)\psi_{\text{cluster}} = E_{\text{cluster}} \psi_{\text{cluster}}$$  (2.3)

All ions within the cluster are thus handled in a rigorous quantum mechanical way and the effect of the interaction of the cluster with the crystal lattice is accounted for by introducing a crystal potential $\hat{V}_{\text{lattice}}$.

For a qualitative description of the electron magnetic resonance phenomena for these ions, the cluster size is restricted to the central transition metal ion itself. The problem is further simplified by restricting the quantum mechanical description to the valence d electrons of the ion, assuming them to be present in the mean field of the central nucleus and the closed shell core electrons. The Hamiltonian for the paramagnetic ion in the crystal then takes the form [SPAE92]

$$\hat{H} = \sum_i \left[ \frac{\vec{p}_i^2}{2m_0} - \frac{Ze^2}{4\pi\varepsilon_0 r_i} + U(\vec{r}_i) + \frac{1}{2} \sum_{j \neq i} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} + \vec{s}_i \cdot \vec{\sigma}_i + \hat{H}_{\text{magn}}(\vec{r}_i, \text{nucleus}) \right]$$

$$+ \sum_n \left[ \hat{c}_n(\vec{r}_i) + \hat{H}_{\text{magn}}(\vec{r}_n, \text{nucleus}_n) \right]$$  (2.4)

with $i$ the summation index for the valence electrons. The terms between the first brackets on the left hand side of equation (2.4) are free ion terms. They are independent of the diamagnetic lattice in which the paramagnetic ion is incorporated. The first of these terms represents the kinetic energy of the valence electrons, the second their attractive coulomb interaction with the central nucleus with
nuclear charge $Ze$ and the third their repulsive interaction with the core electrons. The fourth term describes the Coulomb repulsion between the valence electrons and is the only two-electron term in the Hamiltonian, as a result of which the orbital momenta $\hat{i}_i$ and spin momenta $\hat{s}_i$ of the individual electrons are coupled. The fifth term represents the spin-orbit interaction of the individual electrons. The sixth term is due to the interaction between the magnetic momenta of the central nucleus and each electron. The latter interaction is usually referred to as hyperfine interaction. The terms between the second pair of brackets in equation (2.4) are related to the crystalline environment of the transition metal ion. $\hat{V}_c(\hat{r}_i)$, the crystal lattice potential, represents the Coulomb interaction between the valence electrons and the lattice ions. The last term describes the magnetic interactions of the valence electrons with the lattice nuclei or superhyperfine interactions.

In order to find the energy eigenvalues and eigenstates of the Hamiltonian (2.4) perturbation theory is applied [BOES94a]. In a first step, the Coulomb repulsion term between the electrons is separated into a maximal spherically symmetrical part and a minimal interaction part

$$\frac{1}{2} \sum_i \frac{\hat{r}_i^2}{4\pi\epsilon_0 r_i} = \sum_i \hat{H}_{SS,i}(r_i) + \hat{H}_{\text{int}}$$

(2.5)

The Hamiltonian can then be rewritten, according to the relative magnitude of the terms in (2.4)

$$\hat{H} = \hat{H}_0 + \hat{H}_i + \hat{H}_2,$$

$$\langle \hat{H}_0 \rangle \gg \langle \hat{H}_i \rangle \gg \langle \hat{H}_2 \rangle$$

$$\hat{H}_0 = \sum_i \left( \frac{\hat{p}_i^2}{2m_e} - \frac{Ze^2}{4\pi\epsilon_0 r_i^2} + U(\hat{r}_i) + \hat{H}_{SS,i}(r_i) \right)$$

$$\hat{H}_i = \hat{H}_{\text{int}} + \sum_i \left[ \hat{s}_i \cdot \hat{s}_i + \hat{V}_c(\hat{r}_i) \right]$$

$$\hat{H}_2 = \sum_i \left[ \hat{H}_{\text{magn}}(\hat{r}_i, \text{nucleus}) + \sum_n \hat{H}_{\text{magn}}(\hat{r}_{nn}, \text{nucleus}_n) \right]$$

(2.6)

The eigenstates of the unperturbed Hamiltonian $\hat{H}_0$ are anti-symmetric linear combinations of one-electron wave functions, the so-called Slater determinants, and the energy eigenvalues are the sums of the one-electron energies. A specific distribution of the valence electrons over one-electron wave functions or orbitals is called an electron configuration. The energy separation between different configurations is of the order of 10 eV ($\sim 10^5$ cm$^{-1}$).

The further perturbation handling of the problem depends on the relative magnitude of the three terms in the perturbation Hamiltonian $\hat{H}_i$. The cases in which the spin-orbit coupling term is larger than the Coulomb coupling term $\hat{H}_{\text{int}}$, which are referred to in literature as $j-j$ coupling schemes and only apply to heavy ions, will not be considered here. Three cases still need to be discussed [ORTO68]:

1. $\langle \hat{H}_{\text{int}} \rangle \gg \langle \hat{H}_{\text{SO}} \rangle \gg \langle \hat{H}_c \rangle$ : weak crystal field

First, the angular moments $\hat{i}_i$ and spin moments $\hat{s}_i$ of the individual valence electrons are coupled to the total angular and spin momentum $\hat{L}$ and $\hat{S}$ by $\hat{H}_{\text{int}}$. This coupling scheme is called LS or
Russell-Saunders coupling. The allowed eigenstates of the operators $\hat{L}$ and $\hat{S}$ for a certain electron configuration are called terms. They are characterised by four quantum numbers $ILM_jSM_\theta$ and are $(2L+1)\times(2S+1)$-fold electronically degenerate. Their spectroscopic notation is $^{2S+1}L$. The term with lowest energy (ground state term) is found by applying Hund's rules: it has maximum total spin and total angular momentum. Energy separations between the different terms of an electron configuration are of the order of a few eV. As a result of the interaction between the total orbital and total spin momentum, these are coupled to the total momentum $\hat{J}$. The different $J$ states are again characterised by four quantum numbers $ILSJM_\theta$. $J$ can take up the values $J = L+S, L+S-1, ..., IL-SI$. The ground state value of $J$ is $IL-SI$ for less than half-filled shells, and $L+S$ for more than half-filled shells. The $J$ states are $(2J+1)$-fold degenerate and their spectroscopic notation is $^{2S+1}L$. The energy separation between the different $J$ states within a term of a configuration is of the order 0.1 to 1 eV ($10^3 - 10^4$ cm$^{-1}$). The crystal field $\langle \hat{H}_c \rangle$, at highest of the order of 0.1 eV, now splits these multiplets further into linear combinations of the $ILSJM_\theta$ states which are base functions of the irreducible representations of the point group of the crystal lattice field. For a correct description of odd-electron paramagnetic ions, the double group representations should in principle be used. The case of a weak crystal field only applies to the rare earth and actinide paramagnetic ions. It will not be encountered in this work.

2. $\langle \hat{H}_{\text{int}} \rangle \gg \langle \hat{H}_e \rangle \gg \langle \hat{H}_{\text{SO}} \rangle$ : intermediate crystal field

Again the orbital and spin momenta of the individual valence electrons are coupled to the total angular and spin momentum by $\hat{H}_{\text{int}}$. The ground state electronic configuration again splits up in terms $^{2S+1}L$ with quantum numbers $ILM_jSM_\theta$ and the same ground state term is found as in the previous case. At variance with the previous case the crystal lattice field has to be taken into account as the second perturbation term. $\langle \hat{H}_e \rangle$ is now of the order of a few tenths of an eV ($\sim 10^3$ cm$^{-1}$). This implies that $J$ and $M_j$ are no longer good quantum numbers for the system. Instead, the ground state term $^{2S+1}L$ splits up in linear combinations $ILM_jSM_\theta$ states which are base functions belonging to the irreducible representations of the point group of the crystal lattice field. Their spectroscopic notation is $^{2S+1}\Gamma_\kappa$, in which $\Gamma_\kappa$ is an irreducible representation of the crystal field point group (single group representations. The usual notation for one dimensional many-electron representations is $A$ or $B$. For two and three-dimensional representations $E$ and $T$ are used, respectively. The degeneracy of each of these multiplets is partially lifted by spin-orbit interaction. For systems with an odd number of electrons, the double group formalism should, in principle, again be used.

The case of intermediate crystal fields applies to the first row transition metal ions, which have a 3$d^0$ configuration ($n = 1-9$), with halide or oxygen coordination. It gives rise to so-called high spin configurations. Also this case will not be encountered here.
Figure 2.1: Ground state electronic configuration for transition metal ions in a strong octahedral or tetrahedral crystal field, the so-called low spin complexes. The strong crystal field splits the ten d levels into an orbital triplet $t_{2g}$ (three lines, sixfold degenerate) and an orbital doublet $e_g$ (two lines, fourfold degenerate). The many-electron ground state is indicated for all configurations. The irreducible representation notations are defined in the character table for the octahedral (O) and tetrahedral ($T_d$) point group.
3. \( \langle \hat{H}_c \rangle \gg \langle \hat{H}_{\text{ex}} \rangle \gg \langle \hat{H}_{\text{SO}} \rangle \): strong crystal field

In this case the crystal lattice potential, which is of the order of a few eV, has to be taken into account before the Coulomb interaction term couples the individual angular and spin momenta to the total angular and spin momentum. This implies that \( L, M_L, S \) and \( M_S \) are no longer good quantum numbers. The crystal lattice potential lifts the degeneracy of the one-electron \( d \) orbitals. In a cubic crystal field they split into a two-fold degenerate \( e_g \) level and a three-fold degenerate \( t_{2g} \) level. In octahedral coordination, which is the relevant case for substitutional ions in rock salt lattices, the \( t_{2g} \) level lies lowest, whereas in tetrahedral or cubic coordination, the relevant case for interstitial ions in rock salt lattices, the \( e_g \) level has the lowest energy. The ground state configuration is now found by distributing the valence \( d \) electrons over these energy levels in a way, which minimises the crystal field energy. This gives rise to low spin configurations. The ground state \( d^1 \) configuration then takes the form \( (t_{2g})^1(e_g)^{n-1} \), with \( l + m = n \). This case of strong crystal fields applies to second and third row transition metal ions and also to some first row transition ions in special coordinations, e.g. \( \text{M(CN)}_6 \) complexes. They are called low spin complexes. \( \text{RhCl}_6 \) and similar complexes, in which one or several \( \text{Cl}^- \) ions have been replaced by \( \text{H}_2\text{O} \) or other solvent molecules, are typical examples of low spin complexes.

In figure 2.1, the low spin configurations in an octahedral and tetrahedral coordination are shown [GRIF61]. The Coulomb interaction term couples the individual angular and spin momenta to the total angular and spin momenta. The many-electron states for low spin configurations have again a \( 2S+1\text{I}_K \) notation and are also listed in figure 2.1. Spin-orbit coupling mixes configurations with higher energy into the ground state configuration. It may lift the remaining orbital degeneracy and/or cause a general energy shift of the ground state multiplet.

Finally, the interactions with the central nucleus and neighbouring nuclei cause a splitting of the electronic ground state into \( \prod_j (2I_j + 1) \) levels. The splitting between these levels is usually not larger than 0.1 meV (\( -1 \text{ cm}^{-1} \)).

2.2 The influence of an external magnetic field: the Zeeman effect and magnetic resonance

According to Kramers theorem, the electronic ground state of a system with an odd number of electrons is at least twofold degenerate [ORTO68]. This degeneracy can only be lifted by an external magnetic field. In this magnetic field \( \vec{B} \), the many-electron system acquires an extra potential energy via its magnetic momentum \( \vec{\mu} : E = -\vec{B} \cdot \vec{\mu} \). In the quantum mechanical description of the valence electrons of the transition metal ion, an extra term is introduced: the electronic Zeeman Hamiltonian

\[
\hat{H}_{\text{ez}} = -\vec{B} \cdot \vec{\mu} = \mu_B \vec{B} \cdot \sum_i \left( \vec{l}_i + g_\text{s} \vec{s}_i \right)
\]

(2.7)

in which \( \mu_B \) represents the Bohr magneton \((\hbar/2\pi m_e)\) and \( g_\text{s} (2+\alpha/\pi = 2.0023) \) is the gyro-magnetic ratio for the free electron. In the case of intermediate and weak crystal fields, the electronic Zeeman Hamiltonian is equivalent with
\[ H_{\text{Ez}} = \mu_B B \cdot \left( \hat{L} + g_s \hat{S} \right) \]  

(2.8)

and

\[ H_{\text{Ez}} = g_L \mu_B B \cdot \hat{J}, \quad g_L = 1 + \frac{J(J+1) - L(L+1) + S(S+1)}{2J(J+1)} \]  

(2.9)

respectively. In order to evaluate the effect of the electronic Zeeman Hamiltonian, the simple case of a one-electron system in an external magnetic field, without orbital momentum \(s^1\) configuration) will be considered. In the absence of magnetic fields, the two energy levels of this system are degenerate: the \(m_s = 1/2\) and \(m_s = -1/2\) states of the electron have the same energy. Through the interaction with an external magnetic field, the different \(m_s\) states of the electron obtain a different energy

\[ \langle \pm \frac{1}{2} | H_{\text{Ez}} | \pm \frac{1}{2} \rangle = \mu_B g_e \langle \pm \frac{1}{2} | \vec{B} \cdot \hat{\vec{s}} | \pm \frac{1}{2} \rangle = \mu_B g_e B \langle \pm \frac{1}{2} | s_z | \pm \frac{1}{2} \rangle = \pm \frac{1}{2} \mu_B g_e B \]  

(2.10)

The energy separation between the states is \(\mu_B g_e B\). For magnetic fields ranging between 0.1 and 10 T, this energy separation \((10^{-5} - 10^{-3} \text{ eV}, 0.1 - 10 \text{ cm}^{-1})\) lies in the microwave frequency region of the electromagnetic spectrum \((3 \text{ GHz} - 300 \text{ GHz})\). Magnetic dipole transitions between the \(m_s = -\frac{1}{2}\) and \(m_s = \frac{1}{2}\) states may be induced by microwaves for which \(\nu = \mu_B g_e B\). In other words: this paramagnetic system is able to absorb microwaves which meet the requirement \(\nu = \mu_B g_e B\). This is shown in figure 2.2. More generally, a resonance absorption of microwaves may take place in any paramagnetic system. This phenomenon is called electron paramagnetic resonance or EPR. The microwave-induced transitions are called EPR transitions.

The external magnetic field also interacts with the magnetic momentum of nuclei. This interaction is quantum mechanically described by the nuclear Zeeman Hamiltonian

\[ H_{nz} = -\vec{B} \cdot \vec{\mu}_N = -g_N \mu_N \vec{B} \cdot \vec{\hat{s}} \]  

(2.11)

with \(g_N\) the nuclear gyro-magnetic ratio and \(\mu_N\) the nuclear magneton \((\epsilon h / 2 \pi m_p)\). As the proton/electron mass ratio is approximately 1/1836, the energy separation between the different \(m_I\) states induced by the nuclear Zeeman Hamiltonian is also approximately 1836 times smaller than the separation between the electronic \(m_s\) states, induced by the electronic Zeeman Hamiltonian. Magnetic dipole transitions between the different \(m_s\) states are called nuclear magnetic resonance (NMR) transitions. These transitions involve the absorption of electromagnetic waves in the RF frequency region \((0.1 - 100 \text{ MHz})\).
2.3 The spin Hamiltonian

At temperatures at which magnetic resonance experiments are usually carried out (4 – 300 K), only a few energy levels, which are at maximum a few times $kT$ (0.3 – 26 meV) above the electronic ground state, are thermally populated. As the energy differences between the states involved in magnetic resonance transitions are, even at high magnetic fields, not higher than 1 meV, magnetic resonance only involves these thermally populated, low lying states, which are well-separated from the other electronic states. Therefore, an effective Hamiltonian is used to describe the magnetic resonance properties of paramagnetic systems: the spin Hamiltonian. The number of electronic states, $2S+1$, defines the effective spin $S$ of this effective Hamiltonian. Furthermore, all interactions with surrounding nuclei should be included in the spin Hamiltonian, as they correspond to energy differences of the order of $\mu$eV (typical superhyperfine interactions observable with magnetic resonance spectroscopy are of the order of $10^{-4}$ cm$^{-1}$ or a few MHz). The spin Hamiltonian thus describes a system of $(2S+1)\prod_j (2I_j + 1)$ levels, between which EPR and NMR transitions may take place. Its most general form includes all terms (direct interactions between nuclei neglected) [PILB90]

$$A_{jqr} B^p \hat{S}^q \hat{I}_j^r, \quad q \leq 2S, r \leq 2I_j$$

(2.12)

which are allowed by time reversal symmetry (p + q + r even) and by the symmetry of the paramagnetic defect and its surroundings. A lot of these terms have no direct physical interpretation. They arise due to contributions of excited states in the ground state effective spin multiplet. For the purposes of this work a spin Hamiltonian ($\hat{H}_S$), in which all terms can be physically interpreted, is used

$$\hat{H}_S = \hat{H}_{Sx} + \hat{H}_{FS} + \sum_I (\hat{H}_{IS}^{\text{HF}} + \hat{H}_{IS}^{x} + \hat{H}_{IS}^{y})$$

(2.13)

The various terms in this spin Hamiltonian and their physical interpretation for paramagnetic transition metal complexes are excellently reviewed in several handbooks (see e.g. [PILB90], [ABRA70] and [ORTO68]) and will be briefly discussed in the following.

2.3.1 The electronic Zeeman interaction

This effective Hamiltonian describes the interaction of the effective spin $\hat{\vec{S}}$ with the external magnetic field $\vec{B}$ and takes the form

$$\hat{H}_{Sx} = \mu_B \vec{B} \cdot \vec{g} \hat{\vec{S}}$$

(2.14)

$\vec{g}$ is a symmetrical 3x3 matrix, generally referred to as the $\vec{g}$ tensor. The components of this matrix can be calculated by evaluating the operator

$$\mu_B \vec{B} \cdot \sum_I (\hat{I}_I + g_s \hat{S}_I)$$

(2.15)

in the effective spin multiplet. For low spin $d^0$ complexes, the orbital momentum is to a large extent quenched, as a result of which the principal values of the $\vec{g}$ tensor, $g_x$, $g_y$ and $g_z$ are close to $g_e$. Deviations from $g = g_e$ arise through mixing of excited states into the ground state multiplet by spin-orbit coupling. For a paramagnetic system with $S = 1/2$, without interactions with neighbouring nuclei,
the electronic Zeeman term is the only term in the spin Hamiltonian. For an arbitrary direction of the magnetic field \( \vec{B} \), an EPR transition occurs at

\[
h\nu = g\mu_B B, \quad g = \sqrt{\vec{B} \cdot \vec{g} \cdot \vec{B}}
\]  

(2.16)

The principal values and directions of the \( \vec{g} \) tensor reflect the symmetry of the paramagnetic defect. The electronic Zeeman Hamiltonian, however, always has inversion symmetry. Therefore, the electronic Zeeman Hamiltonian does not make a distinction between centres with and without inversion symmetry. In Table 2.1, an overview of the different \( \vec{g} \) tensor symmetries encountered in rock salt type lattices and the defect symmetries they may correspond to is given.

**Table 2.1: relation between \( \vec{g} \) tensor symmetry and defect symmetry in rock salt type lattices [WATT77]**

<table>
<thead>
<tr>
<th>( \vec{g} ) symmetry</th>
<th>principal directions</th>
<th>principal values</th>
<th>defect symmetries</th>
</tr>
</thead>
<tbody>
<tr>
<td>cubic</td>
<td>〈100〉, 〈010〉, 〈001〉</td>
<td>( g_x = g_y = g_z )</td>
<td>( \text{O}_h, \text{T}_d, \text{T} )</td>
</tr>
<tr>
<td>tetragonal</td>
<td>〈100〉, 〈010〉, 〈001〉</td>
<td>( g_x = g_y \neq g_z )</td>
<td>( \text{D}<em>{4h}, \text{D}<em>4, \text{C}</em>{4v}, \text{D}</em>{2d}, \text{C}_{4h}, \text{S}_4, \text{C}_4 )</td>
</tr>
<tr>
<td>trigonal</td>
<td>〈110〉, 〈111〉, 〈112〉</td>
<td>( g_x = g_y \neq g_z )</td>
<td>( \text{D}_{3h}, \text{D}<em>3, \text{C}</em>{3v}, \text{C}_3, \text{C}_3 )</td>
</tr>
<tr>
<td>orthorhombic I</td>
<td>〈110〉, 〈110〉, 〈001〉</td>
<td>( g_x \neq g_y \neq g_z )</td>
<td>( \text{D}_{2h}, \text{D}<em>2, \text{C}</em>{2v} )</td>
</tr>
<tr>
<td>orthorhombic II</td>
<td>〈100〉, 〈001〉, 〈010〉</td>
<td>( g_x \neq g_y \neq g_z )</td>
<td>( \text{D}_{2h}, \text{D}<em>2, \text{C}</em>{2v} )</td>
</tr>
<tr>
<td>monoclinic I</td>
<td>〈110〉 + ( \alpha ), 〈110〉, 〈001〉 + ( \alpha )</td>
<td>( g_x \neq g_y \neq g_z )</td>
<td>( \text{C}_{2h}, \text{C}_2, \text{C}_2 )</td>
</tr>
<tr>
<td>monoclinic II</td>
<td>〈100〉 + ( \alpha ), 〈001〉 + ( \alpha ), 〈010〉</td>
<td>( g_x \neq g_y \neq g_z )</td>
<td>( \text{C}_{2h}, \text{C}_2, \text{C}_2 )</td>
</tr>
<tr>
<td>triclinic</td>
<td>arbitrary orthogonal directions</td>
<td>( g_x \neq g_y \neq g_z )</td>
<td>( \text{C}_1, \text{C}_1 )</td>
</tr>
</tbody>
</table>

2.3.2 The zero field splitting

For centres with \( S = 1/2 \), Kramers theorem dictates that in the absence of magnetic fields, the two \( M_S \) states are degenerate. For centres with \( S > 1/2 \), a zero field splitting may occur, as shown in figure 2.3 for an \( S = 1 \) system. If \( B = 0 \), the \( M_S = \pm 1 \) levels have a slightly different energy than the \( M_S = 0 \) level. This energy difference is related to the coupling of the unpaired electrons of the system (spin-orbit coupling, Coulomb interaction, magnetic dipole and exchange interactions) and to the crystal lattice potential. For \( B \neq 0 \), two different allowed EPR transitions (\( \Delta M_S = 1 \)) and one forbidden EPR transition (\( \Delta M_S = 2 \)) may take place in this system.

For paramagnetic systems with \( S < 2 \), which include all low spin \( d^1 \) configurations, the zero field splitting Hamiltonian can be represented by

\[
\hat{H}_{ZFS} = \vec{S} \cdot \vec{D} \cdot \vec{S}
\]  

(2.17)

in which \( \vec{D} \) is a traceless 3x3 tensor with principal values \( D_x, D_y \) and \( D_z \) (\( D_x + D_y + D_z = 0 \)). It reflects the symmetry of the paramagnetic defect in the lattice, as a result of which, this term vanishes if the defect has perfect cubic symmetry. For defects with axial (tetragonal, trigonal) symmetry, one defines
2.3.3 The (super)hyperfine interaction

In the spin Hamiltonian formalism, an interaction between the unpaired electrons and a single nuclear spin is represented by

\[ \hat{H}_{(s)HF} = \hat{S} \cdot \vec{A} \cdot \vec{l} \]  

(2.20)

It is referred to as a hyperfine interaction if the interacting nucleus belongs to the central ion, and as superhyperfine or ligand hyperfine interaction if the interacting nucleus belongs to a neighbouring ion.

The symmetrical 3x3 matrix \( \vec{A} \) is called the (super)hyperfine tensor.

Hyperfine and superhyperfine interactions are associated with the unpaired electron distribution over the paramagnetic transition metal ion complex [OWEN66]. For the analysis of (ligand) hyperfine interactions, the \( \vec{A} \) tensor is usually divided into an isotropic part, \( A_0 \), and a traceless anisotropic part. The isotropic part is interpreted as the contact interaction between an unpaired electron and the central or ligand nucleus, which is proportional to the probability of finding the electron at the nucleus, \( lP(0)^2 \). This probability is only non-zero for \( s \) electrons. The isotropic hyperfine and superhyperfine interaction may thus be used to estimate the unpaired electron density in the outer shell \( s \) orbitals of the central ion and ligands, respectively. The unpaired electron or spin density in these \( s \) orbitals is defined as

\[ D = 3/2 D_z = -3D_x = -3D_y \]

and the zero field splitting Hamiltonian may be expressed in the principal direction frame of the \( \vec{D} \) tensor as

\[ \hat{H}_{ZFS} = D \left( \hat{S}_z^2 - \frac{1}{3} \hat{S}_0^2 \right) \]  

(2.18)

Orthorhombic and lower symmetries introduce an extra term

\[ E \left( \hat{S}_x^2 - \hat{S}_y^2 \right) \]  

(2.19)

in the zero field splitting Hamiltonian. For \( S \geq 2 \), also terms in \( \hat{S}_i^4 \) \((i = x, y, z)\) and for \( S \geq 3 \), also terms in \( \hat{S}_i^6 \) should be included in this Hamiltonian. These will not be encountered in this work. Just like the electronic Zeeman Hamiltonian, the zero field splitting Hamiltonian has inversion symmetry. The \( \vec{g} \) and \( \vec{D} \) tensors usually have the same symmetry properties and the same principal directions.
in which $A_s^{100\%}$ is the calculated hyperfine interaction assuming that the unpaired electron is completely localised in the corresponding $s$ orbital. A contribution to the isotropic hyperfine interaction may also arise through core polarisation. An unpaired valence electron in the spin up state interacts differently with the closed shell core electrons in the spin up state, and those in the spin down state, as a result of which the probability of finding this core $s$ electron at the position of the nucleus is different for the spin up and the spin down state. This gives rise to an isotropic hyperfine interaction, which may have either a positive or a negative sign. An estimation of the core polarisation contribution to the hyperfine interaction requires unrestricted (exchange polarised) Hartree Fock calculations of the paramagnetic ion [WATS67]. It is characteristic for the type of ion, but relatively insensitive to its lattice surroundings. If it is known through calculations, the contribution of the isotropic (super)hyperfine constant, solely due to spin density in the outer $s$ orbitals, can be calculated.

The anisotropic part of the (super)hyperfine interaction is interpreted in terms of dipole interactions between the magnetic moment of the unpaired electrons and the nucleus and/or interactions of the orbital motion of the electron and the magnetic moment of the nucleus. It is usually related to the probability of finding the unpaired electrons in $p$ or $d$ type orbitals of the central or ligand ions through the relation

$$f_{p,d} = \frac{A_{p,d}}{A_{100\%}^{p,d}}$$

(2.22)

For the ligand hyperfine interactions, an anisotropic contribution also arises through the point dipole interaction between the unpaired electrons and the ligand nucleus. The unpaired electrons are assumed to be localised at the central nucleus. This point dipole contribution for a nucleus with coordinates $(X,Y,Z)$ with respect to the central nucleus and $R^2 = X^2 + Y^2 + Z^2$ is then given by

$$\tilde{\mathbf{A}}_{dip} = \frac{\mu_0 g_0 \mu_0 \mu_B}{4\pi R^6} \mathbf{g} \cdot \begin{bmatrix} 3X^2 - R^2 & 3XY & 3XZ \\ 3XY & 3Y^2 - R^2 & 3YZ \\ 3XZ & 3YZ & 3Z^2 - R^2 \end{bmatrix}$$

(2.23)

The point dipole contribution is usually subtracted from the superhyperfine tensor before separating it into an isotropic and an anisotropic part.

From the foregoing discussion, it is clear that hyperfine and superhyperfine interactions provide information about the distribution of the unpaired electrons over the transition metal ion complex and hence also about the wave function overlap and covalency effects between the central and ligand ion orbitals. It should, however, be kept in mind that the spin densities, here defined, are derived from spin Hamiltonian properties, and can only be expected to give an indication of the unpaired electron distribution. Only if the effective spin $S$ corresponds to the real electronic spin, and hence all principal $g$ values are very close to the free electron value $g_e$, the spin densities give an accurate estimation of the unpaired electron density over the complex, e.g. as calculated by ab initio quantum chemical methods. In cases which do not meet these restrictions, the calculated "real Hamiltonian" properties should be transformed into spin Hamiltonian parameters before a comparison between both is made.
The hyperfine interaction with the central nucleus of the transition metal ion complex also reflects the symmetry of the complex. As the hyperfine Hamiltonian has inversion symmetry, it gives the same symmetry information as the electronic Zeeman and the zero field splitting Hamiltonian. Ligand hyperfine interactions reflect the local symmetry at the position of the interacting nucleus. The determination of the principal values, principal directions and number of equivalent interacting nuclei in the first shells of neighbouring ions thus provides additional symmetry information, allowing to distinguish between paramagnetic defects with and without inversion symmetry.

2.3.4 The nuclear Zeeman interaction

This Hamiltonian represents the interaction between an external magnetic field and the magnetic moment of the central nucleus or a ligand nucleus

$$\hat{H}_{nz} = -g_n \mu_n \vec{B} \cdot \vec{I}$$  \hspace{1cm} (2.24)

The nuclear $g$ factor is characteristic for each type of magnetic nucleus. Therefore, the measurement of the $g_n$ factor of its nucleus serves as a chemical identification for a certain ion in the paramagnetic complex. The $g_n$ factors for the nuclei which are relevant to this work are given in Table 2.2

**Table 2.2 : $g_n$ factors and quadrupole moments for some magnetic isotopes [BRUK98]**

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Spin</th>
<th>Natural Abundance (%)</th>
<th>$g_n$</th>
<th>$Q \times 10^{-28}$ m$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1$H</td>
<td>1/2</td>
<td>100</td>
<td>5.5856912</td>
<td>---</td>
</tr>
<tr>
<td>$^{23}$Na</td>
<td>3/2</td>
<td>100</td>
<td>1.478391</td>
<td>0.108</td>
</tr>
<tr>
<td>$^{35}$Cl</td>
<td>3/2</td>
<td>75.77</td>
<td>0.5479157</td>
<td>-0.08249</td>
</tr>
<tr>
<td>$^{37}$Cl</td>
<td>3/2</td>
<td>24.23</td>
<td>0.4560820</td>
<td>-0.06493</td>
</tr>
<tr>
<td>$^{103}$Rh</td>
<td>1/2</td>
<td>100</td>
<td>0.4717</td>
<td>---</td>
</tr>
<tr>
<td>$^{107}$Ag</td>
<td>1/2</td>
<td>51.83</td>
<td>0.606282</td>
<td>---</td>
</tr>
<tr>
<td>$^{109}$Ag</td>
<td>1/2</td>
<td>48.17</td>
<td>0.698309</td>
<td>---</td>
</tr>
</tbody>
</table>

2.3.5 The nuclear quadrupole interaction

The nuclear quadrupole interaction arises from the finite extension and the aspherical shape of the nuclear charge distribution. The quadrupole moment of nuclei with $I = \frac{1}{2}$, which have a spherical charge distribution, is zero. Nuclei with $I > \frac{1}{2}$ have a quadrupole moment $Q$ given by

$$Q = \frac{1}{e_v} \int_\nu \rho_n (\vec{r}) (3\vec{z}^2 - r^2) dV$$  \hspace{1cm} (2.25)

with $\rho_n (\vec{r})$ the charge distribution of the nucleus, $V$ the nuclear volume and the $z$ axis taken along the nuclear spin orientation. The values for the nuclei of interest to this work are also given in Table 2.2. The quadrupole moment shows no interaction with a uniform electric field. In a non-uniform electric
field, the quadrupole moment of a nucleus interacts with the electric field gradient. In the spin Hamiltonian formalism, this interaction is described by

\[ \hat{H}_Q = \hat{I} \cdot \vec{Q} \cdot \hat{I} \tag{2.26} \]

in which \( \vec{Q} \) is a traceless 3x3 tensor, called the quadrupole tensor. The components of this tensor are given by the expressions [ATHE93]

\[ Q_{k\ell} = \frac{e Q}{2I(2I-1)} \frac{\partial^2 V(\vec{r}_j)}{\partial \kappa \partial \ell}, \quad k, \ell = x, y, z \tag{2.27} \]

with \( V(\vec{r}_j) \) the electric potential at the position of the nucleus with index \( j \). As Rh has nuclear spin \( I = \frac{1}{2} \), we will be mainly concerned with ligand nuclear quadrupole interactions in this work. Usually, two different contributions to this interaction are considered. A first contribution arises from the non-spherically symmetric unpaired electron distribution over the paramagnetic defect and is related to the unpaired spin density in ligand \( p \) or \( d \) orbitals. The contribution of an unpaired electron density \( f_p \) in a ligand \( np_\ell \) orbital is given by

\[ \vec{Q}_e = \frac{-e^2 Q}{4\pi \varepsilon_0 2I(2I-1)} \frac{2}{5} \left( r^{-3} \right)_{np} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix} \tag{2.28} \]

A second contribution is due to extra charges in the crystal lattice. Due to the perfect crystalline symmetry, the electric field gradient at each nucleus in the defect-free crystal is zero. Extra charges, e.g. substitutional ions in a different valence state than the ion they are replacing or vacancies, introduce electric field gradients in the crystal. The electric field of an extra charge \( ne \) in the lattice, at a position with coordinates \((X,Y,Z)\) with respect to the nucleus for which the quadrupole tensor is considered, is usually calculated using a point charge model for the electric field, leading to a contribution

\[ \vec{Q}_{\text{sh}} = \frac{ne^2 Q(1-\gamma_\nu)}{4\pi \varepsilon_0 2I(2I-1)R^2} \begin{pmatrix} 3X^2 - R^2 & 3XY & 3XZ \\ 3XY & 3Y^2 - R^2 & 3YZ \\ 3XZ & 3YZ & 3Z^2 - R^2 \end{pmatrix}, \quad R = \sqrt{X^2 + Y^2 + Z^2} \tag{2.29} \]

in which \( \gamma_\nu \) is the Sternheimer anti-shielding factor, which is characteristic for each type of nucleus.

Due to their sensitivity to electric field gradients, ligand quadrupole tensors reflect the symmetry of the defect at the position of the ligand nuclei. They provide the same symmetry information as the ligand hyperfine tensors.

In conclusion, the spin Hamiltonian contains a lot of structural information about the paramagnetic defect it describes. The determination of its parameters, the \( \vec{g} \) tensor, zero field splitting constants, (ligand) hyperfine tensors, \( g_N \) factors and quadrupole tensors via electron magnetic resonance experiments allow the experimentalist to construct a detailed model for the paramagnetic centre. The spin Hamiltonian parameters should, however, not be confused with real Hamiltonian parameters, which are e.g. obtained from quantum chemical calculations of optimised structures for the paramagnetic defect in the crystal.
2.4 Electron paramagnetic resonance spectroscopy

2.4.1 Resonance phenomenon and selection rules

The energy eigenvalues \( E(M_s, M_l) \) and eigenstates \( \Psi(M_s, M_l) \) of a paramagnetic system described by a spin Hamiltonian \( \hat{H}_s \), e.g. (2.13), are dependent on the magnitude and the direction of an externally applied magnetic field \( \vec{B} \)

\[
\hat{H}_s(\vec{B})\Psi(M_s, M_l; \vec{B}) = E(M_s, M_l; \vec{B})\Psi(M_s, M_l; \vec{B})
\]  

(2.30)

The externally applied magnetic field will now be considered to consist of a large DC component \( \vec{B}_0 \) and an AC component \( \vec{B}_0 \cos \omega t \) for which \( |\vec{B}_0| \gg |\vec{B}| \). The spin Hamiltonian of the paramagnetic system then consists of a large static component \( \hat{H}_s^0(\vec{B}_0) \) and a small time dependent perturbation \( \hat{H}_s^0(\vec{B}_0) \cos \omega t \) with

\[
\hat{H}_s(\vec{B}) = \mu_B \vec{B} \cdot \vec{g} \cdot \vec{S} - \sum_j g_n \mu_B \vec{B} \cdot \vec{i}_j
\]  

(2.31)

According to time dependent perturbation theory, \( \hat{H}_s^0(\vec{B}_0) \) induces transitions (magnetic dipole transitions) between the eigenstates \( \Psi_0(M_s, M_l; \vec{B}_0) \) and \( \Psi_0(M_s', M_l'; \vec{B}_0) \) of the non-perturbed Hamiltonian \( \hat{H}_s^0(\vec{B}_0) \) if

\[
\hbar \omega = |E^0(M_s, M_l; \vec{B}_0) - E^0(M_s', M_l'; \vec{B}_0)|
\]  

(2.32)

with a transition probability \( W \) proportional to

\[
W \propto \left| \left( \Psi_0(M_s, M_l; \vec{B}_0) \right) \left( \hat{H}_s^0(\vec{B}_0) \right) \Psi_0(M_s', M_l'; \vec{B}_0) \right|^2
\]  

(2.33)

as \( \mu_n \ll \mu_B \). This leads to the selection rules for EPR transitions \( \Delta M_s = 1 \) and \( \Delta M_l = 0 \), \( \forall j \), which hold for paramagnetic systems in which the electronic Zeeman interaction is much larger than all other terms in the spin Hamiltonian.

At variance with conventional spectroscopic techniques, e.g. optical absorption, it is more convenient in EPR experiments to keep the transition frequency \( v = \omega/2\pi \) constant (in the microwave range) and to vary the resonance conditions by slowly varying the magnitude of the magnetic DC field \( B_0 = |\vec{B}_0| \).

As a result of broadening mechanisms of the energy levels, absorption of microwaves not only takes place if the resonance condition is exactly matched, but occurs in a narrow frequency band around the resonance frequency. This is accounted for by introducing a line shape function \( g(v) \) in the transition probability, as a result of which the EPR absorption peaks obtain a finite line width. In order to improve their signal to noise ratio, EPR spectra are usually recorded in first derivative mode. An example of a fictitious EPR spectrum, illustrating the effects of recording the absorption as a function
of $B_0$, the finite line width of the resonances and the detection in first derivative mode is given in figure 2.4.

![Energy level scheme, EPR absorption ($I_{EPR}$) and first derivative ($dI_{EPR}/dB$) for a fictitious paramagnetic system with effective spin $S = 3/2$.](image)

**Figure 2.4**: Energy level scheme, EPR absorption ($I_{EPR}$) and first derivative ($dI_{EPR}/dB$) for a fictitious paramagnetic system with effective spin $S = 3/2$.

2.4.2 Rate equations for a two-level system: relaxation and saturation

![Energy level scheme for the two-level paramagnetic system with spin Hamiltonian (2.34)](image)

**Figure 2.5**: Energy level scheme for the two-level paramagnetic system with spin Hamiltonian (2.34)

In order to explain the phenomenon of saturation of EPR transitions, which is also important for ENDOR, a two-level paramagnetic system ($S = \frac{1}{2}$) with a very simple isotropic spin Hamiltonian is considered

$$\hat{H}_S = g \mu_B \hat{B}_0 \cdot \hat{S} = g \mu_B B_0 \cdot \hat{S}_z$$  \hspace{1cm} (2.34)

The energy levels of this system are given by $E(M_S) = g \mu_B B_0 M_S$, in which $M_S$ can take the values $+\frac{1}{2}$ and $-\frac{1}{2}$. These two levels will be referred to as + and −, respectively. The level scheme is shown in figure 2.5.

A magnetic dipole transition occurs between these levels if $h \nu = g \mu_B B_0$ and

$$W_{+ \rightarrow -} = W_{- \rightarrow +} = W_{EPR} \propto \left| \langle -| g \mu_B \vec{B}_1 \cdot \hat{S} |+ \rangle \right|^2 \neq 0$$  \hspace{1cm} (2.35)

which implies that $\vec{B}_1$ should not be parallel to $\vec{B}_0$.
The equilibrium thermal population of these levels \( N_e \) and \( N_s \) is given by the Boltzmann distribution, according to which

\[
\frac{N_e}{N_s} = e^{-\frac{g_s\mu_B B_0}{kT}}
\]  

(2.36)

The rate equations for the microwave-induced magnetic dipole transitions in this system are:

\[
\frac{dN_e}{dt} = -W_{\text{EPR}} (N_e(t) - N_s(t))
\]

\[
\frac{dN_s}{dt} = -W_{\text{EPR}} (N_s(t) - N_e(t))
\]

(2.37)

One defines the population difference between the levels \( n(t) = N_s(t) - N_e(t) \) and \( N(t) = N_e(t) + N_s(t) \).

The rate equations for \( n(t) \) and \( N(t) \) are

\[
\frac{dN(t)}{dt} = 0 \Rightarrow N(t) = N
\]

\[
\frac{dn(t)}{dt} = -2W_{\text{EPR}} n \Rightarrow n(t) = n_0 e^{-2W_{\text{EPR}} t}
\]

(2.38)

If the populations \( N_e \) and \( N_s \) were initially in thermal equilibrium

\[
n_0 = N \left( \frac{1 - e^{-\frac{g_s\mu_B B_0}{kT}}}{1 + e^{-\frac{g_s\mu_B B_0}{kT}}} \right) = N \tanh \left( \frac{g_s\mu_B B_0}{2kT} \right)
\]

(2.39)

The absorbed microwave power by this system at the resonance frequency is then given by

\[
P_{\text{ABS}} = W_{\text{EPR}} n_0 \nu_{\text{MW}} = W_{\text{EPR}} g_s \mu_B B_0 N \tanh \left( \frac{g_s\mu_B B_0}{2kT} \right) e^{-2W_{\text{EPR}} t}
\]

(2.40)

Thus, no steady state absorption is observed in this system if only microwave-induced transitions are considered. However, if the microwave excitation is no longer applied, the populations of the two states return to their equilibrium values within a characteristic relaxation time \( T_R \), due to interactions of the magnetic moment of the paramagnetic centres with the crystal lattice vibrations (spin-lattice relaxation) and interactions between the magnetic moments of paramagnetic centres in the crystal (spin-spin relaxation). It is customary to define a longitudinal relaxation time \( T_1 \), which shows a complex temperature dependence and is related to spin-lattice relaxation, and a transverse relaxation time \( T_2 \), related to the spin-spin relaxation and practically temperature-independent. These relaxation mechanisms cause broadening of the energy levels and may be related to the line shape function \( g(\nu) \).

From the Bloch equations (see e.g. [SPAE92]) one can calculate the line shape function for homogeneous lifetime broadening to be Lorentzian

\[
g(\nu) = \frac{2T_2}{1 + 4\pi^2 T_2^2 (\nu - \nu_{\text{m}})^2}
\]

(2.41)

Short relaxation times \( T_2 \) caused by a high concentration of paramagnetic centres (many spin-spin interactions) may seriously broaden the EPR absorption peak and prevent it from being detected. Therefore EPR is best observed for paramagnetically dilute systems, e.g. low concentrations of
paramagnetic defects in a diamagnetic host crystal. For defects in solids, one usually finds that $T_2 \ll T_1$. The relaxation time $T_R$ may then be approximated by $T_1$.

Including the effect of relaxation, the rate equation for $n(t)$ becomes

$$\frac{dn(t)}{dt} = -\frac{(n(t) - n_0)}{T_R} - 2W_{EPR}n(t)$$

$$= \frac{n_0}{T_R} - \left(\frac{1}{T_R} + 2W_{EPR}\right)n(t)$$

(2.42)

The steady state solution ($t = \infty$, $dn/dt = 0$) of this problem is

$$n = \frac{n_0}{1 + \frac{2W_{EPR}T_R}{1 + s}} = \frac{n_0}{1 + s}$$

(2.43)

in which $s$ is called the saturation parameter. The steady state absorbed microwave power is

$$P_{ABS} = \frac{N \tanh\left(\frac{g\mu_B B_0}{2kT}\right)g\mu_B B_0 W_{EPR}}{1 + 2W_{EPR}T_R} = \frac{AB_0^2}{1 + CT_R B_0^2} = \frac{AP_{MW}}{1 + CT_R P_{MW}}$$

(2.44)

as $W_{EPR} \approx B_1^2 \approx P_{MW}$, the applied microwave power. The absorbed microwave power as a function of the applied microwave power at a certain temperature and for a certain value of the spin-lattice relaxation time is shown in figure 10. As the intensity of the EPR spectrum $I_{EPR} \propto (P_{ABS})^{1/2}$, the plot also represents the dependence of $I_{EPR}$ from $B_1$. At small applied microwave power, $P_{ABS} \propto P_{MW}$ or $I_{EPR} \propto B_1 \propto (P_{MW})^{1/2}$. For large $P_{MW}$ the signal intensity no longer increases and may even decrease. The EPR transition is then said to be saturated.

For decreasing temperature the absorbed microwave power increases via the $\tanh(g\mu_B B_0/2kT)$ dependence. Usually, the relaxation time $T_1$ also increases when the temperature decreases, as a result of which the maximum absorbed microwave power decreases and saturation sets in at a lower microwave power. An optimum temperature may thus be found for the detection of the EPR signal of a paramagnetic defect.

For transition metal complexes in ionic solids, the optimum detection temperature often lies below room temperature. Hence, the EPR spectrometer should be equipped with a cryostat operating with liquid nitrogen or liquid helium, allowing the detection temperature to be varied between 77 K or 4.2 K and room temperature.

Figure 2.6: Absorbed microwave power as a function of the applied microwave power in the two-level paramagnetic system with spin Hamiltonian (2.34). The dashed line indicates the $P_{ABS} \propto P_{MW}^{1/2}$ law for low microwave power.
2.4.3 The spin Hamiltonian information obtained from an EPR spectrum

As an example, a paramagnetic defect with $S = 1$ interacting with one nucleus with $I = 1$ is considered. For simplicity reasons, the $\tilde{g}$ and $\tilde{A}$ tensor are assumed to be isotropic, the $\tilde{D}$ and $\tilde{Q}$ tensor have axial symmetry and the magnetic field is applied along the symmetry axis of the $\tilde{D}$ and $\tilde{Q}$ tensor. Furthermore, the electronic Zeeman energy is assumed to be much larger than all other terms in the spin Hamiltonian. The spin Hamiltonian for this system is

$$\hat{H}_s = g\mu_B B_z \hat{S}_z + D \left( \hat{S}_z^2 - \frac{1}{3} \hat{S}^2 \right) + A \hat{S} \cdot \hat{I} - g_n \mu_n B_0 \cdot \hat{I} + Q \left( 3\hat{I}_z^2 - \hat{I}^2 \right) \quad (2.45)$$

Via first order perturbation theory, the energy levels for this system can be calculated to be

$$E(M_s, M_I) = g\mu_B B_0 M_s + \frac{D}{3} (3M_s^2 - 2) + AM_s M_I - g_n \mu_n B_0 M_I + Q (3M_I^2 - 2) \quad (2.46)$$

Six allowed EPR transitions ($\Delta M_s = 1$ and $\Delta M_I = 0$) occur in this system. Their transition frequencies at fixed field and transition fields at fixed frequency are given in Table 2.3. If it is further assumed that $D > A$, the EPR spectrum consists of two triplets of lines, as shown in figure 2.7. From the centre of the pattern, $h\nu_{M_I}/\mu_B$, the $g$ value of the paramagnetic system can be deduced. The splitting between the two triplets corresponds to $2D$ and the splitting within the triplets equals $A$, the hyperfine constant. A more accurate determination of the spin Hamiltonian parameters requires the diagonalisation of the spin Hamiltonian.

![Figure 2.7](image-url)  

*Figure 2.7: Calculated EPR spectrum (first order) of the paramagnetic system with spin Hamiltonian (2.45)*
Table 2.3: allowed EPR transitions in the paramagnetic system with spin Hamiltonian (2.45) calculated to first order

| \( |M_S\rangle \rightarrow |M'_S\rangle \) | \( M_I \) | \( h\nu_{res} (B_0 \text{ fixed}) \) | \( B_{res} (\nu_{MW} \text{ fixed}) \) |
|---|---|---|---|
| \( |1\rangle \rightarrow |0\rangle \) | 1 | \( g\mu_B B_0 + D + A \) | \( (h\nu_{MW} - D - A)/g\mu_B \) |
| | 0 | \( g\mu_B B_0 + D \) | \( (h\nu_{MW} - D)/g\mu_B \) |
| | -1 | \( g\mu_B B_0 + D - A \) | \( (h\nu_{MW} - D + A)/g\mu_B \) |
| \( |0\rangle \rightarrow |1\rangle \) | 1 | \( g\mu_B B_0 - D + A \) | \( (h\nu_{MW} + D - A)/g\mu_B \) |
| | 0 | \( g\mu_B B_0 - D \) | \( (h\nu_{MW} + D)/g\mu_B \) |
| | -1 | \( g\mu_B B_0 - D - A \) | \( (h\nu_{MW} + D + A)/g\mu_B \) |

These first order calculations, however, already clearly indicate that the EPR spectrum gives information about the \( \tilde{g} \) tensor, the zero field splitting parameters and the hyperfine tensor.

Recording the spectra as a function of the orientation of the magnetic field with respect to the crystal axes allows the determination of the principal values and axes of the \( \tilde{g} \), \( \tilde{D} \) and \( \tilde{A} \) tensors and provides information on the symmetry of the paramagnetic ion and its lattice surroundings. The \( g_N \) factor of the interacting nucleus (thus, its chemical nature) and its \( \tilde{Q} \) tensor can usually not be determined from the EPR spectrum. One should further notice that the splitting between the transition fields is, to first order, independent of the microwave frequency. The centre of the pattern, on the other hand, is linearly dependent on the microwave frequency. Recording the EPR spectrum at different microwave frequencies enables one to assign observed splittings in the spectra to field-dependent or field-independent terms in the spin Hamiltonian. The spectrum in figure 2.7 could, e.g., also be explained by the presence of two non-interacting paramagnetic centres with \( S = 1/2 \), each interacting with a nucleus with \( I = 1 \), and with different \( g \) values \( g_I \) and \( g_0 \). Recording the spectrum at another microwave frequency would then result in a different splitting between the two triplets.

From the resonance condition for centres with \( S = 1/2 \), \( h\nu = g\mu_B B_0 \), it is easily deduced that the \( g \) factor resolution, the ability to resolve the EPR spectra of two paramagnetic centres with slightly different \( g \) values, increases linearly with microwave frequency

\[
\left| \frac{\partial B_0}{\partial g} \right| = \frac{h\nu}{g^2 \mu_B}
\]

(2.47)

As a second example, a paramagnetic centre with \( S = 1/2 \), interacting with a large number of nuclei with \( I = 1/2 \) is considered. The interaction with each nucleus splits all energy levels in two and doubles the number of allowed EPR transitions. For \( N \) interacting nuclei \( 2^N \) EPR transitions occur. Usually only the interactions with a few nuclei for which the (super)hyperfine coupling is much larger than that for all other nuclei, are resolved in the EPR spectrum. The other (super)hyperfine interactions merely broaden the observed EPR transitions, giving them a Gaussian (inhomogeneously broadened) line shape. The EPR spectrum, however, still contains the information of all interacting nuclei. Hyperfine and superhyperfine interactions are usually better resolved at low microwave frequency than at higher
frequencies. If the paramagnetic centre in the crystal is subject to random strain, its $g$ factor has a random distribution, as a result of which each observed EPR transition obtains an additional line width, which increases linearly with the microwave frequency. Hence, (super)hyperfine interactions, which are resolved at low microwave frequencies may be buried in the line width at higher microwave frequencies.

2.4.4 Experimental detection of EPR transitions

The EPR spectra recorded for this work were measured on a Bruker ESP300E spectrometer operating at X-band (9.5 GHz), equipped with an Oxford ESR10 flow cryostat, and on a Bruker ELEXSYS E500 spectrometer operating at Q-band (34 GHz), equipped with an Oxford CF935 cryostat. In figure 2.8 the block diagram of an EPR spectrometer is shown. It consists of four parts: the microwave bridge, the microwave cavity, the electromagnet and the console. In the following, these four components are briefly discussed.

![Block diagram of an EPR spectrometer](image)

**Figure 2.8**: Block scheme of an EPR spectrometer [BRUK83]. The numbering is explained in the text.

The microwave bridge contains the microwave excitation, detection, control and operation system. A microwave source (1), e.g. a klystron (ESP300E spectrometer) or a gun-diode (ELEXSYS), produces coherent microwaves. The source power is split into a power arm (2) and a reference arm (3). The power arm consists of an attenuator (6) which regulates the power, and a circulator (7), which directs the power from the source to the sample cavity (8) and the power reflected at the cavity to the detector (9). The microwave signal of the reference arm serves as bias signal for the detector diode. The reference arm contains an attenuator (4) and a phase shifter (5). The frequency of the microwave source is stabilised to the resonance frequency of the cavity by the automatic frequency control (AFC)
system. The source frequency $v_s$ is frequency modulated by the signal (10). If $v_s$ deviates from the
cavity resonance frequency $v_{res}$, the reflected signal contains a component at the frequency $|v_s - v_{res}|$,
which is, via a feedback loop, phase sensitively detected by the detector (11), using the modulation
signal as a reference. This detector produces an error signal which is used to correct the central
source frequency.

The microwave cavity (8) contains the specimen
and is placed in the air gap of the electromagnet
(13). The microwave energy is transferred to the
cavity via wave tubes. At the cavity, the microwave
power is partly reflected. The impedance of the
cavity may be matched to that of the waveguides
adjusting a screw, called the iris. The cavity is a
geometric construction of the proper dimensions for
microwave radiation at the cavity resonance
frequency to form standing wave patterns, called
modes. Through the formation of standing waves,
the density of electromagnetic energy in the cavity
increases significantly. In figure 2.9 the energy
density in the cavity as a function of the microwave
frequency is shown. The cavity functions as an
amplifier of microwave frequencies near the cavity
resonance frequency. A characteristic parameter
for the cavity is its quality factor $Q$, defined as

$$Q = \frac{2\pi \text{ energy stored in cavity}}{\text{dissipation in cavity per microwave period}} = \frac{v_{res}}{\Delta v}$$

(2.48)

EPR microwave cavities usually have a $Q$ factor of the order $10^5 - 10^6$. Another important
characteristic of the cavity modes is the spatial separation of the maxima of the electric and magnetic
field amplitudes. The sample is placed in a region of maximum magnetic field intensity, maximising
the magnetic dipole transition probability, and low electric field intensity, minimising the dielectric
losses in the cavity. The presence of the specimen slightly changes the resonance frequency of the
cavity from its unloaded value. If the EPR resonance condition $\Delta E(B_0) = h\nu_{reg}$ is fulfilled, microwave
energy quanta are absorbed by the specimen, changing the quality factor of the cavity and thus also
its reflection coefficient. These changes of the reflected microwave power, EPR signals, are detected
in the microwave bridge. The $Q$ factor, which is a measure for the microwave energy density in the
cavity, is also a measure for the sensitivity of this system. By using a resonance cavity, EPR
spectroscopy is extremely sensitive allowing the detection of paramagnetic centres with absolute
concentrations of about $10^{15}$. The use of a resonance cavity, however, limits the possibilities of
varying the resonance frequency. Therefore, the microwave frequency is kept fixed in EPR
experiments. The dimensions of the waveguides and microwave cavity and maximum specimen size
are dependent on the microwave frequency at which the spectrometer is operated.
The electromagnet (13) provides the static magnetic field $\vec{B}_0$. Its direction is perpendicular to that of the excitation microwave field $\vec{B}_1$, and its magnitude is slowly varied in a linear way. To improve the signal to noise ratio of EPR spectra, phase sensitive detection is applied. Therefore, the amplitude of the static magnetic field is modulated at high frequency (typically $1 - 100$ kHz) with a small amplitude (typically of the order $0.1$ mT). The modulation frequency source (12) supplies a current to the modulation coils (14), which are usually situated inside the cavity. The reference arm (15) supplies an amplitude and phase reference signal to the phase sensitive detector (17). The band pass amplifier (16) only transmits frequencies near the modulation frequency. Phase sensitive detection eliminates all low frequency noise of the detector. As a side product of this detection method, the output of the detector is proportional to the first derivative of the EPR absorption signal. Increasing the modulation amplitude usually results in an increase of the signal intensity and thus improves the signal to noise ratio. It, however, also broadens the EPR lines, as a result of which the resolution of the spectrum decreases.

The control systems of the signal channel, the microwave power and the magnetic field are brought together in a console. The spectrometers used in this work are completely computer controlled. The experimental parameters are given as input to the operation software (ESP300E for the X-band spectrometer, XEPR for the Q-band spectrometer). The spectra are digitised and stored on computer. For accurate measurements of the microwave frequency a digital frequency counter is used (HP5350B at X-band and EIP548B at Q-band). Accurate measurements of the magnetic field are performed with a Bruker ER035M NMR Gaussmeter. The NMR probe is placed outside the microwave cavity, as close as possible to the specimen. In order to correct for possible deviations between intensity of the magnetic field at the position where it is measured and at the position of the specimen, the EPR spectrum of a paramagnetic sample with accurately known $g$ values ($g$ calibration sample) is measured. All magnetic field values are corrected for the deviation of the measured and calculated resonance magnetic field intensity for this calibration sample. At X-band DPPH ($g = 2.0036$) is commonly used as $g$ calibration sample. Due to its $g$ anisotropy, DPPH may no longer be suitable as calibration sample at higher microwave frequencies. At Q-band, a $\text{CO}_3^{3-}$ centre in CaCO$_3$ has been suggested as a reference [MORE00].

2.5 Electron nuclear double resonance spectroscopy and some related techniques

2.5.1 Additional information provided by recording the NMR spectrum

Let us turn back to the examples given in paragraph 2.4.3. In the first example, a paramagnetic centre with $S = 1$ interacting with one nucleus with $I = 1$ was considered (spin Hamiltonian equation (2.45)). From the allowed EPR transitions, calculated with first order perturbation theory, the spin Hamiltonian parameters $g, D$ and $A$ have been deduced. In this system, also 6 allowed NMR transitions ($\Delta M_S = 0$, $\Delta M_I = 1$) take place. Their transition frequencies are given in table 2.4, assuming $A > g\mu_B B > 3Q > 0$. 

Table 2.4: Allowed NMR transitions for the paramagnetic system described by spin Hamiltonian (2.45)

| $M_S$ | $M_i \leftrightarrow M_i'$ | $h\nu_{res} = |E(M_S,M_i) - E(M_S,M_i')|/h$ |
|-------|-----------------------------|-------------------------------------|
| 1     | $1 \leftrightarrow 0$      | $A - g_{\mu_B}B_0 + 3Q$            |
|       | $0 \leftrightarrow -1$     | $A - g_{\mu_B}B_0 - 3Q$            |
| 0     | $1 \leftrightarrow 0$      | $g_{\mu_B}B_0 - 3Q$                |
|       | $0 \leftrightarrow -1$     | $g_{\mu_B}B_0 + 3Q$                |
| -1    | $1 \leftrightarrow 0$      | $A + g_{\mu_B}B_0 - 3Q$            |
|       | $0 \leftrightarrow -1$     | $A + g_{\mu_B}B_0 + 3Q$            |

Figure 2.10: ENDOR spectrum with the magnetic field parallel to the tetragonal axis of the paramagnetic system ($S = 1$ and $I = 1$) described by spin Hamiltonian (2.45).

The NMR spectrum, shown in figure 2.10, consists of three doublets of lines. One of them, corresponding to $M_S = 0$, is centred on the Larmor frequency of the interacting nucleus $g_{\mu_B}B_0/h$ and the other two are separated by twice this value. The centre of the latter two doublets corresponds to the hyperfine parameter $A/h$. The splitting within all three doubles equals $6Q/h$. More generally, recording the NMR spectrum as a function of the orientation of the magnetic field with respect to the crystal axes allows one to determine the $g_{\mu}$ factor of the interacting nuclei, the principal values and directions of the (super)hyperfine and quadrupole tensors. Thus it provides information on the chemical nature and the lattice position of interacting nuclei. It should be remarked that $g_{\mu}$ and quadrupole parameters could, in a first order approximation, not be determined from the EPR
spectrum. If the NMR spectrum is recorded at several static magnetic field intensities $B_0$, the transition frequencies change due to their $g_n \mu_n B_0$ dependence. The splitting of the upper two doublets changes when $B_0$ is changed, although their central position and splitting within these doublets remains, to first order, unchanged. From the $B_0$ dependence of the NMR transition frequencies $g_n$ can be determined and the transitions can be assigned to a particular magnetic nucleus. This is called the magnetic field shift method. In general, the recording of the NMR spectrum at different $B_0$ values enables the experimentalist to assign observed splittings to field-dependent and field-independent terms in the spin Hamiltonian.

In the second example, a paramagnetic centre with $S = \frac{1}{2}$, interacting with a large number $N$ of nuclei with $I = \frac{1}{2}$ was considered. If interactions between the nuclei may be neglected, which is certainly the case in first order calculations, each additional interacting nucleus, with hyperfine coupling constant $A$ and nuclear $g$ factor $g_n$, introduces two additional allowed transitions in the NMR spectrum at $\hbar \nu = |A/2 + g_n \mu_n B_0|$. Hence, the ENDOR spectrum consists of $2N$ transitions, whereas in the EPR spectrum $2^N$ allowed transitions take place. Through this enormous reduction of the number of transitions, NMR acquires a much higher spectral resolution than EPR. Small (super)hyperfine interactions, buried in the EPR line width, may easily be resolved in NMR spectra.

The main drawback of conventional NMR spectroscopy is, however, its much lower sensitivity as compared with EPR. The probability for NMR transitions

$$W_{\text{NMR}} \propto \left| \langle \psi^0 \left( M_0, M_1 \right) | g_n \mu_n \vec{B}_0 \cdot \hat{I} \left| \psi^0 \left( M_0, M_1 \right) \right. \rangle \right|^2$$

(2.49)

is typically a factor of $10^6$ smaller than that for EPR transitions. A much higher concentration than usually encountered for paramagnetic defects in solids would be required for the experimental detection of NMR transitions. With electron nuclear double resonance spectroscopy, the NMR transitions are detected via their effect on the EPR spectrum. In this way ENDOR spectroscopy combines the high sensitivity of EPR (the sensitivity of ENDOR is only a factor of $10^2$ to $10^3$ lower) with the high spectral resolution of NMR.

### 2.5.2 The principles of ENDOR spectroscopy

In order to explain the mechanisms of ENDOR spectroscopy a paramagnetic centre with $S = \frac{1}{2}$, interacting with a single nucleus with $I = \frac{1}{2}$, is considered. The spin Hamiltonian of this system, assuming isotropic $\vec{g}$ and $\vec{A}$ tensors, is

$$\hat{H}_s = g_\mu_B B_0 \hat{S}_z + A \hat{S} \cdot \hat{I} - g_n \mu_n B_0 \hat{I}_z$$

(2.50)

The energy levels for this four-level paramagnetic system are represented in figure 2.11, assuming $A/2 > g_n \mu_B B_0$. The spin relaxation mechanisms between the states are represented by their respective relaxation times: $T_{1e}$ and $T_{1n}$, the electronic and nuclear spin-lattice relaxation times corresponding to the allowed EPR and NMR transitions, and the $T_2$ and $T_{2x}$ cross-relaxation times, corresponding to transitions for which $|\Delta M_0 + \Delta M_1| = 0$ and $2$, respectively. One usually finds $T_{1e} > T_x > T_{2x} < T_{1n}$. In order to observe the ENDOR effect, the static magnetic field $B_0$ is set to one of the allowed EPR transitions, e.g. $E_1$, and a sufficiently high microwave power $P_{EPR} \propto B_1^2$ is applied for the transition to be saturated. The absorbed microwave power is given by equation (2.44) with $T_n = T_{1e}$, as $T_{1e} < T_{1n}$. If a
second time-dependent field $B_z \cos \Omega t$ is applied, with $B_z$ perpendicular to both $B_y$ and $\vec{B}_1$, $\Omega = \omega/2\pi$ in the radio frequency region and $hf = \Delta E(N1)$, an extra relaxation path is created between the levels 1 and 4, via the cross relaxation $T_x$. The relaxation time $T_R$ is hereby reduced:

$$T_R = \frac{1}{\frac{1}{T_{1e}} + \frac{1}{T_{NMR} + T_x}}$$

$$\Delta T_R = \frac{T_{1e} (T_{NMR} + T_x)}{T_{1e} + T_{NMR} + T_x} - T_{1e} = -\frac{T_{1e}^2}{T_{1e} + T_{NMR} + T_x}$$

with $T_{NMR} = 1/(2W_{NMR})$. As a result, the steady state absorbed microwave power $P_{ABS}$ increases, because

$$\frac{\partial P_{ABS}}{\partial T_R} = \frac{ACB^4}{(1 + CT_R B^1)^2}$$

If an RF frequency corresponding to the transition $N2$ is applied, an extra relaxation path is created via the cross relaxation $T_{xx}$. The relaxation time is again changed

$$\Delta T_R = \frac{T_{1e} (T_{NMR} + T_{xx})}{T_{1e} + T_{NMR} + T_{xx}} - T_{1e} = -\frac{T_{1e}^2}{T_{1e} + T_{NMR} + T_{xx}}$$

The NMR transitions can thus be detected by monitoring the intensity of a partially saturated EPR transition as a function of the frequency of an applied RF signal. This effect is called ENDOR. If the other EPR transition, $E2$, is saturated, the same ENDOR transitions are observed. Indeed, for $hf = \Delta E(N1)$ an extra relaxation path is created via $T_{xx}$ and for $hf = \Delta E(N2)$ via $T_x$. More generally, for paramagnetic centres interacting with several nuclei, all having $I = \frac{1}{2}$, the same ENDOR spectrum is recorded at all EPR hyperfine transitions. For nuclei with $I > \frac{1}{2}$, not all ENDOR transitions may be recorded at a certain EPR hyperfine transition, as will be illustrated later in this work.

The actual relaxation mechanisms which determine the magnitude of the ENDOR effect are much more complicated than the ones given here [SPA92]. The intensity of ENDOR spectra can by no means be predicted from the equations (2.52), (2.51) and (2.53), even if the required relaxation times were accurately known. Certain requirements for the relaxation times may nonetheless be deduced from these equations:

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{scheme.png}
\caption{Four level scheme of the paramagnetic system with spin Hamiltonian (2.50), defining the electronic relaxation time $T_{1e}$, the nuclear relaxation time $T_{NMR}$, and the cross relaxation times $T_x$ and $T_{xx}$. The induced NMR transitions are characterised by an effective relaxation time $T_{NMR} = 1/(2W_{NMR})$}
\end{figure}
1. $T_{1n}$ should be sufficiently large in order to prevent paramagnetic ions in the excited nuclear states 1 and 3 from decaying immediately to the states 2 and 4, respectively.

2. $T_{1\theta}$ should be sufficiently large for the EPR transitions to be easily saturated

3. Efficient cross-relaxation paths should be present.

As all these relaxation times are usually strongly temperature-dependent, ENDOR can for many paramagnetic systems only be detected in a very narrow temperature range. For transition metal complexes in ionic solids, ENDOR can usually only be detected at temperatures of the order 10 K.

2.5.3 ENDOR extensions to the EPR spectrometers

As the ENDOR signal is detected as a change in the intensity of the EPR spectrum, ENDOR spectra are recorded with EPR spectrometers with a microwave cavity in which an RF signal $\tilde{B}_2(t)$ can be produced. The simplified block scheme of an ENDOR spectrometer is given in Figure 2.12. A low power frequency modulated RF signal is generated by a synthesiser (1) and amplified by an RF amplifier (2).

![Figure 2.12: Block scheme of an ENDOR spectrometer. The numbering is explained in the text. Extensions to conventional EPR spectrometers are indicated in bold.](image)

Via coaxial cables the amplified RF signal is fed to a metallic helix (ENDOR coil) placed inside the microwave cavity (3) around the specimen, as a result of which the NMR excitation field $\tilde{B}_2(t)$ is produced, perpendicular to the EPR excitation field $\tilde{B}_1(t)$ field generated in the microwave bridge (6) and to the static field $\tilde{B}_0$ produced by the electromagnet (5). To avoid unwanted reflections of the RF power, the RF transmission line is terminated by a 50 $\Omega$ load (4). The amplitude of the EPR signal (7)
(y) is recorded in the signal channel (8) as a function of the RF frequency (x). ENDOR experiments are completely computer controlled (9).

In order to enhance the signal to noise ratio, the ENDOR spectra are phase sensitively detected. To this end the RF signal is frequency modulated. The time dependence of the RF field is given by

\[ \tilde{B}_r(t) = \tilde{B}_r \cos \left( 2\pi \left[ \frac{t}{f_m} + f_r D_{m} \right] t \right) \]

\[ D_{m} = 1, \quad \frac{n}{f_m} < t < \frac{n + 1/2}{f_m} \]

\[ D_{m} = -1, \quad \frac{n + 1/2}{f_m} < t < \frac{n + 1}{f_m} \]  \hspace{1cm} (2.54)

in which \( f_m \) represents the modulation frequency (usually fixed at 12.5 kHz) and \( f_r \) is referred to as the modulation depth. The latter experimental parameter has more or less the same effect on ENDOR spectra as the modulation amplitude has on EPR spectra: a higher modulation depth usually enhances the intensity of the ENDOR signal but it decreases its resolution.

2.5.4 The principles of ENDOR-induced EPR and electron nuclear nuclear triple resonance

Two spectroscopic techniques, related to ENDOR, which are very helpful in the interpretation of complex EPR and ENDOR spectra, will now be briefly discussed. A detailed description of the relaxation mechanisms involved and the experimental requirements for these techniques, can be found in specialised handbooks on multiple magnetic resonance techniques, e.g. [SPAE92].

A first technique is usually referred to as ENDOR-induced EPR (EI-EPR) although the name field-swept ENDOR is also used. In an EI-EPR experiment the RF frequency is kept fixed at the position of a certain ENDOR transition. The intensity of this ENDOR transition is monitored while the static magnetic field \( B_0 \) is swept. In this way, the EPR spectrum of the paramagnetic centre, for which the ENDOR transition has been detected, can be reconstructed. In order to accomplish this effect, the static RF frequency should be corrected for the variation of the ENDOR transition frequency as a function of \( B_0 \). Only if the RF frequency is fixed at a transition of a nucleus with \( I = \frac{1}{2} \), the complete EPR spectrum will be recorded (in non-derivative mode) in the EI-EPR spectrum. This technique is very useful if the EPR spectrum of several paramagnetic centres overlap. If a certain ENDOR transition corresponds to only one of these centres, EI-EPR allows to record the isolated spectrum of this centre. In this way it can also be used to correctly assign the ENDOR transitions to the different paramagnetic centres.

As a second technique, electron nuclear nuclear triple resonance is mentioned. It is also referred to as double ENDOR [SPAE92] or general Triple. In this technique, an RF frequency magnetic field \( \tilde{B}_r \) is applied to the sample (parallel to \( \tilde{B}_0 \)), with a frequency \( f_r \) fixed to one of the transition frequencies in the ENDOR spectrum. The ENDOR spectrum is then again recorded by sweeping the RF frequency \( f_r \) and the effect of the presence of the RF field with frequency \( f_r \) on the intensity of the ENDOR transitions is examined. One finds that the presence of the second RF signal only affects the ENDOR transitions belonging to the same paramagnetic centre (orientation, see paragraph 2.5.6). In this way double ENDOR can also be used to decompose the ENDOR spectra of paramagnetic centres with overlapping EPR spectra. The intensity of ENDOR transitions belonging to the same paramagnetic
centre and the same $M_S$ multiplet as the transition at the pumped frequency $f_2$ is decreased, while the intensity of the transitions belonging to a different $M_S$ multiplet are increased [NIKLB83]. In this way, double ENDOR can be used to determine the relative signs of (super)hyperfine coupling constants for different nuclei, as will be explained further in this work (see chapter 4).

2.5.5 ENDOR spectra for a paramagnetic centre interacting with several nuclei

If the unpaired electrons of a paramagnetic centre interact with many nuclei, the analysis of the magnetic resonance spectra involves the diagonalisation of a spin Hamiltonian matrix with rank

$$ (2S+1) \prod_{j=1}^{N} (2I_j + 1). $$

If several of these nuclei have $I > 1/2$ and the total number of nuclei is large, the dimension of this Hamiltonian matrix becomes very large and even its numerical diagonalisation by computer is very time consuming, especially for spin Hamiltonian fitting programs, which require a large number of diagonalisations. Therefore, one usually makes the assumption that each nucleus interacts with the unpaired electrons, independently from all others, which implies that all interactions between the nuclei are neglected. This approximation usually works very well, except in case the nuclei are equivalent and the (super)hyperfine interaction parameters are sufficiently large. This case will be discussed at the end of this section. First, a few definitions about equivalent nuclei should be given. Nuclei which are transformed into one another by the symmetry operations of the point group of the paramagnetic centre will be referred to as being physically equivalent. Although such nuclei have identical interaction tensors $\vec{A}$, $\vec{Q}$ and identical $g_N$, their NMR transitions will in general only coincide for special orientations of the magnetic field. In these orientations, the nuclei are called magnetically equivalent, or simply equivalent. For orientations of the magnetic field at which the NMR transitions of physically equivalent nuclei do not coincide, the nuclei are called magnetically

![Diagram](image-url)

**Figure 2.13**: Energy level scheme and first order EPR and ENDOR spectra for a paramagnetic centre with $S = 1/2$ interacting with $N$ nuclei with $I = 1/2$ for $N = 1, 2, 3$ and 4.
inequivalent. If physically equivalent nuclei are transformed into one another by inversion, they are magnetically equivalent for all magnetic field orientations.

If the unpaired electrons interact with several equivalent nuclei, a problem arises. This is illustrated in figure 2.13, which shows the first order energy levels, EPR and ENDOR spectra of a paramagnetic centre with $S = \frac{1}{2}$ (isotropic $g$) interacting with an increasing number $N$ of equivalent nuclei with $I = \frac{1}{2}$ (isotropic $A > 2g\mu_BhB_0$, all interactions between nuclei neglected). It is clearly seen that the EPR spectrum contains information about the number of equivalent nuclei. Even if the (super)hyperfine structure is not resolved in the EPR spectrum, it still contains the information on the number of nuclei in its line width. This information is, however, completely lost in the ENDOR spectrum, where the transitions of all equivalent nuclei coincide. Each interaction observed in the ENDOR spectrum may thus be due to several equivalent nuclei. Usually only a few possible combinations of numbers of equivalent nuclei for each interaction are compatible with the symmetry of the centre and its lattice surroundings. The simulation of the resolved hyperfine structure and/or line width of the EPR spectrum then usually allows an unambiguous determination of the number of equivalent nuclei for each interaction.

Although the direct interactions between the nuclear magnetic moments in a paramagnetic complex are very small and only broaden the individual ENDOR transitions, the indirect interaction via the electronic spin between equivalent nuclei may be resolved in the EPR and ENDOR spectra, if the (super)hyperfine coupling constants for these nuclei are sufficiently large [SPAE92]. This will be illustrated by a second order perturbation calculation of the EPR and ENDOR spectra for a paramagnetic centre with $S = \frac{1}{2}$ interacting with two equivalent nuclei, $I_1 = I_2 = \frac{1}{2}$. For simplicity reasons, all spin Hamiltonian terms are assumed to be isotropic. The eigenvalues and eigenstates of this eight-level system are found by diagonalisation of the spin Hamiltonian

$$
\hat{H}_S = g_\mu_B B_0 \hat{S}_z + A \left( \hat{S}_z \hat{I}_{zz} + \frac{1}{2} \left( \hat{S}_z \hat{I}_z + \hat{S}_z \hat{I}_z \right) \right) - g_\mu_B B_0 \hat{I}_z
$$

(2.55)

In the base $|M_S, M_I, M_{Iz}\rangle$, the matrix elements of the spin Hamiltonian are

|           | $|1/2, 1/2, 1/2\rangle$ | $|1/2, -1/2, -1/2\rangle$ | $|1/2, -1/2, 1/2\rangle$ | $|1/2, 1/2, -1/2\rangle$ | $|-1/2, 1/2, 1/2\rangle$ | $|-1/2, -1/2, 1/2\rangle$ | $|-1/2, 1/2, -1/2\rangle$ | $|-1/2, -1/2, -1/2\rangle$ |
|-----------|-------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| $|1/2, 1/2, 1/2\rangle$ | $H_z + H_x - 2H_0$ | 0 | 0 | 0 | 0 | 0 | 0 |
| $|1/2, -1/2, 1/2\rangle$ | 0 | $H_z$ | 0 | $H_x$ | 0 | 0 | 0 |
| $<1/2, -1/2, -1/2|$ | 0 | 0 | $H_z$ | 0 | $H_x$ | 0 | 0 |
| $<1/2, -1/2, -1/2|$ | 0 | 0 | 0 | $H_z - H_x + 2H_0$ | 0 | $H_x$ | $H_x$ | 0 |
| $<1/2, -1/2, -1/2|$ | 0 | $H_x$ | $H_x$ | 0 | $H_z - H_x + 2H_0$ | 0 | 0 | 0 |
| $<1/2, 1/2, -1/2|$ | 0 | 0 | 0 | $H_x$ | 0 | $-H_z$ | 0 | 0 |
| $<1/2, 1/2, -1/2|$ | 0 | 0 | 0 | $H_x$ | 0 | 0 | $-H_z$ | 0 |
| $<1/2, -1/2, -1/2|$ | 0 | 0 | 0 | 0 | 0 | 0 | $-H_z$ | 0 |
with $H_z = \frac{1}{2} g \mu_B B_0$, $H_A = A/2$ and $H_N = \frac{1}{2} g \mu_B B_0$. The spin Hamiltonian may be re-written as

$$\hat{H}_s = g \mu_B B_0 \hat{S}_z + A \left( \hat{S}_+ \hat{i}_z + \frac{1}{2} (\hat{S}_- \hat{i}_z + \hat{S}_+ \hat{i}_z) \right) - g \mu_B B_0 \hat{I}_z$$

(2.56)

with $\hat{I} = \hat{i}_x + \hat{i}_y$. The possible values of the total nuclear spin $I$ are 1 and 0. The spin Hamiltonian can now be represented in the base $|M_S, I, M_I\rangle$, for which the base vectors can be expressed as a linear combination of the base vectors $|M_S, M_I, M_I\rangle$.

$$
\begin{align*}
|M_S, 1, 1\rangle &= |M_S, 1/2, 1/2\rangle \\
|M_S, 1, 0\rangle &= \frac{1}{\sqrt{2}} \left( |M_S, -1/2, 1/2\rangle + |M_S, 1/2, -1/2\rangle \right) \\
|M_S, 1, -1\rangle &= |M_S, -1/2, -1/2\rangle \\
|M_S, 0, 0\rangle &= \frac{1}{\sqrt{2}} \left( |M_S, -1/2, 1/2\rangle - |M_S, 1/2, -1/2\rangle \right)
\end{align*}

(2.57)

From the expression for the spin Hamiltonian (2.55) it is clear that matrix elements between states with different total nuclear spin are zero

$$\langle M_S, I, M_I | \hat{H}_s | M_S', I', M_I' \rangle = \langle M_S, I, M_I | \hat{H}_s | M_S', I, M_I' \rangle \delta (I, I')$$

(2.58)

As a consequence, the submatrices with $I = 0$

<table>
<thead>
<tr>
<th></th>
<th>$I/1/2.0,0&gt;</th>
<th>I/-1/2.0,0&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;1/2,0,0</td>
<td>$ $H_z$</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;-1/2,0,0</td>
<td>$ 0</td>
<td>$-H_z$</td>
</tr>
</tbody>
</table>

and $I = 1$

<table>
<thead>
<tr>
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<th>$I/1/2,1,1&gt;</th>
<th>I/1/2,1,0&gt;</th>
<th>I/1/2,1,-1&gt;</th>
<th>I/-1/2,1,1&gt;</th>
<th>I/-1/2,1,0&gt;</th>
<th>I/-1/2,1,-1&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>$&lt;1/2,1,1</td>
<td>$ $H_z + H_A - 2H_N$</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;1/2,1,0</td>
<td>$ 0</td>
<td>$H_z$</td>
<td>0</td>
<td>$\sqrt{2} H_A$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;1/2,1,-1</td>
<td>$ 0</td>
<td>0</td>
<td>$H_z - H_A + 2H_N$</td>
<td>0</td>
<td>$\sqrt{2} H_A$</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;-1/2,1,1</td>
<td>$ 0</td>
<td>$\sqrt{2} H_A$</td>
<td>0</td>
<td>$-H_z - H_A - 2H_N$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;-1/2,1,0</td>
<td>$ 0</td>
<td>0</td>
<td>$\sqrt{2} H_A$</td>
<td>0</td>
<td>$-H_z$</td>
<td>0</td>
</tr>
<tr>
<td>$&lt;-1/2,1,-1</td>
<td>$ 0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>$-H_z + H_A + 2H_N$</td>
<td>0</td>
</tr>
</tbody>
</table>

can be diagonalised separately. The 2x2 Hamiltonian matrix with $I = 0$ is already diagonal. This two-level sub-system gives rise to just one EPR transition at

$$\hbar \nu = 2H_z = g \mu_B B_0 \quad \Rightarrow \quad B_0 = \frac{\hbar \nu}{g \mu_B}$$

(2.59)

For the 6x6 Hamiltonian matrix with $I = 1$, the first order eigenstates and second order eigenvalues are
\(|\phi_1\rangle = |1/2,1,1\rangle\)
\(|\phi_2\rangle = |1/2,1,0\rangle + \frac{H_A}{\sqrt{2}H_z} | -1/2,1,1\rangle\)
\(|\phi_3\rangle = |1/2,1,-1\rangle + \frac{H_A}{\sqrt{2}H_z} | -1/2,1,0\rangle\)
\(|\phi_4\rangle = | -1/2,1,1\rangle - \frac{H_A}{\sqrt{2}H_z} |1/2,1,1\rangle\)
\(|\phi_5\rangle = | -1/2,1,0\rangle - \frac{H_A}{\sqrt{2}H_z} |1/2,1,-1\rangle\)
\(|\phi_6\rangle = | -1/2,1,-1\rangle\)

\[E_1 = H_z + H_A - 2H_N\]
\[E_2 = H_z + \frac{H_A^2}{H_z}\]
\[E_3 = H_z - H_A + 2H_N + \frac{H_A^2}{H_z}\]
\[E_4 = -H_z - H_A - 2H_N - \frac{H_A^2}{H_z}\]
\[E_5 = -H_z + \frac{H_A^2}{H_z}\]
\[E_6 = -H_z + H_A + 2H_N\]

(2.60)

Three allowed EPR transitions and four allowed NMR transitions take place in this sub-system. The transition frequencies and fields (for EPR transitions) are given in table 2.5. A comparison with the first order calculated spectra in figure 2.14 shows that second order corrections split the central EPR line in the superhyperfine pattern, and split both lines in the ENDOR spectrum. Experimental evidence for the splitting of the central EPR line has, e.g. been observed for the Ag\(^{19}_2\) molecular ion in KCl [ZHI73]. The splittings appear to be inversely proportional to the microwave frequency (or the transition field), as a result of which these second order effects are suppressed when the spectra are recorded at higher microwave frequency bands (Q-band, e.g. instead of X-band). The splittings will only be resolved when they exceed the line width of the individual EPR or ENDOR transitions. Assuming a line width for the EPR transitions of the order of 0.1 mT and for the ENDOR transitions of the order of 0.1 MHz, these second order effects in the EPR and ENDOR spectra become resolved at X-band for \(A/\hbar > 150\) MHz and \(A/\hbar > 40\) MHz, respectively. They will thus be more easily observed in the ENDOR spectrum (as is clear from figure 2.14), which gives also information about the number of equivalent nuclei in this way.

---

**Figure 2.14**: Calculated EPR and ENDOR spectra at 10 GHz for a paramagnetic centre with \(S = 1/2\) \((g = 2)\) interacting with two nuclei with \(I = 1/2\) \((A = 100\) MHz, \(g_I = 0.75)\)
Table 2.5: Transition frequencies and fields for the paramagnetic system described by spin Hamiltonian (2.56) with \( l = 1 \). The \( \phi_n \) eigenfunctions are defined in equation (2.60).

<table>
<thead>
<tr>
<th>Type</th>
<th>Transition frequency ( h\nu_{\text{res}} )</th>
<th>Transition field ( B_{\text{res}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPR</td>
<td>( g_{\mu_B}B_0 + A + \frac{A^2}{2g_{\mu_B}B_0} )</td>
<td>( h\nu_0 ) = ( \frac{A}{g_{\mu_B}} - \frac{A^2}{2g_{\mu_B}h\nu_0} )</td>
</tr>
<tr>
<td></td>
<td>( g_{\mu_B}B_0 + \frac{A^2}{g_{\mu_B}B_0} )</td>
<td>( h\nu_0 ) = ( \frac{A}{g_{\mu_B}} - \frac{A^2}{g_{\mu_B}h\nu_0} )</td>
</tr>
<tr>
<td></td>
<td>( g_{\mu_B}B_0 - A + \frac{A^2}{2g_{\mu_B}B_0} )</td>
<td>( h\nu_0 ) = ( \frac{A}{g_{\mu_B}} - \frac{A^2}{2g_{\mu_B}h\nu_0} )</td>
</tr>
<tr>
<td>NMR</td>
<td>( \frac{A}{2} - g_{n\mu_B}B_0 - \frac{A^2}{2g_{\mu_B}B_0} )</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>( \frac{A}{2} - g_{n\mu_B}B_0 )</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>( \frac{A}{2} + g_{n\mu_B}B_0 )</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>( \frac{A}{2} + g_{n\mu_B}B_0 + \frac{A^2}{2g_{\mu_B}B_0} )</td>
<td>---</td>
</tr>
</tbody>
</table>

2.5.6 Orientation selectivity of ENDOR

In a single crystal, with a symmetry point group \( G \), a paramagnetic defect with symmetry point group \( S \), which is a sub-group of \( G \), can be incorporated in \( h\nu_S \) different, but physically equivalent ways. If an external magnetic field is applied along a certain crystal orientation, these differently oriented defects give rise to EPR absorptions at different magnetic field values \( B_0 \). The defects become magnetically inequivalent. This effect can be easily illustrated for a defect with tetragonal symmetry (e.g. \( D_{4h} \)) and a spin Hamiltonian

\[
\hat{H}_S = \mu_B \vec{B}_0 \cdot \vec{g} \cdot \vec{S}
\]

in a cubic, rock salt type lattice. The defect may be incorporated in the crystal in three physically equivalent ways, as shown in figure 2.15, with the fourfold axis along [100], [010] or [001]. Each of these defect orientations is characterised by a different \( \vec{g} \) tensor, in the crystal reference frame

\[
\vec{g}_{s1} = \begin{pmatrix} g_0 & 0 & 0 \\ 0 & g_0 & 0 \\ 0 & 0 & g_0 \end{pmatrix}, \quad \vec{g}_{s2} = \begin{pmatrix} g_0 & 0 & 0 \\ 0 & g_1 & 0 \\ 0 & 0 & g_0 \end{pmatrix}, \quad \vec{g}_{s3} = \begin{pmatrix} g_0 & 0 & 0 \\ 0 & g_0 & 0 \\ 0 & 0 & g_1 \end{pmatrix}
\]

(2.62)

For an arbitrary orientation of the magnetic field \( \vec{B}_0 = B_0 (l, m, n) \) EPR transitions take place at

\[
B_1 = \frac{h\nu_{\text{MW}}}{\mu_B \sqrt{l^2 g_0^2 + (m^2 + n^2) g_0^2}} \quad B_2 = \frac{h\nu_{\text{MW}}}{\mu_B \sqrt{m^2 g_0^2 + (l^2 + n^2) g_0^2}} \quad B_3 = \frac{h\nu_{\text{MW}}}{\mu_B \sqrt{n^2 g_0^2 + (l^2 + m^2) g_0^2}}
\]

(2.63)
For several orientations of the magnetic field, two of these transition field values may coincide. E.g. for \( \vec{B}_0 \parallel [100] \), \( B_1 \neq B_2 \) = \( B_3 \) and for \( \vec{B}_0 \parallel [110] \), \( B_1 = B_2 \neq B_3 \). If \( \vec{B}_0 \) is parallel to any of the crystal \( \langle 111 \rangle \) directions, \( B_1 = B_2 = B_3 \). If the EPR transition fields for different defect orientations coincide, these orientations are called magnetically equivalent. The angular dependence of the EPR spectrum for the tetragonal defect is shown in figure 2.16a, for rotation of the magnetic field in the \( (001) \) plane from \( [100] \) to \( [010] \). If the reference frame \( x, y, z \) is considered to be fixed to each of the defect orientations (\( z \) along the tetragonal axis), the magnetic field is rotated in the \( yz \) plane of defect orientation \( S_1 \), in the \( yx \) plane of \( S_2 \) and in the \( xy \) plane of \( S_3 \). The angular dependence of the EPR spectrum in figure 2.16a may thus also be regarded as the result of rotating the magnetic field in three perpendicular \( \{100\} \) planes in a reference frame fixed to one defect orientation (e.g. \( S_1 \)). The latter planes will be referred to as \( g \) planes. ENDOR spectra, recorded by saturating the EPR spectrum of one of the physically equivalent but magnetically inequivalent defect orientations, only contain the transitions for this orientation. From the ENDOR viewpoint, magnetically inequivalently oriented defects are regarded as different defects. Their spectra may be recorded separately, if their EPR spectra do not overlap, or may be separated using E1-EPR or double ENDOR, as explained in section 2.5.4. The orientation selectivity of ENDOR in the case of single crystal samples is illustrated in figure 2.16b, in which the angular dependence of the ENDOR spectrum for an interaction with a nucleus with \( I = \frac{1}{2} \) on the axis of the tetragonal defect is shown for the three different defect orientations. We will refer to the angular variation of the ENDOR spectrum of a certain defect orientation as being recorded in a certain \( g \) plane. One should notice that, due to the fourfold symmetry of the defect, the \( zx \) (\( S_1 \)) and the \( yz \) (\( S_2 \)) planes contain the same information. The rotation angle phase shift between both planes is 90°.

The orientation selectivity of ENDOR is even more important in the analysis of paramagnetic defects of polycrystalline materials or powders. In an ideal powder, all single crystal orientations are present with the same probability. The EPR spectrum of a powder is thus the convolution of the EPR spectra for all possible single crystal orientations and hence also for all possible orientations of the magnetic field \( \vec{B}_0 \) with respect to the defect, which is characterised by the polar angles \( \theta \) and \( \phi \)

\[
J_{\text{EPR}}^{\text{powder}} (\vec{B}_0) \approx \int_{0}^{\frac{2\pi}{3}} d\phi \int_{0}^{\pi} d\theta \sin \theta \sum_{\text{single crystal}} (B_0, \theta, \phi)
\]

(2.64)
The powder EPR spectrum of the tetragonal defect with spin Hamiltonian (2.61) is shown in figure 2.17a in non-derivative mode and also in first derivative mode, as it is usually recorded. The latter spectrum allows the determination of the \( g_i \) and the \( g_\perp \) values. The orientation of the principal \( g \) axes with respect to the crystal axes cannot be determined from this spectrum. All angular dependent information is merged into a single spectrum.

For ENDOR the situation is different. If an ENDOR spectrum is recorded at a certain static magnetic field value \( B_0 \) within the EPR powder envelope, only those microcrystal orientations for which the EPR spectrum is saturated contribute to the spectrum. This is generally known as the orientation selection principle and was first introduced by Rist et al. [RIST68]. The contribution of a defect orientation to the ENDOR spectrum recorded at a certain \( B_0 \) value is thus weighed by the intensity of the EPR spectrum of this defect orientation at \( B_0 \):

\[
I_{\text{ENDOR}}(\theta, B_0) \propto \int_0^{2\pi} d\phi \int_0^\tau d\theta \sin\theta I_{\text{ENDOR}}^{\text{single crystal}}(B_0, \theta, \phi) I_{\text{single crystal}}^{\text{ENDOR}}(\theta, B_0, \phi)
\]  

(2.65)

For the tetragonal defect of the example, interacting with one nucleus on its fourfold axis, the single crystal EPR and ENDOR spectra are independent of the azimuth angle \( \phi \). Considering only the defect orientation S3, each \( B_0 \) value corresponds to just one polar angle \( \theta \), because \( B_{\text{res}} = h\nu/g\mu_B \) and

\[
g = \sqrt{g_i^2 \cos^2 \theta + g_\perp^2 \sin^2 \theta}
\]

and thus

\[
\theta = \arccos \frac{g_i^2 - g_\perp^2}{\sqrt{g_i^4 - g_\perp^4}}
\]

(2.66)

Hence, a single crystal-like "angular variation" of the ENDOR spectrum may be obtained by recording spectra at different values of the static magnetic field \( B_0 \) within the powder envelope, as shown in figure 2.17b. Note that the intensity of the powder ENDOR spectrum drastically decreases when the static magnetic field is varied from \( g_i \) (\( \theta = 90^\circ \)) to \( g_\perp \) (\( \theta = 0^\circ \)). For non-axial nuclei or defects with lower than axial symmetry, the variation of the ENDOR spectrum with the magnetic field in general does not resemble the corresponding angular dependence for single crystal samples.
Figure 2.17: (a) Powder EPR spectrum of the paramagnetic centre with spin Hamiltonian (2.61) in non-derivative and first derivative mode. The magnetic field positions at which ENDOR spectra were recorded are indicated with interrupted lines. The corresponding rotation angles $\theta$ were calculated using equation (2.66). (b) ENDOR spectrum as a function of the magnetic field position. The magnification is indicated on each spectrum. The "angular dependence" corresponds to that of defect orientation $S1$. The spin Hamiltonian parameters are identical to those in figure 2.16.
Chapter 3: Magnetic resonance properties of Rh\(^{2+}\) impurities in NaCl and AgCl

3.1. Introduction

Since the late sixties, [RhCl\(_6\)] complexes have been investigated in AgCl single crystals [WILK65]. In the seventies first [RhCl\(_6\)(CN)\(_4\)] [MUNI71] and later also [RhCl\(_6\)] complexes [SHOC75] have been studied in NaCl with EPR. The first ENDOR report on Rh-doped AgCl single crystals appeared in 1988 [OLM88]. Reports on ENDOR results on RhCl\(_6\) complexes in NaCl single crystals were published in 1997 [SPA97, ZDRA97]. The magnetic resonance properties for all these Rh-related defects are very similar. The Rh\(^{2+}\) ion (some species have first erroneously been assigned to Rh\(^0\) [WILK65], but have been reassigned later on [OLM88]) always occupies a substitutional cation position and is octahedrally coordinated by six anions. Due to the Jahn-Teller effect (explained in § 3.2.6) or to the presence of charge compensating neighbouring defects, the octahedral symmetry is lowered to tetragonal. For several species, the EPR spectrum undergoes serious changes as a function of the measuring temperature. At the lowest temperature (typically below 80 K) all these defects are characterised by a (nearly) axial \(\vec{g}\) tensor with \(g_\parallel\) close to the free electron value \(g_e\) and \(g_\perp > g_\parallel\). The EPR spectrum exhibits a resolved superhyperfine structure due to the interaction of the unpaired electron with the two nearest axial anions. The hyperfine interaction with the central \(^{103}\)Rh nucleus is usually not resolved in the EPR spectrum, but can be easily observed in the ENDOR spectrum. The ENDOR spectrum further reveals a strong interaction with the next nearest cation neighbours along the tetragonal axis of the complex.

This chapter is dedicated to the electron magnetic resonance properties of Rh\(^{2+}\) complexes in NaCl and AgCl. In the second section, the electronic ground state of the Rh\(^{2+}\) ion in a distorted octahedral coordination is discussed and its \(\vec{g}\) tensor is calculated in the cases of tetragonal elongation and compression. Special attention is paid to the reported deviations of \(g_\parallel\) from \(g_e\) (\(g_\parallel > g_e\)) and their interpretation. The third section is dedicated to the interaction of the unpaired electron with magnetic nuclei in the system. For the interaction of the unpaired electron with the axial anion ligands, second order perturbation formulae are derived and the EPR and NMR transitions are calculated. The spectra for the weaker interactions with the central \(^{103}\)Rh and the cation neighbours \(^{35}\)Na and \(^{107/109}\)Ag are briefly discussed. The fourth section gives an overview of the rhodium-related centres that have been identified in NaCl and AgCl up to now. The nomenclature used by the various authors which have studied these centres is summarised and the one we will use throughout this work is defined. The way in which the structural models for the centres were deduced from the spectroscopic data is also briefly discussed.
3.2. Electronic ground state and $\tilde{g}$ tensor for Rh$^{2+}$ in tetragonally distorted octahedral coordination

3.2.1. Electronic ground state

Rh$^{2+}$, substitutionally incorporated in NaCl or AgCl, has a 4$d^7$ low spin configuration. In octahedral coordination, this leads to a $(t_{2g}^6e_g^2, 2E_g)$ ground state electron configuration (see figure 2.1), which will here be described as three holes in the $e_g$ shell ($(e_g^3, 2E_g)$ hole configuration). Rather than adopting the double-group formalism for systems with an odd number of electrons (see e.g. [TOWN64]), single-groups will be used to describe the orbital part of the holes’ wave function and their spin will be considered as a separated coordinate. The character table of the single-groups $O_h$ and $D_{4h}$ are given in appendix 1.

Through spin-orbit coupling, the excited states with a hole configuration $e_g^2t_{2g}$ are mixed into the ground state doublet. The allowed terms of the latter configuration may be easily found as follows: $e_g^2$ has the allowed terms $3A_{2g}, 1E_g$ and $1A_1g$ [GRIF61] and $t_{2g}$ has an allowed $2T_{2g}$ term. The allowed terms of $e_g^2t_{2g}$ are found as the direct product of all combinations of terms of $e_g^2$ and $t_{2g}$ as none of these are forbidden by the Pauli exclusion principle. This leads to the following terms:

$$
\begin{align*}
3A_{2g} \otimes 2T_{2g} &= 4T_{1g} \oplus 2T_{1g} \\
1E_g \otimes 2T_{2g} &= 2T_{1g} \oplus 2T_{2g} \\
1A_1g \otimes 2T_{2g} &= 2T_{2g}
\end{align*}
$$

(3.1)

The ground state $e_g^2$ and excited state $e_g^2t_{2g}$ wave functions are given in table 3.1. In this table, the notation $(\phi_0, \phi_1, \phi_2)$ is used for Slater determinants, in which the orbital part is one of the real linear combinations of the $d$ orbitals, compatible with the octahedral symmetry of the complex, and the spin is indicated by $+$ ($m_s = 1/2$) or $-$ ($m_s = -1/2$).

The Coulomb repulsion Hamiltonian $\hat{H}_m$ is not diagonal in this base. Using the matrix elements for a three-holes configuration given by Griffith [GRIF61] and neglecting the influence of $e_g^2t_{2g}$ and $t_{2g}^3$ excited states, the following non-diagonal blocks appear:

| $\hat{H}_m$ | $|\Phi_{2i}\rangle$ | $|\Phi_{3i}\rangle$ |
|------------|-----------------|-----------------|
| $\langle \Phi_{2i} |$ | $21A-34B+17C$ | $-2\sqrt{3}B$ |
| $\langle \Phi_{3i} |$ | $-2\sqrt{3}B$ | $21A-30B+17C$ |
\[
\begin{array}{|c|c|c|}
\hline
| \hat{H}_{\text{int}} | & | \Phi_{x_i} \rangle & | \Phi_{y_j} \rangle \\
\hline
\langle \Phi_{x_i} | & 21A - 30B + 17C & 10B \\
\langle \Phi_{y_j} | & 10B & 21A - 22B + 19C \\
\hline
\end{array}
\]

with \( j = x, y \) or \( z \). \( A, B \) and \( C \) represent the Racah parameters of the ion, defined by [GRIF61]

\[
A = F_0 - 49F_4 \\
B = F_2 - 5F_4 \\
C = 35F_4 
\]

The definition of the two-electron integrals \( F_k \) can e.g. be found in [BOES94a] or [GRIF61].

Diagonalisation of these blocks leads to the following eigenvalues and eigenfunctions [GILL96]

\[
\Phi_{x_i} = \Phi_{y_j} \\
\Phi_{z_j} = \frac{\sqrt{3}}{2} \Phi_{z_j} + \frac{1}{2} \Phi_{y_j} \\
\Phi_{3_j} = -\frac{1}{2} \Phi_{z_j} + \frac{\sqrt{3}}{2} \Phi_{3_j} \\
\Phi_{4_j} = \cos \alpha \Phi_{y_j} + \sin \alpha \Phi_{x_j} \\
\Phi_{5_j} = -\sin \alpha \Phi_{y_j} + \cos \alpha \Phi_{x_j} \\
\tan \alpha = \frac{\sqrt{(4B + C)^2 + (10B)^2} - (4B + C)}{10B}
\]

Using the Racah parameters of the free \( \text{Rh}^{2+} \) ion \((B = 667 \text{ cm}^{-1} \text{ and } C = 2313 \text{ cm}^{-1} \) [GRIF61]), the following sequence of the term energies is found

\[
E(\Phi_1) < E(\Phi_2) < E(\Phi_4) < E(\Phi_3) < E(\Phi_5) \tag{3.4}
\]

The separation between the \( \Phi_{2_j} \) and \( \Phi_{4_j} \) levels is very small: it only amounts to a few hundred wave numbers \((660 \text{ cm}^{-1}, \text{ for the free } \text{Rh}^{2+} \text{ ion})\). The energy level scheme for the ground state and excited state terms is shown in figure 3.1.

If the spin-orbit coupling Hamiltonian

\[
\hat{H}_{\text{SO}} = \zeta_{4d}^n \sum_{i=1}^{3} \langle \hat{\tau}_i \cdot \hat{\tau}_i \rangle 
\]

with \( \zeta_{4d}^n \) the spin-orbit coupling constant for a \( 4d \) hole, is now considered as perturbation the admixing coefficients of the excited state terms can be calculated to first order to be

\[
\frac{\langle \Phi_{5} | \hat{H}_{\text{SO}} | \Phi_{g} \rangle}{E(\Phi_{g}) - E(\Phi_{5})} \tag{3.6}
\]

with \( \Phi_{g} \) and \( \Phi_{e} \) the wave function of the ground state and the excited state, respectively, and \( E(\Phi_{g}) \) the term energy of the wave function \( \Phi_{g} \). As the orbital part of \( \hat{H}_{\text{SO}} \) transforms as \( T_{1g} \) and

\[
E_{g} \otimes T_{1g} = T_{1g} \oplus T_{2g} \tag{3.7}
\]
Table 3.1: Eigenfunctions of the allowed terms of the $e_g$ ground state and the $e_g^2 t_{2g}$ excited state configurations for a system with three unpaired holes in perfect (O₉) and tetragonally distorted (D₄h) octahedral coordination

<table>
<thead>
<tr>
<th>configuration</th>
<th>O₉</th>
<th>D₄h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_g^2$</td>
<td>$^2E_g$</td>
<td>$^2A_g$</td>
</tr>
<tr>
<td>$\Phi_{e_g, 1/2}$</td>
<td>$\left{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$\Phi_{e_g, -1/2}$</td>
<td>$\left{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$^2B_g$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\Phi_{g, 1/2}$</td>
<td>$\left{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right}$</td>
<td></td>
</tr>
<tr>
<td>$\Phi_{g, -1/2}$</td>
<td>$\left{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$e_g^2 t_{2g}$</th>
<th>$^4T_g$</th>
<th>$^4A_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_{e_g^2 t_{2g}, 3/2}$</td>
<td>$\left{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right}$</td>
<td></td>
</tr>
</tbody>
</table>
| $\Phi_{e_g^2 t_{2g}, 1/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}

| $^4A_g$ |
|-----------------|-----------------|
| $\Phi_{e_g^2 t_{2g}, -1/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}

| $^4E_g$ |
|-----------------|-----------------|
| $\Phi_{e_g^2 t_{2g}, -3/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}

<table>
<thead>
<tr>
<th>$^2T_g$</th>
<th>$^2E_g$</th>
</tr>
</thead>
</table>
| $\Phi_{e_g^2 t_{2g}, 1/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}

| $\Phi_{e_g^2 t_{2g}, -1/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}

| $\Phi_{e_g^2 t_{2g}, 3/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}

| $\Phi_{e_g^2 t_{2g}, -3/2}$ | $\left\{ d_{x^2-y^2}, d_{z^2}, d_{x^2-z^2} \right\}$ |}
### Table 3.1: continued

| configuration | $O_h$ | $|\Phi_x, M_s\rangle$ | $D_{4h}$ |
|---------------|-------|---------------------|----------|
| $e_g^2 t_{2g}$ | | | |
| $3\ A_{2g} \otimes 2\ T_{2g}$ | $^2 T_{1g}$ | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{6}} \left[ 2\{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 A_{2g}$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{6}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} + \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - 2\{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 A_{2g}$ |
| $e_g^2 t_{2g}$ | | | |
| $1\ E_g \otimes 2\ T_{2g}$ | $^2 T_{1g}$ | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 E_g$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 E_g$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 E_g$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 E_g$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 E_g$ |
| $e_g^2 t_{2g}$ | | | |
| $1\ A_g \otimes 2\ T_{2g}$ | $^2 T_{2g}$ | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 B_{2g}$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 B_{2g}$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 B_{2g}$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 B_{2g}$ |
| | | $|\Phi_{x, \downarrow/2}\rangle = \frac{1}{\sqrt{2}} \left[ \{d^+_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} - \{d_{x, \downarrow}, d_{y, \downarrow}, d_{z, \downarrow}\} \right]$ | $^2 B_{2g}$ |
all excited state terms of the $e^{2}_{g}t_{2g}$ are mixed into the ground state $^{2}E_{g}$.

Figure 3.1: Ground and first excited states of a $4d^{6}$ hole configuration of Rh$^{2+}$ in perfect (a) and tetragonally distorted (b) octahedral coordination. The energy separations are not drawn to scale.

In $D_{4h}$ symmetry, the doublet $^{2}E_{g}$ splits into a $^{2}A_{1g}$ and a $^{2}B_{1g}$ state and each of the excited orbital triplet states splits into an orbital doublet and singlet

$$T_{1g} = E_{g} \oplus A_{2g}$$
$$T_{2g} = E_{g} \oplus B_{2g}$$

(3.8)

The splitting in a tetragonal crystal field is also depicted in figure 3.1. It is assumed to be much smaller than the separation between the terms. The spin-orbit coupling Hamiltonian may also be written as the sum of a part transforming as $A_{2g}$ and a part transforming as $E_{g}$:

$$T_{1g} = \sum_{i=1}^{3} \frac{e}{\hbar} \sum_{j=1}^{3} \vec{l}_{i} \cdot \vec{S}_{j} + \sum_{i=1}^{3} \left( i_{x} \vec{S}_{x} + i_{y} \vec{S}_{y} \right)$$

(3.9)

In tetragonal symmetry, low spin $d^{7}$ ions may have either a $^{2}A_{1g}$ or a $^{2}B_{1g}$ ground state. In either case, the paramagnetic centre has an effective spin $S = 1/2$. In the following, the $\vec{g}$ tensor for both ground states will be calculated.

3.2.2. $\vec{g}$ tensor in the $^{2}A_{1g}$ ground state

The $^{2}A_{1g}$ ground state, which occurs for elongated complexes, will first be considered. In order to calculate the $\vec{g}$ tensor in this case, the admixing coefficients of the excited states into the ground state
doublet should first be calculated with equation (3.6). As \(B_{s2}\) does not appear in the reduction of \((A_{s2} \otimes E_g) \otimes A_g\), the matrix elements \(\langle \Phi_{s2} M_g | \hat{H}_{SO} | \Phi_0 M_0 \rangle = \langle \Phi_{s2} M_g | \hat{H}_{SO} | \Phi_0 M_0 \rangle = 0\). In order to evaluate the other matrix elements, one has to calculate \(\hat{H}_{SO} | \Phi_0, \frac{1}{2} \rangle\) and \(\hat{H}_{SO} | \Phi_0, -\frac{1}{2} \rangle\). Considering equation (3.5) and making use of the known actions of the orbital and spin momentum operators (see appendix 2), one can calculate, e.g. that

\[
\begin{align*}
(i \hat{t}_z \hat{s}_z + i \hat{t}_x \hat{s}_x + i \hat{t}_y \hat{s}_y) & \left( d_{\alpha' \alpha''}^+ d_{x' y'}^- d_{x'' y''}^- \right) \\
= i \left[ d_{\alpha' y'}^+ d_{x' \alpha''}^- d_{x'' y''}^- \right] + 0 + (i) \left[ d_{\alpha' x'}^+ d_{x' \alpha''}^- d_{y'' y''}^- \right] \\
= (i) \left[ d_{\alpha' x'}^+ d_{x' \alpha''}^- d_{y'' y''}^- \right] - i \left[ d_{\alpha' y'}^+ d_{x' \alpha''}^- d_{y'' y''}^- \right] \\
= -\left[ i \frac{4}{3} | \Phi_{s2}, \frac{1}{2} \rangle - \frac{2}{\sqrt{3}} | \Phi_0, \frac{1}{2} \rangle \right] \tag{3.10}
\end{align*}
\]

leading to the matrix elements

\[
\langle \Phi_{s2}, \frac{1}{2} | \hat{H}_{SO} | \Phi_0, \frac{1}{2} \rangle = -\frac{4}{\sqrt{3}} \zeta_4, \quad \langle \Phi_{s2}, \frac{1}{2} | \hat{H}_{SO} | \Phi_0, -\frac{1}{2} \rangle = 0, \quad \langle \Phi_{s2}, \frac{1}{2} | \hat{H}_{SO} | \Phi_0, 1/2 \rangle = i \frac{2}{\sqrt{3}} \zeta_4 \tag{3.11}
\]

The matrix elements with the \(| \Phi_{s \alpha'} M_{\alpha'} \rangle\) and the \(| \Phi_{s \alpha'} M_{\alpha'} \rangle\) states \((\rho = 1, 2, \ldots, 5)\) may be found by calculating \(\left( i \hat{t}_x \hat{s}_x + i \hat{t}_z \hat{s}_z + i \hat{t}_y \hat{s}_y \right) \left( d_{\alpha' \alpha''}^+ d_{x' \alpha''}^+ d_{x'' \alpha''}^- \right)\) and \(\left( i \hat{t}_y \hat{s}_y + i \hat{t}_z \hat{s}_z + i \hat{t}_x \hat{s}_x \right) \left( d_{\alpha' \alpha''}^+ d_{x' \alpha''}^+ d_{x'' \alpha''}^- \right)\), respectively. Correct to first order in \(\frac{\zeta_4}{\Delta_x}\) the ground state doublet is given by

\[
\begin{align*}
| + \rangle &= | \Phi_0, 1/2 \rangle + i \zeta_4 \left[ \frac{2}{\sqrt{3} \Delta_{1z}} | \Phi_{1z}, \frac{1}{2} \rangle - \frac{\sqrt{2}}{\sqrt{3} \Delta_{3z}} | \Phi_{3z}, \frac{1}{2} \rangle \right] \\
\quad &+ \frac{i \zeta_4}{2} \left[ \frac{1}{\Delta_{1y}} | \Phi_{1y}, \frac{3}{2} \rangle - \frac{\sqrt{3} (\cos \alpha + \sin \alpha)}{\sqrt{2} \Delta_{4y}} | \Phi_{4y}, -\frac{1}{2} \rangle - \frac{\sqrt{3} (\cos \alpha - \sin \alpha)}{\sqrt{2} \Delta_{5y}} | \Phi_{5y}, -\frac{1}{2} \rangle \right] \\
- \frac{i \zeta_4}{2} \left[ \frac{1}{\Delta_{1y}} | \Phi_{1y}, -\frac{1}{2} \rangle - \frac{\sqrt{2}}{\sqrt{3} \Delta_{3y}} | \Phi_{3y}, -\frac{1}{2} \rangle \right] \\
+ \frac{\zeta_4}{2} \left[ \frac{1}{\Delta_{1y}} | \Phi_{1y}, \frac{3}{2} \rangle - \frac{\sqrt{3} (\cos \alpha + \sin \alpha)}{\sqrt{2} \Delta_{4y}} | \Phi_{4y}, -\frac{1}{2} \rangle - \frac{\sqrt{3} (\cos \alpha - \sin \alpha)}{\sqrt{2} \Delta_{5y}} | \Phi_{5y}, -\frac{1}{2} \rangle \right] \\
- \frac{\zeta_4}{2} \left[ \frac{1}{\Delta_{1y}} | \Phi_{1y}, -\frac{1}{2} \rangle - \frac{\sqrt{2}}{\sqrt{3} \Delta_{3y}} | \Phi_{3y}, -\frac{1}{2} \rangle \right] \tag{3.12}
\end{align*}
\]
$$ | - \rangle = | \Phi_0, -1/2 \rangle + i \zeta_{4d} \left[ \frac{2}{\sqrt{3} \Delta_{1z}} | \Phi_{1z}, -1/2 \rangle + \frac{\sqrt{2}}{\sqrt{3} \Delta_{3z}} | \Phi_{3z}, -1/2 \rangle \right]$$

$$ - \frac{i \zeta_{4d}^*}{2} \left[ \frac{1}{\Delta_{1x}} | \Phi_{1x}, -3/2 \rangle + \sqrt{3} \left( \cos \alpha + \sin \alpha \right) | \Phi_{4x}, 1/2 \rangle + \frac{\sqrt{3} \left( \cos \alpha - \sin \alpha \right)}{\sqrt{2} \Delta_{5x}} | \Phi_{5x}, 1/2 \rangle \right]$$

$$ + \frac{i \zeta_{4d}^*}{2} \left[ \frac{1}{\Delta_{1y}} | \Phi_{1y}, 1/2 \rangle + \frac{\sqrt{2}}{\sqrt{3} \Delta_{3y}} | \Phi_{3y}, 1/2 \rangle \right]$$

$$ + \frac{\zeta_{4d}^*}{2} \left[ \frac{1}{\Delta_{1x}} | \Phi_{1x}, -3/2 \rangle + \sqrt{3} \left( \cos \alpha + \sin \alpha \right) | \Phi_{4x}, 1/2 \rangle + \frac{\sqrt{3} \left( \cos \alpha - \sin \alpha \right)}{\sqrt{2} \Delta_{5x}} | \Phi_{5x}, 1/2 \rangle \right]$$

$$ - \frac{\zeta_{4d}^*}{2} \left[ \frac{1}{\sqrt{3} \Delta_{3y}} | \Phi_{1y}, 1/2 \rangle + \frac{\sqrt{2}}{\sqrt{3} \Delta_{3y}} | \Phi_{3y}, 1/2 \rangle \right]$$

The $\tilde{g}$ tensor, which has tetragonal symmetry (see Table 2.1), is then calculated by evaluating the electronic Zeeman Hamiltonian (2.7) in this spin doublet. $g_{||}$, e.g., is calculated from the identity

$$ \langle \pm | \hat{L}_z + g_e \hat{S}_z | \pm \rangle = - \langle - | \hat{L}_z + g_e \hat{S}_z | - \rangle = \frac{1}{2} g_{||} $$

(3.13)

To first order, its value equals

$$ g_{||} = 2 \langle + | \hat{L}_z + g_e \hat{S}_z | + \rangle $$

$$ = g_e + 4 \langle + | \hat{L}_z | \Phi_0, 1/2 \rangle $$

$$ = g_e + 8 \sqrt{2} i \langle + | \hat{S}_z | 1/2 \rangle $$

$$ = g_e $$

(3.14)

as

$$ \hat{L}_z | \Phi_0, 1/2 \rangle = \sum_{i=1}^{3} i \left( \hat{d}_{x}^{+} \hat{d}_{x}^{-} + \hat{d}_{y}^{+} \hat{d}_{y}^{-} \right) $$

$$ = 2 \left( \left( \hat{d}_{x}^{+} \hat{d}_{x}^{-} \right) - \left( \hat{d}_{y}^{+} \hat{d}_{y}^{-} \right) \right) $$

$$ = 2 \sqrt{2} | \Phi_0, 1/2 \rangle $$

(3.15)

In the same way, $g_{\perp}$ can be calculated from the matrix elements

$$ \langle - | \hat{L}_z + g_e \hat{S}_z | + \rangle = \langle - | \hat{L}_z + g_e \hat{S}_z | + \rangle = \frac{1}{2} g_{\perp} $$

(3.16)

resulting in

$$ g_{\perp} = g_e - 3 \zeta_{4d}^* \left( \frac{1 + \sin 2 \alpha}{\Delta_{4xy}} + \frac{1 - \sin 2 \alpha}{\Delta_{5xy}} \right) $$

(3.17)

Concerning these results for the $g$ values, the following remarks should be made:

1. Neglecting the off-diagonal matrix elements of $\hat{H}_{Tz}$, one finds the $g$ values

$$ g_{||} = g_e - 4 \zeta_{4d}^* \left( \frac{1}{\Delta_{3z}} - \frac{1}{\Delta_{2z}} \right) $$

$$ g_{\perp} = g_e - 3 \zeta_{4d}^* \left( \frac{3}{\Delta_{4xy}} + \frac{3}{\Delta_{5xy}} + \frac{1}{\Delta_{3z}} - \frac{1}{\Delta_{2z}} \right) $$

(3.18)
\( \Delta \) now indicates the energy difference between the levels \( \Phi_0 \) and \( \Phi_x \). These results were obtained by Parker and published by Pilbrow et al. [PILB73]. The approximation used by these authors may only be justified if the non-cubic crystal field splittings become comparable to or larger than the Coulomb repulsion splitting between the terms of the excited state configuration. The formulae (3.18) predict a deviation of \( g_\parallel \) from the free electron value \( g_e \) which may be either positive or negative, dependent on the ordering of the energy levels. The discrepancy with the expressions given by Townsend [TOWN64] is most probably due to an error in the sign of the \( g_\parallel \) shift by the latter author. In the perturbation scheme used here, which is relevant for low spin \( d \) ions in a nearly octahedral crystal field, no first order \( g_\parallel \) shift is found.

2. In the literature, one usually works with the electron spin orbit coupling constant \( C_{54d}^s = -C_{54d}^p \).

3. Using the free ion values of the Racah parameters for \( \text{Rh}^{2+} \), one finds
   \[
   \tan \alpha = -0.5, \quad \sin 2\alpha = -0.8
   \]
   \[(3.19)\]
   The main contribution to the \( g_\perp \) shift thus arises from the admixture of \( \Phi_{5x} \) and \( \Phi_{5y} \) into the ground state level. These levels have a predominant \( d_{x^2-r^2} d_{yz} \) and \( d_{x^2-y^2} d_{zx} \) character, respectively. In general, the coupling between the \( \Phi_0 \) and the \( \Phi_{4j} \) or \( \Phi_{5j} \) levels corresponds to a virtual excitation of the unpaired electron from a \( d_{x^2-r^2} (a_{1g}) \) to a \( d_{yz} \) or \( d_{zx} (e_g) \) orbital.

\[\text{Figure 3.2 : Splitting of the d levels in an octahedral, tetragonal and orthorhombic crystal field}\]

Neglecting the energy difference between the \( \Phi_{4j} \) and \( \Phi_{5j} \) levels or taking \( \sin 2\alpha = -1 \) leads to the expressions for the \( g \) values of low spin elongated \( d \) ions, often found in the literature (see e.g. [VERC98a], the original theory is due to Griffith [GRIF58])
   \[
   g_\parallel = g_e
   \]
   \[
   g_\perp = g_e + \frac{6C_{54d}^e}{\delta_{11}}
   \]
   \[(3.20)\]
   in which \( \delta_{11} \) is associated with the energy difference between the one-electron \( a_{1g} \) and \( e_g \) states (see figure 3.2). The expressions in (3.20) are formally identical to the ones obtained for a \( d^1 \) configuration
in which the electron occupies a \( d_{x^2-r^2} \) orbital, except for the sign of the \( g \) shifts. Hence, this approach will be referred to as the one-electron approximation.

3.2.3. \( \bar{g} \) tensor in the \( ^2B_1g \) ground state

Tetragonally compressed complexes have a \( ^2B_1g \) ground state. As \( A_{eq} \) does not appear in the reduction of \( (A_{eq} \otimes E_g) \otimes B_{1g} \), the matrix elements \( \langle \Phi_{\rho} | \hat{H}_{SO} | \Phi'_{\rho'} \rangle (\rho = 1, 2, 3) \) all vanish. All other levels contribute to the ground state doublet

\[
|+\rangle = \Phi_0, 1/2 \rangle + \frac{i_{5d}^h}{\sqrt{2}} \left[ \frac{\cos \alpha \sin \alpha}{\Delta'_{4z}} |\Phi_{4z}, 1/2 \rangle - \frac{\cos \alpha + \sin \alpha}{\Delta'_{5z}} |\Phi_{5z}, 1/2 \rangle \right] \\
\quad + \frac{i_{5d}^h}{2} \left[ \frac{\sqrt{3}}{\Delta'_{1xy}} |\Phi_{1xy}, 3/2 \rangle - \frac{\cos \alpha \sin \alpha}{\sqrt{2} \Delta'_{4xy}} |\Phi_{4xy}, 1/2 \rangle - \frac{\cos \alpha + \sin \alpha}{\sqrt{2} \Delta'_{5xy}} |\Phi_{5xy}, 1/2 \rangle \right] \\
\quad - \frac{i_{5d}^h}{2} \left[ \frac{1}{\Delta'_{1xy}} |\Phi_{1xy}, -1/2 \rangle + \frac{\sqrt{3}}{2 \Delta'_{2xy}} |\Phi_{2xy}, 1/2 \rangle + \frac{1}{\sqrt{2} \Delta'_{3xy}} |\Phi_{3xy}, 1/2 \rangle \right] \\
\quad - \frac{c_{5d}^h}{2} \left[ \frac{\sqrt{3}}{\Delta'_{4xy}} |\Phi_{4xy}, 3/2 \rangle - \frac{\cos \alpha \sin \alpha}{\sqrt{2} \Delta'_{5xy}} |\Phi_{5xy}, -1/2 \rangle \right] \\
\quad - \frac{c_{5d}^h}{2} \left[ \frac{1}{\Delta'_{1xy}} |\Phi_{1xy}, -1/2 \rangle + \frac{\sqrt{3}}{2 \Delta'_{2xy}} |\Phi_{2xy}, -1/2 \rangle + \frac{1}{\sqrt{2} \Delta'_{3xy}} |\Phi_{3xy}, -1/2 \rangle \right] \tag{3.21}
\]

\[
|-\rangle = \Phi_0, -1/2 \rangle - \frac{i_{5d}^h}{\sqrt{2}} \left[ \frac{\cos \alpha \sin \alpha}{\Delta'_{4z}} |\Phi_{4z}, -1/2 \rangle - \frac{\cos \alpha + \sin \alpha}{\Delta'_{5z}} |\Phi_{5z}, -1/2 \rangle \right] \\
\quad - \frac{i_{5d}^h}{2} \left[ \frac{\sqrt{3}}{\Delta'_{1xy}} |\Phi_{1xy}, 3/2 \rangle + \frac{\cos \alpha \sin \alpha}{\sqrt{2} \Delta'_{4xy}} |\Phi_{4xy}, 1/2 \rangle - \frac{\cos \alpha + \sin \alpha}{\sqrt{2} \Delta'_{5xy}} |\Phi_{5xy}, 1/2 \rangle \right] \\
\quad + \frac{i_{5d}^h}{2} \left[ \frac{1}{\Delta'_{1xy}} |\Phi_{1xy}, -1/2 \rangle - \frac{\sqrt{3}}{2 \Delta'_{2xy}} |\Phi_{2xy}, 1/2 \rangle - \frac{1}{\sqrt{2} \Delta'_{3xy}} |\Phi_{3xy}, 1/2 \rangle \right] \\
\quad - \frac{c_{5d}^h}{2} \left[ \frac{\sqrt{3}}{\Delta'_{4xy}} |\Phi_{4xy}, 3/2 \rangle + \frac{\cos \alpha \sin \alpha}{\sqrt{2} \Delta'_{5xy}} |\Phi_{5xy}, -1/2 \rangle \right] \\
\quad - \frac{c_{5d}^h}{2} \left[ \frac{1}{\Delta'_{1xy}} |\Phi_{1xy}, -1/2 \rangle - \frac{\sqrt{3}}{2 \Delta'_{2xy}} |\Phi_{2xy}, -1/2 \rangle - \frac{1}{\sqrt{2} \Delta'_{3xy}} |\Phi_{3xy}, -1/2 \rangle \right] \tag{3.21}
\]

which leads to the principal \( g \) values

\[
g_{ii} = g_e - 4_{5d}^h \left( \frac{1 - \sin 2\alpha}{\Delta'_{4z}} + \frac{1 + \sin 2\alpha}{\Delta'_{5z}} \right) \tag{3.22}
\]

\[
g_{ll} = g_e - 4_{5d}^h \left( \frac{1 - \sin 2\alpha}{\Delta'_{4xy}} + \frac{1 + \sin 2\alpha}{\Delta'_{5xy}} \right) \tag{3.23}
\]

Using the one-electron approximation, the \( g \) values are usually calculated as

\[
g_i = g_e + \frac{8c_{5d}^h}{\delta_{2i}}
\]

\[
g_l = g_e + \frac{2c_{5d}^h}{\delta_{2l}}
\]
in which \( \delta_{3l} \) is associated with the energy difference between the \( d_{xy} \) and the \( d_{x^2-y^2} \) levels, and \( \delta_{4l} \) with the energy difference between the degenerate \( d_{yz} \) and \( d_{zx} \) levels and the \( d_{x^2-y^2} \) level (see figure 3.2 in tetragonal distortion).

If the off-diagonal matrix elements of \( \hat{H}_{\text{el}} \) are neglected, one finds

\[
\begin{align*}
g_{\perp} &= g_e - 4\hbar \left( \frac{1}{\Delta'_{4x}} + \frac{1}{\Delta'_{5z}} \right) \\
g_{\parallel} &= g_e - \frac{\hbar}{2} \left( \frac{1}{\Delta'_{4xy}} + \frac{1}{\Delta'_{5y}} - \frac{3}{\Delta'_{2xy}} - \frac{3}{\Delta'_{3y}} \right)
\end{align*}
\]

as reported by Townsend [TOWN64].

3.2.4. Deviations from \( D_{4h} \)-symmetry

In case that the \( D_{4h} \)-symmetry of the complex is disturbed by, e.g., the presence of a cation vacancy in the equatorial plane, the \( d_{yz} \) and \( d_{zx} \) levels are no longer degenerate and the \( \tilde{g} \) tensor has orthorhombic (or lower) symmetry with (one-electron approximation)

\[
\begin{align*}
\tilde{2}A_{1g} & \quad \begin{cases} 
x = g_e + \frac{6\hbar}{\delta_{1x}} \\
y = g_e + \frac{6\hbar}{\delta_{1y}} \\
z = g_e 
\end{cases} \\
\tilde{2}B_{1g} & \quad \begin{cases} 
x = g_e + \frac{2\hbar}{\delta_{1x}} \\
y = g_e + \frac{2\hbar}{\delta_{1y}} \\
z = g_e + \frac{8\hbar}{\delta_{1z}} 
\end{cases}
\end{align*}
\]

The crystal field splitting parameters \( \delta_{k} \) are explained in figure 3.2 (case of orthorhombic distortion). The knowledge of the free ion spin-orbit coupling constant (1220 cm\(^{-1}\) for Rh\(^{2+}\) [MABB92]) and of the crystal field splittings \( \Delta_{k} \) or \( \delta_{k} \), e.g. from optical absorption measurements, should allow an accurate (to first order) calculation of the \( \tilde{g} \) tensor. The low temperature magnetic resonance properties of Rh\(^{2+}\) centres in NaCl and AgCl are consistent with a \( \tilde{2}A_{1g} \) ground state, which implies that the complexes are elongated.

3.2.5. Corrections due to delocalisation of the unpaired electron to the ligands

Due to overlap and covalency, the unpaired electron wave function (in the one-electron approximation, or the wave function of the three holes in a more rigorous treatment) is not purely composed of metal orbitals, but also contains contributions from the ligands. The transformation properties of the wave functions should, however, be preserved as a result of which the metal orbitals only mix with those linear combinations of the ligand orbitals which transform in the same way under the operations of the point group of the transition metal complex. The transformation properties of the various metal and ligand orbitals in \( O_{h} \) and \( D_{4h} \) symmetry are listed in appendix 1. The \( \tilde{2}A_{1g} \) ground state of tetragonally elongated \( d^{7} \) complexes may be written as
\[
(1 - \beta^2 - \gamma^2) d_{32,41} - \frac{\beta}{\sqrt{2}} \left[ \sqrt{1-\mu^2} (s_5 + s_6) + \mu (-p_{x5} + p_{y6}) \right] \\
- \frac{\gamma}{2} \left[ \sqrt{1-\nu^2} (s_1 + s_2 + s_3 + s_4) + \nu (-p_{x1} + p_{y2} + p_{x3} + p_{y4}) \right]
\]

(3.26)

with \( \frac{\beta^2}{2} \) and \( \frac{\gamma^2}{4} \) the spin densities on the axial and equatorial ligands, respectively, and \( \mu^2 \) and \( \nu^2 \) the degrees of hybridisation of the axial and equatorial ligand orbitals [MORE77]. Similarly, the \(^2B_{1g}\) ground state of tetragonally compressed complexes may be expressed as

\[
\sqrt{1-\varepsilon^2} d_{32,41} - \frac{\varepsilon}{2} \left[ \sqrt{1-\lambda^2} (s_1 - s_2 + s_3 - s_4) + \lambda (-p_{x1} + p_{y2} + p_{x3} - p_{y4}) \right]
\]

(3.27)

with \( \frac{\varepsilon^2}{4} \) the spin density on the equatorial ligands and \( \lambda^2 \) the degree of hybridisation of their orbitals.

In order to calculate the \( \vec{g} \) tensor for such transition metal complexes, first order corrections to the ground state due to metal and ligand spin-orbit coupling should be calculated and the electronic Zeeman Hamiltonian should be evaluated in the corrected spin doublet. This is usually dealt with in a phenomenological way by introducing an orbital reduction factor \( k \), which is related to the spin density on the metal orbitals [OWEN68]. The principal \( \vec{g} \) tensor components for the \(^2A_{1g}\) and \(^2B_{1g}\) ground states may then be written as (one electron approximation, tetragonal distortion)

\[
{^2A_{1g}} \begin{cases} 
    g_{_1} = g_e \\
    g_{_2} = g_e + \frac{6k e_0}{\delta_{1l}}
\end{cases}, \quad {^2B_{1g}} \begin{cases} 
    g_{_1} = g_e + \frac{8k e_0}{\delta_{2l}} \\
    g_{_2} = g_e + \frac{2k e_0}{\delta_{2l}}
\end{cases}
\]

(3.28)

A further consequence of the covalency and metal-ligand wave function overlap will be discussed in the next subsection.

3.2.6. The positive \( g \) shift in the \(^2A_{1g}\) ground state

The calculation of the \( \vec{g} \) tensor in § 3.2.2 or § 3.2.3 has shown that the important deviations from \( g = g_e \) arise from contributions of the \( \Phi_{42} \) and \( \Phi_{52} \) excited states to the \( \Phi_0 \) and \( \Phi_0' \) ground states. As \( \Phi_{42} \) and \( \Phi_{52} \) do not contribute to \( \Phi_0 \), the first order deviation of \( g_1 \) or \( g_2 \) from \( g_e \) in the \(^2A_{1g}\) ground state is zero. Higher order corrections to the \( g \) values predict a negative contribution to \( g_1 \). In the one-electron approximation e.g., this second order contribution can be calculated to be [ARAM83]

\[
g_1 - g_e = -3 \left( \frac{e_0}{\delta_{1l}} \right)^2
\]

(3.29)

Experimentally observed \( g_1 \) shifts are, however, often positive for \([\text{RhCl}_6]^{2+}\) complexes and similar hydrated species in AgCl and NaCl. Also for \( d^7 \) transition ions, which have similar \( g \) values in the case of tetragonally compressed six-fold coordination [ABRA70], a similar effect has been observed. In the literature, this anomaly has been explained in two different ways [PILB64, MORE77, ARAM83].

A first explanation is in principle only valid for complexes which originally had exact octahedral symmetry. For such complexes the main cause of the \( \vec{g} \) tensor anisotropy is the Jahn-Teller effect. The
Jahn-Teller theorem states that for a molecule or complex in a solid with an orbitally degenerate ground state there exists a distortion which lifts the orbital degeneracy and lowers the energy and the symmetry [STON75]. The energy difference between the high symmetry degenerate state and the distorted state of lowest energy is defined as the Jahn-Teller coupling $E_{JT}$. If the Jahn-Teller coupling is much larger than the thermal energy $kT$, the molecule or complex undergoes a static distortion (static Jahn-Teller effect). However, for sufficiently high temperatures the distortion axes of the molecule or complex may hop between the different physically equivalent directions in the crystal. As a result, the original high symmetry of the molecule or complex is, on average, restored. For octahedral $d^3$ and $d^6$ complexes, the orbital degeneracy of the $^2E_g$ ground state is lifted by a tetragonal distortion (elongation or compression). Due to the original degeneracy of the $\Phi_0$ and $\Phi_1^0$ states, the electronic ground state at low temperature may be a vibronic mixture of these two states

$$\Phi = \eta \Phi_0 + \sqrt{1 - \eta^2} \Phi_1^0 \quad (3.30)$$

The principal $g$ values may in this case be calculated (in the one-electron approximation) to be [ABRA70]

$$g_{ii} = \eta^2 g_s + (1 - \eta^2) \left( g_s + \frac{8c_{dd}}{\delta_{ii}} \right) = g_s + (1 - \eta^2) \frac{8c_{dd}}{\delta_0} \quad (3.31)$$

$$g_\perp = \eta^2 \left( g_s + \frac{6c_{dd}}{\delta_{11}} \right) + (1 - \eta^2) \left( g_s + \frac{2c_{dd}}{\delta_{22}} \right) = g_s + (2 + 4\eta^2) \frac{c_{dd}}{\delta_0}$$

assuming that the splitting due to the tetragonal distortion is much smaller than the octahedral crystal field splitting. This mechanism has been used to explain the $g_{ii}$ shift of Cu$^{2+}$ ions ($3d^9$ configuration) in NH$_4$Cl and NH$_4$Br single crystals (PILB64) and later also for [Rhb$_{9a}$] complexes in AgBr [EACH74] and [Rhb$_{9a}$] complexes in NaCl [VERC98a].

An alternative explanation for $d^6$ [MORE77] and $d^9$ ions [ARAM83] has been presented, which takes into account the overlap and covalency effects in the MX$_n$ complexes ($M$ = transition metal, $X$ = anion ligands and $n$ = coordination number). As the main deviations of $g_{ii}$ from $g_s$ arise from virtual excitations from the $^2A_{1g}$ ground state to $^2A_{2g}$ excited states (the orbital part of $\hat{H}_{SO}$ and $\hat{H}_{EZ}$, both involving an operator $\hat{L}_z$, transform as $^2A_{2g}l$) and none of the transition metal orbitals transforms in this way, crystal field theory predicts these deviations to be negative and very small (higher order effects). In a molecular orbital approach, the ligand spin-orbit coupling produces virtual excitations between the $^2A_{1g}$ ground state and the non-bonding $^2A_{2g}$ excited state, consisting of ligand $p_s$ orbitals (see appendix 1). This so-called charge transfer excitation produces a first order shift [ARAM83]

$$g_{ii} - g_s = 2\gamma^2 \Gamma^{-1}(\nu) \frac{\zeta_L}{\delta} \quad (3.32)$$

in which $\zeta_L$ is the ligand spin-orbit coupling constant and $\delta^*$ the energy difference between the $^2A_{1g}$ ground state and the $^2A_{2g}$ excited level. $\gamma$ and $\nu$ are defined in equation (3.26) and

$$\Gamma(\nu) = \nu - \sqrt{1 - \nu^2} R_{eq} \left| \left\langle s \left| \frac{\partial}{\partial \nu} \right| p_s \right\rangle \right.$$
with $R_{eq}$ the equatorial metal to ligand distance and $\left\langle s \frac{\partial}{\partial y} \rho_y \right\rangle$ an atomic integral with a value close to 0.8Å⁻¹ for Cl⁻ and Br⁻. The value of the $g_{\|}$ shift, which may be either positive or negative, thus strongly depends on the degree of hybridisation of the equatorial ligands, $\nu$. As up to now no reliable data on the unpaired spin distribution on the equatorial ligands are available for these complexes, the value of this contribution cannot be evaluated in a quantitatively correct manner. However, a qualitative argument in favour of this mechanism is provided by the fact that the observed $g_{\|}$ shifts for rhodium and palladium hexabromide complexes are roughly four times as large as those for the corresponding hexachloride complexes. This is in good agreement with the expected linear dependence of the $g_{\|}$ shift on the ligand spin-orbit coupling constant, as $s_{3p}(Br^-)/s_{3p}(Cl^-) = 4$ [FROE76].

In the analysis of the positive $g_{\|}$ shift for the most stable [RhCl₄]⁺ complex in solution-grown NaCl, Vercammen et al. [VERC99a] used the expression for $g_{\|}$ in the $^2A_{1g}$ ground state given by Townsend [TOWN64], which gives the wrong sign for the first order shift. The excellent agreement between the experimental $g$ values for this centre and those calculated from their optical absorption data should be considered as fortuitous. The assignments of the observed optical transitions in [VERC99a] should, most probably, be reconsidered.

3.3. Superhyperfine interactions : EPR and ENDOR spectra for the $^2A_{1g}$ ground state

In the previous section it has already been argued that in [RhCl₄]⁺ complexes and their hydrated variants incorporated in AgCl and NaCl have an effective spin $S = 1/2$, with the unpaired electron mainly localized in a $d_{3z^2-\rho^2}$ orbital. It will, hence, primarily interact with the nuclei of the two Cl⁻ ligands on the $g_z$ or $g_{\|}$ axis of the complex, which have $I = 3/2$. This interaction will be considered in § 3.3.1. In many cases, it is the only interaction resolved in the EPR spectrum, those with the central Rh nucleus and with other neighbouring nuclei being buried in the EPR line width. In the ENDOR spectrum, the latter interactions may be resolved. The expected ENDOR spectra for these nuclei are discussed in § 3.3.2. In order to describe the interaction of the unpaired electrons with all these nuclei, the spin Hamiltonian formalism (see § 2.3) is again adopted.

3.3.1. Interaction of the unpaired electron with two equivalent axial Cl nuclei

If no other defects are in the neighbourhood, the axial Cl⁻ ligands are, from the physical point of view, equivalent. There are, however, two magnetic Cl isotopes, $^{35}\text{Cl}$ and $^{37}\text{Cl}$, both with spin 3/2 and with relative natural abundances 3:1 (see table 2.2). The two equivalent nuclei thus come in $^{35}\text{Cl}^{35}\text{Cl}$, $^{35}\text{Cl}^{37}\text{Cl}$ and $^{37}\text{Cl}^{37}\text{Cl}$ pairs with relative abundances 9:6:1. In the first and the last case, the interacting nuclei are equivalent and the indirect interaction between the nuclei via the electron spin is expected to be important (see § 2.5.5). In the $^{35}\text{Cl}^{37}\text{Cl}$ pairs, the nuclei are inequivalent and the second order indirect interaction between the nuclei vanishes. In the latter case, the nuclei may in a very good approximation be assumed to interact with the unpaired electron independently from one another. For
the $^{35}\text{Cl}-^{35}\text{Cl}$ pairs, which occur most frequently, the EPR and ENDOR spectra will be calculated using second order perturbation theory.

Castner and Känzig [CAST57] reported second order splittings observed in the EPR spectrum of the $V_K$ centre $\text{Br}_2^-$. They did not give a detailed calculation of the second order energy levels, though. Schoemaker presented general second order perturbation calculations of the energy levels and EPR spectra for a paramagnetic centre with $S = 1/2$ interacting with two equivalent nuclei and applied the obtained formulae to the $\vec{B} \parallel (110)$ spectra of the $V_K$ and $V_F$ centres $I_2^-$ in various alkali halides [SCHO68]. He calculated the EPR spectra in two limiting cases, for the second order hyperfine interaction much larger or much smaller than the quadrupole interaction, and found out that the latter case is valid for the $V_K$ and $V_F$ centres. Feuchtwang [FEUC62] calculated second order the ENDOR spectrum of two equivalent $I > 1/2$ nuclei for an $S = 1/2$ system (i.e. the $^{39}\text{K}$ interaction in the $F$ centre in $\text{KCl}$) in the case of strong quadrupole interaction.

In order to understand the essential features of the EPR and ENDOR spectra of the axial Cl$^-$ ligands of Rh$^{2+}$ impurities in NaCl and AgCl, it is sufficient to consider perfectly axial superhyperfine and quadrupole tensors and to calculate the spectra with the magnetic field parallel to the $g_{\parallel}$ symmetry axis of the centre. With these assumptions, the calculations become considerably less complicated. The results correspond to the strong quadrupole interaction limit.

**Second order perturbation calculation of the energy levels**

The spin Hamiltonian describing the interaction of an unpaired electron ($S = 1/2$), interacting with two equivalent nuclei with $I = 3/2$, is given by

$$\hat{H}_S = g_{\parallel} \mu_B \vec{B}_\parallel \vec{S} + \sum_{j=1}^{N} \left[ A_j \vec{S} \cdot \vec{j} + \frac{A_{\perp}}{2} \left( \vec{S} \cdot \vec{j}_- + \vec{S} \cdot \vec{j}_+ \right) - g_{\perp} \mu_B \vec{B}_\perp \vec{j} + \frac{C}{2} \left( \vec{S} \cdot \vec{j}_z \right) \right]$$

(3.34)

The electronic Zeeman interaction is assumed to be much larger than all terms involving the nuclear spins, which are treated as a perturbation. As we expect the nuclear spins $\vec{j}_1$ and $\vec{j}_2$ to be coupled to the total nuclear spin $\vec{I} = \vec{j}_1 + \vec{j}_2$, the Hamiltonian (3.34) is evaluated in the base $|M_S, I, M_I\rangle$. The possible values for $I$ are 3, 2, 1 and 0. The $|M_S, I, M_I\rangle$ states are linear combinations of the $|M_S, M_I, M_Z\rangle$ states:
\begin{align}
|M_{5,3,3}\rangle &= |M_{5,3/2,3/2}\rangle \\
|M_{5,3,2}\rangle &= \frac{1}{\sqrt{2}} (|M_{5,3/2,1/2}\rangle + |M_{5,1/2,3/2}\rangle) \\
|M_{5,3,1}\rangle &= \frac{1}{\sqrt{5}} (|M_{5,3/2,-1/2}\rangle + \sqrt{3} |M_{5,1/2,1/2}\rangle + |M_{5,-1/2,3/2}\rangle) \\
|M_{5,3,0}\rangle &= \frac{1}{\sqrt{20}} (|M_{5,3/2,-3/2}\rangle + 3|M_{5,1/2,-1/2}\rangle + 3|M_{5,-1/2,1/2}\rangle + |M_{5,-3/2,3/2}\rangle) \\
|M_{5,3,-1}\rangle &= \frac{1}{\sqrt{5}} (|M_{5,1/2,-3/2}\rangle + \sqrt{3} |M_{5,-1/2,-1/2}\rangle + |M_{5,-3/2,1/2}\rangle) \\
|M_{5,3,-2}\rangle &= \frac{1}{\sqrt{2}} (|M_{5,-1/2,-3/2}\rangle + |M_{5,-3/2,-1/2}\rangle) \\
|M_{5,3,-3}\rangle &= |M_{5,-3/2,-3/2}\rangle \\
|M_{5,2,2}\rangle &= \frac{1}{\sqrt{2}} (|M_{5,3/2,1/2}\rangle - |M_{5,1/2,3/2}\rangle) \\
|M_{5,2,1}\rangle &= \frac{1}{\sqrt{2}} (|M_{5,3/2,-1/2}\rangle - |M_{5,-1/2,3/2}\rangle) \\
|M_{5,2,0}\rangle &= \frac{1}{2} (|M_{5,3/2,-3/2}\rangle + |M_{5,1/2,-1/2}\rangle - |M_{5,-1/2,1/2}\rangle - |M_{5,-3/2,3/2}\rangle) \\
|M_{5,2,-1}\rangle &= \frac{1}{\sqrt{2}} (|M_{5,1/2,-3/2}\rangle - |M_{5,-3/2,1/2}\rangle) \\
|M_{5,2,-2}\rangle &= \frac{1}{\sqrt{2}} (|M_{5,-1/2,-3/2}\rangle - |M_{5,-3/2,-1/2}\rangle) \\
|M_{5,1,1}\rangle &= \frac{1}{\sqrt{10}} (\sqrt{3} |M_{5,3/2,-1/2}\rangle - 2|M_{5,1/2,1/2}\rangle + \sqrt{3} |M_{5,-1/2,3/2}\rangle) \\
|M_{5,1,0}\rangle &= \frac{1}{\sqrt{20}} (3|M_{5,3/2,-3/2}\rangle - |M_{5,1/2,-1/2}\rangle - |M_{5,-1/2,1/2}\rangle + |M_{5,-3/2,3/2}\rangle) \\
|M_{5,1,-1}\rangle &= \frac{1}{\sqrt{10}} (\sqrt{3} |M_{5,1/2,-3/2}\rangle - 2|M_{5,-1/2,-1/2}\rangle + \sqrt{3} |M_{5,-3/2,1/2}\rangle) \\
|M_{5,0,0}\rangle &= \frac{1}{2} (|M_{5,3/2,-3/2}\rangle - |M_{5,1/2,-1/2}\rangle + |M_{5,-1/2,1/2}\rangle - |M_{5,-3/2,-1/2}\rangle) \\
\end{align}

The perturbation Hamiltonian

\begin{equation}
\hat{H}_5^I = A_i \hat{S}_i^2 - g_i \mu_i B_0 \hat{J}_z + \frac{A_i}{2} (\hat{S}_i^+ \hat{J}_+ + \hat{S}_i^- \hat{J}_-) + \frac{Q_i}{2} \sum_{j=1}^4 (3 \hat{J}_z^2 - \hat{J}_z^2) \tag{3.39}
\end{equation}

is not diagonal in this base, due to its third and the fourth term. The third term produces, like in § 2.5.5, produces non-zero matrix elements between states with different \( M_z \), and will give rise to second order corrections. The fourth term, the nuclear quadrupole Hamiltonian \( \hat{H}_0 \), produces non-zero off-diagonal matrix elements within the two \( M_5 \) multiplets. The Hamiltonian (3.39) should first be diagonalised within the \( M_5 \) multiplets. Because \( \hat{H}_0 \) is diagonal in the orthogonal base \( |M_5, M_1, M_2\rangle \), non-zero matrix elements only exist between states with identical \( M_5 \). Furthermore, it can be easily verified that \( \hat{H}_0 \), the \( I = 3 \) and \( I = 1 \) states transform as \( A_{1^+} \), whereas the \( I = 2 \) and \( I = 0 \) states transform as \( A_{2^+} \). As a consequence, \( \hat{H}_0 \) only has non-zero off-diagonal matrix elements between
states with $l = 1$ and $l = 3$ and between states with $l = 0$ and $l = 2$. The non-zero off-diagonal matrix elements are

$$\langle M_s, 2, 0 | \hat{H}_d | M_s, 0, 0 \rangle = 3Q$$

$$\langle M_s, 3, 1 | \hat{H}_d | M_s, 1, 1 \rangle = \frac{3\sqrt{6}}{5} Q$$

$$\langle M_s, 3, 0 | \hat{H}_d | M_s, 1, 0 \rangle = \frac{9}{5} Q$$

$$\langle M_s, 3, -1 | \hat{H}_d | M_s, 1, -1 \rangle = \frac{3\sqrt{6}}{5} Q$$

(3.40)

The diagonalisation of the 16x16 matrices corresponding to each $M_s$ multiplet is thus reduced to a diagonalisation of four matrices of dimensions 2x2. The diagonal element for each $|M_s, l, M_i\rangle$ state is given by

$$A_l M_s M_i - g g_{M_s} B_l M_i = \frac{Q}{2} \left( 3 (l, M_i | \hat{I}_{zz}^2 | l, M_i) - \frac{15}{2} \right)$$

(3.41)

The 2x2 matrices to be diagonalised are ($H_z$ and $H_N$ have the same definition as in § 2.5.5)

| $\hat{H}_z + \hat{H}_{s}$ | $| M_s, 2, 0 \rangle$ | $| M_s, 0, 0 \rangle$ |
|--------------------------|-------------------|-------------------|
| $\langle M_s, 2, 0 |$ 2$H_z M_s$ | 3$Q$ |
| $\langle M_s, 0, 0 |$ 3$Q$ $2H_z M_s$ |

which has the eigenvalues and eigenstates

$$E(\langle M_s, 2, 0 \rangle) = 2H_z M_s + 3Q, |M_s, 2, 0\rangle = \frac{1}{\sqrt{2}} (|M_s, 2, 0\rangle + |M_s, 0, 0\rangle)$$

$$E(\langle M_s, 0, 0 \rangle) = 2H_z M_s - 3Q, |M_s, 0, 0\rangle = \frac{1}{\sqrt{2}} (|M_s, 2, 0\rangle - |M_s, 0, 0\rangle)$$

(3.42)

| $\hat{H}_z + \hat{H}_{s}$ | $| M_s, 3, \pm 1 \rangle$ | $| M_s, 1, \pm 1 \rangle$ |
|--------------------------|-------------------|-------------------|
| $\langle M_s, 3, \pm 1 |$ $(2H_z \pm A_l) M_s \mp 2H_N - \frac{9}{5} Q$ | $\frac{3\sqrt{6}}{5} Q$ |
| $\langle M_s, 1, \pm 1 |$ $3\frac{\sqrt{6}}{5} Q$ | $(2H_z \pm A_l) M_s \mp 2H_N - \frac{6}{5} Q$ |

with the eigenvalues and eigenstates

$$E(\langle M_s, 3, \pm 1 \rangle) = 2H_z M_s \pm A_l M_s \mp 2H_N, |M_s, 3, \pm 1\rangle = \frac{1}{\sqrt{5}} (\sqrt{2} |M_s, 3, \pm 1\rangle \pm \sqrt{3} |M_s, 1, \pm 1\rangle)$$

$$E(\langle M_s, 1, \pm 1 \rangle) = 2H_z M_s \pm A_l M_s \mp 2H_N - 3Q, |M_s, 1, \pm 1\rangle = \frac{1}{\sqrt{5}} (\sqrt{3} |M_s, 3, \pm 1\rangle - \sqrt{2} |M_s, 1, \pm 1\rangle)$$

(3.43)

and
with the eigenvalues and eigenstates

\[
E(M_s, \bar{3}, 0) = 2H_2 M_s + 3 Q, \quad E(M_s, 3, 0) = \frac{1}{\sqrt{10}} (E(M_s, 3, 0) + 3 E(M_s, 1, 0))
\]

\[
E(M_s, \bar{1}, 0) = 2H_2 M_s - 3 Q, \quad E(M_s, 1, 0) = \frac{1}{\sqrt{10}} (3 E(M_s, 3, 0) - E(M_s, 1, 0))
\]

(3.44)

All remaining non-zero off-diagonal matrix elements are of the type

\[
\langle \frac{1}{2}, \bar{l}, M_f | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, l, M_i \rangle = \langle -\frac{1}{2}, \bar{l}, M_i | \frac{A_1}{2} \hat{S}_z \hat{i} | \frac{1}{2}, l, M_f \rangle
\]

(3.45)

with the restriction that for the pure \( l \) states, \( l' = l \). The matrix elements to be calculated are

\[
\begin{align*}
\langle \frac{1}{2}, 2, 1 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 2, 2 \rangle &= A_1 \\
\langle \frac{1}{2}, 2, 0 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 2, 1 \rangle &= \frac{\sqrt{3}}{2} A_1 \\
\langle \frac{1}{2}, 0, 0 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 2, 1 \rangle &= \frac{\sqrt{3}}{2} A_1 \\
\langle \frac{1}{2}, 2, -1 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 2, 0 \rangle &= \frac{\sqrt{3}}{2} A_1 \\
\langle \frac{1}{2}, 2, -1 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 0, 0 \rangle &= \frac{\sqrt{3}}{2} A_1 \\
\langle \frac{1}{2}, 2, -2 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 2, -1 \rangle &= A_1 \\
\langle \frac{1}{2}, 3, 2 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 3, 3 \rangle &= \frac{\sqrt{6}}{2} A_1 \\
\langle \frac{1}{2}, 3, 1 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 3, 2 \rangle &= A_1 \\
\langle \frac{1}{2}, 1, 1 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 3, 2 \rangle &= \frac{\sqrt{6}}{2} A_1 \\
\langle \frac{1}{2}, 3, 0 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 3, 1 \rangle &= \frac{\sqrt{3}}{2} A_1 \\
\langle \frac{1}{2}, 3, -3 | \frac{A_1}{2} \hat{S}_z \hat{i} | -\frac{1}{2}, 3, -2 \rangle &= \frac{\sqrt{6}}{2} A_1
\end{align*}
\]

(3.46)

The second order energy levels are thus given by
\[ E(\{\mathbf{2}, 3, 0\}) = \frac{1}{2} g_\mu B_\text{s} + 3Q + \frac{3A'}{4g_\mu_\mu_\text{s} B_\text{s}} \]

(3.47)

\[ E(\{\mathbf{2}, 2, 2\}) = \frac{1}{2} g_\mu B_\text{s} + A - 2g_\mu_\mu_\text{s} B_\text{s} \quad E(\{-\mathbf{2}, 2, 2\}) = -\frac{1}{2} g_\mu B_\text{s} - A - 2g_\mu_\mu_\text{s} B_\text{s} - \frac{3A'}{2g_\mu_\mu_\text{s} B_\text{s}} \]

\[ E(\{\mathbf{2}, 2, 1\}) = \frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} - g_\mu_\mu_\text{s} B_\text{s} + \frac{A'}{g_\mu_\mu_\text{s} B_\text{s}} \quad E(\{-\mathbf{2}, 2, 1\}) = -\frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} - g_\mu_\mu_\text{s} B_\text{s} - \frac{3A'}{2g_\mu_\mu_\text{s} B_\text{s}} \]

\[ E(\{\mathbf{2}, 2, 0\}) = \frac{1}{2} g_\mu B_\text{s} + 3Q - \frac{3A'}{4g_\mu_\mu_\text{s} B_\text{s}} \quad E(\{-\mathbf{2}, 2, 0\}) = -\frac{1}{2} g_\mu B_\text{s} + 3Q - \frac{3A'}{4g_\mu_\mu_\text{s} B_\text{s}} \]

\[ E(\{\mathbf{2}, 2, -1\}) = \frac{1}{2} g_\mu B_\text{s} - \frac{A}{2} + g_\mu_\mu_\text{s} B_\text{s} + \frac{3A'}{2g_\mu_\mu_\text{s} B_\text{s}} \quad E(\{-\mathbf{2}, 2, -1\}) = -\frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} + g_\mu_\mu_\text{s} B_\text{s} - \frac{3A'}{2g_\mu_\mu_\text{s} B_\text{s}} \]

\[ E(\{\mathbf{2}, 2, -2\}) = \frac{1}{2} g_\mu B_\text{s} - A + 2g_\mu_\mu_\text{s} B_\text{s} \quad E(\{-\mathbf{2}, 2, -2\}) = -\frac{1}{2} g_\mu B_\text{s} + A + 2g_\mu_\mu_\text{s} B_\text{s} \]

\[ E(\{\mathbf{2}, 1, 0\}) = \frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} - g_\mu_\mu_\text{s} B_\text{s} - 3Q + \frac{3A'}{2g_\mu_\mu_\text{s} B_\text{s}} \quad E(\{-\mathbf{2}, 1, 0\}) = -\frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} - g_\mu_\mu_\text{s} B_\text{s} - 3Q - \frac{2A'}{g_\mu_\mu_\text{s} B_\text{s}} \]

\[ E(\{\mathbf{2}, 1, 1\}) = \frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} - g_\mu_\mu_\text{s} B_\text{s} - 3Q + \frac{11A'}{4g_\mu_\mu_\text{s} B_\text{s}} \quad E(\{-\mathbf{2}, 1, 1\}) = -\frac{1}{2} g_\mu B_\text{s} + \frac{A}{2} - g_\mu_\mu_\text{s} B_\text{s} - 3Q - \frac{11A'}{4g_\mu_\mu_\text{s} B_\text{s}} \]

\[ E(\{\mathbf{2}, 0, 0\}) = \frac{1}{2} g_\mu B_\text{s} - 3Q + \frac{3A'}{4g_\mu_\mu_\text{s} B_\text{s}} \quad E(\{-\mathbf{2}, 0, 0\}) = -\frac{1}{2} g_\mu B_\text{s} - 3Q - \frac{3A'}{4g_\mu_\mu_\text{s} B_\text{s}} \]

(3.50)

These energy levels, along with the allowed EPR and ENDOR transition are shown in figure 3.3.
Figure 3.3: Energy level scheme for the paramagnetic system with spin Hamiltonian (3.34).
The allowed EPR ($E_i - E_{i0}$) and ENDOR ($N_{i1}, N_{i2}, M_i, -M_{i2}$) are indicated.

EPR spectrum
The transition fields of the allowed EPR transitions are summarised in table 3.2. For the Rh$^{5+}$
complexes in NaCl and AgCl, $A_\perp$ is typically of the order of 40 MHz. The quantity $\frac{A_i^2}{g_i \mu_B \hbar \nu_{MW}}$ then
amounts to 6 $\mu$T at $\nu_{MW} = 10$ GHz. The second order splittings of the EPR transitions are much
smaller than the expected line widths of the transitions (> 0.1 mT) and the splittings due to the isotopic
distribution of the axial Cl' pairs. For the calculation of the EPR spectrum, first order perturbation
results are sufficiently accurate. For axial $^{35}$Cl and $^{37}$Cl pairs, the calculations give rise to a seven line
superhyperfine pattern in the EPR spectrum, as shown in figure 3.4a and b, respectively
($g_i = 2.019, A_i (^{35}$Cl$) = 75.5$ MHz, $\nu_{MW} = 9.56$ GHz). For $^{35}$Cl-$^{37}$Cl pairs, the EPR transitions may be
calculated to first order to occur at
\[ B(M_i[^{35}Cl], M_j[^{37}Cl]) = \frac{1}{g_i\mu_B} \left( h\nu_{MW} - A_i[^{35}Cl]M_i[^{35}Cl] - A_j[^{37}Cl]M_j[^{37}Cl] \right) \]  

(3.51)

**Table 3.2**: Transition fields of the allowed EPR transitions in the system with spin Hamiltonian (3.34). To zero order, all transitions have equal probability. The transition numbers are given figure 3.3.

<table>
<thead>
<tr>
<th>(N^0)</th>
<th>Transition field at (\nu_{MW})</th>
<th>(N^0)</th>
<th>Transition field at (\nu_{MW})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E_1)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - 3A_i - \frac{3A_i^2}{2h\nu_{MW}} \right))</td>
<td>(E_9)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - \frac{11A_i^2}{2h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_2)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - 2A_i - \frac{4A_i^2}{h\nu_{MW}} \right))</td>
<td>(E_{10})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} + A_i - \frac{7A_i^2}{2h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_3)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - A_i - \frac{5A_i^2}{2h\nu_{MW}} \right))</td>
<td>(E_{11})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - 2A_i - \frac{A_i^2}{h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_4)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - \frac{3A_i^2}{2h\nu_{MW}} \right))</td>
<td>(E_{12})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - A_i - \frac{5A_i^2}{2h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_5)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} + A_i - \frac{5A_i^2}{2h\nu_{MW}} \right))</td>
<td>(E_{13})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - \frac{3A_i^2}{2h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_6)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} + 2A_i - \frac{4A_i^2}{h\nu_{MW}} \right))</td>
<td>(E_{14})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} + A_i - \frac{5A_i^2}{2h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_7)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} + 3A_i - \frac{3A_i^2}{2h\nu_{MW}} \right))</td>
<td>(E_{15})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} + 2A_i - \frac{A_i^2}{h\nu_{MW}} \right))</td>
</tr>
<tr>
<td>(E_8)</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - A_i - \frac{7A_i^2}{2h\nu_{MW}} \right))</td>
<td>(E_{16})</td>
<td>(\frac{1}{g_i\mu_B} \left( h\nu_{MW} - \frac{3A_i^2}{2h\nu_{MW}} \right))</td>
</tr>
</tbody>
</table>

**Figure 3.4**: Superhyperfine structure in the EPR spectrum due to two equivalent Cl ions, calculated to first order (a) interaction with two ^{35}Cl nuclei, (b) interaction with two ^{37}Cl nuclei, (c) interaction with one ^{35}Cl and one ^{37}Cl nucleus, and (d) interaction with two Cl nuclei occurring in their natural abundances.
The spectrum of the latter pairs is shown in figure 3.4c. If the Cl isotopes occur in their natural abundances, the spectrum in figure 3.4d, which is the weighed sum of spectra a, b and c, is expected to be observed. As the line width of an individual EPR transition is very small (0.1 mT) in the spectra in figure 3.4, the effect of the different isotopes is clearly observed. If the line width is a factor of 10 larger, as is the case for the Rh\textsuperscript{2+} complexes in NaCl and AgCl, the spectrum for the interaction with two \textsuperscript{35}Cl nuclei resembles very well the spectrum in which the natural abundances of the Cl isotopes are taken into account. This is illustrated in figure 3.5. To a good approximation, the Rh\textsuperscript{2+} EPR spectra may thus be calculated assuming that the \textsuperscript{35}Cl isotope is 100% abundant. This is frequently done in the calculation of powder EPR spectra, where the spectrum needs to be calculated for a lot of microcrystal orientations, in order to reduce the computing time.

The spectrum of the latter pairs is shown in figure 3.4c. If the Cl isotopes occur in their natural abundances, the spectrum in figure 3.4d, which is the weighed sum of spectra a, b and c, is expected to be observed. As the line width of an individual EPR transition is very small (0.1 mT) in the spectra in figure 3.4, the effect of the different isotopes is clearly observed. If the line width is a factor of 10 larger, as is the case for the Rh\textsuperscript{2+} complexes in NaCl and AgCl, the spectrum for the interaction with two \textsuperscript{35}Cl nuclei resembles very well the spectrum in which the natural abundances of the Cl isotopes are taken into account. This is illustrated in figure 3.5. To a good approximation, the Rh\textsuperscript{2+} EPR spectra may thus be calculated assuming that the \textsuperscript{35}Cl isotope is 100% abundant. This is frequently done in the calculation of powder EPR spectra, where the spectrum needs to be calculated for a lot of microcrystal orientations, in order to reduce the computing time.

**ENDOR spectrum**

The frequencies and probabilities of the allowed ENDOR transitions are given in table 3.4. The relative values for the transition probabilities were obtained by calculating

\[ |\langle M_s, \bar{J}, M_l | \bar{J}_l | M_s, \bar{J}_l \rangle|^2 \]

(3.52)

neglecting terms of first and higher order in \[ \frac{A_{12}}{g_H \mu_B B_0} \].

If second and higher order corrections are neglected, the ENDOR frequencies for the interaction with two (or any other number of) equivalent Cl\textsuperscript{−} ions are identical to those for the interaction with a single nucleus. These six transitions occur at

\[ f = \left| A_{12} M_s - g_N \mu_B B_0 + 3QM_0 \right| \]

(3.53)
with $M_Q = M_I + M_r$ for a transition between the levels $|M_B M_r⟩ ↔ |M_B M_r⟩$ (interaction with a single nucleus). Two triplets of transitions are thus expected, with a splitting of $3\Omega/h$ within the triplets and a splitting of $2g_i\mu_B B/h$ between the triplets. In figure 3.6 the experimental and calculated $g_i$ ENDOR spectrum (at superhyperfine line 4) for the interaction with two equivalent Cl' ions of the so-called RTAX centre (see table 3.5) in NaCl are shown. Both $^{35}\text{Cl}$ and $^{37}\text{Cl}$ isotopes are observed in the experimental spectrum (indicated with arrows) and taken into account in the simulation. It is clearly seen that the $^{35}\text{Cl}$ ENDOR transitions with $M_Q = 0$ are split due to the indirect coupling between the two equivalent $^{35}\text{Cl}$ nuclei.

Table 3.4: Frequencies and probabilities of the ENDOR transitions for the system with spin Hamiltonian (3.34). The transition numbers are defined in figure 3.3.

| $N^o$ | $h \Delta f_{\text{res}}$ | $W_{\text{NMR}}$ | $N^o$ | $h \Delta f_{\text{res}}$ | $W_{\text{NMR}}$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>$A_1/2 - g_i\mu_B B_0 + 3\Omega - 3A_1^2/2g_i\mu_B B_0$</td>
<td>6</td>
<td>N13</td>
<td>$A_1/2 - g_i\mu_B B_0 - 5A_1^2/4g_i\mu_B B_0$</td>
<td>8</td>
</tr>
<tr>
<td>N2</td>
<td>$A_1/2 - g_i\mu_B B_0 + A_1^2/2g_i\mu_B B_0$</td>
<td>4</td>
<td>N14</td>
<td>$A_1/2 - g_i\mu_B B_0 + 3A_1^2/4g_i\mu_B B_0$</td>
<td>8</td>
</tr>
<tr>
<td>N3</td>
<td>$A_1/2 - g_i\mu_B B_0 - 3\Omega + A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
<td>N15</td>
<td>$A_1/2 + g_i\mu_B B_0 + 5A_1^2/4g_i\mu_B B_0$</td>
<td>8</td>
</tr>
<tr>
<td>N4</td>
<td>$A_1/2 - g_i\mu_B B_0 + 3\Omega - 3A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
<td>N16</td>
<td>$A_1/2 + g_i\mu_B B_0 - 3A_1^2/4g_i\mu_B B_0$</td>
<td>8</td>
</tr>
<tr>
<td>N5</td>
<td>$A_1/2 - g_i\mu_B B_0 - A_1^2/g_i\mu_B B_0$</td>
<td>4</td>
<td>N17</td>
<td>$A_1/2 - g_i\mu_B B_0 - A_1^2/g_i\mu_B B_0$</td>
<td>4</td>
</tr>
<tr>
<td>N6</td>
<td>$A_1/2 - g_i\mu_B B_0 - 3\Omega + A_1^2/g_i\mu_B B_0$</td>
<td>6</td>
<td>N18</td>
<td>$A_1/2 - g_i\mu_B B_0 - 3\Omega - A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>N7</td>
<td>$A_1/2 + g_i\mu_B B_0 + 3\Omega + 3A_1^2/2g_i\mu_B B_0$</td>
<td>6</td>
<td>N19</td>
<td>$A_1/2 - g_i\mu_B B_0 + 3\Omega - 3A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>N8</td>
<td>$A_1/2 + g_i\mu_B B_0 - A_1^2/2g_i\mu_B B_0$</td>
<td>4</td>
<td>N20</td>
<td>$A_1/2 - g_i\mu_B B_0 + A_1^2/2g_i\mu_B B_0$</td>
<td>4</td>
</tr>
<tr>
<td>N9</td>
<td>$A_1/2 + g_i\mu_B B_0 - 3\Omega - A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
<td>N21</td>
<td>$A_1/2 + g_i\mu_B B_0 + A_1^2/g_i\mu_B B_0$</td>
<td>4</td>
</tr>
<tr>
<td>N10</td>
<td>$A_1/2 + g_i\mu_B B_0 + 3\Omega + 3A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
<td>N22</td>
<td>$A_1/2 + g_i\mu_B B_0 - 3\Omega - 3A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>N11</td>
<td>$A_1/2 + g_i\mu_B B_0 + A_1^2/g_i\mu_B B_0$</td>
<td>4</td>
<td>N23</td>
<td>$A_1/2 + g_i\mu_B B_0 + 3\Omega + 3A_1^2/4g_i\mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>N12</td>
<td>$A_1/2 + g_i\mu_B B_0 - 3\Omega - A_1^2/g_i\mu_B B_0$</td>
<td>6</td>
<td>N24</td>
<td>$A_1/2 + g_i\mu_B B_0 - A_1^2/2g_i\mu_B B_0$</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 3.4: continued

<table>
<thead>
<tr>
<th>$N^a$</th>
<th>$h f_{res}$</th>
<th>$W_{NMR}$</th>
<th>$N^a$</th>
<th>$h f_{res}$</th>
<th>$W_{NMR}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_1$</td>
<td>$A_1/2 - g_n \mu_B B_0 + 3Q$</td>
<td>6</td>
<td>$M_9$</td>
<td>$A_1/2 - g_n \mu_B B_0 + 6Q + 5A_i^2/4g_i \mu_B B_0$</td>
<td>0</td>
</tr>
<tr>
<td>$M_2$</td>
<td>$A_1/2 - g_n \mu_B B_0 + 3Q - 7A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
<td>$M_{10}$</td>
<td>$A_1/2 + g_n \mu_B B_0 - 3Q - 3A_i^2/4g_i \mu_B B_0$</td>
<td>0</td>
</tr>
<tr>
<td>$M_3$</td>
<td>$A_1/2 - g_n \mu_B B_0 + 6Q - 5A_i^2/4g_i \mu_B B_0$</td>
<td>0</td>
<td>$M_{11}$</td>
<td>$A_1/2 + g_n \mu_B B_0 - 3Q - 5A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>$M_4$</td>
<td>$A_1/2 - g_n \mu_B B_0 - 6Q + 3A_i^2/2g_i \mu_B B_0$</td>
<td>0</td>
<td>$M_{12}$</td>
<td>$A_1/2 + g_n \mu_B B_0 - 3Q + A_i^2/2g_i \mu_B B_0$</td>
<td>6</td>
</tr>
<tr>
<td>$M_5$</td>
<td>$A_1/2 - g_n \mu_B B_0 - 3Q + 5A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
<td>$M_{13}$</td>
<td>$A_1/2 - g_n \mu_B B_0 + 3Q + A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>$M_6$</td>
<td>$A_1/2 - g_n \mu_B B_0 - 3Q - A_i^2/2g_i \mu_B B_0$</td>
<td>6</td>
<td>$M_{14}$</td>
<td>$A_1/2 - g_n \mu_B B_0 - 3Q - 3A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>$M_7$</td>
<td>$A_1/2 + g_n \mu_B B_0 + 3Q$</td>
<td>6</td>
<td>$M_{15}$</td>
<td>$A_1/2 + g_n \mu_B B_0 + 3Q - A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
</tr>
<tr>
<td>$M_8$</td>
<td>$A_1/2 + g_n \mu_B B_0 + 3Q + 7A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
<td>$M_{16}$</td>
<td>$A_1/2 + g_n \mu_B B_0 - 3Q + 3A_i^2/4g_i \mu_B B_0$</td>
<td>3</td>
</tr>
</tbody>
</table>

For the $M_Q = \pm 1$ transitions, no splitting is resolved, but the lines are clearly broadened. The line splitting is proportional to $\frac{A_i^2}{h g_i \mu_B B_0}$ (see table 3.4) and can, as a consequence, be suppressed by recording the spectrum at a higher static magnetic field value $B_0$ when the EPR spectrum is recorded at higher microwave frequency. A similar line splitting occurs for the interaction with two equivalent $^{37}$Cl nuclei. It is expected to be some 30% smaller than the splitting for the $^{35}$Cl transitions ($A_i^2 (^{37}\text{Cl})/A_i^2 (^{35}\text{Cl}) = 0.69$). However, the observed $^{37}$Cl transitions mainly arise from the more abundant axial $^{35}$Cl-$^{37}$Cl pairs, in which the $^{35}$Cl and $^{37}$Cl transitions show no second order splitting. The transitions for these pairs were calculated by diagonalisation of the spin Hamiltonian for the interaction of a paramagnetic system with $S = 1/2$ with a single nucleus with $I = 3/2$. The splitting of the $^{37}$Cl transitions is usually not observed due to the low natural abundance of the $^{37}$Cl pairs (6.25%). They were not taken into account in the calculated spectra.

The agreement between the experimental and the calculated spectra in figure 3.6 is satisfactory. It should be remarked that an intensity difference between the $M_5 = 1/2$ and the $M_5 = -1/2$ transitions is observed, which is not explained by the calculated transition probabilities in table 3.4. Considering the thermal populations of the levels involved, the intensity of the transitions within the $M_5 = -1/2$ multiplet would indeed be expected to be higher than that for the transitions within the $M_5 = 1/2$ multiplet. This effect is, however, very small, even at temperatures of the order of 20 K, at which the ENDOR spectra were recorded. It cannot account for the observed intensity difference. We found no suitable
explanation for this phenomenon, but handled it in a phenomenological way by introducing the intensity ratio as an empirical parameter. For the calculated spectra in figure 3.6 the intensity ratio was, quite arbitrarily taken to be $R = I(-1/2)/I(1/2) = 2$. A similar effect is also observed for the interactions with other nuclei.

![ENDOR spectra](image)

**Figure 3.6**: Experimental (a) and simulated (b) ENDOR spectrum of the interaction with two equivalent axial Cl ions. Expected positions for the interactions with one $^{35}$Cl (full lines) and one $^{37}$Cl nucleus are marked with arrows. The $M_s$ number of each transition is indicated. The calculated ENDOR spectrum is the result of adding the spectrum of two equivalent $^{35}$Cl nuclei and that of a $^{35}$Cl-$^{37}$Cl pair in intensity ratios 9:6.

If the static magnetic field is set to one of the superhyperfine lines in the EPR spectrum, not all ENDOR transitions in table 3.4 can be detected. Indeed, if a certain superhyperfine line in the EPR spectrum is saturated, only those ENDOR transitions, which involve an energy level also involved in the saturated EPR transition, are observed. The transition $N_1$, e.g., can only be observed at the EPR transitions $E_1$ and $E_2$ and the transition $M_1$ is only observed if the EPR transitions $E_2$ or $E_6$ are saturated. Therefore, the ENDOR spectrum recorded at each of the superhyperfine transitions is different. For Rh$^{2+}$ centres in NaCl and AgCl, we have argued that second order effects in the EPR spectrum may safely be neglected and the EPR transitions with the same $M_s$ coincide. With this assumption the ENDOR spectra at the 7 superhyperfine EPR lines were calculated in two cases: a) $A_{1i}Q > 0$ and b) $A_{1i} > 0, Q < 0$ ($A_{1i}$ is assumed to have the same sign as $g_N$, thus positive). The results are shown in figure 3.7. The calculated spectra in this figure include the contribution of the $^{35}$Cl-$^{35}$Cl pairs and the $^{35}$Cl-$^{37}$Cl pairs, added in ratios 9:6. The much less abundant $^{37}$Cl-$^{37}$Cl spectra were again neglected. Part c of this figure presents the experimentally recorded spectra at the
different EPR superhyperfine transitions of the \( g_{||} \) component of the RTAX centre in NaCl. From the comparison of the spectra it is clear that \( A_y \) and \( Q \) have different signs in this case. Recording the ENDOR spectrum at different EPR superhyperfine transitions thus presents a way of determining the relative signs of the principal \( A \) and \( Q \) values.

![Diagram of EPR spectra](image)

**Figure 3.7**: Variation of the ENDOR spectrum of two equivalent Cl ions when recorded at different EPR superhyperfine transitions. (a) calculated spectra assuming \( A_y \), \( Q > 0 \), (b) calculated spectra assuming \( A_y > 0 \) and \( Q < 0 \), and (c) experimental spectra recorded at \( g_\perp \) of the RTAX centre in NaCl.

3.3.2. Interaction with other nuclei

**Interaction with the central \(^{103}\text{Rh} \) nucleus**

In the literature several cases of \( \text{Rh}^{5+} \) EPR spectra with resolved hyperfine structure are known (see e.g. [TOWN64], [MUNI70], [LUZ77], [ABEL79] and [SAST80]). For \([\text{RhCl}_6]^{4-}\) complexes and their hydrated variants in AgCl and NaCl, the hyperfine structure is almost never resolved in the EPR spectrum. In the ENDOR spectrum, on the other hand, interactions with the central Rh nucleus may be expected. As Rh has one magnetic isotope \( (^{103}\text{Rh}) \) with 100% natural abundance, \( I = 1/2 \) and low magnetic moment (see table 2.2), the ENDOR spectrum is expected to consist of two transitions at frequencies

\[
hf_{\text{res}} = \left| A^{\text{Rh}} M_g - g^{\text{Rh}}_\perp \mu_B B_0 \right|
\]

with \( A^{\text{Rh}} \) the hyperfine interaction parameter. As the nuclear \( g \) factor for \(^{103}\text{Rh} \) is very small, the transition frequencies are expected to be centred on \( A^{\text{Rh}}/2h \). The splitting between the lines is given by
Assignments of ENDOR transitions to the central $^{103}$Rh nucleus are based on the observation of this splitting. In figure 3.8 a simulated $^{103}$Rh ENDOR spectrum is shown. The unpaired spin density $I_{4d}^{\text{un}}$ in the $4d_z^2$ orbital of the central Rh ion may be estimated from the principal values of the hyperfine tensor. In the one-electron approximation for a tetragonal Rh$^{2+}$ complex in the $^2A_{1g}$ ground state these are given by [ABEL79]

\[
\begin{align*}
A_1^{\text{un}} &= \frac{\mu_0}{4\pi} g_s g_N^\text{un} \mu_H \mu_N \langle r^{-3} \rangle_{4d} \left[-\kappa + \frac{4}{7} I_{4d}^{\text{un}} - \frac{6c_\delta^4}{7\delta_1}\right] \\
A_2^{\text{un}} &= \frac{\mu_0}{4\pi} g_s g_N^\text{un} \mu_H \mu_N \langle r^{-3} \rangle_{4d} \left[-\kappa - \frac{2}{7} I_{4d}^{\text{un}} + \frac{45c_\delta^4}{7\delta_1}\right]
\end{align*}
\]

(3.55)

in which $\kappa$ is related to core polarisation.

**Figure 3.8**: ENDOR spectrum for an interaction of the unpaired electron with the central $^{103}$Rh nucleus ($A^{\text{un}} = 11.16$ MHz, $B_e = 339.3$ mT).

**Figure 3.9**: ENDOR spectrum for an interaction of the unpaired electrons with an Ag nucleus ($A(^{107}\text{Ag}) = 12.8$ MHz, $B_e = 339.6$ mT).

Interactions with second and fourth shell cations.

The interactions of the unpaired electron with the surrounding cations are expected to be much weaker than the interaction with the axial Cl$^-$ ions. Although the observation of an interaction with fourth shell cations in the EPR spectrum has been reported for Co$^{2+}$, Rh$^{2+}$ and Ir$^{2+}$ complexes in NaCl [PINH85], it is in general not expected that these interactions would be resolved in the EPR spectrum. Therefore, the discussion will again be confined to the ENDOR spectrum. As Rh$^{2+}$ complexes are studied both in AgCl and in NaCl, the expected ENDOR spectra for the interaction with silver and sodium nuclei are considered in the following.

Silver has two magnetic isotopes ($^{107}\text{Ag}$ and $^{109}\text{Ag}$) both with $I = 1/2$ and small $g_N$ values (see table 2.2). They are approximately equally abundant. For each interaction with a silver nucleus, two doublets of ENDOR transitions are thus expected in the ENDOR spectrum. As in the case of $^{103}\text{Rh}$,
each of the doublets is expected to be centred on $\frac{A}{2h}$ of the corresponding silver isotope because the value $g_n^\text{Na} \mu_B B_0 / h$ is very small at the microwave frequencies used in this work. The ratio of the superhyperfine parameters of the Ag isotopes should be equal to the ratio of their nuclear $g$ factors. An example of a simulated ENDOR spectrum for a silver interaction is shown in figure 3.9. ENDOR transitions are only then assigned to an interaction with silver nuclei if the transitions with both isotopes are observed.

Na has one magnetic isotope ($^{23}\text{Na}$) with 100% natural abundance, $I = 3/2$ and a large magnetic moment (see table 2.2). As the expected $A$ values are considerably smaller than those of the axial Cl nuclei, second order corrections do not have to be considered. The transition frequencies are given by an expression similar to (3.53). Whereas for the axial Cl interaction the contribution of the superhyperfine interaction term to the transition frequencies was dominant, for $^{23}\text{Na}$ interactions it is expected that $g_n^\text{Na} \mu_B B_0 > \frac{A_n^\text{Na}}{2} > 3Q_n^\text{Na}$. As a result, the transition frequencies are centred on the $^{23}\text{Na}$ Larmor frequency $g_n^\text{Na} \mu_B B_0 / h$. The latter frequency is usually marked by an intense and rather broad ENDOR transition, due to the interaction with a large number of remote $^{23}\text{Na}$ nuclei with very small hyperfine and quadrupole parameters. The ENDOR spectrum for an interaction with a Na nucleus typically looks like the one in figure 3.10. Pairs of ENDOR transitions centred on the $^{23}\text{Na}$ Larmor frequency are assigned to interactions with $^{23}\text{Na}$ nuclei.

Figure 3.10: ENDOR spectrum for an interaction of the unpaired electron with a nearby $^{23}\text{Na}$ nucleus ($A_n^\text{Na} / h = 4.29$ MHz, $Q_n^\text{Na} / h = 0.08$ MHz, $B_0 = 338.3$ mT) and with remote $^{23}\text{Na}$ nuclei ($A / h = Q / h = 0$ MHz).
The interaction with the nearest shell of cations, which are the nearest neighbours of the central ion along the crystal (110) axes, are usually dominated by the point dipole interaction. An expression for the tensor in this case is given in equation (2.23). The interaction with the fourth shell cations along the z axis of the complex is usually found to be stronger than that with the nearer second shell of cations. This has been explained by a transfer of unpaired spin density onto the fourth shell axial cations via overlap with the axial Cl\textsuperscript{-} ions [PINH85].

In the presentation of experimental results (§ 3.4 and chapters 4 – 6), the spin Hamiltonian will be expressed in frequency units \( \frac{\hbar}{\hbar} \). Zero field splitting, (super)hyperfine and quadrupole parameters will thus be given in MHz and \( \mu_B \) and \( \mu_N \) will be expressed in units MHz/T.

3.4. Rhodium-related paramagnetic centres in NaCl and AgCl

3.4.1. Literature data

In the introduction to this chapter it has already been mentioned that the structure of paramagnetic [RhCl\textsubscript{6}]\textsuperscript{3-} centres have been studied in AgCl since the sixties [WILK65, SHOC75] and in NaCl since the seventies [SHOC75, PINH85]. The only centre for which a complete structural model had been derived was, the primary \([\text{RhCl}_6]\textsuperscript{3-}\) complex in AgCl [VANR85, OLM88]. A renewed interest in the subject resulted from a study by Endo et al. [ENDO90], which indicated that hydrated \([\text{RhCl}_6]\textsuperscript{3-}\) complexes may be incorporated in AgCl and AgBr emulsion microcrystals and that the hetero ligands influence the trapping behaviour (efficiency, depth, stability) of the Rh\textsuperscript{3+} ion. In an attempt to unravel the structure of such complexes, paramagnetic Rh\textsuperscript{2+} complexes have been studied (and in some cases reinvestigated) using electron magnetic resonance techniques in AgCl emulsion microcrystals [VERC96, MOEN96, SCHW97, VRIE98b, VERC98c, PAWL98, VRIE99 and VRIE00] and in model systems like melt-grown AgCl [DASS95, VRIE98b, VRIE00], solution-grown NaCl [ZDRA97, CALL98, VERC98a, SABB98b] and melt-grown NaCl [SCHW97, SABB98a]. In the course of this investigation, a Rh\textsuperscript{3+} dimer centre [SCHW97, VERC98b] and a Rh\textsuperscript{3+} centre [VRIE98a] have also been identified. Our research on this subject was carried out in collaboration with the EPR research group of the University of Antwerp (U.I.A.) (Vercammen et al.) and Agfa-Gevaert research laboratories (Dr. D. Vandenbroucke). Two other research groups have been working on this subject: the research group of Prof. Dr. Spaeth at the Paderborn University (Germany) (Schweizer et al.) and the Eastman-Kodak research group (Pawlik et al.).

Only a few topics of the study of Rh complexes in NaCl and AgCl will be presented as personal experimental work (see chapters 4 – 6). We will make use of the results of three basic studies: the X-band ENDOR study of the primary Rh\textsuperscript{2+} centre in melt-grown AgCl ([OLM88] and the reanalysis [VRIE98b]), the identification of three Rh\textsuperscript{2+} – vacancy complexes in NaCl [ZDRA97, CALL98, VERC98a] and the X-band EPR study of Rh\textsuperscript{2+} complexes in AgCl emulsion microcrystals [VERC98c].

Table 3.5 gives an overview of the rhodium-related centres which have thus far been identified in NaCl single crystals, either grown from the melt or from aqueous solution. Some of these centres have been described by several authors giving them different labels. All labels are included in the table with
a reference to the paper in which they are defined. For each centre, the symmetry and the principal EPR parameters are given. For centres which have been described by several authors, the most recent or most accurate (smallest error) values are presented. When available, ENDOR data for the superhyperfine parameters are given. The structural models for some of these centres are shown in figure 3.11. In all these models, Rh ions are in substitutional cation positions. A next nearest neighbour (NNN) cation vacancy is indicated by Vac. Some of the centres undergo thermal reorientations at higher temperatures. The spin Hamiltonian parameters in table 3.5 only apply to the low temperature variants (measured at 5 - 50 K) of the centres. A similar overview of the rhodium-related centres identified in AgCl is given in Table 3.6.

We will use the [RhCl₆]⁺⁻nVac notation for the hexachloro complexes in NaCl, not making use of the labels defined in the literature. For the other centres in NaCl we will use the labels B-centre, Rh⁺ and Rh-dimer. The labels R4, R5, R6 and R6' will be used to indicate the doubly, the singly and the two non-hydrated [RhCl₆]⁺ complexes in AgCl. R6 and R6' will also be referred to as [RhCl₆]⁺⁻.0Vac and [RhCl₆]⁺⁻.1Vac, respectively.

**Table 3.5**: Paramagnetic rhodium-related centres in NaCl. The experimental error for the EPR parameters is given as a subscript. The zero field splitting and superhyperfine parameters for the interaction with the axial Cl⁻ ions (¹²Cl isotope) are given in MHz.

<table>
<thead>
<tr>
<th>Growth</th>
<th>Label</th>
<th>Symmetry</th>
<th>EPR parameters</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>solu./melt</td>
<td>O(I) a</td>
<td>orthorhombic I</td>
<td>$g_x = 4.27974, A_x = 33.9_1$</td>
<td>cis-[RhCl₆]⁺⁻.2Vac (Fig. 3.11a)</td>
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<td>Axial I b</td>
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<td>$g_y = 4.7124, A_y = 33.9_1$</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>$g_z = 2.0118_9, A_z = 72.7_2$</td>
<td></td>
</tr>
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<td>orthorhombic II</td>
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<td>[RhCl₆]⁺⁻.1Vac (Fig. 3.11b)</td>
</tr>
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<td>$g_y = 4.3014, A_y = 34.1_2$</td>
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<td></td>
<td></td>
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</tr>
<tr>
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<td>A-centre e</td>
<td>tetragonal</td>
<td>$g_x = 2.4510_9, A_x = 33.9_1$</td>
<td>[RhCl₆]⁺⁻.0Vac (Fig. 3.11c)</td>
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<tr>
<td>solution</td>
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<td>monoclinic II ?</td>
<td>$g_x = 2.503_1$</td>
<td>[RhCl₆H₂O]⁺⁻ or [RhCl₆OH]⁺⁻ tentative</td>
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<td>$g_z = 2.010_1$</td>
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<tr>
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<td>$g = 2.45$</td>
<td>[RhCl₆]⁺⁻</td>
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<td>Secondary b</td>
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<td>$^{2+}$-Rh²⁺⁻.2Vac (Fig. 3.11d)</td>
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<td>Rh-dimer g,i</td>
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<td></td>
<td>$g_z = 2.008_1, D_z = 0.20, A_z = 72.4_1$</td>
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</tbody>
</table>

References:

- a [CALL98]
- b [SCHW97]
- c [VERC98a]
- d [SABB98a, SABB98b]
- e [SHOC75]
- f [ZDRA97]
- g [VERC99]
- h [VRIE98a]
- i [VERC98b]
Figure 3.11: structural model for some of the Rh-related centres identified in NaCl and AgCl.
(a) [RhCl$_6^{2-}$].2Vac
(b) [RhCl$_6^{2-}$].1Vac
(c) [RhCl$_6^{2-}$].0Vac
(d) Rh-dimer

For the ions indicated in colour, the interactions have been observed in the EPR and/or ENDOR spectrum:
green: first shell axial Cl ions in (0,0,1) positions
purple: fourth shell axial cations in (0,0,2) positions
orange: second shell equatorial cations in (1,1,0) positions
red: second shell non-equatorial cations in (1,0,1) and (0,1,1) positions
Table 3.6: Paramagnetic rhodium-related centres in AgCl. The experimental error for the EPR parameters is given as a subscript. The $^{32}$Cl superhyperfine parameters are given in MHz. The spin Hamiltonian parameters for the primary centre in melt-grown AgCl crystals are taken from [OLM88] and [VRIE98b], those for the complexes in emulsion microcrystals are taken from the X-band powder EPR study by Vercammen et al. [VERC98c].

<table>
<thead>
<tr>
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<th>Label</th>
<th>Symmetry</th>
<th>EPR parameters</th>
<th>Model</th>
</tr>
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<tr>
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<td></td>
<td></td>
<td>$g_z=2.011_{2}$ $A_z^{Cl}=78.9_{5}$</td>
<td></td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
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<td>high temp^d</td>
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<td>$g_y=2.409_{15}$ $A_y^{Cl}=40_{5}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$g_z=2.011_{1}$ $A_z^{Cl}=78_{5}$</td>
<td></td>
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<td>$g_z=2.011_{5}$ $A_z^{Cl}=78_{5}$</td>
<td></td>
</tr>
<tr>
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<td>$g_z=2.011_{5}$ $A_z^{Cl}=78_{5}$</td>
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</tr>
</tbody>
</table>

^a [OLM88] ^b [VRIE00] ^c [VERC98c] ^d [PAWL99] ^e [VRIE99]

3.4.2. Structure and stability of [RhCl₄]^n Vac centres in NaCl and AgCl

The [RhCl₄]^n Vac centres are probably the most thoroughly studied and the proposed structural models for these centres are very well established. These models have been deduced from the observed symmetry and thermal stability of the centres in solution-grown and melt-grown NaCl single crystals. The symmetry was in each case determined from the angular dependence of the EPR spectrum, although for the [RhCl₄]^2 Vac centre, Q and W-band frequencies were required to separate the $g_x$ and $g_y$ components. In the ENDOR spectrum, interactions of the unpaired electron with the first shell of neighbours, consisting of the two axial Cl⁻ ions in (0,0,1) positions, the second shell, consisting of four equatorial Na ions in (1,1,0) positions and eight non-equatorial Na ions in (1,0,1) and (0,1,1) positions, and the axial fourth shell Na ions in (0,0,2) positions were observed. These nuclei are marked in the models in figure 3.11a-c. The ENDOR results thus indicate that the nearest positions in which charge compensating cation vacancies may be localised are the fourth shell equatorial Na (2,0,0) or (0,2,0) positions. Interactions with the first shell equatorial Cl⁻ ions were either not observed [ZDRA97, CALL98] or could not be completely analysed [SCHW97, SABB98b].

A puzzling fact in the ENDOR analysis was the absence of the $^{169}$Rh interaction for the [RhCl₄]^3 Vac centre [ZDRA97], although it had clearly been observed for the other centres [CALL98, SCHW97].

The fact that the charge compensation occurs through cation vacancies was most clearly demonstrated by pulse annealing experiments on Rh₃⁺ doped NaCl single crystals grown from aqueous solution. In a pulse annealing experiment, paramagnetic centres are created in a sample at low temperature and the EPR (and ENDOR) spectra are recorded below that temperature. The
thermal stability and interconversion of paramagnetic centres is then monitored by heating the samples above the temperature, at which paramagnetic centres were originally created in the sample, and recording the the spectra again at the measuring temperature. The results of such experiments for solution-grown NaCl:Rh^{3+} crystals can be summarised as follows. After irradiation with X-rays at liquid nitrogen temperature (77 K), only [RhCl_{6}]^{4-}.2Vac centres are produced. This indicates that all [RhCl_{6}]^{3-} complexes present in the crystals (or at least all those acting as an electron trap) have two NNN cation vacancies in a cis-configuration. The diamagnetic precursor centres are thus fully charge compensated. Only one cation vacancy is required to compensate the charge of the [RhCl_{6}]^{4-} centre, but the vacancies are immobile at 77 K and below. When the crystal is annealed to 220 K, the majority of the [RhCl_{6}]^{4-}.2Vac centres are converted into [RhCl_{6}]^{4-.1}Vac centres. This conversion could be very well monitored by X-band EPR and higher resolution magnetic resonance techniques like W-band EPR and X-band ENDOR [SABB98b]. The latter techniques demonstrated that the conversion is not complete: a fraction of the centres remains compensated by 2 cation vacancies. Rather surprisingly, when the crystals are annealed to room temperature for a long time (typically a few days), the majority of the [RhCl_{6}]^{4-} complexes lose all cation vacancies. It turns out that the non-locally charge compensated [RhCl_{6}]^{4-.0}Vac centre is the most stable in NaCl single crystals grown from aqueous solution. In melt-grown NaCl, paramagnetic Rh^{2+} centres are present in as-grown crystals. [RhCl_{6}]^{4-.2}Vac and [RhCl_{6}]^{4-.1}Vac centres appear to be present in a fixed concentration ratio (estimated at 1:3) which cannot be changed by irradiating or heating the crystals [SABB98a]. A very small concentration of [RhCl_{6}]^{4-.0}Vac centres was also found in these crystals (W-band EPR measurements). The stability of the [RhCl_{6}]^{4-.n}Vac complexes in melt-grown NaCl is thus completely different from that in solution-grown crystals.

Olm et al. established the structural model of the [RhCl_{6}]^{4-.1}Vac centre in melt-grown AgCl single crystals. Although ENDOR spectra due to the central Rh^{2+} ion, two equivalent first shell axial Cl ions and two equivalent fourth shell axial Ag^{+} ions were observed, the identification of the centre was mainly based on the thermal behaviour of the EPR spectrum. The low temperature {\textsuperscript{5}A_{1}} ground state of the centre was explained by a Jahn-Teller elongation. Its deviation from tetragonal symmetry was attributed to the presence of a charge compensating NNN cation vacancy in the equatorial plane. At temperatures above approximately 80 K (strongly dependent on the dopant concentration) the superhyperfine structure on the EPR spectrum of this centre disappears, the spectral g components broaden and the g_{\perp} and g_{\|} component gradually disappear. At higher temperatures a new component arises at \( g = \sqrt{\frac{g_{\perp}^2 + g_{\|}^2}{2}} \) in the spectrum with \( \vec{B}_{0} \parallel \{100\} \). It turns out to be the perpendicular component of a tetragonal centre with \( g_{\perp} \) very close to the \( g_{\|} \) value of the centre at low temperature. This behaviour has been attributed to a thermally assisted reorientation of the elongation axis between the \( y \) and \( z \) directions of the complex, as a result of which a motionally averaged \( g \) value is detected. It has also been observed for the [RhCl_{6}]^{4-.1}Vac centre in NaCl [SABB98a]. The centre then appears to have a \({\textsuperscript{5}B}_{1}\) ground state. As the reorientations of the centre involve the \( y \) and \( z \) axes of the complex, the cation vacancy was proposed to be localised on the \( x \) axis. Close to room temperature, the tetragonal centre is reversibly converted into a centre with isotropic \( g \) value. This surprising phenomenon, which is not observed for the corresponding centre in NaCl, has been
attributed to a reversible migration of the cation vacancy, away from the centre when raising the temperature or towards the centre when lowering the temperature. The experimental data on [RhCl₄]⁺λVac centres in AgCl are still rather limited. They will be discussed in chapter 6 of this work. No evidence for the presence of [RhCl₄]⁺λ.2Vac centres in AgCl has been found up to now.

It should be noted that for all [RhCl₄]⁺λVac complexes, both in NaCl and AgCl, the cation vacancies were always found in NNN positions. The most direct evidence for the presence and the position of these vacancies will be presented in chapter 5. From purely electrostatic considerations, one would expect complexes with nearest neighbour (NN) vacancies to be more stable, as the distance between the central ion with an extra positive charge and the vacancies with an extra negative charge is smaller. Atomistic simulations for the [RhCl₄]⁺λVac centre in AgCl by Baetzold indeed favour the NN above the NNN positions for the vacancies by 0.1-0.2 eV. The experimental evidence, however, clearly contradicts these calculations. The results of computer simulations by Bannon et al. on divalent cation - vacancy association and aggregation in alkali [BANN85a] and silver halides [BANN85b] are in this respect very interesting, although no calculations for Rh³⁺ complexes are included. These simulations indicate that for divalent cations with a small ionic radius, relative to that of the ion it is replacing, the association with a NNN cation vacancy may become energetically more favourable than that with a NN vacancy. Furthermore, the association energy of divalent cation - vacancy defect pairs were found to decrease as the ionic radius of the divalent cation decreases. The calculated association energy for NN vacancies was, as expected, found to be larger than for NNN vacancies. In view of these results and the enormous progress made in the last few decades in the field of ab initio and density functional calculations, it appears worth the effort to recalculate the optimal structures of the [RhCl₄]⁺λVac complexes in NaCl and AgCl.

3.4.3. The hydrated Rh³⁺ complexes in AgCl

The existence of [RhXₙ(νH₂O)ₖ₋ₙ]ⁿ⁻⁻₃⁻ (X = Cl or Br, n = 4, 5 and 6) complexes in aqueous solutions in which RhCl₄⁺xH₂O was dissolved, was demonstrated by Endo et al. [ENDO90]. They correlated thermodynamical calculations of the equilibrium concentrations for these complexes as a function of the Cl⁻ concentration of the solution with experimental optical absorption results. They also studied the influence of the concentration of [RhXₙ(νH₂O)ₖ₋ₙ]ⁿ⁻⁻₃⁻ complexes in dopant solutions of AgX emulsions on the macroscopic sensitizer properties of the resulting emulsions. The sensitivity in general decreases dramatically by Rh³⁺ incorporation in the crystals. As the H₂O coordination number of the Rh³⁺ ions in the dopant solution increased, the sensitivity of cubic grain AgX emulsions appeared to be less decreased. The sensitivity of tabular AgBr emulsions, on the other hand, seemed not to be affected by the H₂O coordination of the Rh³⁺ ions in the dopant solution. These results indicate that the Rh³⁺ ion in AgX emulsion microcrystals may be ligated by molecules of the solvent and that the presence of these hydroxides has an effect on the electron trapping properties of the complexes and/or on the concentration of Ag⁺ interstitials in the crystals. Endo et al. suggest the latter possibility.

Vercammen et al. found a correlation between the concentration of the R4, R5 and R6 centres (Rn centres, with n = 4, 5 and 6, respectively), produced after X-ray or UV irradiation of AgCl emulsion microcrystals, and the concentration of [RhCl₄(νH₂O)ₖ₋ₙ]ⁿ⁻⁻₃⁻ complexes in the dopant solution
[VERC98c]. The $g$ values for the R6 centre were close to those reported for the dominant [RhCl$_6$]$^{3+}$ centre in melt-grown AgCl single crystals. The centre appeared to have axial symmetry, rather than orthorhombic, though. Therefore, Vercammen et al. identified it as a [RhCl$_6$]$^{3+}$ complex without near cation vacancies. This assignment will be confirmed in chapter 6. The other two centres were attributed to singly (R5) and doubly hydrated (R4) complexes. These assignments are confirmed by the ENDOR studies of Pawlik et al. [PAWL98] and Vrielinck et al. [VRIE99, VRIE00]. They will be discussed in detail in chapter 6. Vercammen et al. [VERC98c] further demonstrated that the thermal stability of the Rn centres decreases as the number of hydroxyl groups increases. The decrease in trapping depth for water coordinated complexes explains the decreased desensitisation by these complexes, as reported by Endo et al. [ENDO90], very well.

3.4.4. Other rhodium-related centres in NaCl

The identification of the Rh$^+$ centre in NaCl was based on ENDOR measurements [VRIE98a]. It was found to have octahedral symmetry. The details about the magnetic resonance properties of this centre, its formation and stability will be discussed in chapter 4. For the B-centre, only limited experimental results are available. The centre was tentatively identified as a hydrated Rh$^{2+}$ complex, by analogy with the Rn complexes in AgCl. Some EPR and ENDOR results on this centre, which have not yet been published, will also be mentioned in chapter 4.

The structure of the Rh-dimer centre was proposed by Vercammen et al. [VERC98b]. It consists of two weakly interacting [RhCl$_6$]$^{3+}$:1Vac complexes along a $(110)$ direction at a distance $2\sqrt{2}a$ ($a$ = cation-anion distance) from one another with the vacancies arranged in a way that the complex acquires orthorhombic $I$ ($D_{2h}$) symmetry. The structure is shown in figure 3.11d. Sabbe [SABB00] performed ENDOR measurements for this centre. For the interpretation of the spectra, the Rh-dimer was described as an $S = 1$ system, rather than as a pair of weakly interacting $S = 1/2$ centres. It is interesting to note that Bannon et al. [BANN85a, BANN85b] calculated the structure in figure 3.11d to be the most stable for divalent cation dimers in alkali and silver halide crystals. They indicate that the formation of these centres requires the presence of divalent cation monomers associated with a NNN cation vacancy. This may explain why the Rh-dimer is formed in NaCl crystals grown from the melt and not in solution-grown crystals, in which most of the Rh$^{2+}$ ions are not associated with a NNN cation vacancy. It is, however, also believed that the Rh concentration in the latter crystals is lower than in melt-grown crystals.
Chapter 4: Magnetic resonance study of Rh\(^+\) and the B-centre in NaCl single crystals

4.1. Introduction
X-ray irradiation at room temperature produces three stable rhodium-related paramagnetic centres in solution-grown NaCl doped with Rh\(^{3+}\). The primary centre centre has been identified as a non-locally charge compensated [RhCl\(_6\)]\(^+\) complex, substituting for [NaCl\(_6\)]\(^+\) [ZDRA97], based on an X-band EPR and ENDOR study. A secondary centre in these crystals, referred to as the B-centre, also observed with X-band EPR, was in the same study tentatively assigned to a pentachloro Rh\(^{2+}\) complex with one water or hydroxyl ligand. Some additional magnetic resonance results for this centre will be presented at the end of this chapter. These data do not provide sufficient evidence to propose a complete microscopic model for the centre(s) involved. The third centre could at X-band frequencies only be observed with ENDOR. The identification of this centre as a substitutional Rh\(^+\) ion is the main topic of this chapter. The data obtained at two microwave frequency bands provide complementary information for the centre; whereas the ENDOR spectrum for most interactions can only be recorded at X-band, the best EPR information is obtained at Q-band. Special attention will be paid to the ground state electronic properties of the Rh\(^+\) ion (4d\(^5\) configuration) in NaCl. The formation properties of this centre in solution-grown and melt-grown NaCl will also be discussed.

4.2. Identification of a cubic Rh\(^+\) centre in X-ray irradiated NaCl single crystals

4.2.1. X-band ENDOR spectrum

After X-ray irradiation at room temperature of solution-grown NaCl single crystals, doped with Na\(_3\)RhCl\(_6\)\cdot12H\(_2\)O, an intense ENDOR spectrum is observed at X-band frequencies (9.56 GHz) in a very wide magnetic field range (265 - 315 mT, independent of the orientation of the magnetic field) at temperatures below 15 K. The optimum detection parameters for this spectrum are given in table 4.1.

<table>
<thead>
<tr>
<th>T</th>
<th>(v_{MW})</th>
<th>(P_{MW})</th>
<th>(P_{RF})</th>
<th>RF range</th>
<th>modulation depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-7K</td>
<td>9.56 GHz</td>
<td>20 mW</td>
<td>200 W</td>
<td>0.8-30.8 MHz</td>
<td>50 kHz</td>
</tr>
</tbody>
</table>

When the magnetic field is set to \(g = 2.45\), the intensity of the spectrum reaches a maximum. In figure 4.1 the ENDOR spectrum recorded at 6 K with the static magnetic field \(\vec{B}_0 \parallel \langle 100 \rangle\) at \(g = 2.45\) is shown. As the spectrum is observed in a large magnetic field range, the magnetic field shift method (see § 2.5.1) may be applied to assign each ENDOR transition to a particular nucleus. One set of two transitions in the high frequency region of this spectrum could be attributed to the interaction of the unpaired electrons with the central \(^{103}\)Rh nucleus. The other transitions in this region are due to interactions with \(^{35}_{57}\)Cl nuclei. The transitions below 6 MHz are attributed to interactions with \(^{22}\)Na nuclei. They are centred around the Larmor frequency of this magnetic isotope. None of the
observed or known EPR spectra in the magnetic field range around \( g = 2.45 \) (\( g_\perp \) range of the \([\text{RhCl}_6]^{4-}\) or \(\text{N Vac}\) centres and of the B-centre) could be related to this ENDOR spectrum. ENDOR-Induced EPR (EI-EPR) experiments were carried out in order to reconstruct the EPR spectrum of the centre. Very intense EI-EPR signals were detected, but they exhibit a very complex and strongly angular dependent structure, which we could, up to now, not interpret.

![ENDOR spectrum](image)

**Figure 4.1**: ENDOR spectrum recorded at 6 K with the magnetic field along a crystal \(<100>\) direction after X-ray irradiation at room temperature of Rh\(^{2+}\) doped solution-grown NaCl single crystals. The ENDOR transitions can be assigned (magnetic field shift method) to \(^{23}\text{Na}, ^{35/37}\text{Cl}\) and \(^{103}\text{Rh}\) nuclei.

4.2.2. Determination of the effective spin

At temperatures around 10 K and high microwave power (> 10 mW) a very weak transition is observed in the X-band EPR spectrum at \( g = 4.90 \), as shown in figure 4.2 (\( \vec{B}_0 \parallel \langle 100 \rangle \)). When the static magnetic field is set to the centre of this line, an ENDOR spectrum can be observed which is very similar to the one recorded at \( g = 2.45 \), but which has a much lower intensity. Figure 4.3 shows the 15 – 30 MHz part of the ENDOR spectrum recorded at both magnetic field positions. The transitions observed at the low field EPR transition can be calculated.

![ΔM_s = 2](image)

**Figure 4.2**: \( \Delta M_s = 2 \) EPR transition recorded at 7 K and 9.56 GHz.
from those recorded at \( g = 2.45 \) merely by rescaling the Larmor frequency of the corresponding nuclei. The occurrence of this low field EPR line is explained by assigning it to a \( \Delta M_S = 2 \) forbidden transition of the paramagnetic centre. Indeed, the fact that essentially an identical ENDOR spectrum is observed at both magnetic field positions indicates that the EPR transitions are due to the same centre.

**Figure 4.3**: High frequency part (15 - 30 MHz) of the ENDOR spectrum recorded at 6 K with the magnetic field parallel to \( <100> \) and set to values corresponding with \( g = 2.45 \) (upper trace) and \( g = 4.90 \) (lower trace). The two spectra are essentially identical: they can be converted into one another by rescaling the Larmor frequency (half the splitting between the transitions indicated with arrows) of the nuclei responsible for the transitions. \(^{35}\text{Cl} \) transitions are indicated with *.

**Figure 4.4**: Low frequency part of the ENDOR spectrum recorded at 6 K with the magnetic field parallel with \( <100> \) set to \( g = 2.45 \) (upper trace) and to \( g = 4.90 \) (lower trace). In the \( g = 2.45 \) spectrum, the \( M_s = -1 \) and \( M_s = 0 \) multiplets are clearly observed. The \( M_s = 1 \) multiplet is not resolved. Its expected position is indicated with dashed lines. In the \( g = 4.90 \) spectrum, the \( M_s = 0 \) transitions are also missing.

In addition, from the resonance conditions for a \( \Delta M_S = 2 \) transition (\( \nu_{\text{MW}} = 2g\mu_B B_{\text{res}} \), zero field splitting neglected) it can be calculated to occur at twice the \( g \) value of the centre (\( \nu_{\text{MW}} = 2g \)) or at half the magnetic field value (\( B_{\text{res}} = \frac{\nu_{\text{MW}}}{2g\mu_B} \)) of the \( \Delta M_S = 1 \) transition (\( \nu_{\text{MW}} = g\mu_B B_{\text{res}} \)). This implies that the centre has an effective spin \( S > 1/2 \). If no zero field splitting occurs, the \( \Delta M_S = 1 \) transitions should all
coincide and the effective spin of the centre can be determined from the number of $M_S$ multiplets in the ENDOR spectrum. We determined $S$ from the $^{23}$Na transitions. Figure 4.4 shows the $^{23}$Na ENDOR spectra recorded with $\vec{B}_0 \parallel (100)$ at $g = 2.45$ and at $g = 4.90$. Contrary to figure 4.3, the spectra are not identical in this case: in the spectrum recorded at the low field transition the central part close to the $^{23}$Na Larmor frequency is missing. This leads to the conclusion that $S = 1$, as can be explained with the aid of the energy level scheme in figure 4.5a. At $g = 2.45$, the two allowed EPR transitions of the $S = 1$ system ($M_S : 1 \rightarrow 0$ and $M_S : 0 \rightarrow -1$) coincide. As a result the ENDOR spectrum consists of NMR transitions within all three $M_S$ multiplets, and in the spectrum three groups of lines should be observed. The $M_S = 1$ transitions appear to have very low intensity, though, and are hardly observed. The $\Delta M_S = 2$ transition at $g = 4.90$ only involves the $M_S = 1$ and $M_S = -1$ levels. The NMR transitions within the $M_S = 0$ multiplet should thus not be observed at this EPR transition. As they contain, to first order, no contribution of the superhyperfine tensor, these NMR transitions are expected in the close neighbourhood of the $^{23}$Na Larmor frequency. It is indeed observed that these transitions are missing in the ENDOR spectrum recorded at the low field EPR line. Assuming $S = 1$, the observed ENDOR spectra can be very well explained.

![Energy level scheme](image)

**Figure 4.5**: Energy level scheme for a paramagnetic system with (a) $S = 1$ and (b) $S = 2$ interacting with a nucleus with $I = 3/2$ ($g_{\text{nH}} < 2\Delta$). For the $S = 1$ system, the $M_S = 0$ level is not involved in the $\Delta M_S = 2$ transition, whereas for the $S = 2$ system it is involved in two of the $\Delta M_S = 2$ EPR transitions.

Moreover, for $S > 1$, the $\Delta M_S = 2$ transitions involve all $M_S$ multiplets, as illustrated in figure 4.5b for an $S = 2$ system. If, again, the zero field splitting is neglected, all $\Delta M_S = 2$ transitions coincide at the half field EPR line and essentially the same ENDOR spectrum should be recorded as at the $\Delta M_S = 1$ EPR lines. The fact that not all NMR transitions can be observed at the $\Delta M_S = 2$ EPR spectrum is thus very specific for an $S = 1$ system.

As $S = 1$, the ENDOR spectra for each nucleus should be analysed using a spin Hamiltonian

$$
\hat{H}_S = \mu_B \vec{B}_0 \cdot \vec{g} \cdot \vec{S} + \frac{\hbar}{2} \vec{S} \cdot \vec{\Delta} \cdot \vec{S} + \frac{\hbar}{2} \vec{S} \cdot \vec{\eta} \cdot \vec{S} - g_n \mu_n \vec{B}_0 \cdot \vec{I} + \vec{I} \cdot \vec{Q} \cdot \vec{I} 
$$

(4.1)
with \( S = 1 \) and \( \vec{Q} = \vec{0} \) if \( I = 1/2 \). In the next paragraph, it will be shown that the centre has cubic symmetry. As a result, the \( \vec{g} \) tensor is isotropic and \( \vec{D} = \vec{0} \) in equation 4.1. Calculated to first order, the ENDOR transitions occur at

\[
|AM_S - g_n \mu_B B_0 + 3QM_0|
\]

(4.2)

In principle three \( M_S \) multiplets are expected for each interaction: the \( M_S = \pm 1 \) multiplets give rise to a spectrum very similar to that for the interaction with magnetic nuclei in an \( S = 1/2 \) centre (see § 3.3), whereas the transitions within the \( M_S = 0 \) multiplet should be close to the Larmor frequency of the nucleus involved (see § 2.5.1).

4.2.3. Determination of the symmetry

Although no accurate information about the \( \Delta M_S = 1 \) EPR spectrum could be obtained at X-band, the symmetry of the centre could still be determined to be cubic. A first indication for the cubic symmetry is provided by the angular dependence of the \( \Delta M_S = 2 \) EPR transition, whose magnetic field position does not change when the orientation of the magnetic field is rotated in a \{100\} plane. However, this EPR line has an asymmetrical line shape and very low intensity. The symmetry can be determined more accurately from the angular dependence of the ENDOR spectrum recorded at \( g = 2.45 \). In figure 4.6, a model for the Rh ion on a substitutional cation position in the NaCl lattice is shown. In this figure, the nuclei for which the NMR transitions have been identified in the ENDOR spectra are indicated in colour.

![Figure 4.6: Microscopic model of a Rh ion in a substitutional cation position in the NaCl lattice without nearby lattice defects or relaxations. For an arbitrary orientation of the magnetic field, three magnetically inequivalent sets of neighbours along the <100> axes are observed, indicated in red, green and blue.](image)

![Figure 4.7: Angular variation of the \(^{101}\)Rh transitions recorded at X-band (9.56 GHz). Black dots represent experimental data points. Full lines are calculated with the spin Hamiltonian parameters in table 4.3.](image)
The angular dependence of the NMR transitions was studied by rotating the magnetic field in the crystal (001) plane from [100] (θ = 0°) to [110] (θ = 45°) and recording the ENDOR spectrum with 5° intervals. Figure 4.7 shows the angular dependence of the $^{103}$Rh ENDOR spectrum. The position of the transition frequencies does not move when the magnetic field is rotated in the (001) plane. The angular dependence can be perfectly fitted with an isotropic $\tilde{A}$ tensor. This gives already a more accurate indication for the cubic symmetry of the centre. Only two transitions ($M_s = \pm 1$) are observed for each angle. The $M_s = 0$ transition is not observed, because the Larmor frequency of $^{103}$Rh (0.38 MHz at 280 mT) lies below the detection limit of our ENDOR spectrometer.

Even more convincing evidence for the cubic symmetry of the centre is obtained from the ENDOR spectrum for the interaction with the first shell of $\text{Cl}^-$ ions and with the fourth shell of $\text{Na}^+$ ions. The angular dependence of the spectra, shown in figure 4.8 for the $^{35}$Cl isotope and in figure 4.9 for $^{23}$Na and fitted with axial $\tilde{A}$ and $\tilde{O}$ tensors, proves that in each of these shells all six ions are physically equivalent.

**Figure 4.8:** Angular variation in the (001) plane of the first shell $^{35}$Cl transitions, recorded at X-band (9.56 GHz) and 6 K. For an arbitrary orientation in the rotation plane, three magnetically inequivalent sets of nuclei are observed (red, green and blue). Only the $M_s = -1$ and $M_s = 1$ multiplets are observed.

**Figure 4.9:** Angular variation in the (001) plane of the fourth shell $^{23}$Na transitions, recorded at X-band (9.56 GHz) and 6 K. For an arbitrary orientation in the rotation plane, three magnetically inequivalent sets of nuclei are observed (red, green and blue). The $M_s = -1$ and $M_s = 0$ multiplets are clearly observed in the spectrum, the $M_s = 1$ transitions have very low intensity and cannot be followed throughout the complete angular range.

However, if a magnetic field is applied, three sets of two ions become magnetically inequivalent. These sets are indicated in different colours in figure 4.6. If $\vec{B}_0 \parallel \langle 100 \rangle$ two of these sets (indicated in red and green) become magnetically equivalent. Their transition frequencies coincide, while those for the third set (in blue) reach a maximum. If the magnetic field is rotated in the (001) plane, the frequency positions of the set indicated in red do not change, while those for the sets indicated in
green and blue move towards each other. For \( \vec{B}_0 \parallel \langle 110 \rangle \) the latter sets become magnetically equivalent. For the fourth shell \( ^{23}\text{Na} \) interaction, the \( M_S = 0 \) and \( M_S = -1 \) multiplets are observed for all magnetic field orientations. The \( M_S = 0 \) transitions have a much higher intensity than those with \( M_S = -1 \). The \( M_S = 1 \) transitions occur at low frequencies and appear to have low intensity. They cannot be followed throughout the angular variation. For the first shell \( \text{Cl} \) interaction, only the \( M_S = \pm 1 \) transitions have been observed at X-band. The \( M_S = 0 \) transitions are, rather surprisingly, missing. They are expected to lie in the same frequency region as the \( ^{23}\text{Na} \) transitions.

The X-band EPR results, the isotropic \( ^{103}\text{Rh} \) hyperfine interaction and the equivalence of all ions in the first and the fourth coordination shells provide sufficient evidence to conclude that the centre has indeed cubic symmetry.

4.2.4. ENDOR spin Hamiltonian parameters: delocalisation of the unpaired electrons to the ligands

The spin Hamiltonian parameters obtained from a least squares error fitting of calculated transition frequencies (by diagonalisation of the spin Hamiltonian 4.1) to the experimental data are shown in table 4.2.

**Table 4.2**: spin Hamiltonian parameters for the interactions identified in the ENDOR spectrum. The principal hyperfine and quadrupole values are given in MHz. The error in these parameters is given as a subscript. The principal directions of the (super)hyperfine and quadrupole tensors are along the crystal \( \langle 100 \rangle \) axes.

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>( A_i )</th>
<th>( A_\perp )</th>
<th>( Q_i )</th>
<th>( Q_\perp )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^{103}\text{Rh} )</td>
<td>21.61</td>
<td>21.61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^{35}\text{Cl} )</td>
<td>23.91</td>
<td>11.41</td>
<td>1.22(_3)</td>
<td>-0.61(_2)</td>
</tr>
<tr>
<td>( ^{23}\text{Na} )</td>
<td>2.08(_1)</td>
<td>1.31(_1)</td>
<td>-0.074(_5)</td>
<td>0.037(_3)</td>
</tr>
</tbody>
</table>

ENDOR experiments alone give no information about the absolute signs of these values. In § 2.5.4 it has been explained that the relative signs of hyperfine interaction constants can be determined with double ENDOR, which we used to determine the signs of the \( ^{103}\text{Rh} \) hyperfine value, assuming that the principal superhyperfine tensor components for the first shell Cl nuclei are positive. In figure 4.10 the ENDOR (a) with \( \vec{B}_0 \parallel \langle 001 \rangle \) and double ENDOR spectra when pumping the \( ^{103}\text{Rh} \) transitions (b and c) are shown. When the ENDOR line at 21.2 MHz is pumped, the intensity of the \( M_S = -1 \) Cl transitions decrease and those for the \( M_S = 1 \) multiplet increase. When the line at 21.9 MHz is pumped, the \( M_S = -1 \) Cl transitions increase in intensity, while the \( M_S = 1 \) multiplet decreases. Double ENDOR experiments thus indicate that the transition at 21.2 MHz is an \( M_S = -1 \) transition and the one at 21.9 MHz belongs to the \( M_S = 1 \) multiplet. This may only happen if the hyperfine constant and \( g_N \) have different signs. As \( g_M^{(103}\text{Rh}) < 0 \), \( A^{(103}\text{Rh}) \) should be positive. In [VRIE98a] the hyperfine value was erroneously stated to be negative. The relatively large value of \( A \) and its sign opposite to that of the nuclear magnetic moment indicate that the main contribution to the hyperfine constant arises through core polarisation.
Figure 4.10: High frequency part of the ENDOR (a) and double ENDOR spectra with the second RF frequency set to 21.2 MHz (b) and to 21.9 MHz (c), recorded with the magnetic field parallel to <100>. The arrows in the double ENDOR spectra indicate that the intensity of the corresponding transition has increased (arrow up) or decreased (arrow down).
As the intensity of the $^{23}\text{Na}$ transitions did not significantly change if the $^{35}\text{Cl}$ or $^{103}\text{Rh}$ transitions were pumped and vice versa, we were unable to determine the signs of the superhyperfine constants for this interaction. Attempts to determine the signs of the principal $\bar{Q}$ components for $^{35}\text{Cl}$ and $^{23}\text{Na}$ from the variation of the spectrum by changing the magnetic field position (see § 3.3.1 ENDOR spectrum, figure 3.7) also failed.

From the superhyperfine values of the first and fourth shell ions, the unpaired spin density on these ions can be calculated, as explained in § 2.3.3. The total spin density for a centre with effective spin $S = 1$ is normalised on $2S = 2$ (which corresponds to the two unpaired electrons in this system). The spin density on each of the Cl ligands is calculated to be 0.075, which results in a total spin density of 0.45 on the first shell of ligands. The total spin density in the second shell only amounts to 0.005. It most probably arises through overlap of the fourth shell Na$^+$ s and p orbitals with those of the first shell Cl ions (super-superhyperfine interaction [PINH85]). As no other large interactions have been detected in the ENDOR spectra, the remaining 1.545 spin density should be localised on the central Rh ion. No information about the spin density in the Rh d orbitals could be obtained because the hyperfine tensor shows no anisotropy.

4.2.5. Identification of the centre as Rh$^+$

The X-band magnetic resonance data for the centre ($S = 1$, cubic symmetry and strong interaction with nuclei on the $\langle 100 \rangle$ axes) lead to its identification as a Rh$^+$ ion, substituting for Na$^+$. Indeed, Rh$^+$ has a $4d^8 (t^6_2 e^2_0)$ ground state electron configuration or an $e^2_0$ hole configuration. The allowed terms for this configuration are $^3A_2g$, $^1E_g$ and $^1A_1g$, with the triplet state lying lowest [GRIF61]. The effective spin of this state, which corresponds to the real spin in this case, is $S = 1$. The base functions for this state may be expressed as Slater determinants of the Rh$^+$ d functions

$$\begin{align*}
|\Phi_{0,1}\rangle &= \left\{ d_{3z^2-r^2}^+ d_{x^2-y^2}^+ \right\} \\
|\Phi_{0,0}\rangle &= \frac{1}{\sqrt{2}} \left[ \left\{ d_{3z^2-r^2}^+ d_{x^2-y^2}^- \right\} + \left\{ d_{3z^2-r^2}^- d_{x^2-y^2}^+ \right\} \right] \\
|\Phi_{0,-1}\rangle &= \left\{ d_{3z^2-r^2}^- d_{x^2-y^2}^- \right\}
\end{align*}$$

(4.3)

The unpaired electrons (or holes) are thus mainly localised in the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals of the central ion and are expected to interact strongly with the nuclei along the $\langle 100 \rangle$ axes of the complex. Rh$^+$ has the same valence state as Na$^+$. The presence of charge compensating vacancies, which could lower the symmetry of the centre, is not required. The ground state of the ion is orbitally non-degenerate and no Jahn-Teller distortion is expected. Rh$^+$ should thus have perfect cubic symmetry, as was observed for the centre under study.

As Rh$^+$ substitutes for Na$^+$ and no vacancies are in its neighbourhood, the quadrupole interaction observed for the first shell of Cl nuclei and the fourth shell of Na nuclei should be solely due to the unpaired electron distribution over the [RhCl$_6$]$^{5-}$ complex. This contribution can be calculated from the anisotropic superhyperfine interaction in the way indicated in § 2.3.5. Such calculations lead to values
of $q = Q/2$ of 0.5 MHz for the first shell $^{35}$Cl nuclei and $-0.02$ MHz for the fourth shell $^{23}$Na nuclei. These values are in reasonably good agreement with the experimentally observed values, especially in view of the approximations made. It is, e.g., assumed that the substitution of Na$^+$ by Rh$^+$ induces no electric field gradients in the crystal. Our choice of the sign for the quadrupole parameters is inspired by these calculations.

4.2.6. **Ground state electronic properties of Rh$^+$ in a distorted octahedral crystal field**

For $d^8$ ions the strong and intermediate crystal field approximations lead to the same ground state electronic properties. In this paragraph, we will adopt the strong crystal field approach. The perturbation scheme and the calculation of the $\tilde{g}$ tensor are very similar to those for the Rh$^{3+}$ ion (see § 3.2). It will be shown that in the particular case of the Rh$^+$ ion in NaCl, the crystal field splitting of the $d$ levels and the Coulomb splitting between the allowed terms of the ground and the excited state configurations are of the same order of magnitude. For simplicity reasons, the hole formalism is again adopted.

As was already argued in the previous paragraph, the ground state term of the strong crystal field $e_g^2$ configuration is the $^3A_{2g}$ state. Via spin-orbit coupling, this state will be mixed with the $e_g t_{2g}$ configuration states. An overview of the terms of the ground state and the excited states, along with their crystal field and Coulomb interaction energies, is given in table 4.3. It should be noted that the Coulomb interaction mixes higher excited state terms (with $t_{2g}$ configuration) into some of these states ($e_g^1A_{1g}$, $e_g t_{2g}^3T_{1g}$ and $e_g t_{2g}^1T_{2g}$). This configuration interaction will be neglected here. It has no significant implications on the results.

**Table 4.3**: Allowed terms of the ground and first excited configurations of a $d^8$ ion in a strong octahedral crystal field. The crystal field and Coulomb interaction energies are calculated relative to the energy of the ground state level. $\Delta$ indicates the cubic crystal field splitting of the $d$ orbitals of the ion. $B$ and $C$ represent the Racah parameters. The Coulomb interaction energy values were taken from [GRIF61].

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Crystal field energy</th>
<th>Term</th>
<th>Coulomb interaction energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>$e_g^2$</td>
<td>0</td>
<td>$^3A_{2g}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^1E_g$</td>
<td>$8B + 2C$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^1A_{1g}$</td>
<td>$16B + 4C$</td>
</tr>
<tr>
<td>$e_g t_{2g}$</td>
<td>$\Delta$</td>
<td>$^3T_{2g}$</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^3T_{1g}$</td>
<td>$12B$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^1T_{2g}$</td>
<td>$8B + 2C$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^1T_{1g}$</td>
<td>$12B + 2C$</td>
</tr>
</tbody>
</table>

Using the free ion values of the Racah parameters for the Rh$^+$ ion ($B = 596$ cm$^{-1}$ and $C = 3236$ cm$^{-1}$), this leads to an arrangement of the ground state and excited state levels, as given in figure 4.11. As
the singlet states of the $e_g^2$ configuration do not contribute to the magnetic resonance properties of the ion, they are not considered in figure 4.11. Spin-orbit interaction only couples the $T_{2g}$ excited states to the $3A_{2g}$ ground state, as

$$T_{1g} \otimes A_{2g} = T_{2g}$$

(4.4)

The wave functions of the $^1T_{2g}$ and $^3T_{2g}$ states are given in table 4.4.

The $\tilde{g}$ tensor will be calculated in the more general case of a tetragonally distorted octahedral crystal field. The ground state triplet then has $B_{1g}$ symmetry, and the excited states of interest split in a $B_{2g}$ ($z$) and an $E_g$ ($x$ and $y$) level. The splitting due to lowering of the symmetry of the complex is also shown in figure 4.11. The energy differences which play an important role in the calculation of the magnetic resonance properties are defined in this figure.

![Diagram](image)

**Figure 4.11:** Ground state term of the $e_g^2$ hole configuration and allowed terms of the $e_g^2$ excited state hole configuration for a $d^l$ ion in perfect (a) and tetragonally distorted (b) octahedral coordination. Spin-orbit coupling mixes only the $T_{2g}$ terms in the $A_{2g}$ ground state term.

The first order contributions of the excited state levels to the ground state wave function arising from spin-orbit coupling can, in an analogous way as in § 3.2, be calculated from the matrix elements

$$\langle \Phi_s, M_s | \hat{H}_{SO} | \Phi_o, M_o \rangle = \langle \Phi_s, M_s | \sum_{4d}^n \left( \hat{a}_1 \cdot \hat{s}_1 + \hat{a}_2 \cdot \hat{s}_2 \right) | \Phi_o, M_o \rangle$$

(4.5)

The first order corrected ground state wave functions are

$$|1\rangle = |\Phi_o, 1\rangle - \frac{i \sum_{4d}^n}{\Delta_{1z}} |\Phi_{1z}, 1\rangle + \frac{i \sum_{4d}^n}{\sqrt{2} \Delta_{3z}} \left( |\Phi_{1x}, 0\rangle + i |\Phi_{1y}, 0\rangle \right)$$

$$|0\rangle = |\Phi_o, 0\rangle + \frac{i \sum_{4d}^n}{\Delta_{3z}} |\Phi_{3z}, 0\rangle + \frac{i \sum_{4d}^n}{\sqrt{2} \Delta_{3y}} \left( |\Phi_{1x}, 1\rangle - i |\Phi_{1y}, 1\rangle + |\Phi_{1x}, -1\rangle + i |\Phi_{1y}, -1\rangle \right)$$

(4.6)

$$|-1\rangle = |\Phi_o, -1\rangle + \frac{i \sum_{4d}^n}{\Delta_{1z}} |\Phi_{1z}, -1\rangle + \frac{i \sum_{4d}^n}{\sqrt{2} \Delta_{1y}} \left( |\Phi_{1x}, 0\rangle - i |\Phi_{1y}, 0\rangle \right) - \frac{i \sum_{4d}^n}{\sqrt{2} \Delta_{3y}} \left( |\Phi_{3x}, 0\rangle - i |\Phi_{3y}, 0\rangle \right)$$
The second order energy corrections due to spin-orbit coupling of these states are
\[
\Delta E_{SO}(|1\rangle) = -\left(\frac{\hbar}{\lambda_{1z}}\right)^2 \left(\frac{1}{\Delta_{1z}} + \frac{1}{\Delta_{1xy}} + \frac{1}{\Delta_{3xy}}\right)
\]
\[
\Delta E_{SO}(|0\rangle) = -\left(\frac{\hbar}{\lambda_{3z}}\right)^2 \left(\frac{1}{\Delta_{3z}} + \frac{2}{\Delta_{1xy}}\right)
\]
\[
\Delta E_{SO}(|-1\rangle) = -\left(\frac{\hbar}{\lambda_{1z}}\right)^2 \left(\frac{1}{\Delta_{1z}} + \frac{1}{\Delta_{1xy}} + \frac{1}{\Delta_{3xy}}\right)
\]

(4.7)

**Table 4.4**: Wave functions of the $^1T_{2g}$ and $^3T_{2g}$ terms of the $e_g^{1} t_{2g}$ excited state configuration in perfect and tetragonally distorted octahedral symmetry.

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>Wave functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^3T_{2g}$</td>
<td>$</td>
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<tr>
<td></td>
<td>$</td>
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<td>$</td>
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<td></td>
<td>$</td>
</tr>
<tr>
<td>$^1T_{2g}$</td>
<td>$</td>
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<td>$</td>
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<td>$</td>
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</tr>
</tbody>
</table>

From equation 4.7 the zero field splitting for the $S = 1$ system can be calculated.
\[
D = E(|\pm 1\rangle) - E(|0\rangle) = (\frac{\hbar}{\Delta})^2 \left( \frac{1}{\Delta_{1xy}} - \frac{1}{\Delta_{1z}} - \frac{1}{\Delta_{3xy}} + \frac{1}{\Delta_{3z}} \right)
\]  
(4.8)

If no tetragonal distortion occurs, \(\Delta_{1z} = \Delta_{1xy}\) and \(\Delta_{3z} = \Delta_{3xy}\), and the zero field splitting vanishes. As the \(\Phi_{ij}\) levels lie well below the \(\Phi_{3j}\), the sign of the zero field splitting is dominated by the term \(\left( \frac{1}{\Delta_{1xy}} - \frac{1}{\Delta_{1z}} \right)\). \(D\) will thus be positive for elongated complexes (\(\Delta_{1xy} < \Delta_{1z}\)) and negative for compressed complexes (\(\Delta_{1z} < \Delta_{1xy}\)).

The \(\tilde{g}\) tensor for the \(d^5\) hole configuration can be calculated by evaluating the electronic Zeeman operator (2.7) in the spin triplet of equation (4.6). The principal \(g\) values are given by

\[
g_{1z} = g_0 - \frac{4\zeta_d}{\Delta_{1z}} = g_0 + \frac{4\zeta_d}{\Delta_{1z}}
\]

\[
g_{xy} = g_0 - \frac{4\zeta_d}{\Delta_{1xy}} = g_0 + \frac{4\zeta_d}{\Delta_{1xy}}
\]

In perfect octahedral coordination, \(g_{1z} = g_{xy}\). The results calculated here are in perfect agreement with the magnetic resonance properties for \(d^8\) ions given by Mabbs and Collison [MABB92] and by Abragam and Bleaney [ABRA70]. The latter authors [ABRA70] did not consider contributions from the \(^1T_{2g}\) excited state, though.

4.2.7. The EPR spectrum: aspects discussed in the literature and experimental observation at Q-band

d\(^5\) complexes of the first row transition metal ions Ni\(^{2+}\) and Co\(^{2+}\) have been extensively studied. However, only a few publications discuss these ions in a perfect cubic crystalline environment. The \(g\) values for these ions are in some cubic host lattices are given in table 4.5.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Host lattice</th>
<th>(g) value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(^{2+})</td>
<td>CaO</td>
<td>2.327</td>
<td>[LOW65]</td>
</tr>
<tr>
<td>MgO</td>
<td>2.2122</td>
<td>[ORTO60]</td>
<td></td>
</tr>
<tr>
<td>AgBr</td>
<td>2.238</td>
<td>[BUSS63]</td>
<td></td>
</tr>
<tr>
<td>AgCl</td>
<td>2.276</td>
<td>[HOHN69]</td>
<td></td>
</tr>
<tr>
<td>Co(^{2+})</td>
<td>MgO</td>
<td>2.1728</td>
<td>[ORTO60,ORTO61]</td>
</tr>
<tr>
<td>CaO</td>
<td>2.2756</td>
<td>[LOW65]</td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>2.14</td>
<td>[JAIN70]</td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>2.14</td>
<td>[MEHE75]</td>
<td></td>
</tr>
</tbody>
</table>

For most of these centres, the following EPR characteristics were observed [ABRA70]. The \(\Delta M_S = 1\) EPR spectrum consists of a broad and structureless transition, in the case of Co\(^{2+}\) possibly split in 8
components by hyperfine interaction ($I(^{69}\text{Co}) = 7/2$). At higher microwave power, a much sharper but phase inverted EPR line appears in the centre of the broad line (or in the centre of each of the hyperfine splitted lines). At approximately half the magnetic field value at which the $\Delta M_S = 1$ line is observed, a rather narrow EPR transition with an asymmetrical line shape occurs, which is attributed to the $\Delta M_S = 2$ transition. This line exhibits a sharp cut-off at the high field side and a more gradual tail to the low field end. At very low temperatures and even higher microwave powers, very sharp transitions which are not phase inverted appear in the centre of the $\Delta M_S = 1$ EPR spectrum. In MgO and CaO even the hyperfine splitting of Ni$^{2+}$ ($I(^{61}\text{Ni}) = 3/2$ with a natural abundance of only 1.13 %) was resolved. The $g$ value of the centre can be determined very accurately from the latter EPR lines. They are attributed to so-called double quantum transitions, for which two microwave quanta are absorbed simultaneously by a paramagnetic system with $S > 1/2$. As double quantum transitions are due to second order processes, their transition probability is expected to be proportional to $B_t^4$ ($B_t$ is the microwave excitation field, see § 2.4.2) or to $P_{MW}^{4/3}$ [VAND98]. The intensity of the double quantum EPR line is then expected to be proportional to $P_{MW}^{4/3}$ [VAND98], whereas that of single quantum transitions is known to be proportional to $P_{MW}^{7/2}$ for low microwave power. For several $S > 1/2$ paramagnetic systems, deviations from these relations have been reported [VAND98]. The intensity of the double quantum transitions is at least expected to increase much faster with increasing microwave power than that of the single quantum transition. All these EPR characteristics have been explained by assuming that very small local departures from exact cubic symmetry may occur for these centres. If only tetragonal distortions are considered, the EPR spectrum can be analysed with the aid of a spin Hamiltonian ($S = 1$)

$$\hat{H}_S = g_\mu_B B_0 \hat{S}_z + g_\mu_B B_z \hat{S}_x + D \left( \hat{S}_z^2 - \frac{1}{3} \hat{S}_z \right)$$

(4.10)

The EPR transitions which may occur for this system, calculated to second order, if the magnetic field $B_0$ is parallel to $\langle 100 \rangle$, are summarised in table 4.6. The transition fields and probabilities were obtained by calculating the eigenvalues of the Hamiltonian (4.10) to second order in $\frac{D}{g\mu_B B_0}$ and the eigenstates to first order in $\frac{D}{g\mu_B B_0}$. It should be noted that the $\Delta M_S = 2$ transition requires a microwave excitation field $B_t$ parallel to $B_0$ [ABRA70].

If the zero field splitting is, e.g., assumed to have a Gaussian distribution, centred around 0 with a dispersion $D_0$, the probability of finding a centre with $D = D^*$ is given by

$$P(D^*) = \frac{1}{(2\pi D_0)^{1/2}} e^{-\frac{(\sigma_D)^2}{2(\sigma_D)^2}}$$

(4.11)
Table 4.6: EPR transitions for an $S = 1$ paramagnetic system with tetragonal symmetry in the strong field approximation $g \mu_B B_0 >> D$

<table>
<thead>
<tr>
<th>$B_0$ orientation</th>
<th>type of transition</th>
<th>resonance magnetic field</th>
<th>transition probability</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\vec{B}_0 \parallel z$</td>
<td>single quantum $\Delta M_S = 1$</td>
<td>$\frac{1}{g\mu_B}(h\nu_{MW} - D)$</td>
<td>$\frac{1}{2}B_i^2$</td>
</tr>
<tr>
<td></td>
<td>$\Delta M_S = 2$</td>
<td>$\frac{1}{2g\mu_B}(h\nu_{MW} + D)$</td>
<td>$\frac{1}{2}B_i^2$</td>
</tr>
<tr>
<td></td>
<td>double quantum $\Delta M_S = 1+1$</td>
<td>$\frac{1}{g\mu_B}(h\nu_{MW})$</td>
<td>$\frac{1}{4}B_i^4$</td>
</tr>
</tbody>
</table>

| $\vec{B}_0 \parallel x$ | single quantum $\Delta M_S = 1$ | $\frac{1}{g\mu_B}(h\nu_{MW} + \frac{D}{2} - \frac{D^2}{8h\nu_{MW}})$ | $\frac{1}{2}(1 + \frac{D}{2h\nu_{MW}})B_i^2$ |
|                        | $\Delta M_S = 2$ | $\frac{1}{2g\mu_B}(h\nu_{MW} - \frac{D}{2} - \frac{D^2}{8h\nu_{MW}})$ | $\frac{1}{2}(1 - \frac{D}{2h\nu_{MW}})B_i^2$ |
|                        | double quantum $\Delta M_S = 1+1$ | $\frac{1}{g\mu_B}(h\nu_{MW} - \frac{D^2}{4h\nu_{MW}})$ | $\frac{1}{4}(1 - \frac{D^2}{4(h\nu_{MW})^2})B_i^4$ |

The $\Delta M_S = 1$ single quantum transition EPR spectrum with $\vec{B}_0 \parallel \langle 100 \rangle$ then consists of two broad EPR lines with approximately Gaussian line shapes and approximate line widths $\sqrt{(D_0)^2 + (\Delta B_0)^2}$ ($\vec{B}_0 \perp z$) and $\sqrt{(2D_0)^2 + (\Delta B_0)^2}$ ($\vec{B}_0 \parallel z$), with $\Delta B_0$ the initial line width of the EPR transitions (not due to the zero field splitting distribution). The occurrence of the phase inverted narrower lines has been attributed to saturation [LOW65]: the main saturation effect is expected to occur when the splitting between the levels corresponding to the two $\Delta M_S = 1$ transitions are exactly equal.

As the $\Delta M_S = 2$ single quantum and the $\Delta M_S = 1$ double quantum transition fields show only a second order dependence on $D$, their EPR spectrum is expected to be much narrower than that of the $\Delta M_S = 1$ single quantum transition. For $D = 0$, the $\Delta M_S = 2$ transition occurs at exactly $2g$, but its transition probability is zero. For $D \neq 0$, it obtains a finite probability and it occurs at a lower magnetic field value. This explains the shape of the EPR spectrum for this transition, with a sharp cut-off at the high field side and a tail towards lower magnetic fields. The double quantum transition in principle only
Magnetic resonance study of Rh⁺ and the B-centre in NaCl single crystals

occurs if the intermediate level (\(M_S = 0\)) lies exactly half way between the initial and the final state \((M_S = \pm 1)\), in other words if \(D = 0\). Hence, it gives the most accurate indication of the \(g\) value of the centre. At X-band, only a \(\Delta M_S = 2\) EPR spectrum is observed for the cubic Rh⁺ ion in NaCl. Along with the fact that its ENDOR spectrum can be observed in a very wide magnetic field range, this indicates that the centre is subjected to a distribution of local distortions, resulting in a distribution of the zero field splitting parameter. At Q-band, the \(\Delta M_S = 1\) EPR spectrum of the centre can be observed. It shows all the above mentioned characteristics.

Figure 4.12 shows the spectrum recorded with \(\hat{B}_0 \parallel \langle 100 \rangle\) at 30 K and \(P_{MW} = 1\) mW (figure 4.12a), and at 8 K and 40 mW (figure 4.12b). Although the spectrum at high temperature and low power is dominated by the EPR transitions of the \([\text{RhCl}_6]^{3+}\cdot0\text{Vac}\) centre at \(g = 2.4510\), a broad line at slightly higher \(g\) value can be clearly distinguished. At the centre of this broad line, a phase inverted line appears to be present. The spectrum at low temperature and high microwave power is dominated by a rather sharp EPR line which exhibits a partially resolved (super)hyperfine structure.

This structure can be perfectly simulated assuming an interaction of the unpaired electrons with the central \(^{103}\text{Rh}\) nucleus, with two equivalent Cl nuclei along the \(\langle 100 \rangle\) direction parallel to the magnetic field \(\hat{B}_0\) and four equivalent Cl nuclei along the \(\langle 100 \rangle\) directions perpendicular to \(\hat{B}_0\), using the (super)hyperfine values given in table 4.2. As a consequence, we attribute this line to the double quantum transition for the cubic Rh⁺ centre. The intensity of this transition increases much faster with increasing microwave power than that of the single quantum transition, as can be seen in figure 4.13a. It does not obey the expected \(I_{\text{double}} \propto P_{MW}^{3/2}\) law, though, but rather increases linearly with microwave power at low power, as indicated in figure 13b. At low power, the intensity of the single quantum transition appears to increase with microwave power as \(P_{MW}^{1.8}\), also slightly deviating from the expected \(P_{MW}^{3/2}\) law. If the magnetic field is rotated in a \(\langle 100 \rangle\) plane, the position of the double quantum transition does not change, within experimental error. This is additional strong evidence for the (on average) cubic symmetry of the centre. The isotropic \(g\) value for the centre can be determined very
accurately from this double quantum transition: \( g = 2.4229 \pm 0.0005 \). Via equation (4.9) this leads to an estimation for the crystal field splitting

\[
\Delta_i = \Delta_{1x} = \Delta_{1z} = \frac{4\xi_{4d}^{e}}{g - g_e}
\]

Using the free ion value of \( \xi_{4d}^{e} \) for Rh\(^{3+} \) (1060 cm\(^{-1} \) [MABB92]) one can calculate \( \Delta = 10000 \) cm\(^{-1} \). This value is of the same order of magnitude as the splitting between the allowed terms in the ground state configuration \( (t_{2g}^{6}e_{g}^{2}) \) and in the excited state configuration \( (t_{2g}^{5}e_{g}^{3}) \) due to the Coulomb repulsion between the valence electrons. In principle, neither the strong nor the intermediate crystal field limit cases are good approximations for this paramagnetic system. However, for \( d^{8} \) ions in octahedral coordination, both approximations lead to exactly the same results for the ground state magnetic properties. Thus, as long as the

**Figure 4.13:** (a) Q-band EPR spectrum of NaCl:Rh\(^{3+} \) crystals after X-ray irradiation at room temperature recorded at 8 K with the magnetic field along <100>. The microwave power at which the spectra were taken is indicated on the left side of each spectrum. (b) Contributions of the single quantum (full circles) and the double quantum transition (open squares) to the spectra in (a). At low microwave power, the power dependence of the contributions is well described as a power law \((P)^{r} \) with \( r = 0.6 \) for the single quantum and \( r = 1.0 \) for the double quantum transition (straight lines).

**Figure 4.14:** Angular variation of the Q-band ENDOR spectrum of the Rh\(^{3+} \) centre in NaCl, recorded at 8 K. Black dots represent experimental data points, the full lines are the angular variation of the \( M_s = 0 \) transitions for the three sets of first shell Cl ions (see figure 4.6) calculated using the spin Hamiltonian parameters in table 4.2.
spin-orbit coupling remains sufficiently small, the magnetic resonance parameters calculated in § 4.2.6 are, to first order, correct. Through a simulation of the $\Delta M_S = 1$ single quantum transition (figure 4.12a), the dispersion of the zero field splitting parameter $D_0$ was estimated at $(450 \pm 60)$ MHz. The $\Delta M_S = 2$ transition could not be observed at Q-band. This could be a result of its transition probability being inversely proportional to the microwave frequency. It should be noted that at X-band its intensity is already very small.

The Q-band ENDOR spectra for the Rh$^+$ centre consist of broad phase inverted lines in the frequency region $0 \sim 12$ MHz. Their angular dependence is shown in figure 4.14. They can be attributed to the $M_S = 0$ NMR transitions of the first shell Cl nuclei. These are exactly the transitions which were missing in the X-band ENDOR spectra. The fact that no other ENDOR transitions can be observed is probably a temperature effect: the minimum temperature attainable with the Q-band cryostat is considerably higher than that with the X-band cryostat.

4.2.8. Formation of Rh$^+$ centres in NaCl

In order to unravel the reaction mechanism through which Rh$^+$ centres are formed, Rh-doped NaCl single crystals, grown both from aqueous solution and from the melt, have been irradiated with X-rays and/or heat treated under various conditions. As already mentioned in the last section of chapter 3, Rh is incorporated in its diamagnetic 3+ valence state in solution-grown NaCl crystals. An X-band ENDOR study has demonstrated that all [RhCl$_6$]$^{3+}$ complexes (or at least all acting as an electron trap) are charge compensated by two next-nearest neighbour cation vacancies in a cis-configuration [CALL98]. X-ray irradiation leads to the formation of a [RhCl$_6$]$^{4+}.2$Vac centre in these crystals, which loses one vacancy after anneal at T > 200 K and eventually loses both vacancies when the crystal is brought to room temperature [VERC98a]. In melt-grown crystals, Rh is incorporated in the paramagnetic divalent state. The majority of these ions is charge compensated by one next nearest neighbour cation vacancy [SCHW97]. [RhCl$_6$]$^{4+}.2$Vac centres also occur in appreciable concentrations in these crystals, whereas only a very small concentration of [RhCl$_6$]$^{4+}.0$Vac centres has been detected [SABB98a].

No signals of the Rh$^+$ centre could be detected in as-grown Rh-doped NaCl crystals grown from solution. A very strong Rh$^+$ spectrum is observed after X-ray irradiation of these crystals at room temperature, but it is not produced by X-ray irradiation at 77 K, nor after subsequent anneal of these crystals. This implies that vacancy motion is a necessary intermediate step in the formation of Rh$^+$ centres from the Rh$^{3+}$ precursor centres in NaCl: the [RhCl$_6$]$^{3+}.2$Vac centre can trap one electron, but it cannot trap another before vacancies have migrated away from the centre. In solution-grown NaCl single crystals containing [RhCl$_6$]$^{4+}.2$Vac complexes, the cubic Rh$^+$ centre can be produced in two distinct ways. First, it is produced if the crystals are annealed to room temperature and afterwards again X-ray irradiated at liquid nitrogen temperature, without subsequently annealing the crystals. The cubic Rh$^+$ is thus formed through electron trapping by [RhCl$_6$]$^{4+}.0$Vac centres. Alternatively, Rh$^+$ centres are also detected after annealing the [RhCl$_6$]$^{4+}.2$Vac containing crystals to 220 K for a short time, reirradiating at liquid nitrogen temperature and subsequently again annealing the crystals to 220 K. In the first annealing step, [RhCl$_6$]$^{4+}.1$Vac centres are formed, which trap an electron during
irradiation at low temperature and lose their cation vacancy during the second annealing step. It should be noted that before the second annealing step no Rh⁺ spectra are detected. The possible formation paths of the cubic Rh⁺ centre in solution-grown NaCl crystals are summarised in figure 4.15.

![Diagram showing possible paths leading to the production of the cubic Rh⁺ centre from the [RhCl₆]²⁺.2Vac precursor in solution-grown NaCl crystals.](image)

*Figure 4.15: Possible paths leading to the production of the cubic Rh⁺ centre from the [RhCl₆]²⁺.2Vac precursor in solution-grown NaCl crystals. Horizontal arrows correspond to the trapping of an electron at temperatures below 200 K. Vertical arrows correspond to the migration of a cation vacancy at temperatures above 200 K or at room temperature. The complexes which have been experimentally observed with electron magnetic resonance techniques are indicated with rectangles. The barred complexes are not produced in these crystals. The production of the cubic Rh⁺ centre occurs through the reactions indicated with solid arrows.*

Contrary to what was originally thought, Rh⁺ can also be produced in melt grown NaCl:Rh²⁺ crystals. After X-ray irradiation at room temperature or X-ray irradiation at liquid nitrogen temperature and subsequent thermal anneal to 220 K, strong X-band ENDOR signals of this centre have been detected. Again, no Rh⁺ spectra could be detected before the annealing step. Cubic Rh⁺ is thus produced through electron trapping at [RhCl₆]²⁺.1Vac complexes and vacancy migration. Production via electron trapping at [RhCl₆]²⁺.0Vac centres appears to be negligible, as would be expected from the low concentration of the latter centres in melt-grown crystals.

4.2.9. The [RhCl₆]⁵⁻.1Vac centre

The study of the formation properties of the cubic Rh⁺ centre in NaCl demonstrates that an intermediate Rh⁺ complex associated with one next nearest neighbour cation vacancy exists. Such a centre has C₄ᵥ symmetry. In order to know whether it should be paramagnetic, we need to estimate the splitting between the d₅z²−r² and the dₓ²−r² levels, induced by a next nearest cation vacancy on the z axis of the complex. We may expect it to have the same order of magnitude as the splitting between the dₓ and the dᵧ levels induced by the vacancy on the x axis in the [RhCl₆]⁴⁺.1Vac centre in NaCl, as estimated from the orthorhombicity of its ȳ tensor. Using the expressions (3.25) for the ȳ tensor of a ñ' ion in the A's ground state (one electron approximation) one finds

\[ E(dₓ) - E(dᵧ) = \delta_{r} - \delta_{t} = \delta_{t} \delta_{t} \frac{g_x - g_y}{6s_{0}d_{4d}} = \delta_{t} \frac{g_x - g_y}{6s_{0}d_{4d}} \]  \hspace{1cm} (4.13)
in which $\zeta_{4d}$ represents the spin-orbit coupling constant for Rh$^{2+}$ and $\delta_{1L}$ is estimated from

$$\frac{1}{2} (g_x + g_y) = g_s + \frac{6\zeta_{4d}}{\delta_{1L}}$$  \hspace{1cm} (4.14)$$

Using the free Rh$^{2+}$ ion value for $\zeta_{4d}$ and the $g$ values for the [RhCl$_6$]$^{3-}$1 Vac centre given in table 3.5, one finds a splitting of approximately 1700 cm$^{-1}$. For the Ni$^{2+}$ ion (3$d^9$ configuration) associated with a next nearest neighbour cation vacancy in AgCl, from the magnetic resonance properties ($g = 2.281$ and $D = -2.96$ cm$^{-1}$ [HOLM77]), the splitting between the $d_{x^2-y^2}$ and the $d_{z^2}$ levels may be estimated at approximately 600 cm$^{-1}$. For the Rh$^+$ ion, which belongs to the next transition row in the periodic table (4$d^8$ configuration), the splitting is expected to be larger than for the Ni$^{2+}$ ion. Thus, it seems reasonable to estimate the splitting between the $d_{x^2-y^2}$ and the $d_{z^2}$, $d_{x^2-y^2}$ levels for the [RhCl$_6$]$^{3-}$1 Vac complex at 1000 cm$^{-1}$. Even if it were to be a factor of 2 or 3 larger, it would still be considerably smaller than the cubic crystal field splitting and the splitting between the allowed terms of the ground state for the Rh$^+$ ion. As a consequence, this complex is still expected to have a $^3A_{2g}$ paramagnetic ground state. Nevertheless, it could not be detected with EPR or ENDOR at X-band, nor at Q-band. This is most probably due to the large zero field splitting expected for this centre.

Indeed, from equation (4.8), assuming $\Delta_1 = 10000$ cm$^{-1}$ and $E(d_{x^2-y^2}) - E(d_{z^2}) = 1000$ cm$^{-1}$, $D$ may be estimated at -11 cm$^{-1}$ or -330 GHz. $D$ thus appears to be much larger than the microwave quantum (10 GHz at X-band and 34 GHz at Q-band) and huge magnetic fields would be required to observe the allowed EPR transition between the $M_S = 0$ and $M_S = 1$ levels ($\vec{B}_0 \parallel \langle 001 \rangle$), occurring at

$$\nu_{MW} = |D + g\mu_B B_0| \Rightarrow B_0 = \frac{D + \nu_{MW}}{g\mu_B}$$  \hspace{1cm} (4.15)$$

The EPR transitions for this centre may possibly be observed at high microwave frequencies (W-band, D-band,...).

### 4.2.10. Conclusions

The cubic rhodium-related centre produced after X-ray irradiation at room temperature in Rh$^{3+}$-doped NaCl crystals grown from aqueous solution is identified as a Rh$^+$ ion, substituting for Na$^+$. This centre has a $4d^8 \ A_{2g}$ ground state configuration with $S = 1$. Its unpaired electrons, mainly localised in the transition metal $d_{x^2-y^2}$ and $d_{z^2}$ orbitals, strongly interact with the central $^{103}$Rh nucleus and with the nuclei of six equivalent first shell Cl$^-$ ions and six equivalent fourth shell Na$^+$ ions, resulting in an intense ENDOR spectrum observed at X-band. Most of the EPR characteristics of the centre, on the other hand, could only be observed at Q-band. Random local distortions broaden the $\Delta M_S = 1$ single quantum transition, preventing it from being detected in the X-band spectrum, which is dominated by the overlapping [RhCl$_6$]$^{3-}$0 Vac spectrum. At Q-band, the latter spectrum is better separated from that of Rh$^+$. In addition, at low temperature and high microwave power, a sharp double quantum transition is observed which exhibits hyperfine structure due to the interaction with the central $^{103}$Rh nucleus and with the first shell Cl nuclei. The two microwave bands thus provide complementary information about the paramagnetic properties of the cubic Rh$^+$ centre in NaCl.
The study of the formation properties of the centre have shown that it may only be produced in solution-grown Rh\(^{3+}\)-doped NaCl crystals through X-ray irradiation at temperatures at which cation vacancies are mobile. Its Rh\(^{2+}\) precursor centres in these crystals are [RhCl\(_6\)]\(^{+}\).0Vac and [RhCl\(_6\)]\(^{3+}\).1Vac. The latter centre is also the precursor of the cubic Rh\(^{3+}\) centre in melt-grown NaCl crystals. The production of cubic Rh\(^{3+}\) from [RhCl\(_6\)]\(^{+}\).1Vac complexes involves the formation of a [RhCl\(_6\)]\(^{3+}\).1Vac intermediate. This centre also has a \(^5\)A\(_{2g}\) ground state, but is, due to a very large zero field splitting, EPR silent at X and Q-band microwave frequencies. In addition to [RhCl\(_6\)]\(^{3+}\).2Vac, it has been demonstrated that also [RhCl\(_6\)]\(^{+}\).0Vac and [RhCl\(_6\)]\(^{3+}\).1Vac act as deep permanent electron traps in NaCl. In AgCl, no Rh\(^{3+}\) ions have been detected. These complexes are probably not stable in AgCl, which may be related with the narrower band gap of this crystal, as compared with NaCl.

4.3. Magnetic resonance results for the B-centre in solution-grown NaCl single crystals

4.3.1. Introduction

The first report of the so-called B-centre is due to Shock and Rogers [SHOC75]. In their X-band EPR study of \(\gamma\)-irradiated (irradiation at room temperature) Rh\(^{3+}\)-doped solution-grown NaCl single crystals, they observed a weak spectrum on the low field side of the \(g_L\) component of the primary spectrum, due to the [RhCl\(_6\)]\(^{+}\).0Vac complex, which they labeled the A-centre. The \(g_L\) part of the X-band EPR spectrum recorded with \(\vec{B}||\langle 100\rangle\) is shown in figure 4.16. The B-centre EPR signals could not be followed throughout the complete angular variation, though.

In a later X-band ENDOR study of stable paramagnetic Rh centres in solution-grown NaCl:Rh\(^{3+}\) produced by X-ray irradiation at room temperature, Zdravkova et al. also report the presence of the B-centre [ZDRA97]. They assign it, tentatively, to a [RhCl\(_6\)H\(_2\)O]\(^3\) or a [RhCl\(_6\)OH]\(^{+}\) complex. Vercammen studied the angular dependence of the W-band EPR spectrum of similar crystals after X-ray irradiation at 77 K and subsequent anneal to room temperature for a long time [VERC99b]. He discovered that even after very long annealing times not all [RhCl\(_6\)]\(^{+}\).2Vac and [RhCl\(_6\)]\(^{+}\).1Vac complexes have been converted to [RhCl\(_6\)]\(^{+}\).0Vac. In addition to the [RhCl\(_6\)]\(^{+}\).nVac (n = 0, 1 and 2) spectra, he observed weak EPR signals of a Rh\(^{2+}\) related centre with monoclinic symmetry. Thus, the spectrum observed at X-band at the low field side of \(g_L\) of the [RhCl\(_6\)]\(^{+}\).0Vac centre is in fact a superposition of the spectra of [RhCl\(_6\)]\(^{+}\).1Vac, [RhCl\(_6\)]\(^{+}\).2Vac and a third centre, which is now called the B-centre.
In order to verify the assignment of Zdravkova et al., the B-centre should be studied with ENDOR. This is, however, not trivial from the experimental point of view. First, it should be noted that the intensity of its EPR spectrum is much lower than that of the \([\text{RhCl}_6]^4\)^-.-n\(\text{Vac}\) centres, as a result of which its ENDOR spectra are expected to be of poorer quality. Moreover, a correct ENDOR analysis at X-band microwave frequencies seems a priori excluded, because the EPR spectrum of the B-centre strongly overlaps with those of the \([\text{RhCl}_6]^4\)^-.-n\(\text{Vac}\) complexes. ENDOR measurements should thus be preferably carried out at Q-band or even higher microwave frequency. The W-band EPR data of Vercammen indicate that even at 95 GHz, the angular dependence of the spectrum cannot be followed completely due to overlap with other centres. The situation at Q-band is not expected to be better. In view of all these difficulties, our Q-band ENDOR results are rather limited and will not lead to the determination of a microscopic model for the B-centre.

The assignment of the centre to a hydrated complex also implies that it does not have the \([\text{RhCl}_6]^3\)\(\cdot\)\(2\text{Vac}\) complex as precursor. As a consequence, a (or several) B-centre like paramagnetic complex(es) should be produced in the crystals by X-ray irradiation at liquid nitrogen temperature. At X-band, the only rhodium-related paramagnetic centre, observed in crystals treated in this way, was \([\text{RhCl}_6]^4\)^-\(2\text{Vac}\). Our main effort in the Q-band EPR study of the B-centre has been directed towards the question: which centres are produced by X-ray irradiation at liquid nitrogen temperature in solution-grown NaCl:Rh\(^{3+}\) crystals?

4.3.2. Q-band EPR data

In figure 4.17 the Q-band EPR spectrum, recorded with \(\vec{B}||\langle 100\rangle\), of solution-grown NaCl:Rh\(^{3+}\) crystals is shown, immediately after X-ray irradiation at liquid nitrogen temperature. The most intense component in this spectrum is due to the \(V_\text{K}\) centre. This component is indeed so strong, that it makes the observation of all other spectral components in the \(g \approx 2\) region (\(g_\text{i}\) region of the \([\text{RhCl}_6]^4\)^-\(2\text{Vac}\) centres, e.g.) difficult. The occurrence of the \(V_\text{K}\) centre, however, ensures that the temperature has not risen above 150 K during irradiation and transfer into the microwave cavity. In spite of the strong \(V_\text{K}\) signal, the spectrum of the irradiated quartz tube and the high field septet of the \([\text{RhCl}_6]^4\)^-\(2\text{Vac}\) centre are still clearly visible in the EPR spectrum. The low field end of the spectrum is dominated by the septet of \([\text{RhCl}_6]^4\)^-\(2\text{Vac}\) at \(\sqrt{(g^2_x + g^2_y)}/2\). In addition, two clearly resolved components occur at \(g = 2.509\) and \(g = 2.449\), and two components, which exhibit a partially resolved superhyperfine structure, are not completely resolved from the \([\text{RhCl}_6]^4\)^-\(2\text{Vac}\) spectrum. Although not seen in this spectrum, additional B-centre components are expected in the \(g \approx 2\) region. This is confirmed by the angular dependence of the spectrum, shown in figure 4.18 for a rotation of the magnetic field in a \(\{100\}\) plane. The occurrence of (at least) four components in the \(g = 2.4 - 2.5\) range either indicates that the B-type centre exhibits an additional fine structure or hyperfine structure splitting, or that more than one B-type centre is produced by X-ray irradiation at liquid nitrogen temperature. In view of the difference in intensity of the various components, the latter assumption appears to be the most plausible.
Considering the angular dependence of the spectrum in figure 4.18, the components of the $[\text{RhCl}_6]^+\cdot2\text{Vac}$ centre can be clearly distinguished for all angles. A simulation of the angular dependence of the spectrum for this centre, using the best fit $g$ values in table 4.6, is indicated in red in the figure.

The component at $g = 2.449$ for $\vec{B}_0 \parallel \langle 100 \rangle$ can be followed in nearly all spectra. The component at $g = 2.509$, on the other hand, can only be followed for about 20°. Both components split in two, one of which approximately remains in its original position, while the other moves to $g = 2$. Assuming that these components belong to the same centre with monoclinic II symmetry (see table 2.1), a reasonably good simulation of the angular dependence can be obtained, as indicated in green in figure 4.18 (best fit parameters in table 4.6). However, the spectra show insufficient resolution to allow a complete and consistent analysis: a much better fitting of a part of the data is obtained by combining the component at $g = 2.449$ with one of the unresolved components, partially hidden under the $[\text{RhCl}_6]^+\cdot2\text{Vac}$ spectrum when $\vec{B}_0 \parallel \langle 100 \rangle$. The best fit parameters for this fitting are also given in table 4.6. Considering the data in this table, the $g$ values of the $[\text{RhCl}_6]^+\cdot2\text{Vac}$ centre appear to be systematically shifted towards higher values, as compared with the W-band results of Vercammen (see table 3.5). This discrepancy would, most probably, be removed if both sets of data were to be calibrated with the same $g$ marker (DPPH, $\text{CO}_3^{3-}$ in calcite, ...). If the systematical shift is corrected, the agreement between the two sets of results is in fact much better than the indicated experimental
error. Although the experimental parameters of the first fitting of the B-type centre are within (the very large) experimental error identical to those obtained for the B-centre by Vercammen, it is rather doubtful that exactly the same centre would be involved (the reason for the large errors given on the parameters for this fitting is its large sum of least squares error, indicating that the fitting is rather poor). The difference between the sets of data can in this case not be explained by a systematic shift of the $g$ values.

![Graph](image)

**Figure 4.18**: Angular dependence of the Q-band EPR spectrum of solution-grown NaCl:Rh$^+$ crystals, after X-ray irradiation at 77 K. The calculated angular variation for the [RhCl]$_2$ vac centre is indicated in red lines and that for the B-type centre, assuming - among other things - that the transitions at $g = 2.509$ and $g = 2.448$ belong to the same centre, in green lines. The parameters used for the simulations are given in Table 4.7.
Table 4.6: Best fit $g$ values extracted from the angular dependence of the EPR spectrum of solution-grown NaCl:Rh$^{3+}$ crystals irradiated with X-rays at 77 K, as shown in figure 4.18. The tilting angles are given in degrees. The error in the last digits is given as a subscript.

<table>
<thead>
<tr>
<th>centre</th>
<th>symmetry</th>
<th>EPR parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>[RhCl$_6$]$^{4+}$.2Vac</td>
<td>Orthorhombic I</td>
<td>$g_x((110))$</td>
<td>2.4812$_{10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$g_y((110))$</td>
<td>2.4745$_{10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$g_z((001))$</td>
<td>2.0135$_{15}$</td>
</tr>
<tr>
<td>B-type, assuming the components at $g = 2.509$ and $g = 2.449$ to belong to the same centre</td>
<td>Monoclinic II</td>
<td>$g_x((100)+\alpha)$</td>
<td>2.510$_{10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$g_y((010)+\alpha)$</td>
<td>2.448$_7$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$g_z((001))$</td>
<td>2.010$_{20}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha$</td>
<td>12$_8$</td>
</tr>
<tr>
<td>B-type, assuming that the component at $g = 2.449$ belongs to the same centre as one of the components under the [RhCl$_6$]$^{4+}$.2Vac spectrum</td>
<td>Monoclinic II</td>
<td>$g_x((100)+\alpha)$</td>
<td>2.483$_{10}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$g_y((010)+\alpha)$</td>
<td>2.448$_3$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$g_z((001))$</td>
<td>2.0124$_{40}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\alpha$</td>
<td>5.5$_{4.0}$</td>
</tr>
</tbody>
</table>

Pulse annealing experiments further support the hypothesis that the centre(s) observed immediately after X-ray irradiation at 77 K is (are) not identical to the one studied by Vercammen. Figure 4.19 shows the low field part of the EPR spectrum of solution-grown NaCl:Rh$^{3+}$, X-ray irradiated at 77 K, before (figure 4.19a) and after (figure 4.19b) a short pulse anneal to room temperature. Besides the conversion of [RhCl$_6$]$^{4+}$.2Vac centres into [RhCl$_6$]$^{4+}$.1Vac and [RhCl$_6$]$^{4+}$.0Vac complexes during the pulse anneal, the spectrum also seems to have undergone changes in the $g = 2.50$ range: the position of the components does not appear to have changed much, but a much better resolved superhyperfine structure is observed. A more detailed interpretation of the changes, e.g. via the analysis of the angular variation of this EPR spectrum, is hindered by the fact that now all three [RhCl$_6$]$^{4+}$.nVac complexes are simultaneously present. It is e.g. not clear whether the component at $g = 2.449$ in figure 4.19a has been affected by the pulse anneal or not, due to the presence of the very intense [RhCl$_6$]$^{4+}$.0Vac spectrum. Finally, these spectra are also compared with that of crystals irradiated at room temperature (a long time after irradiation), shown in figure 4.19c. The B-type components in this spectrum are shifted in position as compared with the previous two spectra, and they exhibit a less resolved structure. The interpretation of the angular dependence of the spectrum of the B-type centre(s) in these crystals is again not obvious due to the presence of the [RhCl$_6$]$^{4+}$.nVac complexes and the Rh$^+$ centre.
4.3.3. Q-band ENDOR data

Up to now Q-band ENDOR experiments have only been performed on crystals irradiated at room temperature for \( \vec{B}_0 \parallel (100) \). The most intense spectrum for B-type centres is obtained by setting the magnetic field to \( g = 2.505 \) (indicated in figure 4.19c). This spectrum is shown in figure 4.20. In the 5 – 30 MHz part of the spectrum (figure 4.20a), interactions of the unpaired electrons with \( ^{35/37}\text{Cl} \) and \(^{23}\text{Na} \) nuclei are expected. The most intense transition in the spectrum is situated at the Larmor frequency of \(^{23}\text{Na} \), corresponding to the interaction with remote Na\(^+\) ions. Based on the analysis of the \([\text{RhCl}_6]^{\text{4-}}.n\text{Vac} \) complexes, we were able to identify the interaction with two types of Na\(^+\) ions (in the second and the fourth shell) and with the axial Cl\(^-\) ions (in (0,0,1) positions), which are indicated in the spectrum. As no angular dependence of the spectrum has been recorded, the principal \( \hat{A} \) and \( \hat{Q} \) tensor components and orientations for these interactions cannot be determined. The order of
magnitude of some of these parameters can, however, be estimated from the spectrum. It is given in table 4.7. Centred around the proton Larmor frequency, four partially overlapping ENDOR transitions are observed, which are attributed to the interaction with two \( ^1\text{H} \) nuclei (see figure 4.20b). The estimated parameters for these interactions are also given in table 4.7. An interaction with a remote proton has also been observed for the \([\text{RhCl}_6]^{4+}.2\text{Vac}\) [CALL98] and the \([\text{RhCl}_6]^{4+}.0\text{Vac}\) [ZDRA97] centre in solution-grown NaCl. The ENDOR data for these interactions are also included in the table. From the comparison with the data for the B-type centre, one is tempted to conclude that the interaction, labeled H1 corresponds to a remote proton, whereas the interaction H2, which is significantly larger, is due to a proton in one of the first few neighbouring shells. As the superhyperfine tensor for the latter interaction is not completely known, the actual distance between the central Rh\(^{2+}\) ion and the proton cannot be estimated.

**Table 4.7**: Estimated superhyperfine and quadrupole parameters (given in MHz, no error indicated) for a B-type centre as obtained from the Q-band ENDOR spectrum.

<table>
<thead>
<tr>
<th>Centre</th>
<th>Nucleus</th>
<th>position with respect to Rh(^{2+})</th>
<th>( A )</th>
<th>( Q )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-type</td>
<td>( ^{35}\text{Cl} )</td>
<td>(0,0,1)</td>
<td>33.7</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td>( ^{23}\text{Na} )</td>
<td>second shell</td>
<td>0.71</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>( ^{23}\text{Na} )</td>
<td>(0,0,2)</td>
<td>3.4</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>( ^{1}\text{H} )</td>
<td>remote</td>
<td>0.24</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( ^{1}\text{H} )</td>
<td>one of the first few neighbouring shells</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>([\text{RhCl}_6]^{4+}.2\text{Vac})</td>
<td>( ^{1}\text{H} )</td>
<td>remote</td>
<td>( A^\text{a}_1 = 0.26 )</td>
<td></td>
</tr>
<tr>
<td>([\text{RhCl}_6]^{4+}.0\text{Vac})</td>
<td>( ^{1}\text{H} )</td>
<td>remote</td>
<td>( A^\text{b}_1 = 0.22 )</td>
<td></td>
</tr>
</tbody>
</table>

\(^\text{a}\) [CALL98] \quad \(^\text{b}\) [ZDRA97]

### 4.3.4. Conclusions

From our limited Q-band EPR and ENDOR results, the following information concerning the B-centre is obtained. X-ray irradiation at liquid nitrogen temperature produces at least two Rh\(^{2+}\)-related paramagnetic centres in solution-grown NaCl:Rh\(^{3+}\), different from the dominant \([\text{RhCl}_6]^{4+}.2\text{Vac}\) complex. These centres are most probably very closely related with the B centre studied by Vercammen at W-band in solution-grown NaCl:Rh\(^{3+}\) crystals, irradiated at 77 K and annealed to room temperature, and are called B-type centres. Annealing to room temperature changes the EPR spectrum of the B-type centres significantly, indicating that some of these centres decay and/or undergo structural changes (e.g. through the migration of charge compensating vacancies). Also X-ray irradiation at room temperature produces (most probably several different) B-type centres in solution-grown NaCl:Rh\(^{3+}\) crystals. The lack of resolution and intensity of the spectra prevented us from concluding whether identical centres are present in crystals irradiated at room temperature and crystals irradiated at 77 K, annealed to room temperature. For one of the B-type centres produced by
room temperature irradiation, the ENDOR spectrum suggests that a proton is present in one of the first few neighbouring shells around the central Rh$^{2+}$ ion. This and the fact that B-type centres have a precursor different from that of the [RhCl$_6$]$^4-$:nVac centres support the identification of these centres as Rh$^{2+}$ complexes in which one of the Cl ligands is exchanged with a water molecule or a hydroxyl ion. More detailed information on these centres might be obtained from the analysis of the angular dependence of the ENDOR spectrum for the B-type centres produced by irradiation at 77 K. In view of the low intensity of the EPR spectra and the overlap with other centres in the crystals, recording and analysing these spectra is not expected to be a trivial task.
Chapter 5: Detection of cation vacancies near \( \text{Rh}^{2+} \) ions in \( \text{AgCl} \) and \( \text{NaCl} \) using Q-band ENDOR

5.1. Introduction

The X-band EPR and ENDOR study of the \([\text{RhCl}_6]^{\text{4+}}.n \text{Vac}\) centres in \( \text{NaCl} \) (\( n = 2,1,0 \)) has lead to their identification as \( \text{Rh}^{2+}\)-centred complexes charge compensated by two, one and no next nearest neighbour (NNN) cation vacancies. In the case of the \([\text{RhCl}_6]^{\text{4+}}.2 \text{Vac}\) centre, Q and W-band EPR were helpful in determining the symmetry of the centre as orthorhombic I. As explained in § 3.4.2, the identification of the \( \text{Rh}^{2+}\)-vacancy centres was mainly based on the results of pulse annealing experiments on solution-grown crystals, in which the two-vacancies centre, produced by X-ray irradiation at 77 K, transforms into the \([\text{RhCl}_6]^{\text{4+}}.1 \text{Vac}\) by annealing to \( T = 220 \) K and further to \([\text{RhCl}_6]^{\text{4+}}.0 \text{Vac}\) by annealing to room temperature.

The purpose of the Q-band ENDOR study of the \([\text{RhCl}_6]^{\text{4+}}.n \text{Vac}\) centres is different. The primary issue is not their identification, but finding out whether the NNN cation vacancies in the models of these centres can be detected in a more direct way. Therefore, the results for the \([\text{RhCl}_6]^{\text{4+}}.1 \text{Vac}\) centre in \( \text{AgCl} \) (\( n = 1,0 \)) are also included in the study. It will be demonstrated that the presence of NNN vacancies in the \( g_r-g_y \) plane of these complexes may be quasi-directly observed through the ENDOR spectrum of the Cl\(^-\) ligands along the \( g_z \) axis. It will further be shown that for a correct analysis of the latter interaction, the ENDOR spectra need to be recorded at higher microwave frequencies than the conventional X-band.

In § 5.2 some examples of the detection of charge compensating vacancies near transition metal ions in ionic solids from the literature are discussed. The influence of the NNN cation vacancies on the EPR and X-band ENDOR spectra of \([\text{RhCl}_6]^{\text{4+}}.n \text{Vac}\) centres in \( \text{NaCl} \) and \( \text{AgCl} \) is considered in detail. In § 5.3 the Q-band ENDOR results for the \([\text{RhCl}_6]^{\text{4+}}.1 \text{Vac}\) complexes in \( \text{AgCl} \) and \( \text{NaCl} \) and for the \([\text{RhCl}_6]^{\text{4+}}.2 \text{Vac}\) complex in \( \text{NaCl} \) are presented and analysed. Section 5.4 gives a tentative interpretation of the influence of the cation vacancies on the ENDOR spectrum of the axial Cl\(^-\) ligands. Finally, § 5.5 summarises the conclusions of this study and gives some prospects for future studies of \( d^2 \) ions associated with charge compensating cation vacancies. The results presented in this chapter are the subject of two recent publications [VRIE01a, VRIE01b].

5.2. Detection of charge compensating vacancies near transition metal ions in ionic solids with electron magnetic resonance spectroscopy

Cation vacancies play an important role in the charge compensation of alioivalent transition metal ions in ionic solids, e.g., alkali or silver halides. Their presence and configuration can have an important influence on the electronic and magnetic properties of the transition metal ion complex. E.g., if the ion acts as an electron trap, the trap depth and trapping efficiency are expected to depend on the number of charge compensating vacancies and on their positions. Diffusion of the vacancies may stabilise the trapped electron centre. In spite of the apparent importance of the subject, the detection of vacancies in the neighbourhood of transition metal ions incorporated in ionic solids is far from obvious. For paramagnetic transition metal complexes EPR and ENDOR are probably the most promising
spectroscopic techniques for vacancy detection. However, cation vacancies have neither electronic nor nuclear spin. Magnetic resonance techniques will therefore only provide indirect information about their presence.

5.2.1. Determining the vacancy configuration from the EPR spectrum

A nearby cation vacancy changes the symmetry of the transition metal complex, which will be reflected in the angular dependence of the EPR spectrum (\( \tilde{g} \) tensor and, for systems with \( S > 1/2 \), zero field splitting terms, hyperfine interaction). As a consequence, in many studies the vacancy configuration of the complex has been inferred from its symmetry as determined with EPR. However, this rarely leads to an unambiguous determination of the vacancy configuration of the complex. In most cases additional assumptions have to be made in order to restrict the number of possible models, e.g. the assumption of complete local charge compensation for stable centres to determine the number of vacancies and a restriction to nearest neighbour (NN) and NNN vacancies to determine their positions. This method has been applied to identify the various [Cr(CN)\(_6\)]\(^{3+}\) [WANG86, WANG89] and [Fe(CN)\(_6\)]\(^{3-}\) [WANG90a] complexes in AX host lattices (A = Na, K and X = Cl, Br). As these complexes substitute for [AX\(_6\)]\(^{5-}\) units in the host lattice, they introduce a net charge of +2e. Complete local charge compensation via cation vacancies thus requires two vacancies in the close neighbourhood. They are assumed to be in NN or NNN positions with respect to the central ion. In figure 5.1 all possible vacancy configurations for these complexes, meeting the above-mentioned restrictions, are shown.

![Diagram of possible configurations for two cation vacancies](image)

**Figure 5.1**: Possible configurations for the two cation vacancies (open squares) near the [M(CN)]\(^{j+}\) complexes (M = Cr\(^{3+}\) or Fe\(^{2+}\), indicated with a filled small circle) in alkali (small open circles) halides (large open circles) with the NaCl structure, assuming that the vacancies are in NN or NNN positions. The point group and \( g \) tensor symmetry of these configurations are given in table 5.1 [WANG89].
In table 5.1 the point group symmetry and the $\tilde{g}$ tensor symmetry for all these configurations are listed. The $\tilde{g}$ tensor symmetry is the symmetry which can be determined by the analysis of the EPR spin Hamiltonian

$$\hat{H}_s = \mu_0 \tilde{B}_0 \cdot \tilde{g} \cdot \hat{S} + \hat{D} \cdot \hat{S} + \hat{A} \cdot \hat{I}$$  \hspace{1cm} (5.1)

In this spin Hamiltonian, only the interaction of the unpaired electron(s) with the central nucleus is considered, because in most cases interactions with the ligand nuclei are not resolved in the EPR spectrum. For the same reasons, the nuclear Zeeman and quadrupole interactions are not mentioned in equation (5.1).

**Table 5.1**: Point group and $\tilde{g}$ tensor symmetry for the vacancy configurations of the complexes in figure 5.1.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Point group symmetry</th>
<th>$\tilde{g}$ tensor symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C$_3$</td>
<td>monoclinic I</td>
</tr>
<tr>
<td>2</td>
<td>C$_{2v}$</td>
<td>orthorhombic II</td>
</tr>
<tr>
<td>3</td>
<td>C$_2$</td>
<td>monoclinic I</td>
</tr>
<tr>
<td>4</td>
<td>D$_{2h}$</td>
<td>orthorhombic I</td>
</tr>
<tr>
<td>5</td>
<td>C$_3$</td>
<td>monoclinic II</td>
</tr>
<tr>
<td>6</td>
<td>C$_2$</td>
<td>monoclinic I</td>
</tr>
<tr>
<td>7</td>
<td>C$_2$</td>
<td>monoclinic II</td>
</tr>
<tr>
<td>8</td>
<td>D$_{4h}$</td>
<td>tetragonal</td>
</tr>
<tr>
<td>9</td>
<td>C$_{2v}$</td>
<td>orthorhombic I</td>
</tr>
</tbody>
</table>

From table 5.1, it is clear that in many cases the assignment of a spectrum to a particular vacancy configuration from its symmetry as determined by analysis of the angular dependence of the EPR spectrum remains ambiguous. This is mainly due to the fact that EPR does not allow the determination of the exact symmetry of the paramagnetic centre, because of the inversion symmetry of the EPR spin Hamiltonian (5.1). Indeed, the energy eigenvalues remain unchanged under inversion of the magnetic field vector ($\tilde{B}_0 \rightarrow -\tilde{B}_0$) and as a result the EPR spectrum does not change. As long as no ligand interactions are considered in the spin Hamiltonian, the distinction between centres with inversion symmetry and centres without inversion symmetry cannot be made. E.g., EPR is unable to make the distinction between configurations 4 and 9, which clearly have different symmetries (D$_{2h}$ and C$_{2v}$, respectively), but which both give rise to an orthorhombic $\tilde{g}$ tensor with identical principal axes (orthorhombic I symmetry, also the zero field splitting and hyperfine tensors exhibit this type of symmetry). In addition to this problem, the initial assumptions of complete local charge compensation and considering only NN and NNN vacancies may also be incorrect. In solution-grown NaCl, e.g., the most stable paramagnetic [RhCl$_6$]$^{3+}$ complex is non-locally charge compensated [ZDRA97]. It may be concluded that it is practically impossible to deduce the vacancy configuration of paramagnetic transition metal ions unambiguously from the angular dependence of their EPR
spectrum alone. However, changes in the angular dependence of the EPR spectrum as a function of temperature, related with the (reversible) interconversion of various vacancy configurations or the irreversible migration of vacancies, may provide additional evidence in favour of certain configurations. Theoretical calculations of the energy or the magnetic resonance properties (\(\tilde{g}\) tensor, zero field splitting) of transition metal – vacancy complexes may also be used to determine which configurations are experimentally observed. Finally, the analysis of the ligand hyperfine and quadrupole interactions, e.g. by ENDOR or electron spin echo envelope modulation (ESEEM), allow a more detailed determination of the symmetry of paramagnetic centres and hence provide additional information on the presence and the position of charge compensating vacancies.

5.2.2. Determining the vacancy configuration from the ENDOR spectrum

As cation vacancies influence the charge and the unpaired spin distribution over transition metal – vacancy complexes, a detailed study of the ligand hyperfine interactions with ENDOR or ESEEM can provide more direct evidence for their presence. The principal directions of the interaction tensors of ligand nuclei with the unpaired electrons of the paramagnetic centre reflect the true symmetry of the complex and may even allow an unambiguous determination of the vacancy configuration.

An example of a successful determination of the vacancy configuration of a transition metal complex from the ligand hyperfine structure is the study of the \([\text{Fe(CN)}_6]^{3-}\) \(I_s\) centre in NaCl (using ENDOR [KIRM91]) and KCl (using ENDOR and ESEEM [WANG90b]). The structure of this centre, shown in figure 5.2, corresponds to configuration 4 in figure 5.1. The angular dependence of the EPR spectrum could in fact only determine that the centre has orthorhombic \(I\) symmetry (principal axes along \([110]\) (g\(x\)), \([\bar{1}10]\) (g\(y\)) and \([001]\) (g\(z\)).

The observation with ENDOR and ESEEM that the two CN' ligands along the g\(x\) axis are physically equivalent and that also the four CN' ligands in the g\(x\)-g\(y\) plane are physically equivalent determines the symmetry of the complex unambiguously to be \(D_{2h}\). In addition, for the complex in NaCl an interaction with two equivalent \(^{23}\)Na nuclei along the g\(y\) axis of the complex was observed.

The two NN cation vacancies could thus be determined to be located on the g\(x\) axis (g\(x\) > g\(y\) > g\(z\)). As a second example the study by Chung et al. [CHUN79] of the Fe\(^{3+}\) centre with orthorhombic I
symmetry (principal axes along [110] \(g_x\), [\(\bar{1}10\)] \(g_y\) and [001] \(g_z\)) in NaF single crystals is mentioned. This centre is produced by X-ray irradiation of NaF:Fe\(^{2+}\) crystals at temperatures below 60 K. The substitutional Fe\(^{2+}\) ion in NaCl is expected to be associated with one charge compensating cation vacancy. The observation of a centre with orthorhombic I symmetry using EPR [GARR67] led to the conclusion that the vacancy is in a NN position. The model of this centre is shown in figure 5.3. Although ligand hyperfine structure was resolved in the EPR spectrum, the EPR study failed to demonstrate that the centre has C\(_{2v}\) rather than D\(_{2h}\) symmetry. Using ENDOR, Chung et al. demonstrated that the physically equivalent \(F^{-}\) (\(^{19}\)F : \(I = 1/2\), 100% abundant) ligands along the \(g_z\) axis of the complex are equivalent when the magnetic field is rotated in the \(g_x\)-\(g_y\) plane, but become inequivalent if the magnetic field has an arbitrary orientation in the \(g_x\)-\(g_y\) plane (\(g_y > g_x > g_z\)). The inequivalence arises, because the principal superhyperfine tensor axes of these ligands are allowed to be tilted in the \(\bar{1}10\) symmetry plane of a centre with C\(_{2v}\) symmetry. Indeed, symmetry only requires that one of the principal hyperfine axes for the \(F^{-}\) ions along \(g_z\) is perpendicular to \(\bar{1}10\), whereas the other two may have arbitrary directions in the \(\bar{1}10\) plane (they should, however, still be perpendicular to one another). The ENDOR study not only explicitly confirmed the model for the centre, already proposed from EPR measurements, but also determined unambiguously that the Na\(^{+}\) vacancy is located on the \(g_z\) axis of the centre. Based on the EPR results Garrison erroneously assumed the vacancy to be located on the \(g_x\) axis (corresponding to the largest \(g\) value).

5.2.3. Vacancy detection for the \([\text{RhCl}_6]^{4-}\)\(n\) Vac complexes in NaCl and AgCl

As explained in § 3.4.2, X, Q and W-band EPR data and X-band ENDOR data have led to the conclusion that \([\text{RhCl}_6]^{4-}\) complexes in NaCl and AgCl may be accompanied by two (only in NaCl), one or zero charge compensating NNN cation vacancies. The models for these three paramagnetic centres are shown in figure 3.11a-c. They have \(C_{2v}\) (\(C_2\) along \(\bar{1}10\)), \(C_{2v}\) (\(C_2\) along \(100\)) and \(D_{4h}\) symmetry, respectively. The \(\bar{g}\) tensor symmetry determined at low temperatures (20 – 50 K) for these centres is orthorhombic I (\(C_{2v}\) or \(D_{2h}\)), orthorhombic II (\(C_{2v}\) or \(D_{2h}\)) and tetragonal (\(C_{4v}\) or \(D_{4h}\)). From the angular dependence of the EPR spectrum alone, the determination of the number and position of the cation vacancies is still rather ambiguous. In chapter 3 (§ 3.4.2) it has been explained
how changes in the EPR spectrum as a function of the annealing or recording temperature provided additional evidence for the proposed models. These effects did however not allow a determination of the exact symmetry of the complexes and hence did not provide more direct proof for the exact vacancy configurations.

All three complexes in NaCl have been studied with X-band ENDOR. For the complexes in AgCl, a complete angular dependence of the X-band ENDOR spectrum was only recorded for the $[\text{RhCl}_6]^{3+}.1\text{Vac}$ centre. The results on the other Rh$^{2+}$ centre observed in melt-grown AgCl single crystals, presumably $[\text{RhCl}_6]^{3+}.0\text{Vac}$, are still rather limited. They will be discussed in detail in chapter 6. The X-band ENDOR results, which are expected to give more detailed information on the vacancy presence, are summarised in Table 5.1.

Comparing the data for the complexes in NaCl, definite trends in the principal (super)hyperfine and quadrupole parameters for certain nuclei are observed as a function of the number of cation vacancies. The z component of the superhyperfine tensor of the first shell axial Cl$^-$ ions, e.g., clearly increases if the number of vacancies in the complex decreases. In figure 5.4 the X-band ENDOR spectra recorded at $g_\perp$ for the three complexes in NaCl are shown. The shift towards higher frequencies when the number of vacancies decreases is clearly visible. The axial Cl$^-$ interaction has therefore been used to monitor the conversion of the $[\text{RhCl}_6]^{3+}.2\text{Vac}$ complex to $[\text{RhCl}_6]^{3+}.1\text{Vac}$ and eventually $[\text{RhCl}_6]^{3+}.0\text{Vac}$ by thermal anneal of solution-grown NaCl:Rh$^{3+}$ single crystals, irradiated at 77 K. The superhyperfine values for the fourth shell Na$^+$ ions clearly shift towards lower values as the number of vacancies decreases. Also the $^{103}\text{Rh}$ hyperfine values decrease (for the $[\text{RhCl}_6]^{3+}.0\text{Vac}$ complex, no Rh hyperfine interaction was observed, it is possibly below the detection limit of the X-band ENDOR spectrometer). Although these trends are most probably not "coincidental", they do not give direct evidence for the number and the position of cation vacancies around the complexes, as they give no additional information on the symmetry. First principles quantum chemical calculations could, however, give a deeper insight into the significance of these observed trends.

More detailed information about the symmetry of the complexes can be obtained by considering the number of physically inequivalent neighbouring ions around the central Rh$^{2+}$ ion. The non-equatorial NN Na$^+$ interactions, e.g. present a fine example. In figure 5.5, the models of the three $[\text{RhCl}_6]^{3+}$ complexes are shown again. Their principal symmetry axes and planes are indicated and the physically inequivalent sets of non-equatorial NN Na$^+$ ions are shown in different colours. For the $[\text{RhCl}_6]^{3+}.0\text{Vac}$ complex all eight ions were found to be physically equivalent, which serves as a direct proof for the $D_{2h}$ symmetry of this complex. In this case, the inversion symmetry of the centre was also (and more directly) demonstrated by other interactions (with the axial Cl$^-$ and Na$^+$ ions). In the case of the $[\text{RhCl}_6]^{3+}.1\text{Vac}$ complex, three physically inequivalent sets of non-equatorial NN Na$^+$ ions were detected, proving the centre has $C_{2v}$ symmetry. In $D_{2h}$ symmetry, only two physically inequivalent sets are expected. Finally, for the $[\text{RhCl}_6]^{3+}.2\text{Vac}$ centre, two physically inequivalent sets were observed, directly indicating that the centre has $C_{2v}$ symmetry, as in $D_{2h}$ symmetry, all non-equatorial NN Na$^+$ ions should be physically equivalent. However, the analysis of these interactions is far from obvious and may be criticised. The interaction parameters for the various sets of ions are small and very close to one another, resulting in angular dependent ENDOR patterns close to the $^{23}\text{Na}$
Table 5.1: (Super)hyperfine and quadrupole data for the [RhCl₆]⁺-nVac centres in NaCl and AgCl as determined from X-band ENDOR studies. The principal values are given in MHz and the error is given as a subscript. The principal directions are indicated below the table. ¹H data, which are available for the two and zero vacancies complexes, but are not essential to the model for these centres are not mentioned. Also the data on Cl(1,0,0) or Cl(1,1,1) interactions, which were less accurately determined, are not included.

<table>
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<th>Host</th>
<th>Complex</th>
<th>Nucleus</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>$Q_x$</th>
<th>$Q_y$</th>
<th>$Q_z$</th>
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<td>NaCl</td>
<td>[RhCl₆]⁺-2Vac</td>
<td>$^{35}$Cl(0,0,1)$^a$</td>
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<td>33.9₁</td>
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<td>0.67₂</td>
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<td>$^{23}$Na(0,0,2)$^a$</td>
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<td>3.31₃</td>
<td>4.76₃</td>
<td>-0.03₁</td>
<td>-0.03₁</td>
<td>0.06₁</td>
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<td>-0.40₃</td>
<td>1.38₃</td>
<td>-0.20₁</td>
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<td>-0.14</td>
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<td>14.3₀₁</td>
<td>11.1₆₁</td>
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<td>74.5₂</td>
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<td>3.1₇₃</td>
<td>4.5₉₃</td>
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<td>-0.0₂₂</td>
<td>0.0₈₂</td>
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<td>-0.2₀₂</td>
<td>0.1₁₂</td>
<td>-0.₀₉₂</td>
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<td>0.₁₃₃</td>
<td>-0.₁₅₃</td>
<td>0.₀₃₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{23}$Na1(1,1,0)$^c$</td>
<td>1.₁₇₃</td>
<td>0.₂₄₅</td>
<td>0.₁₉₅</td>
<td>0.₈₈₂</td>
<td>0.₀₂₂</td>
<td>-0.₁₀₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{103}$Rh(0,0,0)$^a$</td>
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<td>9.₇₄₂</td>
<td>8.₁₈₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[RhCl₆]⁺-0Vac</td>
<td>$^{35}$Cl(0,0,1)$^a$</td>
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<td>33.9₁</td>
<td>75.₅₂</td>
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<td>2.₈₈₃</td>
<td>2.₈₈₃</td>
<td>4.₂₉₂</td>
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<td>-0.₄₁</td>
<td>0.₀₈₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{23}$Na1(1,0,1)$^b$</td>
<td>-1.₀₃₃</td>
<td>-0.₉₂₃</td>
<td>1.₂₄₃</td>
<td>-0.₁₈₁</td>
<td>0.₁₀₁</td>
<td>0.₀₈₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{23}$Na1(1,1,0)$^c$</td>
<td>1.₁₇₃</td>
<td>0.₂₆₃</td>
<td>0.₁₅₃</td>
<td>0.₀₆₁</td>
<td>0.₀₃₁</td>
<td>-0.₀₉₁</td>
</tr>
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<td></td>
<td></td>
<td>$^{103}$Rh(0,0,0)$^a$</td>
<td>8.₀₁₂</td>
<td>9.₇₄₂</td>
<td>8.₁₈₂</td>
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<tr>
<td>AgCl</td>
<td>[RhCl₆]⁺-1Vac</td>
<td>$^{35}$Cl(0,0,1)$^a$</td>
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<td>3₉.₁₂</td>
<td>7₈.₉₂</td>
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<td>[VRIE98b]</td>
<td>$^{109}$Ag(0,0,2)$^a$</td>
<td>-₉.₈₁</td>
<td>-₉.₈₁</td>
<td>-₁₂.₈₂</td>
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<tr>
<td></td>
<td></td>
<td>$^{103}$Rh(0,0,0)$^a$</td>
<td>-₅.₆₉₅</td>
<td>-₆.₆₆₅</td>
<td>-₉.₄₆₅</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$ principal $\hat{A}$ and $\hat{Q}$ directions along [100], [010] and [001]

$^b$ principal $\hat{A}$ and $\hat{Q}$ directions along [010], [10T] and [101]

$^c$ principal $\hat{A}$ and $\hat{Q}$ directions along [110], [1T10] and [001]

$^d$ principal directions of $\hat{A}$ along the (100) axes, and of $\hat{Q}$ rotated by 6° about the [010] axis

$^e$ principal $\hat{A}$ and $\hat{Q}$ directions along [100], [01T] and [011]

$^f$ principal $\hat{A}$ directions rotated by 6° and principal $\hat{Q}$ directions rotated by 3° about the [010] axis in the [010], [10T], [101] coordinate system

$^g$ principal directions of $\hat{A}$ along the (100) axes, and of $\hat{Q}$ rotated by 2° about the [010] axis
Figure 5.4: ENDOR spectrum of the axial Cl ions recorded at g, for the [RhCl₄]⁺.nVac centres in NaCl, (a) solution-grown NaCl, X-ray irradiated at 77 K (n = 2), (b) melt-grown NaCl (n = 1 and n = 2), (c) solution-grown NaCl, X-ray irradiated at 298 K (n = 0). The contribution of the n = 2 spectrum in (b) is indicated with arrows.

Figure 5.5: Models for the [RhCl₄]⁺.nVac centres in NaCl and AgCl, indicating the number of inequivalent sets (different colours) of non-equatorial NN cations and the main symmetry elements for (a) n = 2, (b) n = 1 and (c) n = 0.
Larmor frequency which are strongly overlapping. Due to their low site symmetry, it is difficult to
determine the principal directions of these interactions. The situation gets even worse if one considers
that in many cases, several $[\text{RhCl}_6]^{3-}.n\text{Vac}$ complexes with overlapping X-band EPR spectra are
simultaneously present in NaCl crystals. It should further be noted that for the complex in AgCl no
similar interaction could be identified in the ENDOR spectrum. In conclusion, the non-equatorial NN
cations in principle supply the required symmetry information on the complexes, but in practice their
analysis is too complicated to serve as direct evidence for the presence and the position of the
vacancies. The inequivalence of ions in the $g_x-g_y$ plane of the complexes would also serve as direct
indications for vacancy presence. Only for the $[\text{RhCl}_6]^{4-}.1\text{Vac}$ complex, a set of ENDOR transitions,
which could not be followed throughout the whole angular dependence and whose spin Hamiltonian
parameters could not be determined very accurately, has been assigned to equatorial Cl [OLM88,
SCHW97, SABB98a]. The equatorial NN cation interactions also appeared to be difficult to analyse:
no such interactions have been reported for the complex in AgCl and in NaCl only one set of
equivalent ions was observed for each complex. Thus, also the equatorial neighbours cannot be used
to determine the symmetry of the complex and the number and position of nearby cation vacancies.
For a direct demonstration of the presence of cation vacancies in the $g_x-g_y$ plane of the complexes, we
should thus turn to the interactions with ions on the $g_z$ axis. The axial Cl$^-(0,0,1)$ ions exhibit a large
interaction with the unpaired electron, which is well-separated from all other interactions in the ENDOR
spectrum. If the symmetry of the complex could be determined from this interaction, it would serve as
the most direct and unambiguous evidence for the presence of the vacancies.
In all three complexes, the two axial Cl$^-$ ligands are physically equivalent, as they are transformed into
one another by a symmetry transformation of the complex (by $\sigma_h$, the equatorial mirror plane). In the
$[\text{RhCl}_6]^{3-}.0\text{Vac}$ complex, the ions are magnetically equivalent for all magnetic field orientations,
because they are transformed into one another by inversion symmetry. This has been confirmed by
the EPR and X-band ENDOR spectra recorded for this centre. In the other two complexes the axial
Cl$^-$ ions would also be magnetically equivalent for all magnetic field interactions, if the complexes were
to have $D_{5h}$ symmetry. In $C_{2v}$ symmetry these ions may become inequivalent for certain magnetic field
orientations. This can be explained as follows. For both complexes the axial ligands are situated in a
vertical mirror plane (indicated with $\sigma_v$ in figures 5.5a and 5.5b). For the $[\text{RhCl}_6]^{4-}.2\text{Vac}$ complex, this
is the $\{110\}$ plane and for $[\text{RhCl}_6]^{3-}.1\text{Vac}$ this is $\{010\}$. Symmetry requires that one of the principal
$\bar{A}$ and $\bar{Q}$ axes of these ligands are perpendicular to this plane. We will indicate this direction as $y$. It
corresponds to $[110]$ and $[010]$ for the complex with two vacancies and one vacancy, respectively.
The other two principal axes may have arbitrary directions in the mirror plane. However, one of these
axes, which we indicate as $z$, is expected to be close to $[001]$ corresponding to the Rh-Cl bond axis.
Figure 5.6 presents a cross-section of the figures 5.5a and 5.5b in their $\sigma_v$ mirror planes, defining the $x$
and $z$ axes of an interaction tensor $\bar{T}$ and also the tilting angle $\theta_T$ in this plane. If the tilting angle $\theta_T =
$0, the Cl$^-$ ions are equivalent for all magnetic field orientations. The angle between the magnetic field
direction and the principal $z$ or $x$ axes are identical for the two ligands. If $\theta_T \neq 0$, the Cl$^-$ ions become
inequivalent if the magnetic field is rotated away from the principal \( \tilde{g} \) axes in this plane. The inequivalence of these ions is expected to be observed as a splitting of the ENDOR transitions: the ENDOR transitions of the two Cl⁻ ions coincide if the magnetic field is along one of the principal \( \tilde{g} \) axes in the mirror plane, whereas they occur at different frequencies for other orientations in this plane. On the other hand, the two Cl⁻ ions remain equivalent for magnetic field rotations in the \( \sigma_h \) mirror plane and in the plane perpendicular to \( \sigma_h \) and \( \sigma_v \). The ENDOR transitions recorded in this plane should not split up. \( \sigma_h \) corresponds to the \( g_x g_y \) plane of the centre. Dependent on the position of the vacancies with respect to the \( \tilde{g} \) tensor axes, \( \sigma_v \) either corresponds to the \( g_x g_y \) plane or to the \( g_x g_x \) plane. In conclusion, the experimental observation of the splitting of the ENDOR transitions of the axial Cl⁻ in the \( g_x g_x \) or the \( g_x g_y \) plane serves as a direct proof for the \( C_{2v} \) symmetry of these complexes. It explicitly rules out the possibility that they would have \( D_{2h} \) symmetry. In addition, the position of the cation vacancies in the models with respect to the \( \tilde{g} \) tensor axes can be determined in an unambiguous way. Indeed, the \( g \) plane in which the ENDOR transitions split up is immediately identified as the \( \sigma_c \) plane of the complex. This information cannot be directly deduced from the angular dependence of the EPR spectrum. For the [RhCl₂]⁺.1 Vac complex, the temperature dependence of the EPR spectrum suggests that the vacancy is situated on the \( g_x \) axis. If this hypothesis is correct, the axial Cl⁻ ENDOR transitions should split up in the \( g_x g_x \) plane and should not split up in the \( g_x g_y \) plane. For the [RhCl₂]⁺.2 Vac complex, the EPR and X-band ENDOR study did not find an answer to the question which of the principal \( \tilde{g} \) directions corresponds to the \( C_2 \) symmetry axis of the complex. Recording the axial Cl⁻ ENDOR spectrum in the \( g_x g_x \) and the \( g_x g_y \) plane should provide this additional
information.

As the distance between the axial Cl⁻ ions and the NNN cation vacancies is rather large (≈ \( \sqrt{5}a \), with a
the anion – cation distance in the lattice), the tilting angles of the \( \bar{A} \) and \( \bar{Q} \) tensors and the resulting
splitting of the ENDOR transitions are expected to be quite small. In fact they escaped the attention of
several authors studying the \([\text{RhCl}_6]^{3+}\cdot n\text{Vac}\) complexes \( (n = 1, 2) \) in NaCl [SCHW97, CALL98] and
AgCl [OLM88] using X-band ENDOR. The lack of \( g \) resolution and the splitting of the Cl⁻ ENDOR
transitions due to the indirect interaction between the two equivalent Cl⁻ nuclei prevent an accurate
analysis of this interaction at X-band frequencies, as will be explained in the following section. Nonetheless, Vrielinck et al. [VRIE98b] and Sabbe et al. [SABB98a] proposed from a detailed analysis
of the X-band ENDOR spectrum of the axial Cl⁻ ions of the \([\text{RhCl}_6]^{3+}\cdot 1\text{Vac}\) centre (in AgCl and NaCl,
respectively) that the quadrupole tensor should be slightly tilted in the \( g_x - g_y \) plane. Although the Q-
band ENDOR analysis will prove their interpretation of the observed splitting of the ENDOR transitions
to be wrong, they already demonstrated the \( C_{2v} \) symmetry of this complex. At Q-band microwave
frequencies, the splitting of the ENDOR transitions is much better observed. It should be noted that in
principle the inequivalence of the axial Cl⁻ ligands could also be determined from the EPR spectrum,
as their superhyperfine structure is resolved. However, the effect of cation vacancies is too small to
be observed with EPR, so higher resolution techniques like ENDOR or ESEEM are required.

The splitting of the ENDOR transitions in the \( g_x - g_y \) or \( g_x' - g_y' \) plane of the ligands along the \( g_z \) axis of
complexes with orthorhombic I or orthorhombic II \( \bar{g} \) tensor symmetry, serves as a direct proof for their
\( C_{2v} \) symmetry, independent of any analysis of the data. In the case of the \([\text{RhCl}_6]^{3+}\cdot n\text{Vac}\) centres in
NaCl and AgCl, it also explicitly confirms the models for the centres and identifies the positions of the
cation vacancies. Although all this information can be obtained without any spin Hamiltonian analysis
of the spectra, we will still try to determine the \( \bar{A} \) and \( \bar{Q} \) tensors for this interaction very accurately, in
order to find out whether NNN cation vacancies have a systematic influence on these parameters and
how this can be physically interpreted. The information thus obtained should allow us to identify the
presence of NNN cation vacancies from their influence on the spin Hamiltonian parameters in
complexes for which the models are not yet as well established.

5.3. X versus Q-band ENDOR

The axial Cl⁻ interaction is studied in order to observe a very small splitting of the ENDOR transitions in
one of the vertical \( g \) planes due to the inequivalence of the axial ligands. Therefore, all other splittings
of the ENDOR transitions should be avoided and a very good orientation and species selection is
required. As the axial Cl⁻ ions are for all magnetic field orientations expected to be nearly equivalent,
the indirect interaction between the nuclear spins via the electron spin may be important for these
nuclei. In § 3.3.1 we demonstrated that this interaction causes a splitting of the ENDOR transitions,
calculated by diagonalisation of the spin Hamiltonian describing the interaction of the unpaired
electron with one \( I = 3/2 \) nucleus

\[
\hat{H}_S = \mu_B \hat{B}_0 \cdot \hat{g} \cdot \hat{S} + \hat{S} \cdot \hat{A} \cdot \hat{I} - g_n \mu_n \hat{B}_0 \cdot \hat{I} + \hat{I} \cdot \hat{Q} \cdot \hat{I}
\]  

(5.2)
The splitting is inversely proportional to the microwave frequency. A good orientation selection can only be obtained with a sufficiently high g factor resolution. The second order splitting of the ENDOR transitions and the poor orientation and species selection render the X-band ENDOR analysis of the axial Cl− interaction practically impossible. These problems are overcome at Q-band. The spectra for the [RhCl6]4−.1Vac centre in AgCl serves as a good illustration.

Figure 5.7 presents the X and Q-band ENDOR spectra of Rh2+ doped (1000 ppm) melt-grown AgCl single crystals, recorded at the gz component of the [RhCl6]4−.1Vac complex. Although the EPR spectrum of [RhCl6]4−.1Vac overlaps with that of another [RhCl6]4− centre in this magnetic field region, only one set of 35/37 Cl transitions is observed. This either indicates that the concentration of the secondary species is too low to give rise to a detectable ENDOR signal or that the transitions of the two centres accidentally coincide. In the X-band ENDOR spectrum (figure 5.7a), the M0 = 0 transitions of the 35Cl isotope show a well-resolved second order splitting. Indeed, the second order splitting can be estimated as \( A_\perp^2 / \hbar \nu_{\text{mw}} \), which at X-band (9.56 GHz) corresponds to 160 kHz (\( A_\perp = 39.1 \) MHz, see table 5.1). At Q-band (34.00 GHz), the splitting is expected to be roughly 3.5 times smaller (45 kHz). As can be seen in figure 5.7b, it is no longer resolved. Although the second order splitting might be expected to hinder the observation of splittings due to the inequivalence of the Cl− ions, the analysis of the X-band spectrum in figure 5.7a certainly appears feasible. However, when the magnetic field is rotated away from the gz axis of the complex towards the gx-gy plane, all ENDOR transitions exhibit a complicated second order splitting. Moreover, due to the poor g factor resolution at X-band and the fact that \( g_x = g_y \), the EPR spectra of different symmetry related orientations of the complex overlap one another and the spectrum of the other [RhCl6]4− centre. As a result, the X-band ENDOR spectra become composite. The combined effect of the second order splitting and the poor orientation and species selection is illustrated in figure 5.8a, which presents gx and gy components of the spectra. The various components in the EPR spectrum are not resolved. The ENDOR spectra were recorded with the magnetic field set to the gx and gy components of the [RhCl6]4−.1Vac centre and the to \( g_\perp \) component.
of the axial [RhCl₆]⁺ centre. The ENDOR spectra are very complicated and their analysis does not appear feasible. An additional splitting due to the inequivalence of the axial Cl⁻ ions would not be easily detected. In contrast, the corresponding Q-band spectra (see figure 5.8b) are very simple: the EPR spectra of the different g components are nearly completely resolved, the ENDOR spectra are non-composite and show no second order splitting. Their analysis is much easier and less ambiguous than that of the X-band spectra. A splitting due to the inequivalence of the Cl⁻ ions would be easily detected in these Q-band spectra.

![EPR and ENDOR spectra](image)

\[ \nu_{\text{AB}} = 9.56 \text{ GHz} \]
\[ \nu_{\text{AV}} = 34.00 \text{ GHz} \]

**Figure 5.8**: EPR and ENDOR spectra in the g₁-gₓ region of the [RhCl₆]⁺.1Vac centre in AgCl (magnetic field along <100>) recorded at (a) X-band and (b) Q-band.

The example clearly illustrates why the study of the axial Cl⁻ interaction is performed at Q-band microwave frequency. In the previous section it has been explained that in order to determine the symmetry of the [RhCl₆]⁺.n Vac complexes and the position of the vacancies, ENDOR spectra have to be recorded in the gₓ-gₓ and gₓ-gᵧ planes. In spite of the enhanced g factor resolution as compared with X-band, the EPR spectra of these symmetry related orientations may still overlap. In figure 5.9 the calculated EPR angular variation of the three centres which have been studied ([RhCl₆]⁺.1Vac in AgCl and NaCl, [RhCl₆]⁺.2Vac in NaCl) are shown. For the [RhCl₆]⁺.2Vac complex, even at Q-band, gₓ-gₓ and gᵧ-gᵧ plane components of the spectra partly overlap for all magnetic field orientations. The different contributions to the composite ENDOR spectra can be separated by recording the spectra at magnetic field positions in the EPR superhyperfine patterns where the g components do not overlap.
Figure 5.9: Calculated angular variation of the EPR spectrum of (a) RhCl₂‒Vac in AgCl, (b) RhCl₂‒Vac in NaCl, and (c) RhCl₂‒Vac in NaCl using the EPR parameters in Tables 3.5 and 3.6. The bold coloured lines and green lines represent the central superhyperfine transition of each g component. The other superhyperfine transitions are indicated in black. The g, s, and g'-g' planes, in which the ENDOR spectra need to be recorded, are drawn in green.
5.4. Experimental results

5.4.1. Study of the [RhCl₆]⁺:1 Vac centre in AgCl

In figure 5.10a, the high field part of the Q-band EPR spectrum, recorded with the magnetic field parallel to a (110) direction, is shown. The spectrum is a superposition of two seven line superhyperfine patterns corresponding to the components recorded in the \( g_r g_x \) and in the \( g_r g_y \) plane. In the centre of each pattern (indicated in figure 5.10a) there is no overlap with the other component, though. The ENDOR spectra recorded at these positions are presented in figures 5.10b and 5.10c. The spectrum recorded in the \( g_r g_y \) plane corresponds to one set of equivalent Cl nuclei, whereas at the \( g_r g_x \) component the spectrum consists of twice as many transitions with approximately half the intensity. As explained previously, the splitting of the ENDOR transitions arises because the two axial Cl ions become inequivalent when the magnetic field is rotated in the \( g_r g_x \) plane, whereas they remain equivalent under rotation in the \( g_r g_y \) plane. Without any further analysis of the spectra, this proves that the centre has \( C_{2v} \) symmetry and that its \( \sigma_v \) mirror plane is the \( g_r g_x \) plane (its \( C_2 \) axis is the \( g_r \) axis).

![Diagram](image)

**Figure 5.10**: (a) High field part of the Q-band (34.00 GHz) EPR spectrum of AgCl:Rh⁺⁺ single crystals recorded with the magnetic field along <110>. The spectrum is the superposition of two superhyperfine septets, indicated with vertical lines. The ENDOR spectra (b) and (c) were recorded with the magnetic field set to the centre of the two superhyperfine patterns, indicated with arrows. Experimental conditions for ENDOR: \( T = 22\, K, P_{uv} = 4\, mW, P_{w} = 100\, W, \) modulation frequency = 12.5 kHz, modulation depth = 200 kHz.
In order to obtain a quantitative understanding of the effect of the NNN cation vacancy on the ENDOR spectrum of the axial Cl\textsuperscript{-} ions, the $\tilde{\Omega}$ and $\tilde{\Omega}$ tensors for this interaction are determined very accurately. Simulations of the $M_S = -1/2$ multiplet of the $^{35}\text{Cl}$ spectrum were carried out, assuming different causes for the splitting of the ENDOR transitions in figure 5.10b. The results of these simulations are shown in figure 5.11. First of all, a tilting of the rotation plane cannot be responsible for the splitting, because it does not render the axial Cl\textsuperscript{-} ions inequivalent. This is confirmed by the simulation in Figure 5.11a, in which no splitting of the ENDOR transitions arises. Tilting angles of the superhyperfine and/or quadrupole tensor principal axes in the $g_r g_x$ plane render the axial Cl\textsuperscript{-} ions inequivalent, if the magnetic field is rotated in this plane, away from the $g_\text{r}$ or $g_\text{x}$ axes (see figure 5.6b). In figures 5.11b-c the effect of two possible axis tiltings is considered. Figure 5.11b shows the simulation for a tilting of the principal $\tilde{\Omega}$ axes of about 5° without a tilting of the $\tilde{\Omega}$ axes, as previously reported for the [RhCl\textsubscript{6}]\textsuperscript{4-}:1Vac complexes in AgCl [VRIE98b] and NaCl [SABB98a]. In this case, the $M_O = \pm 1$ transitions are split, whereas the $M_O = 0$ transition remains unsplit. As this does not agree with the experimentally observed effect, the splitting cannot be explained by a tilting of the $\tilde{\Omega}$ tensor alone. The effect of a tilting of the $\tilde{\Omega}$ tensor of about 50' (0.8°) (no tilting of $\tilde{\Omega}$) is presented in Figure 5.11c. All $M_O$ transitions are split and the simulated spectrum agrees fairly well with the experimental spectrum (figure 5.11d). The observed splitting is thus mainly due to a tilting of the $\tilde{\Omega}$ tensor in the $g_r g_x$ plane. In order to determine the principal values and directions of the $\tilde{\Omega}$ and $\tilde{\Omega}$ tensors more accurately, these parameters were fitted (least squares error procedure) to the ENDOR angular dependence data. ENDOR transition frequencies were calculated by diagonalisation of the spin Hamiltonian (5.2). The best agreement between experimental and calculated transition frequencies was obtained with the parameters listed in table 5.2. The experimental (squares) and calculated (full lines) ENDOR angular variations in the $g_r g_x$ and the $g_r g_y$ plane are shown in Figures 5.12a and 5.12b, respectively. Apart from the fact that for some orientations the experimental $M_O = -1$ transition of the $M_S = 1/2$ multiplet for the $^{35}\text{Cl}$ isotope is missing due to overlap with the $M_S = -1/2$ multiplet of the $^{37}\text{Cl}$ isotope, the agreement is excellent. The $M_S = 1/2$ transitions for the $^{37}\text{Cl}$ isotope are not observed, due to their low signal intensity.

Concerning the parameters in table 5.2 the following should be noted. The $\tilde{\Omega}$ tensor is clearly
orthorhombic but no significant tilting of its principal axes is observed ($\theta_0 = 0^\circ$). Within experimental error, the $\tilde{A}$ tensor is axial. Although the tilting angle of this tensor ($\theta_A$) is very small (less than a degree), it is significantly different from zero, as it causes a splitting of the ENDOR transitions in the $g_x-g_y$ plane.

Table 5.2: Best fit spin Hamiltonian parameters for the $[\text{RhCl}_6]^{n^-}$.$n\text{Vac} (n = 0, 1, 2)$ in AgCl and NaCl. The principal values are given in MHz and the tilting angles are given in minutes. The experimental error is given as a subscript. The principal directions and tilting angles are defined in Figure 5.6. The data for the zero-vacancy complex were determined at X-band and are included for comparison.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>$\theta_A$</th>
<th>$Q_x$</th>
<th>$Q_y$</th>
<th>$Q_z$</th>
<th>$\theta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{RhCl}_6]^{4-}$.$0 \text{Vac in NaCl}$</td>
<td>33.91</td>
<td>33.91</td>
<td>75.52</td>
<td>0</td>
<td>0.722</td>
<td>0.722</td>
<td>-1.442</td>
<td>0</td>
</tr>
<tr>
<td>$[\text{RhCl}_6]^{4-}$.$1 \text{Vac in AgCl}$</td>
<td>39.12</td>
<td>39.12</td>
<td>78.82</td>
<td>48.10</td>
<td>0.421</td>
<td>0.291</td>
<td>-0.712</td>
<td>0.50</td>
</tr>
<tr>
<td>$[\text{RhCl}_6]^{4-}$.$1 \text{Vac in NaCl}$</td>
<td>33.82</td>
<td>34.02</td>
<td>74.32</td>
<td>51.10</td>
<td>0.701</td>
<td>0.701</td>
<td>-1.402</td>
<td>100.50</td>
</tr>
<tr>
<td>$[\text{RhCl}_6]^{4-}$.$2 \text{Vac in NaCl}$</td>
<td>33.549</td>
<td>33.549</td>
<td>72.62</td>
<td>10.10</td>
<td>0.642</td>
<td>0.692</td>
<td>-1.333</td>
<td>120.30</td>
</tr>
</tbody>
</table>

Figure 5.12: Angular variation of the axial Cl ENDOR spectrum of the $[\text{RhCl}_6]^{n^-}$.$1\text{Vac centre in AgCl}$ recorded in the $g_x-g_y$ plane (a) and $g_x-g_z$ plane (b). Experimental data points are represented by black squares, simulations, using the best fit parameters in Table 5.2 are indicated with solid lines (green: $^{35}\text{Cl}$ isotope and red: $^{37}\text{Cl}$ isotope).

The accuracy with which the spin Hamiltonian parameters, and especially the tilting angles, could be determined, deserves some further explanation. The Q-band ENDOR spectrometer allows the rotation of a crystal, fixed in a sample tube, in a certain plane, but does not allow any tilting of the rotation plane. The AgCl crystals were cleaved under liquid nitrogen ($\{100\}$ cleavage planes) and

...
Detection of cation vacancies near Rh$^{3+}$ ions in AgCl and NaCl using Q-band ENDOR

stuck with a $\{100\}$ face to the inner wall of a sample tube (inner diameter approximately 1.4 mm, crystal dimensions approximately 0.5 mm $\times$ 0.5 mm $\times$ 2.0 mm) using vacuum grease. The rotation plane could be determined by analysis of the angular dependence of the EPR spectrum. No indications for tiltings out of a $\{100\}$ plane were observed (estimated experimental error: 15°). The crystals were oriented ($\tilde{B}_b$, along $\langle 011 \rangle$) by observation of the coincidence of the EPR transitions of the $g_r g_x$ and $g_r g_y$ planes and the coincidence of the transitions of the $g_r g_z$ and $g_r g_y$ planes (minimisation of the width of the high field part of the EPR spectrum, estimated error 15°). The angular variation of the ENDOR spectrum was recorded with 5° intervals (estimated error 15°). In view of all these experimental errors, one might wonder how the tilting angles of the $\tilde{A}$ and $\tilde{O}$ tensors could be determined so accurately. It should be noted that the tilting angles are determined from the splitting of ENDOR transitions in the $g_r g_x$ plane. In this plane, the splitting reaches a maximum, as a result of which the fitting results for these angles are insensitive to tiltings of the rotation plane up to a few degrees. In order to eliminate the error induced by the inaccuracy of the rotation angles in the $g_r g_x$ plane, the following procedure was used. An initial fitting was carried out using experimental data points for the $\langle 110 \rangle$ and the $\langle 100 \rangle$ directions only. The $\langle 110 \rangle$ direction could be determined very accurately and the splitting of the ENDOR transitions in the $g_r g_x$ plane reaches a maximum for this orientation. The spectra recorded at $g_x$, $g_y$ and $g_z$ ($\tilde{B}_b \parallel \langle 100 \rangle$) are quite insensitive for small misorientations of the crystal. In this way an initial fitting of the principal values and directions of the tensors was obtained, which is relatively independent of the errors in the orientation of the crystal. Afterwards, small corrections for the rotation angles of all recorded ENDOR spectra were carried out (all corrections were smaller than 30°) in order to obtain a better agreement with the simulated angular dependence using the initial fitting parameters. Finally, these corrected data points were used for a final fitting of the spin Hamiltonian parameters, the results of which are listed in table 5.2. An identical procedure was followed for the fitting of the data for the [RhCl$_6$]$^{3+}$:1Vac centre in NaCl, described in the following section.

5.4.2. Study of the [RhCl$_6$]$^{3+}$:1Vac centre in NaCl

The ENDOR analysis for the [RhCl$_6$]$^{3+}$:1Vac complex in NaCl is very similar to that in the case of AgCl. A few remarkable differences occur, though. In figure 5.13, simulated and experimental $M_S = -1/2$ spectra for the $^{35}$Cl isotope are presented (corresponding to figure 5.11 in the AgCl case). The experimental spectra (5.13a and 5.13b) were again recorded at the $g_r g_y$ and the $g_r g_x$ component of the EPR spectrum with $\tilde{B}_b \parallel \langle 011 \rangle$. It is again clearly seen that in the $g_r g_y$ spectrum the ENDOR transitions are not split (figure 5.13a). Due to the larger quadrupole interaction as compared to the AgCl case, the $^{35}$Cl resonances are not as well separated from the $^{37}$Cl transitions, which are marked (#) in the experimental spectra. In the spectrum recorded in the $g_r g_x$ plane (figure 5.13b), two of the three $^{35}$Cl transitions are clearly split. These transitions seem to undergo a large splitting due to the inequivalence of the Cl ions and an additional smaller splitting. It is unclear how the latter splitting arises. We checked that it is not due to second or higher order interactions between the slightly
inequivalent Cl' ions. In principle, a splitting would arise when the orientation to the [101] crystal direction is not perfect: the overlapping EPR spectra with the magnetic field at 45°±δ and 45°-δ (δ being a very small angle) in the $g_x-g_z$ plane would give rise to a splitting of all transitions in two. However, a splitting in more than two components is observed and an expected similar splitting of the $g_x-g_y$ component spectrum does not occur. Moreover, the splitting is also observed for orientations near [101], where the 45°+δ and 45°-δ spectra (δ now being larger) no longer overlap. The splitting due to the inequivalence of the Cl' ions can, however, be clearly distinguished from this smaller splitting. Again, without any further analysis of the spectra, it is demonstrated that the centre has C$_{2v}$ symmetry with the $g_x-g_z$ plane as the vertical mirror plane.

Whereas in the case of AgCl the splitting of all $M_\text{Q}$ transitions is essentially equal, in this case the magnitude of the splitting is clearly increasing when $M_\text{Q}$ increases. This is related to a tilting of the principal axes of the $\bar{Q}$ tensor. In Figure 5.13c, a tilting of the $\bar{A}$ tensor axes alone is considered. As in Figure 5.11c, the magnitude of the splitting of each $M_\text{Q}$ transition is essentially equal. In Figures 5.13d and 5.13e a tilting of the $\bar{Q}$ tensor axes is also taken into account (θ = 100°). If the tilting of the $\bar{Q}$ tensor is in the opposite direction as that of $\bar{A}$ (Figure 5.13d), the magnitude of the splitting decreases with increasing $M_\text{Q}$, whereas it increases if both tensors are tilted in the same direction (Figure 5.13e). Although the assignment of the transitions to a certain $M_\text{Q}$ value is dependent on the sign of the quadrupole value (here taken negative, in agreement with the literature), the simulated spectrum does not change if the signs of the principal $\bar{Q}$ values are reversed. By comparison with the experimental spectrum, it is obvious that the $\bar{A}$ and $\bar{Q}$ tensor principal axes are tilted in the same direction.

The principal values and directions of $\bar{A}$ and $\bar{Q}$ were again determined by least squares error fitting of the calculated angular dependence of the ENDOR frequencies to the spectra recorded in the $g_x-g_z$ and $g_x-g_y$ plane. If the transitions were additionally split, the centre of the lines was taken as the
experimental transition frequency. The optimum parameters are given in table 5.2. A comparison between calculated and experimental transition frequencies in the $g_x^c-g_x$ and $g_x^c-g_y$ plane is presented in figure 5.14, indicating that the fitting is again excellent.

![Figure 5.14: Angular variation of the axial Cl ENDOR spectrum of the [RhCl₄]⁺.1Vac centre in NaCl recorded in the $g_x^c-g_x$ plane (a) and $g_x^c-g_y$ plane (b). Experimental data points are represented by black squares, simulations, using the best fit parameters in table 5.2 are indicated with solid lines (green: $^{35}$Cl isotope and red: $^{37}$Cl isotope).](image)

The following differences with the parameters for AgCl are remarkable. The principal axes of both the $\tilde{A}$ and the $\tilde{Q}$ tensor are tilted in the $g_x^c-g_x$ plane. The tilting of $\tilde{Q}$ is larger than that of $\tilde{A}$, but also the indicated error is larger. It was indeed observed that changes in $\theta_A$ have a more prominent influence on the calculated spectra than changes in $\theta_Q$. $\theta_Q$ is significantly different from 0°, though. No significant difference between $Q_x$ and $Q_y$ was found in the present case, although in AgCl the $\tilde{Q}$ tensor was clearly rhombic. The $\tilde{A}$ tensor was found again to be axial ($A_x = A_y$), within experimental error. Finally, it is worth noting that for the Cl⁻ interaction of both complexes $\theta_A$ is equal, within experimental error.

5.4.3. Study of the [RhCl₄]⁺.2Vac centre in NaCl

From the experimental point of view, the study of the [RhCl₄]⁺.2Vac complex in NaCl is much more difficult than that of the previous two complexes. First, the deviation from axial $\tilde{g}$ tensor symmetry in the present case is much smaller than for the [RhCl₄]⁺.1Vac centres. For the orientation selection of the [RhCl₄]⁺.2Vac complex the limits of the resolving power of our Q-band ENDOR spectrometer were nearly reached. In addition, the study of the axial Cl⁻ interaction in the $g_x^c-g_x$ and $g_x^c-g_y$ planes requires a rotation of the crystal in a {110} plane. As NaCl crystals cleave (at room temperature) with {100}
faces, the crystals need to be polished in order to allow a rotation in a \{110\} plane. Crystals, with approximate dimensions of 1 mm x 1 mm x 10 mm (long edge along \{110\}) were stuck with their \{001\} face to the inner wall of the sample tubes using vacuum grease. The resulting rotation plane of the crystals is not expected to correspond perfectly to a \{110\} plane. Finally, the concentration of the [RhCl\(_6\)]\(^{+}\).2Vac complex is lower than that of the [RhCl\(_6\)]\(^{+}\).1Vac centres, resulting in a lower signal to noise ratio for the ENDOR spectra. The highest concentration of [RhCl\(_6\)]\(^{+}\).2Vac centres is found in melt-grown NaCl single crystals. It is about 1/3 of the concentration of the [RhCl\(_6\)]\(^{+}\).1Vac complex in these crystals [SCHW97, SABB98a]. As the EPR spectra of these complexes overlap in a very large angular range in the \{110\} plane and the optimal experimental conditions for ENDOR detection are very similar for both, the ENDOR spectra in these crystals are dominated by the contribution of the [RhCl\(_6\)]\(^{+}\).1Vac centre. As a result, a very accurate determination of the spin Hamiltonian parameters of the axial Cl\(^-\) interaction for the [RhCl\(_6\)]\(^{+}\).2Vac complex from melt-grown crystals is very difficult. In solution-grown NaCl:Rh\(^{3+}\) doped crystals, X-ray irradiated at 77 K, the [RhCl\(_6\)]\(^{+}\).2Vac complex is present as primary Rh\(^{2+}\) species. \(V_K\) and B-type centres are also produced during irradiation, but the presence of these centres does not seem to affect the ENDOR spectra in the used experimental conditions. The ENDOR spectra recorded for these crystals will thus be solely due to the hexachloro rhodate complex with two vacancies. The detection of the \(V_K\) centre demonstrates that the temperature has not risen above 150 K [SCHO68] during irradiation and subsequent transfer of the specimen into the microwave cavity. As we irradiated as-grown crystals and because the temperature was kept well below that at which cation vacancies become mobile, no other [RhCl\(_6\)]\(^{+}\).nVac than with \(n = 2\) are present in the crystals. The concentration of the desired Rh\(^{2+}\) complexes in these complexes is, however, much lower than in melt-grown crystals.

We decided to record a complete angular dependence of the ENDOR spectrum in the \(g_r-g_s\) and \(g_r-g_y\) planes for solution-grown crystals, and to check the results for a few orientations on melt-grown crystals. The polar angles of the rotation plane of the crystal, for which the complete angular dependence was recorded (determined by the angular dependence of the EPR spectrum for [RhCl\(_6\)]\(^{+}\).0Vac after annealing the crystal to room temperature for one day), were \(\theta = 89^\circ 45'\) and \(\phi = -44^\circ 8'\). The small deviation from the \{110\} plane (with \(\theta = 90^\circ\) and \(\phi = -45^\circ\)) was taken into account in the fitting of the spin Hamiltonian parameters, but did not affect the results in a significant way. It will not be mentioned in the presentation of the results. As all ENDOR spectra in the angular dependence needed to be recorded on the same crystal (identical rotation plane) and this crystal could not be annealed to temperatures above 220 K, the spectra had to be recorded during one measuring day (at longest 14 - 15 h). Therefore, we decided to record the spectra with 10\(^\circ\) intervals and to record some additional spectra in the range where the splitting of the axial Cl\(^-\) transitions is best observed. In spite of all these experimental difficulties, we succeeded in demonstrating the \(C_{2v}\) symmetry of the complex and in determining its \(\sigma_v\) plane.
Figure 5.15: Low field part of the Q-band (34.00 GHz) EPR spectrum recorded with the magnetic field rotated 15° away from <110> in a {110} plane of solution-grown NaCl:Rh<sup>2+</sup>, after X-ray irradiation at 77 K, and ENDOR spectra recorded in the g<sub>r</sub>-g<sub>r</sub> (b) and g<sub>r</sub>-g<sub>r</sub> plane (c). The experimental conditions are the same as in figure 5.13. The ENDOR spectra were recorded at the central positions of the superhyperfine patterns of the two [RhCl<sub>4</sub>]<sup>2+</sup>.2Vac g components in this magnetic field region (indicated with arrows).

Figure 5.16: Low field part of the Q-band (34.00 GHz) EPR spectrum recorded with the magnetic field rotated 15° away from <110> in a {110} plane of melt-grown NaCl:Rh<sup>2+</sup>, and ENDOR spectra recorded in the g<sub>r</sub>-g<sub>r</sub> (b) and g<sub>r</sub>-g<sub>r</sub> plane (c). The experimental conditions are the same as in figure 5.13. The ENDOR spectra were recorded at the magnetic field positions indicated with an arrow.

The splitting of the axial Cl ENDOR transitions is best observed if the magnetic field is rotated 15° away from the (110) orientation in the (near to) {110} plane. The EPR and ENDOR spectra recorded on solution-grown crystals for this magnetic field orientation are shown in figure 5.15. Figure 5.15a presents the low field part of the EPR spectrum. Although the g<sub>r</sub>-g<sub>r</sub> and the g<sub>r</sub>-g<sub>y</sub> components of the spectrum can be clearly distinguished, they overlap. The ENDOR spectra recorded at the centre of the superhyperfine patterns for each of these components (35Cl isotope, M<sub>S</sub> = -1/2 multiplet, figures 15b-c) are expected to contain small contributions of the spectrum for the other complex orientation. For melt-grown crystals, ENDOR spectra could also be recorded at other transitions in the superhyperfine pattern of the two components, where the contributions of the other complex
orientation are expected to be negligible. Figure 5.16 presents spectra nearly identical to those in figure 5.15, recorded on melt-grown crystals. The small differences between the spectra are due to the fact that the orientation of the magnetic field is slightly different (the crystals have slightly different rotation planes). In both figures, it is clearly observed that the ENDOR transitions recorded in the \( g_x-g_z \) plane are split, whereas those recorded in the \( g_x-g_y \) plane are not. Without any further analysis of the spectra, the \( C_{2\nu} \) symmetry of the complex is thus demonstrated. Furthermore, the \( g_x-g_z \) plane is identified as the \( \sigma_v \) mirror plane. The latter information could not be obtained from the \( X, Q \) and \( W \)-band EPR or X-band ENDOR analysis.

In the spectrum recorded in the \( g_x-g_z \) plane (see figures 5.15b and 5.16b), the \( M_Q = \pm 1 \) transitions are split, whereas the \( M_Q = 0 \) transition appears not to be split. In figure 5.11b it is shown that such a situation occurs when \( \theta_x = 0 \) and \( \theta_0 \neq 0 \). Figure 5.17a shows a simulation of the spectrum in figure 5.15b (or 5.17d) assuming that \( \theta_A = 0 \) and \( \theta_Q = 120' \). A comparison with the experimental spectrum (figure 5.17d) indicates that the correspondence between experimental and simulated spectrum could still be further improved: in the simulated spectrum, the splitting of the \( M_Q = 1 \) transition is slightly smaller than in the experimental spectrum, and the simulated splitting of the \( M_Q = -1 \) transition is slightly too large. A small tilting of the \( \bar{A} \) tensor axes should remove this discrepancy. A simulation with \( \theta_Q = 120' \) and \( \theta_A = -10' \) (tilting angles in opposite directions) is shown in figure 5.17b. By introducing such a tilting angle, the splitting of the \( M_Q = 1 \) transition decreases and that of the \( M_Q = -1 \) increases, which is exactly the opposite of the desired effect. A tilting of the \( \bar{A} \) tensor axes in the same direction as those of that of the \( \bar{Q} \) tensor (figure 5.17c) produces a perfect match between observed and simulated splittings. The spin Hamiltonian parameters were again obtained by fitting the calculated angular dependence of the transition frequencies (diagonalisation of spin Hamiltonian (5.2)) to the experimentally observed resonance positions. The results of the fitting are presented in table 5.2 and a comparison between the experimental and the calculated angular dependence is shown in figure 5.18.

![Figure 5.17: \( g_x-g_z \) ENDOR component of the spectrum in figure 5.15. (a) Simulation with \( \theta_x = 0 \) and \( \theta_0 = 120' \), (b) simulation with \( \theta_A = -10' \) and \( \theta_Q = 120' \), (c) simulation with \( \theta_A = 10' \) and \( \theta_0 = 120' \), (d) experimental spectrum.](image)

The best fit spin Hamiltonian parameters show the following characteristics. The \( \bar{A} \) tensor is, within experimental error, axial. No significant improvement of the fitting results could be obtained by taking \( A_x \neq A_y \). On the other hand, \( Q_x \) and \( Q_y \) differ slightly but significantly. These results can be directly
Detection of cation vacancies near Rh\(^{2+}\) ions in AgCl and NaCl using Q-band ENDOR

**Figure 5.18**: Angular variation of the axial Cl ENDOR spectrum of the [RhCl\(_4\)]\(^{-}\).2Vac centre in NaCl recorded in the \(g_x\)-\(g_y\) plane (a) and \(g_y\)-\(g_z\) plane (b). Experimental data points are represented by black squares, simulations, using the best fit parameters in Table 5.2 are indicated with solid lines (green: \(^{35}\)Cl isotope and red: \(^{37}\)Cl isotope).

\[
A/2 + g_{xx}B_0 \approx A/2 + g_{yy}B_0
\]

\(\approx 6Q_x\)

\(\approx 6Q_y\)

**Figure 5.19**: ENDOR spectra recorded at the \(g_x\) and \(g_y\) components of the [RhCl\(_4\)]\(^{-}\).2Vac EPR spectrum in melt-grown NaCl single crystals (magnetic field parallel with <110>).

Observed by comparing the ENDOR spectra recorded at the \(g_x\) and the \(g_y\) component of the EPR spectrum (\(\vec{B}_0 \parallel \langle 110 \rangle\)), as shown in Figure 5.19. The \(M_0 = 0\) transition occurs, within experimental error, at the same frequency in the two ENDOR spectra, whereas the splitting between the \(M_0 = \pm 1\) transition clearly differs. The tilting angle of the \(\vec{Q}\) tensor is small but highly significantly different from 0°. Also \(\theta_A\) may be regarded as significantly different from 0°, although it is considerably smaller than \(\theta_Q\).
5.5. Discussion

5.5.1. Proof for the vacancy presence

The Ω-band ENDOR study of the axial Cl⁻ interaction of the [RhCl₆]⁺ₙVac (n = 1, 2) complexes in AgCl and NaCl allowed us to determine the exact symmetry of these centres and to identify the g₁g₂ plane as their vertical mirror plane. This information strongly supports the models proposed for these centres, but does not serve as a direct proof for the presence of cation vacancies near the Rh²⁺ ions. Indeed, the presence of, e.g., substitutional (non-magnetic) impurities at the positions of the cation vacancies would produce a similar effect. However, in view of the fact that cation vacancies in ionic solids have neither electronic nor nuclear spin, the tilting Ħ and Š tensor of the axial Cl⁻ ions is about the most direct evidence for the vacancy presence one can expect. Considering also the additional evidence, which originally lead to the identification of these centres (e.g. only [RhCl₆]⁺₂Vac complexes are produced by X-ray irradiation at temperatures, at which vacancies are frozen in, and [RhCl₆]⁺₂Vac is converted into [RhCl₆]⁺₁Vac at temperatures at which vacancies become mobile in NaCl), little doubt is left that the models proposed for the [RhCl₆]⁺ₙVac centres are describing their microscopic structure correctly. The present study then unambiguously determines the position of the cation vacancies with respect to the principal ħ tensor axes.

5.5.2. Physical interpretation of the superhyperfine and quadrupole tensor tilting

Now that the presence and the position of the cation vacancies near the various [RhCl₆]⁺ complex in NaCl and AgCl are known, we may try to find a physical interpretation for the influence of the vacancies on superhyperfine and quadrupole tensors of the axial Cl⁻ ions. Our ultimate objective is to find some kind of fingerprint for the vacancy presence and configuration, that could later on be used to identify paramagnetic complexes, for which the vacancy association is not well established yet. In a first quantitative approach to the influence of the vacancies, we will assume that their presence does not disturb the electronic ground state properties of the [RhCl₆]⁺ complex too much and that they do not induce any important lattice relaxations. Under these conditions, the main effect of the vacancies would be the introduction of electric field gradients near the [RhCl₆]⁺ complex, which should be reflected in the quadrupole tensor of the axial Cl⁻ ions. However, it will be shown that the calculated effects of one and two NNN vacancies on this tensor do not even in a qualitative manner agree with the experiments. This indicates that the unpaired electron distribution over the complex is affected by the presence of the vacancies and/or lattice relaxations around the vacancies are important. The fact that important lattice distortions may be induced around vacancies was already experimentally observed by Halliburton et al. for the F⁺ centre in MgO (electron trapped at a O⁰ vacancy) [HALL73]. We will consider an off-centre displacement of the Rh²⁺ ion as a possible physical interpretation for the tilting of the principal Ħ tensor axes. A more detailed interpretation of the lattice distortions in the [RhCl₆]⁺ₙVac centres requires quantum chemical calculations for the complexes in the appropriate crystal lattices. To our knowledge, no results of such calculations for Rh²⁺ complexes in NaCl and AgCl have been published yet and they are beyond the scope of the present work. In our
discussion, lattice distortions will only be used as a qualitative interpretation of the superhyperfine and quadrupole tensor tiltings.

Calculation of the axial Cl\(^{-}\) quadrupole tensor for Rh – vacancy complexes

As mentioned above, we assume in this paragraph that the only effect of a NNN cation vacancy near a [RhCl\(_{6}\)]\(^{4+}\) complex is to induce an electric field gradient in the crystal. A cation vacancy represents an effective negative charge \(-e\) (considered as a point charge) in the NaCl or AgCl lattice, which will contribute to the quadrupole tensor of the axial Cl\(^{-}\) ions. Other contributions to this tensor are expected from the unpaired electron density on the Cl\(^{-}\) ion and from the effective positive charge of the Rh\(^{3+}\) ion (see § 2.3.5). From equations (2.28) and (2.29) the \(\tilde{Q}\) tensor may be calculated if the unpaired electron density on the Cl\(^{-}\) ligand is known. We do not expect a very good quantitative agreement with the experimental results from such calculations. We only want to verify whether experimental trends in the quadrupole parameters as a function of the number and positions of cation vacancies can be reproduced, in other words, if the vacancies have a predictable influence on the quadrupole tensor of the axial Cl\(^{-}\) ligands. The assumption that the vacancies do not affect the unpaired electron distribution over the complex seems to be reflected by the fact that the anisotropic part of the superhyperfine tensor for the various [RhCl\(_{6}\)]\(^{4+}\) complexes in AgCl and NaCl does not differ very much (the maximum difference is found between the zero and two-vacancies complexes in NaCl and only amounts to about 3 \%). Therefore, we neglect this difference and assume that for all complexes the unpaired electron density on each of the Cl\(^{-}\) ions is 0.11. We further neglect the difference between the lattice parameters of NaCl and AgCl in calculating the contributions of the point charges in the lattice.

From equation (2.28) the contribution to \(\tilde{Q}\) from the unpaired electron density may be calculated to be (using the atomic and nuclear data by Koh and Miller [KOH85]) :

\[
\tilde{Q}_e = 0.818 \text{ MHz} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}
\]  

(5.3)

The contribution of the effective charge of the Rh\(^{3+}\) ion \((+e)\) at coordinates \((0,0,-1)\) with respect to the Cl\(^{-}\) ion is :

\[
\tilde{Q}_{\text{Rh}^{3+}} = -1.28 \text{ MHz} \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 2 \end{pmatrix}
\]  

(5.4)

For the zero-vacancy complex, these are the only two contributions. For the [RhCl\(_{6}\)]\(^{4+}\).1Vac complex, the effect of a NNN cation vacancy with coordinates \((2,0,-1)\) should also be considered :

\[
\tilde{Q}_{\text{Vac},-} = 0.023 \text{ MHz} \begin{pmatrix} 7 & 0 & -6 \\ 0 & -5 & 0 \\ -6 & 0 & -2 \end{pmatrix}
\]  

(5.5)

and the two-vacancies centre has an additional vacancy with coordinates \((0,2,-1)\) :
\[ \tilde{Q}_{\text{vac-y}} = 0.023 \, \text{MHz} \begin{pmatrix} -5 & 0 & 0 \\ 0 & 7 & -6 \\ 0 & -6 & -2 \end{pmatrix} \] (5.6)

The calculated principal values and tilting angles for the three \([\text{RhCl}_6]^{+}\)\(_n\text{Vac}\) complexes are given in table 5.3.

**Table 5.3:** Calculated principal values (in MHz) and tilting angles (principal directions defined in figure 5.6) for the \([\text{RhCl}_6]^{+}\)\(_n\text{Vac}\) centres.

<table>
<thead>
<tr>
<th>n</th>
<th>(Q_x)</th>
<th>(Q_y)</th>
<th>(Q_z)</th>
<th>(\theta_\alpha)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.46</td>
<td>0.46</td>
<td>-0.92</td>
<td>0°</td>
</tr>
<tr>
<td>1</td>
<td>0.63</td>
<td>0.35</td>
<td>-0.98</td>
<td>300°</td>
</tr>
<tr>
<td>2</td>
<td>0.54</td>
<td>0.51</td>
<td>-1.05</td>
<td>435°</td>
</tr>
</tbody>
</table>

A comparison with the experimental values in table 5.2 leads to the conclusion that the influence of the cation vacancies on the quadrupole tensor of the axial Cl\(^-\) ions cannot be predicted from these simplified calculations. Indeed, for the one-vacancy centre the calculations predict an orthorhombic \(\tilde{Q}\) tensor with appreciable axis tilting. The complex in AgCl has a clearly orthorhombic quadrupole tensor, but no tilting is observed. On the other hand, for the complex in NaCl a significant tilting of the quadrupole axes is found, but \(Q_x = Q_y\), within experimental error. For the effect of a second NNN vacancy, calculations predict a decrease in the degree of orthorhombicity and an increase of the tilting angle. When comparing the experimental results of the \([\text{RhCl}_6]^{+}\)\(_1\text{Vac}\) and \([\text{RhCl}_6]^{+}\)\(_2\text{Vac}\) complexes in NaCl, the increase in the tilting angle is observed. However, contrary to the expectations, the degree of orthorhombicity increases as a result of the additional vacancy (although it remains very small). Finally, calculations predict a decrease in the \(Q_x\) value (increase in the absolute value) as the number of vacancies increases, whereas experimentally exactly the opposite is observed.

We conclude that no systematic or predictable (from these simplified calculations) trend is found in the experimental principal values or tilting angles for the quadrupole tensor of the axial Cl\(^-\) ions. The fact that our calculations cannot even qualitatively explain the observed changes in these parameters indicates that the vacancies have an non-negligible influence on the unpaired electron density over the complex and do induce displacements of the ions in the complex.

**Off-centre displacement of the Rh\(^{3+}\) ion as physical interpretation of the tilting of the superhyperfine tensor**

Considering the experimental results in table 5.2, it is striking that for the two \([\text{RhCl}_6]^{+}\)\(_1\text{Vac}\) centres, in similar but different hosts, within experimental error the same tilting angle for the superhyperfine axes is found. Hence, it seems interesting to verify whether the number and position of cation vacancies may have a systematic influence on \(\theta_\alpha\). If, as often assumed, the principal superhyperfine axis corresponding to the largest principal value \((A_0)\) is considered to be directed along the transition metal – ligand bond axis, the tilting can be physically interpreted as a displacement of the central ion or of the axial ligands in the complex from their normal lattice positions.
Lattice relaxations around the extra positive charge of the Rh$^{2+}$ ion and the effective negative charge of the cation vacancies may indeed be expected. The Rh$^{2+}$ ion would attract its first few shells of anions, causing a displacement of these ions towards the central ion, and repel its first few shells of cations, causing a displacement away from the central ion. These displacements may be asymmetrical (e.g. a different displacement for the axial ligands from that for the equatorial ligands, as a result of the Jahn-Teller elongation), but do not cause a tilting of the superhyperfine tensor of the axial Cl$^-$ ions. The effective negative charge of a cation vacancy is expected to repel the first few shells of anions and to attract the first few shells of cations around it. The displacement directions for the central Rh$^{2+}$ ion and the axial Cl$^-$ ligands in the case of the one-vacancy centre are indicated with arrows in figure 5.20a.

Figure 5.20: Expected displacements (indicated in blue) of the ions in the [RhCl$_4$]$^{+}$.1Vac complex (a) considering only the electrostatic interaction between the vacancy and the Rh$^{2+}$ and axial ligands, (b) considering also the repulsive interaction between the vacancy and its first shell of anions. The Rh - Cl bond axes are indicated in red.

It is clear that the expected displacement of the central Rh$^{2+}$ ion and of the Cl$^-$ ligands have an identical effect: a tilting of the $\hat{A}$ tensor axes in the $\sigma_v$ plane of the complex. Thus, displacements of the Rh$^{2+}$ ion and/or axial Cl$^-$ ions offer a possible physical interpretation of the observed tilting of the principal superhyperfine directions. From the experimental point of view, the distinction between the displacement of the central ion and that of the ligands cannot be made. We choose to consider only a displacement of the Rh$^{2+}$ ion. Further assuming that the Rh$^{2+}$ - Cl$^-$ distance is equal to the cation – anion distance in the lattice (281 pm in NaCl and 278 pm in AgCl), the displacement of the Rh$^{2+}$ ion is estimated at 4 pm in the [RhCl$_4$]$^{+}$.1Vac complex and at 0.8 pm in the [RhCl$_6$]$^{4+}$.2Vac complex. These values should only be considered as indications for the order of magnitude of the displacement, because all lattice relaxations caused by the extra positive charge of the Rh$^{2+}$ ion and/or the Jahn-Teller distortion are neglected.

Although from the electrostatic point of view a displacement of the Rh$^{2+}$ ion towards the cation vacancies would be expected, the experimental observation of the tilting angle for the $\hat{A}$ tensor only indicates that a displacement might exist. It gives no information on whether the Rh$^{2+}$ ion should move towards or away from the vacancies. A displacement away from the vacancies is not a priori excluded: the outward relaxation of the first shell of anions around a vacancy might be so large that the Rh$^{2+}$ ion is pushed away from that vacancy in spite of the electrostatic attractive force between both, as indicated in figure 5.20b. Ab initio calculations of Ge$^{2+}$, Sn$^{2+}$ and Pb$^{2+}$ ions associated with a
NNN cation vacancy in NaCl predict such a displacement [AGUA01]. These calculations, however, also predict that the first shell anions in the plane perpendicular to the impurity – vacancy axis exhibit a distortion perpendicular to that plane, away from the vacancy and comparable in size to that of the central impurity ion. Considering only the relative displacement of the Rh\(^{2+}\) ion with respect to the axial Cl\(^-\) ligands, this would result in a very small displacement either towards, but, according to these calculations, most probably away from the vacancy. Similar calculations have not been performed for Rh\(^{2+}\) ions yet. However, two experimental observations for these complexes, which will discussed below, indicate that the Rh\(^{2+}\) ion relaxes towards the cation vacancies.

For a first indication, we turn back to the calculations for the quadrupole tensor. For both vacancy configurations, the calculated \(Q_x\) axis tilting is directed towards the cation vacancies. In the cases where both the superhyperfine and quadrupole tensors are tilted, the direction of the tilting angle is the same. As a consequence, the Rh\(^{2+}\) ion would exhibit a displacement towards the cation vacancies.

We already indicated that the cation vacancies do not appear to have a predictable influence on the \(\bar{Q}\) tensor for the axial Cl\(^-\) ligands. Therefore, the observation that \(\bar{A}\) and \(\bar{Q}\) are tilted in the same direction will only be considered as an indication for a displacement towards the cation vacancies.

A second indication comes from the analysis of the \(\bar{g}\) tensor for the [RhCl\(_6\)]\(^{2+}\).2Vac centre in NaCl. Callens et al. [CALL98] attributed the nearly axial symmetry of this tensor to the accidental degeneracy of the \(d_{yz}\) and \(d_{xz}\) orbital of the Rh\(^{2+}\) ion when the angle between the Rh – Vac axes is exactly 90\(^\circ\). Indeed, in the one-electron approximation the principal \(g\) values are given by equation (3.25) for the \(^2\text{A}_1\) ground state. If the \(d_{yz}\) and \(d_{xz}\) levels are exactly degenerate, like in figure 5.21a, \(g_x\) and \(g_y\) should be exactly equal.

\[
\begin{array}{c}
\text{Vac - Rh}^{2+} - \text{Vac} = 90^\circ \\
\text{Vac - Rh}^{2+} - \text{Vac} < 90^\circ \\
\text{Vac - Rh}^{2+} - \text{Vac} > 90^\circ \\
\end{array}
\]

\[
\begin{array}{c}
d_{x^2-y^2} \quad d_{3z^2-r^2} \\
d_{xy} \quad \delta_{1\perp} \\
d_{yz},d_{zx} \\
\end{array}
\quad
\begin{array}{c}
d_{x^2-y^2} \quad d_{3z^2-r^2} \\
\delta_{2\perp} \quad \delta_{1\parallel} \\
d_{xy} \quad d_{yz} \quad d_{zx} \\
\end{array}
\quad
\begin{array}{c}
d_{x^2-y^2} \quad d_{3z^2-r^2} \\
\delta_{1\parallel} \quad \delta_{2\parallel} \\
d_{xy} \quad d_{yz} \quad d_{zx} \\
\end{array}
\]

\(\text{Figure 5.21} : \) Arrangement of the \(d\) levels, expected from electrostatic considerations, for the [RhCl\(_6\)]\(^{2+}\).2Vac centre if (a) the angle between the Rh – Vac axes is 90\(^\circ\), (b) the angle between the Rh – Vac axes is smaller than 90\(^\circ\), and (c) the angle between the Rh – Vac axes is larger than 90\(^\circ\).

As \(g_x\) and \(g_y\) are slightly different, the degeneracy of these levels is lifted. This can be accomplished by admixture of the equatorial ligand wave functions or if the angle between the Rh – Vac axes is different from 90\(^\circ\). We consider only the latter effect here. From the purely electrostatic viewpoint, one would expect that the energy of the \(d_{yz}\) level is lower than that of the \(d_{zx}\) if the angle is smaller.
than 90° (figure 5.21b, x corresponding to the C2 axis of the complex), whereas the energy of the \( d_{zx} \) level is lower than that of the \( d_{yz} \) if the angle is larger 90° (figure 5.21c). In the former case, \( g_x < g_y \) and in the latter \( g_x > g_y \). The experimental observation that \( g_x > g_y \) thus suggests that the angle between the Rh – Vac axes is larger than 90°. This can either be explained by assuming that the cation vacancies repel one another, as shown in figure 5.22a, or by an off-centre displacement of the Rh\(^{2+}\) ion towards the vacancies, illustrated in figure 5.22b. So also the \( \tilde{g} \) analysis gives an indication that the displacement of the Rh\(^{2+}\) ion is directed towards the vacancies. Again, this serves as an indication and not as a proof. Indeed, there is no a priori information about the relative importance of the repulsion between the vacancies and the possible displacement of the Rh\(^{2+}\) ion in determining the angle between the Rh – Vac axes. A relatively large repulsion between the vacancies in combination with a small displacement of the Rh\(^{2+}\) ion away from the vacancies may still result in an angle slightly larger than 90°. Moreover, the approach of using simple electrostatic considerations to determine the ordering of the \( d \) levels of the Rh\(^{2+}\) ion and first order one-electron formulae to calculate the principal \( g \) values may be inaccurate. E.g. for the [RhCl\(_6\)]\(^{4+}\).1Vac centre, electrostatic considerations would predict that the energy of the \( d_{zx} \) level is higher than that of the \( d_{yz} \) level, whereas the analysis of the principal \( g \) values (\( g_x > g_y \)) leads to exactly the opposite conclusion.

**Figure 5.22**: Cross section of the model for the [RhCl\(_6\)]\(^{4+}\).2Vac complex in the horizontal mirror plane. The angle between the Rh\(^{2+} \) - Vac axes (indicated in green) is larger than 90° (a) if a repulsion between the vacancies is considered, or (b) if the Rh\(^{2+}\) ion undergoes an off-centre displacement towards the vacancies.

Finally, a remark should be made on the magnitude of the displacement. It is not a priori clear why the displacement in the case of the [RhCl\(_6\)]\(^{4+}\).2Vac complex should be much smaller than in the case of [RhCl\(_6\)]\(^{4+}\).1Vac. Indeed, the electrostatic interaction between the central ion and the vacancies in the former case is larger by a factor of \( \sqrt{2} \) than in the latter. One might note that in the one-vacancy complex, the Rh\(^{2+}\) ion moves along the [100] direction, directly towards a Cl\(^-\) ligand, by which it is attracted, whereas in the two-vacancies complex, the displacement occurs in the [110] direction, directly towards a NN Na\(^+\), by which the Rh\(^{2+}\) ion is repelled.
It may be concluded that simple electrostatic calculations, treating the ions and vacancies as point charges, are most probably inappropriate to describe the many relaxation processes occurring in and around the [RhCl₆]⁺.nVac complexes. The results of quantum chemical calculations for these complexes in the appropriate crystal environment should be awaited in order to verify whether the number and the position of charge compensating cation vacancies have a predictable (characteristic) influence on the tilting angle of the $\tilde{A}$ tensor, as we suggest here. Such calculations are in progress (performed by the research group of prof. M. Moreno, University of Cantabria, Santander, Spain), but the results for the complexes with nearby vacancies are not yet available.

5.5.3. Determining the point group symmetry of paramagnetic complexes using Q-band ligand ENDOR: suggestions for further research

Although we are up to now not able to fully explain the effect of nearby cation vacancies on the ENDOR parameters of the axial anion ligands for low spin $d^7$ complexes in the $^2A_1$ ground state, the method of determining the point group symmetry of these complexes by observing a splitting of the ENDOR transitions for the axial anion ligands due to tiltings of the superhyperfine and/or quadrupole tensors is very generally applicable. In the following, two suggestions for further investigation employing this method will be given.

The Rh-dimer centre in melt-grown NaCl crystals

The proposed model for this centre is given in figure 3.11d. The centre has been described by Vercammen et al. [VERC98b] as a pair of weakly interacting [RhCl₆]⁺.1Vac centres with $S = 1/2$ along a [110] direction at a distance $2\sqrt{2}a$ from one another with the two vacancies arranged in such a way that the centre acquires orthorhombic I ($D_{2h}$) symmetry. The arguments for assuming that the interaction between the Rh$^{2+}$ ions is weak, were based on the observation that the $\tilde{g}$ tensor and superhyperfine interaction with the axial Cl⁻ ligands does not differ much from those for the [RhCl₆]⁺.2Vac centre. According to their description, both Rh$^{2+}$ ions in this complex would approximately behave like an isolated [RhCl₆]⁺.2Vac centre, experiencing the presence of the nearby paramagnetic Rh$^{2+}$ ion only via the magnetic dipole interaction between both. As a consequence, the unpaired electron on each of the ions would primarily interact with its own two axial Cl⁻ ligands. Vercammen et al. indeed attributed the observed superhyperfine structure observed for this centre to an interaction with two equivalent Cl⁻ ions. Later Q-band EPR measurements by Sabbe [SABB00a] demonstrated that the observed superhyperfine structure is actually due to four equivalent Cl⁻ ions, suggesting that the wave functions of the neighbouring Rh$^{2+}$ ions strongly overlap and that the centre should be described as an $S = 1$ system, centred on the Na⁺ ion between the Rh$^{2+}$ ions. Furthermore, the analysis of the Q-band ENDOR results by Sabbe suggests that the $\tilde{D}$ tensor analysis by Vercammen et al. is incorrect, casting doubt on the proposed model for the centre. The model proposed by Vercammen et al. has $D_{2h}$ symmetry. One of the vertical mirror planes of this complex, \((\bar{1}10)\), contains the axial ligands, which strongly interact with the unpaired electrons. If this model is correct, the ENDOR transitions for this interaction should split up in the $g_x-g_y$ or $g_x$-$g_y$ plane,
but not in both. If the centre were to have C<sub>2v</sub> symmetry (e.g. because one of the vacancies is missing), no vertical mirror plane of the complex contains the axial ligands, their principal A and Ñ directions are completely arbitrary and their ENDOR transitions will split up in both vertical Ï g planes. Thus, the study of the ENDOR spectrum of the axial ligands for this complex is expected to offer important information in favour of or excluding the proposed model. Moreover, if the centre should be described as an S = 1 system, centred on the Na<sup>+</sup> ion between the Rh<sup>2+</sup> ions, rather than as two weakly interacting [RhCl<sub>6</sub>]<sup>4-</sup>:1Vac complexes, the z directions of the superhyperfine tensors are expected to be strongly tilted towards the centre of the complex, whereas in the other case, the axis tilting is expected to be mainly due to the presence of the cation vacancies and should be comparable to that for the [RhCl<sub>6</sub>]<sup>4-</sup>:2Vac centre. In this respect, the study of the axial Cl<sup>-</sup> interaction at Q-band is expected to reveal information on the spatial distribution of the wave function of the unpaired electrons.

**Ir<sup>2+</sup> complexes in NaCl**

Recent EPR studies at X, Q and W band and ENDOR studies at X and Q band [ZDRA99, SABB00a] indicated that after X-ray irradiation at low temperature of solution and melt-grown NaCl crystals doped with Ir<sup>2+</sup>, paramagnetic Ir<sup>2+</sup> centres are produced, which are very similar to the Rh<sup>2+</sup> centres in NaCl and AgCl. As most of these complexes occur both in solution-grown and in melt-grown crystals, cation vacancies, rather than other impurities, are expected to play an important role in the charge compensation of these complexes. One should, however, be careful in extrapolating conclusions for Rh<sup>2+</sup> complexes to Ir<sup>2+</sup> centres. Calculations by Bannon et al. [BANN84a, BANN85b] indicate that configurations involving NN vacancies become more stable as the size of the substitutional impurity increases. Therefore, NN vacancies may also play a role in the charge compensation of Ir<sup>2+</sup> and Ir<sup>2+</sup> complexes.

The primary centre produced in the crystals by irradiation at 77 K has, within the experimental limits of X-band EPR, axial g symmetry. Its X-band ENDOR properties are very similar to those of the [RhCl<sub>6</sub>]<sup>4-</sup>:nVac centres in NaCl and after a short pulse anneal to 220 K it is transformed into a centre with a g tensor which clearly has orthorhombic II symmetry. In view of the similarities with the [RhCl<sub>6</sub>]<sup>4-</sup>:2Vac centre, it was assigned to a cis-[IrCl<sub>6</sub>]<sup>4-</sup>:2Vac complex, with the two vacancies in NNN positions [ZDRA99]. However, the Q and W-band EPR results for this centre suggest that it has orthorhombic II rather than orthorhombic I symmetry [SABB00a]. Sabbe therefore proposed a model involving two NN cation vacancies in the equatorial plane, with the angle between the Ir – Vac axes very close to 90°. This model is shown in figure 5.23a. Although the model perfectly explains the observed g tensor symmetry of the complex, it appears rather surprising that at temperatures at which vacancies become mobile, one of the vacancies would migrate away, while the other one would move from a NN to a NNN position. Alternatively, a trans-[IrCl<sub>6</sub>]<sup>4-</sup>:2Vac complex may be proposed as a model for this centre, as shown in figure 5.23b. Although one would expect the degree of orthorhombicity for such a centre to be larger than for a [IrCl<sub>6</sub>]<sup>4-</sup>:1Vac complex, whereas the opposite is observed, the model cannot a priori be excluded. The two models in figure 5.23 have different point group symmetries (C<sub>2v</sub> and D<sub>2h</sub> for model a and b, respectively). For the model a, a tilting of the
principal $\tilde{A}$ and $\tilde{Q}$ tensors in the (010) plane should be observed, whereas for the model b, symmetry forbids such a tilting. Thus, the analysis of the axial Cl$^-$ ions should in principle allow to exclude one of these models. As in the case of the $[\text{RhCl}_6]^4$.2Vac centre, the nearly axial $\tilde{g}$ tensor and the large resolved hyperfine and superhyperfine structure in the EPR spectrum may hinder an accurate orientation selection. The Q-band EPR study of the $[\text{IrCl}_6]^4$.1Vac complex may, on the other hand, further contribute to our knowledge of the influence of cation vacancies on the $\tilde{A}$ and $\tilde{Q}$ tensors of the axial Cl$^-$ ligands.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure523.png}
\caption{Models for the Ir$^{3+}$ centre produced in melt-grown NaCl:Ir$^{3+}$ by X-ray irradiation at 77 K, in agreement with the observed orthorhombic \& tensor symmetry, (a) vacancy configuration with two NN vacancies leading to $C_{\infty v}$ symmetry, (b) vacancy configuration with two NNN vacancies leading to $D_{\infty h}$ symmetry.}
\end{figure}

5.6. Conclusions

Whereas the study of the EPR spectrum of low spin elongated $d^2$ complexes only allows to determine the $\tilde{g}$ tensor symmetry for these complexes as a result of the inversion symmetry of the EPR spin Hamiltonian, the study of the interaction with the axial ligands reveals their complete point group symmetry. For two $[\text{RhCl}_6]^4$ complexes, associated with NNN cation vacancies, the $C_{2v}$ symmetry could be directly demonstrated by observing a splitting of the ENDOR transitions of the axial Cl$^-$ ligands for rotations of the magnetic field in their $g_x$-$g_y$ plane, while no splitting is observed if the magnetic field is rotated in the $g_x$-$g_z$ plane. This experimental observation can be explained as follows: symmetry allows that the principal superhyperfine and quadrupole directions for this interaction are tilted in the mirror plane of the complex containing the axial ligands, as a result of which these ligands become slightly inequivalent as the magnetic field is rotated in this mirror plane. The $g_x$-$g_y$ plane is, as a consequence, immediately identified as the vertical mirror plane of the complex. If NNN cation vacancies are the only lattice defects considered to be present near the Rh$^{3+}$ ion, this
information unambiguously determines their number and positions. Nevertheless, it can still not be regarded as a direct proof for the vacancy presence. All the above-mentioned information can be directly deduced from the ENDOR spectra recorded in the $g_x g_y$ and the $g_x g_y$ planes. It requires no detailed spin Hamiltonian analysis of the data. For a clear observation of the effect, the spectra should be recorded at higher microwave frequencies than the conventional X-band (e.g. at Q-band).

At X-band, the lack of $g$ factor resolution and the splitting of ENDOR transitions due to the indirect interaction between the nearly equivalent Cl' ligands hinder the identification of the splitting due to the tilting of the interaction tensors for these ligands.

From the angular dependence of the Q-band ENDOR spectrum, the superhyperfine and quadrupole tensors for the axial Cl' interactions could be determined very accurately. We have tried to find an influence characteristic for the number and the positions of the vacancies, in order to find a way of directly deducing the vacancy configuration of M – nVac complexes (M = low spin elongated $d^8$ ion) for which the model is not yet well-established. Apparently, the number and position of vacancies have no characteristic or predictable influence on the $\tilde{Q}$ tensor of the axial Cl' ligands, although such an influence would be expected in view of the sensitivity of this tensor to electric field gradients in the crystal. A possible characteristic influence has been found on the tilting angle of the $\tilde{A}$ tensor of the axial ligands. We propose an off-centre displacement of the Rh$^{2+}$ ion towards the cation vacancies as a physical interpretation for this tilting. This hypothesis should be tested by performing quantum chemical calculations for the [RhCl$_4$]$^{n^+}$.nVac complexes in an appropriate crystalline environment. Such calculations are in progress, but the results are not available yet.
Chapter 6: Powder EPR and ENDOR study of Rh$^{2+}$ complexes in AgCl emulsion microcrystals

6.1. Introduction

The study of rhodium impurity centres in AgCl and NaCl single crystals have provided detailed structural information about [RhCl$_6$]$^{n+}$ ($n = 3$, 4, 5) complexes in these host lattices, as discussed in the previous chapters (§ 3.4, § 4.2 and chapter 5). Nevertheless, the study of rhodium-doped AgCl emulsion microcrystals remains interesting, both for its photographic relevance and as fundamental research. From the photographic viewpoint, rhodium-doped emulsion microcrystals which can be studied with electron magnetic resonance spectroscopy very closely resemble the AgCl grains in practically applied photographic emulsions. They only differ from the latter by the absence of a gelatine layer and in dopant concentration (100 ppm for research purposes, 0.1 – 1 ppm in practical applications [ENDO90, MARC92]). For photographic research, it is interesting to find out which of the [RhCl$_6$] complexes are stable and which other complexes (hydrated [RhCl$_6$]) may be incorporated in AgCl emulsion microcrystals. From the viewpoint of fundamental research, the latter complexes are the most interesting ones. Although association with solvent molecules (H$_2$O, OH) has been suggested for some Rh$^{2+}$-related centres (B-type) in solution-grown NaCl single crystals, the microscopic structure of such centres could not be determined (see § 4.3). Previous work by Endo et al. [ENDO90] and Vercammen et al. [VERC98c] indicate that hydrated rhodium-centred complexes are present in AgCl emulsion microcrystals, leaving them as the only systems in which such complexes can be studied. At X and Q-band microwave frequencies, a single crystal study of rhodium-doped AgCl emulsion microcrystals is impossible (edge length ~ 0.2 µm [VERC98c]). They should thus be studied in powder samples.

As compared with single crystal magnetic resonance, powder EPR and ENDOR have some important draw-backs. It has already been explained in § 2.5.6 that a lot of the angular dependent information is lost in the powder EPR spectrum, because all single crystal orientations are simultaneously present. If the paramagnetic centre has $\tilde{g}$ tensor anisotropy, part of this information may be recovered by recording the ENDOR spectrum at several magnetic field positions within the EPR powder envelope (see figure 2.17). Via the so-called “orientation selection principle”, the “angular dependence” of the interaction of the unpaired electrons with surrounding magnetic nuclei can then be recorded. Nonetheless the information obtained in this way is much less detailed than that obtainable from a single crystal study. E.g., in a single crystal one is able to determine the principal axes of the $\tilde{g}$ tensor and of the zero field splitting, (super)hyperfine and quadrupole tensors with respect to the principal axes of the crystal by recording the angular dependence of the spectra. In powders, this notion of an absolute reference frame is lost. The principal axes of the $\tilde{D}$, $\tilde{A}$ and $\tilde{Q}$ tensors can only be determined with respect to the $\tilde{g}$ tensor axes. An a priori or a posteriori assumption about the orientation of the latter axes should thus be made in order to obtain a complete model for the paramagnetic centre. Moreover, powder ENDOR spectra have lower resolution than the
corresponding single crystal spectra. This is easily understood: single crystal ENDOR spectra correspond to a single crystal orientation, whereas powder ENDOR spectra contain contributions from all single crystal orientations for which the EPR spectrum has an appreciable intensity at the magnetic field position at which the spectrum is recorded. As a result of this loss in resolution, a very detailed analysis involving very small tilting angles of superhyperfine an quadrupole tensors, like in chapter 5, is impossible in a powder ENDOR study.

In spite of all these difficulties, it will be shown that a powder EPR and ENDOR study at X and Q-band microwave frequencies of Rh²⁺ complexes in AgCl microcrystals leads to very detailed information on the structure of these complexes, if the knowledge obtained by studying single crystal model systems is applied. The fact that magnetic resonance spectra at two microwave bands are available and that for some of the centres a direct comparison between single crystal and powder spectra is possible, is hereby very helpful.

In the second section of this chapter, the various Rh²⁺ species in AgCl microcrystals are introduced and the problems concerning their structure we can solve using magnetic resonance techniques are defined. The third section discusses the powder EPR spectra of Rh²⁺ complexes in AgCl emulsion microcrystals and their simulation. The fourth and most extensive section is dedicated to the analysis of the powder ENDOR spectra for these complexes. In the fifth section our results will be compared to those of the Eastman Kodak group, which has studied the same complexes [PAWL98]. The results of the powder EPR and ENDOR study are used to construct microscopic models for the paramagnetic centres in the sixth section, where they will also be compared to those proposed by Pawlik et al. Finally, in section 8 the conclusions of this study are summarised. The results of this study have been published in two articles [VRIE99, VRIE00]. The simulation programs developed during this study are modified versions of the powder ENDOR simulation program by Van Doorslaer et al. [VAND95]. They were further used in the powder ENDOR study of Ir²⁺ complexes in AgCl emulsion microcrystals [SABB00b].

6.2. Paramagnetic Rh species in AgCl emulsion microcrystals

6.2.1. Identification of the R4, R5 and R6 species with X-band EPR

The emulsions studied here were prepared using the double jet precipitation method at low Cl⁻ concentration and low pH. The dopant salt Na₆RhCl₆.12H₂O, dissolved in an aqueous NaCl solution, was added as a separate flow during precipitation. The resulting cubic AgCl core/shell microcrystals contain approximately 100 ppm Rh³⁺ in the core. The emulsions were enzymatically degelled and dried at 80°C in order to obtain a powder suitable for EPR and ENDOR measurements.

Paramagnetic Rh²⁺ species can be produced in these samples either by UV or X-ray irradiation or by heating the samples to 350°C in vacuum. The relative concentrations of the various Rh⁵⁺ species formed by irradiation further depend on the NaCl concentration of the dopant flow. Figure 6.1 presents the X-band EPR spectra of Rh²⁺-containing emulsion microcrystals. Figure 6.1a and b show spectra of irradiated emulsion microcrystals for which the NaCl concentration of the dopant flow is different. Spectrum c is that of heated Rh³⁺-doped microcrystals. Three main components,
corresponding to different paramagnetic species, have been identified in these spectra, [VERC98c]. They are clearly different in the \( g_x - g_y \) region, but all have overlapping \( g_z \) components. They are indicated in figure 6.1 with R4, R5 and R6. The spin Hamiltonian parameters for these centres determined from their X-band EPR analysis are listed in table 3.6. In microcrystals doped with a flow with low NaCl concentration, relatively more R4 and R5 species are formed, whereas at high NaCl concentration the R6 species is dominant. By heating the emulsions to 350°C, apparently only R6 species are formed. Vercammen et al. [VERC98c] found a correlation between the concentration of the dopant flow and the relative concentrations of Rn (n = 4, 5 or 6) species in irradiated microcrystals. Furthermore, Endo et al. had concluded that the relative concentrations of \([\text{RhCl}_4(\text{H}_2\text{O})_2]^+\), \([\text{RhCl}_6\text{H}_2\text{O}]^3^-\) and \([\text{RhCl}_6]^5^-\) complexes in an aqueous solution are dependent on its Cl\(^-\) concentration [ENDO90] :

as the Cl\(^-\) concentration increases, Rh\(^{3+}\) complexes with a higher number of Cl\(^-\) ligands become more abundant. Based on these results, Vercammen et al. assigned the R4 species to a \([\text{RhCl}_4(\text{H}_2\text{O})_2]^+\) complex, R5 to \([\text{RhCl}_6\text{H}_2\text{O}]^3^-\) and R6 to \([\text{RhCl}_6]^5^-\). However, more direct experimental evidence for such assignments is desirable. Vercammen et al. further found that the thermal stability of the Rn complexes increases as n increases. Heating the irradiated emulsion microcrystals to temperatures above 110°C eliminates the R4 component from the spectra. The R5 component can be eliminated by heating to \( T > 150°C \). Meanwhile, the concentration of R6 centres apparently remains unchanged. The R4 and R5 species can be regenerated to their original concentrations by reirradiating the heated crystals. This led to the conclusion that the decay of these centres is due to a thermal excitation of the trapped electron to the conduction band and not to structural changes in the complexes (e.g. in the ligand structure). The difference in thermal stability presents a possibility of isolating the R4, R5 and

Figure 6.1: X-band EPR spectra (9.54 GHz) recorded at low temperature (20-40 K) of Rh\(^{3+}\)-containing AgCl emulsion microcrystals: (a) X-ray irradiated microcrystals doped with a flow with low NaCl concentration, (b) X-ray irradiated microcrystals doped with a flow with high NaCl concentration, (c) microcrystals heated to 350°C in vacuum.
R6 EPR spectra (directly for the R6 spectrum, through computer manipulation of the spectra for R4 and R5). It can also explain the observations of Endo et al. [ENDO90] that the effect (decrease in sensitivity, increase in contrast) of the rhodium doping decreases as the concentration of H2O-ligated Rh3+ complexes in the dopant solutions increases.

6.2.2. Remaining questions to be solved by a Q-band EPR and X and Q-band ENDOR study

Concerning the R4 and R5 centres, the most important issue is to find direct experimental evidence for the Cl ligand exchange by H2O. Therefore, these complexes should be studied with ENDOR, in order to detect interactions with neighbouring ¹H nuclei. The information we obtain in this way is still ambiguous with respect to the nature of the exchanged ligands: any proton containing solvent molecule (e.g. also OH⁻) is a candidate. A second question concerns the position of the exchanged ligands and possible nearby defects preserving the charge compensation of these complexes. In addition to the ENDOR results, EPR also provides important symmetry information, which limits the number of possible structures. As no single crystal data are available for these complexes, it may be expected that the fine details of the structure, e.g. the number and the positions of nearby vacancies, cannot be determined unambiguously. The general conclusions of our studies of Rh3+ complexes in single crystal model systems can be used to propose the most likely structures for the R4 and R5 complexes, compatible with the experimental magnetic resonance results.

The R6 species is believed to be a [RhCl6]⁴⁻ complex. Such complexes can also be studied in large, melt-grown AgCl single crystals. A direct comparison between species in single crystals and microcrystals is thus possible, very easily leading to detailed (e.g. with respect to the vacancy compensation) microscopic models for the complex(es) involved.

6.3. Powder EPR study of Rh2⁺ complexes in AgCl microcrystals at X and Q-band

6.3.1. The R4 centre

In figure 6.2a, the low field part of the EPR spectrum of the R4 centre is shown. The \( g_x - g_y \) component of the spectrum is not completely resolved: it partly overlaps with the R5 spectrum. Nonetheless, it is clearly seen that it consists of two well-resolved seven-line superhyperfine septets. The nature of the splitting between the septets cannot be unambiguously determined from the X-band EPR spectrum alone. It may either be due to the rhombicity of the \( \vec{g} \) tensor \( (g_x \neq g_y) \) or it may be the result of a (super)hyperfine interaction with a nucleus with \( I = \frac{1}{2} \). As explained in §2.4.3, in the former case the splitting is dependent on the microwave frequency, whereas in the latter it is not. The low field part of the Q-band R4 EPR spectrum is shown in figure 6.2c. Although the whole spectrum is shifted to higher magnetic field values, its structure is identical to that of the X-band spectrum. This demonstrates that the splitting between the Cl superhyperfine septets is due to a hyperfine interaction. It further indicates that the centre has an axial \( \vec{g} \) tensor \( (g_x = g_y) \). The hyperfine interaction can either be due to a ligand nucleus (Ag or H) or to the central Rh nucleus. In view of the axial symmetry of the complex and the fact that an interaction with only one nucleus with \( I = \frac{1}{2} \) occurs, an assignment to the central Rh nucleus is the most obvious. This will be further supported by the ENDOR results.
Figure 6.2: Powder EPR spectrum of the R4 centre (a) recorded at 9.54 GHz and 40 K, (b) simulated with the parameters in table 6.1, (c) recorded at 34.00 GHz and 40 K. The two axial CI superhyperfine septets are indicated. The splitting between them is due to a Rh hyperfine interaction.

In order to extract spin Hamiltonian parameters from the spectra, powder EPR simulations should be carried out. As pointed out in § 2.5.6, a powder EPR spectrum is a superposition of the spectra for all microcrystal orientations. In order to simplify the discussion about powder EPR and ENDOR spectrum simulations, we will consider paramagnetic centres to be present in only one of their physically equivalent orientations in the microcrystals. Hence the microcrystal orientation with respect to the external magnetic field becomes equivalent to the orientation of the paramagnetic complex with respect to the external magnetic field. We consider the polar angles $\theta = 0^\circ$, $\phi = 0^\circ$ to correspond to the $g_z$ axis of the complex, $\theta = 90^\circ$, $\phi = 0^\circ$ to $g_x$ and $\theta = 90^\circ$, $\phi = 90^\circ$ to $g_y$.

In general, for computer simulations, the integration in equation (2.64) is replaced by a summation over microcrystal orientations:

\[ I_{\text{powder}}^{\text{EPR}} (B_0) = \sum_{i=0}^{N_0} \sum_{j=0}^{N_p} I_{\text{single crystal}}^{\text{EPR}} (B_0, \theta_i, \phi_i) \sin \theta_i, \quad \theta_i = \frac{i\pi}{N_0}, \phi_i = \frac{j2\pi}{N_p} \tag{6.1} \]

In order to calculate $I_{\text{single crystal}}^{\text{EPR}} (B_0, \theta_i, \phi_i)$, the single crystal EPR spectrum is assumed to consist of transitions between the first order energy eigenvalues of the spin Hamiltonian:
\[ \hat{H}_S = \mu_B \mathbf{B}_0 \cdot \mathbf{g} \cdot \mathbf{S} + \sum_k \mathbf{S} \cdot \mathbf{A}_k \cdot \mathbf{l}_k \]  

(6.2)

with the index \( k \) running over all interacting nuclei in the complex for which the superhyperfine structure is resolved. Thus, for each microcrystal orientation, a set of EPR transition fields can be calculated. Each of these EPR transitions is assumed to have a Gaussian line shape, as a result of unresolved (super)hyperfine interactions. One finally obtains for a spectrum containing \( M \) transitions at magnetic field positions \( B_{\text{real}} \)

\[ I_{\text{single crystal}}(B, \theta, \phi) = \sum_{m=1}^{M} \frac{e^{-\left\{ \frac{(B_{\text{real}} - B_{m})^2}{2\Gamma^2} \right\}^2}}{\Gamma \sqrt{2\pi}} \]  

(6.3)

The parameter \( \Gamma \) is related to the peak to peak width of the EPR line (difference in magnetic field position between the minimum and the maximum of the first derivative of the EPR line):

\[ \Delta B = 2\Gamma \]  

(6.4)

In the case of an axial centre like R4, the EPR transition field positions are independent of the angle \( \phi \). Therefore, only the summation over \( i \) is left in equation (6.2).

For the R4 centre, the resolved hyperfine structure is due to the interaction with one nucleus with \( I = 1/2 \) and with two equivalent nuclei with \( I = 3/2 \). For each crystal orientation \( \theta \), the single crystal spectrum thus consists of two seven line superhyperfine patterns with intensity ratios 1:2:3:4:3:2:1. In principle, the isotopic distribution of Cl pairs should be taken into account. In § 3.3.1 (figure 3.5) we already indicated that no significant error is introduced by assuming that the \( ^{35}\text{Cl} \) isotope is 100% abundant. With given \( \mathbf{g} \), \( \mathbf{A}^{Rh} \) and \( \mathbf{A}^{Cl} \) tensors, the powder EPR spectrum can thus be calculated (FORTRAN77 program R4EPRPO). By fitting the simulated to the experimental spectrum, these spin Hamiltonian parameters can be determined. There is however a problem: only the \( g_\parallel \) component of the spectrum is well known. At X-band, the \( g_\parallel \) component of R4 strongly overlaps with that of the other \( \text{Rh}^{3+} \) species in the microcrystals and at Q-band, we did not succeed in resolving the \( g_\parallel \) part of the R4 spectrum due to the presence of other, more intense EPR spectra in the \( g = 2 \) region (surface Ag\(^{2+}\) and gelatin hole [EACH00b], Mn\(^{2+}\)). Therefore simulations were carried out with the parallel components of the \( \mathbf{g} \) and \( \mathbf{A} \) tensors as determined by Vercammen from the X-band spectrum. The simulated \( g_\perp \) component is not very sensitive to changes in \( g_\parallel \) and quite insensitive to changes in \( A^{Rh} \) and \( A^{Cl} \). A very good simulation of the X and Q-band EPR spectrum may be obtained (see figure 6.2b) without a detailed knowledge of these parameters. The spin Hamiltonian parameters determined from fitting the low field feature of the spectrum are listed in table 6.1.
Table 6.1: Spin Hamiltonian parameters obtained by fitting the low field part of the powder EPR spectra of R4, R5, R6, and R6' in AgCl microcrystals. Hyperfine and superhyperfine values are given in MHz and the error is given as a subscript. The linewidth parameters are given in mT.

<table>
<thead>
<tr>
<th>Centre</th>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$A_{L}^{Rh}$</th>
<th>$A_x^{CI}$</th>
<th>$A_y^{CI}$</th>
<th>$\Delta B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R4</td>
<td>2.5355_{10}</td>
<td>2.5355_{10}</td>
<td>63_{3}</td>
<td>38_{1}</td>
<td>38_{1}</td>
<td>0.9</td>
</tr>
<tr>
<td>R5</td>
<td>2.4832_{10}</td>
<td>2.4353_{10}</td>
<td>---</td>
<td>39_{1}</td>
<td>39_{1}</td>
<td>1.4</td>
</tr>
<tr>
<td>R6</td>
<td>2.4102_{10}</td>
<td>2.4102_{10}</td>
<td>---</td>
<td>39_{1}</td>
<td>39_{1}</td>
<td>1.2</td>
</tr>
<tr>
<td>R6'</td>
<td>2.4265_{10}</td>
<td>2.3950_{10}</td>
<td>---</td>
<td>39_{1}</td>
<td>39_{1}</td>
<td>1.2</td>
</tr>
</tbody>
</table>

6.3.2. The R5 centre

In figure 6.3, the low field part of the experimental X-band (a) and Q-band (b) spectra are shown. In contrast with the R4 spectra, the structure of the X and Q-band spectra of R5 are clearly different. In the X-band spectrum, traces of a partially resolved superhyperfine structure are seen, but the spectrum roughly consists of one broad component. Nevertheless, Vercammen et al. [VERC98c] had to assume a rhombic $\tilde{g}$ tensor in order to reproduce the powder spectrum. In the Q-band spectrum, the $g_x$ and $g_y$ components are clearly resolved. Both X and Q-band spectra can be very well simulated using the spin Hamiltonian parameters in table 6.1. For simulating the R5 spectrum, the FORTRAN77 program RSEPRPO was used, which explicitly takes into account the rhombicity of the centre by taking the summation both over $\tilde{a}$ and $\tilde{b}$ in equation (6.1). As no Rh hyperfine structure is resolved in this spectrum, the resonance fields for the transitions between the first order eigenvalues of the spin Hamiltonian

$$\hat{H}_S = \mu_B \tilde{B}_0 \cdot \tilde{g} \cdot \hat{S} + \sum_{k=1}^{2} \hat{S} \cdot \tilde{A}^{CI} \cdot \hat{I}_k$$

(6.5)
are calculated. So, each microcrystal orientation gives rise to a seven line superhyperfine pattern with intensity ratios 1:2:3:4:3:2:1. The simulated low field parts of the X and Q-band EPR spectra are shown in figures 6.3a and b in red. Again, the Q-band EPR spectrum reveals no information about the $g_\perp$ part of the spectrum. In the simulations, the values by Vercammen et al. [VERC98c] for $g_\parallel$ and $A^\text{Cl}_l$ were used.

6.3.3. $[\text{RhCl}_6]^{4-}$ centres

From a study of the second derivative of the X-band EPR spectrum, Vercammen et al. [VERC98c] concluded that the R6 complex, produced in emulsion microcrystals by UV or X-ray irradiation, has axial rather than rhombic $\tilde{g}$ symmetry. This would imply that the R6 centre is not identical to the dominant Rh$^{2+}$ centre in melt-grown AgCl single crystals, which is accompanied by one next nearest neighbour (NNN) cation vacancy and has an orthorhombic $\tilde{g}$ tensor.

The X-band ENDOR study of a $[\text{RhCl}_6]^{4-}$ centre in heated AgCl emulsion microcrystals by Moens et al. [MOEN96] also indicated that this centre might be different from the $[\text{RhCl}_6]^{4-}:1\text{Vac}$ complex, but further proved that it has rhombic symmetry. A direct comparison between X-band ENDOR spectra of AgCl:Rh$^{2+}$ single crystals and heated emulsion microcrystals on the other hand, suggests that the centres in both systems are identical [VRIE98b].

In order to elucidate this rather puzzling situation, we directly compared Q-band EPR spectra of emulsion microcrystals, in which Rh$^{2+}$ species were produced in different ways, with single crystal and powder EPR spectra of melt-grown AgCl. This comparison is shown in figure 6.4. Spectrum (a) is recorded for irradiated emulsion microcrystals. The R6 spectrum observed for such samples is typical of a centre with an axial $\tilde{g}$ tensor. Spectrum (b) is a simulation of the $g_\perp$ component of R6.

![Figure 6.4: Q-band (34.00 GHz) EPR spectra of $[\text{RhCl}_6]^{4-}$ complexes in AgCl. (a) X-ray irradiated microcrystals, (b) simulated R6 spectrum, (c) heated emulsion microcrystals, (d) simulation assuming both R6 and R6$'$ components are present, (e) ground melt-grown single crystals, (f) single crystals with the magnetic field along a $<100>$ direction.](image-url)
using the spin Hamiltonian parameters in table 6.1. The simulation was carried out with the program R4EPRPO, assuming the $A^{\text{th}}$ parameters to be zero. The spectrum of heated emulsion microcrystals, shown in (c), is clearly different from that in (a) and (b). The axial R6 component still seems to be present, but on the left and the right hand side of this spectrum additional components appear. The spectrum can be very well simulated assuming that an additional rhombic component, R6', is present, as shown in (d). The R6' spectrum was simulated with the R5EPRPO program, using the spin Hamiltonian parameters in table 6.1. These parameters are, within experimental error, identical to those of the $[\text{RhCl}_6]^{2-}\cdot1$ Vac centre in melt-grown AgCl. In order to check whether the R6' centre is indeed identical to $[\text{RhCl}_6]^{2-}\cdot1$ Vac, the spectrum of ground melt-grown AgCl single crystals is also included in the comparison (spectrum (e)). The latter spectrum also contains both an R6 and an R6' component, and resembles the spectrum of heated emulsion microcrystals very well. Finally, spectrum (f) presents the $g_r g_y$ part of the single crystal EPR spectrum, recorded with the magnetic field along a $\langle 100 \rangle$ direction. Also in the single crystal spectrum, the presence of the R6 centre, next to the dominant R6' or $[\text{RhCl}_6]^{2-}\cdot1$ Vac centre is clearly observed.

A direct comparison of the Q-band ENDOR spectra of various $[\text{RhCl}_6]^{2+}$-containing AgCl samples provides a lot of detailed structural information about the complexes. The results are essentially in agreement with the studies by Vercammen et al. [VERC98a], our own X-band ENDOR results [VRIE98b] and those of Moens et al. [MOEN96]. The centre produced by UV or X-ray irradiation of emulsion microcrystals is different from the dominant Rh$^{2+}$ centre in melt-grown AgCl single crystals. However, if the emulsion microcrystals are heated, essentially the same distribution of Rh$^{2+}$ centres is obtained as in the single crystals. A powder ENDOR analysis of heated emulsion microcrystals may lead to a set of spin Hamiltonian parameters different from those for the $[\text{RhCl}_6]^{2+}\cdot1$ Vac centre in AgCl single crystals, because besides the latter centre, also a centre with axial symmetry is present. It should, however, be noted that the spin Hamiltonian parameters one obtains from analysing powder ENDOR spectra strongly depend on the way in which the spectra are simulated. The problem of finding a correct way to simulate the powder ENDOR spectra for the various interactions in the R4, R5, R6 and R6' complexes will be dealt with in the following section.

6.4. Powder ENDOR study of Rh$^{2+}$ complexes in AgCl emulsion microcrystals

6.4.1. Aims of the ENDOR study for the various Rh$^{2+}$ complexes

The R6' centre is found to be identical to the $[\text{RhCl}_6]^{2-}\cdot1$ Vac complex. Thus, it requires no further ENDOR study. It may, however, serve as an ideal (or nearly ideal, because it is always accompanied by the R6 centre, for which the spin Hamiltonian parameters are not a priori known) test case for the powder ENDOR simulation programs.

The R6 centre has, within experimental error, an axial $\bar{g}$ tensor. From the study of $[\text{RhCl}_6]^{2+}$ complexes in NaCl single crystals, it is known that for a non-locally charge compensated complex $g_x$ exactly equals $g_y$, whereas a complex with two NNN vacancies in a cis-configuration has $g_x$ and $g_y$ values very close to one another, which may, even at Q-band, not be resolved. In principle, both are possible models for the R6 centre. It has been shown in chapter 5 that Q-band ENDOR offers a
possibility of distinguishing between these two cases, by recording the axial Cl ENDOR spectrum in the vertical $g$ planes of the complex. In the case of a two-vacancies model, these correspond to {110} planes. If in one of the $g$ planes a splitting of the Cl ENDOR transitions is observed, the centre has $C_{2v}$ rather than $D_{4h}$ symmetry and the presence of two NNN vacancies is demonstrated. A complete angular dependent single crystal study of the R6 centre was not succesful, because of two reasons. First, we did not succeed in polishing an AgCl crystal, allowing rotation in a {110} plane. Second, the R6 species is a minority centre in AgCl single crystals, in which the R6' centre is dominant. The R6 EPR spectrum is only in a very limited angular range partially resolved from that of R6' and the optimum conditions for ENDOR detection are identical. In the angular range where the EPR spectra overlap, all ENDOR transitions could be assigned to the dominant R6' centre, indicating that the contribution of the R6 spectra is too small to be detected or overlaps the R6' spectra. The R6 centre should thus be studied in irradiated emulsion microcrystals. The main issue there is finding a way of isolating the R6 ENDOR spectra from those of R5 and R4. Studying a powder system, we cannot expect to resolve tilting angles of the axial Cl superhyperfine and quadrupole tensors. Therefore, the powder ENDOR study of the R6 centre will not reveal the vacancy configuration of the complex involved. On the other hand, it might provide spin Hamiltonian parameters for this centre, which are interesting for comparison, and the absence of interactions with nearby magnetic nuclei other than Rh, Ag or Cl can support the hypothesis that no ligand exchange has taken place in this complex. Although this is already suggested by the $g$ values for this centre, which are very close to those of R6', it may be further supported by ENDOR.

For the R4 and R5 centres, we already mentioned the main objective of the ENDOR study to be the detection of interactions with nearby protons. Determining the spin Hamiltonian parameters for the main interactions with other nuclei in these systems may be interesting in order to compare the data for the various Rh$^{2+}$ complexes in AgCl. One important problem in analysing the spectra for these centres is the fact that they are simultaneously present. They have different thermal stability, though. A part of the R4 centres, produced upon UV or X-ray irradiation, decays at room temperature, as illustrated in figure 6.5. By recording ENDOR spectra immediately after irradiation and after, e.g., one week storage at room temperature, the spectra of R4 and R5 can be separated.

![Figure 6.5: X-band (9.54 GHz) EPR spectrum of X-ray irradiated AgCl emulsion microcrystals (dopant solution with 1 M NaCl) (a) immediately after irradiation, (b) after four days storage at room temperature](image)
6.4.2. Simulation of the powder ENDOR spectra: selecting orientations

The orientation selectivity of ENDOR in the case of powder samples has already been discussed in § 2.5.6, where the orientation selection principle has been explained with the aid of a fictitious paramagnetic centre with \( S = \frac{1}{2} \), with axial \( \vec{g} \) symmetry for which no (super)hyperfine structure is resolved in the EPR spectrum, interacting with a nucleus on the main symmetry axis of the centre. In the present section, the effect of resolved (super)hyperfine structure on the orientation selection is illustrated. In the examples, the EPR spin Hamiltonian parameters of the R6 centre are used. The resolved superhyperfine structure is thus a seven line pattern due to the interaction with two equivalent \( ^{35}\text{Cl} \) nuclei, which are again assumed to be 100 % abundant. The extensions to the more general cases of additional resolved splittings in the EPR spectrum and rhombicity are rather straightforward and will be discussed only briefly.

According to the orientation selection principle for powder ENDOR, each microcrystal orientation for which the EPR spectrum is saturated contributes to the powder ENDOR spectrum. For a centre with axial symmetry and without resolved (super)hyperfine structure, each magnetic field position within the EPR powder envelope corresponds to a single value of the polar angle \( \theta \), as illustrated in figure 2.17. If in addition the EPR spectrum for each microcrystal orientation has zero line width and only interactions with nuclei on the main symmetry axis of the centre are considered, a single crystal ENDOR spectrum can be recorded at each magnetic field position in the EPR powder pattern. Due to the finite line width of the EPR transitions for each microcrystal orientation, the recorded spectra are not identical to single crystal spectra. They are only single crystal like, i.e. the result of an integration over a relatively narrow distribution of \( \theta \) angles around that given by equation (2.66).

The situation changes if the EPR spectrum of each microcrystal orientation exhibits a resolved superhyperfine pattern. This is illustrated in figure 6.6 with the example of the R6 centre. The EPR spectrum of each microcrystal consists of seven transitions. Even if the line width of each of these transitions would be zero, the powder ENDOR spectrum would still contain contributions of seven distinct microcrystal orientations. Again, as a result of the finite line width of the EPR transitions also orientations in the close neighbourhood of these seven contribute to the powder ENDOR spectrum. In order to simulate such spectra, for each "selected" microcrystal orientation the single crystal ENDOR spectrum at the corresponding superhyperfine EPR transition should be calculated. In the following a distinction between two types of nuclei is made.

*Figure 6.6:* Non-derivative X-band (9.5 GHz) powder EPR spectrum of R6 and single crystal spectra for which one of the superhyperfine transitions corresponds to \( B_0 \), illustrating the orientation selection principle for paramagnetic centres with axial symmetry and resolved (super)hyperfine structure.
Figure 6.7: (a) Selection of microcrystal orientations at X-band (9.5 GHz) for a centre with axial symmetry and resolved superhyperfine structure of two equivalent nuclei with $I = 3/2$ (spin Hamiltonian parameters of the R6 centre in AgCl, $\Gamma_{zz} = 0.6 \text{ mT}$). (b) Simulated powder ENDOR spectra for a nucleus with $I = 1/2$, $g_n = 0.3$ and a strongly anisotropic superhyperfine tensor ($A_z = 10 \text{ MHz}$, $A_y = 20 \text{ MHz}$) ($\Gamma_{\text{ENDOR}} = 50 \text{ kHz}$, $R = 2$).

For a first type of nuclei, the ENDOR spectrum recorded at each EPR superhyperfine transition of a microcrystal spectrum is identical (except for changes due to the field dependent terms in the ENDOR spin Hamiltonian). In principle, this is only the case for nuclei with $I = 1/2$. It is, however, also a very
good approximation for nuclei with \( l > \frac{1}{2} \), as long as the superhyperfine splitting of the nucleus involved is not resolved in the EPR spectrum, thus, for small superhyperfine interactions. In the case of the example, the powder ENDOR spectrum recorded at a certain magnetic field value \( B_0 \) can then be calculated as follows. In a first step, the EPR spectrum is calculated for a large number \((N_m = 401)\) of equally spaced polar angles \( \theta \). In our simulation programs the transition fields are calculated to first order assuming an interaction with two equivalent \(^{35}\text{Cl} \) nuclei, giving rise to a set of seven transition fields \( B_{\text{m}}, m = 1,\ldots,7 \). This approximation has been justified in \( \S \) 3.3.1 (see figure 3.5). For each of these transition fields, a Gaussian weight factor

\[
w_m(\theta) = e^{-\frac{(B_0 - B_{\text{m}}(\theta))^2}{2\Gamma_{\text{m}}^2}}, \quad m = 1,\ldots,7
\]

(6.6)
is calculated. The line profile of each microcrystal EPR transition is thus assumed to be Gaussian with a width \( 2\Gamma_{\text{EPR}} \). The weight factor for the contribution of a microcrystal ENDOR spectrum to the powder ENDOR spectrum is then given by

\[
w(\theta) = \sin \theta \sum_{m=1}^{7} n_m w_m(\theta)
\]

(6.7)

with \( n_m \) the intensity ratio of the \( m^{\text{th}} \) superhyperfine line \((1:2:3:4:3:2:1)\). The ENDOR transition frequencies are calculated to second order, assuming an interaction with a single nucleus, which is a good approximation as long as the superhyperfine values are small. The ENDOR transitions are assumed to have a Gaussian line profile with a width \( 2\Gamma_{\text{ENDOR}} \). The intensity ratio \( R \) between the \( M_S = -\frac{1}{2} \) and \( M_S = \frac{1}{2} \) transitions (see \( \S \) 3.3.1) is given as an experimental parameter. The quality of the powder ENDOR simulation (assuming that the spin Hamiltonian and line width parameters are known), mainly depends on the accuracy with which the single crystal EPR and ENDOR spectra are calculated.

In figure 6.7a, the weight factors at X-band frequency as a function of the polar angle \( \theta \) are shown for three different \( B_0 \) values in the R6 EPR spectrum. In the neighbourhood of \( g_i \), \( w(\theta) \) is a single broad line. As the magnetic field moves towards \( g_i \), a superhyperfine like structure begins to emerge. For a magnetic field value in the centre of the EPR powder spectrum, \( w(\theta) \) has seven maxima, approximately corresponding to the microcrystal orientations presented in figure 6.6. For these
orientations, one of the superhyperfine EPR transitions exactly occurs at the magnetic field value at which the ENDOR spectrum is calculated. For magnetic field values in the neighbourhood of $g_{1}$, $w(\theta)$ exhibits less than seven maxima, because some of the superhyperfine lines can no longer be selected. The latter effect is illustrated in figure 6.8.

Figure 6.7b shows calculated powder ENDOR spectra at these three magnetic field positions for a fictitious interaction with a nucleus with $l = \frac{1}{2}$ and a strongly anisotropic superhyperfine tensor. Close to $g_{1}$, the ENDOR spectrum is still single crystal like: like in a single crystal spectrum, only two transitions occur. At variance with single crystal spectra, the shape of the transitions is asymmetrical, as a result of the relatively wide (but structureless) distribution of microcrystal orientations contributing to the spectrum. For magnetic field positions closer to $g_{0}$, the spectrum is no longer single crystal like. It rather looks like a superposition of single crystal spectra of clearly distinct microcrystal orientations. For a magnetic field value in the central part of the EPR powder spectrum, a seven line superhyperfine like structure is seen for the two ENDOR transitions, as a result of the seven maxima in $w(\theta)$. As the magnetic field approaches $g_{0}$, the number of "superhyperfine" lines on the ENDOR transitions decreases in accordance with the number of maxima in $w(\theta)$. It will be shown (§ 6.3.3) that for the $^{103}$Rh interaction of the R4 centre a superhyperfine like structure on the ENDOR transitions is clearly observed and can be very well simulated.

It should be noted that the "superhyperfine" structure on the ENDOR spectrum is not always resolved. It disappears if the EPR line width is too large (i.e. if the superhyperfine structure in the EPR spectrum is no longer resolved), if the ENDOR line width is too large or if the $\bar{A}$ tensor of the interaction is insufficiently anisotropic. In the latter two cases, the "superhyperfine" lines in the ENDOR spectrum overlap and give rise to broadened single lines. For the Ag interactions of the various Rh$^{2+}$ centres in AgCl and the $^{103}$Rh interaction for R5 and R6', broadened single lines are observed at each magnetic field position in the EPR envelope. The "angular" variation of the powder ENDOR spectrum with the magnetic field position in the EPR envelope can then be easily represented in "transition frequency versus magnetic field" plots, similar to those used to represent the angular variation of single crystal ENDOR spectra ("transition frequency versus complex orientation" plots).

For nuclei with $l > \frac{1}{2}$ giving rise to resolved (super)hyperfine structure in the EPR spectrum, the single crystal ENDOR spectra recorded at different superhyperfine EPR transitions are no longer identical. In order to calculate powder ENDOR spectra in a correct way for such nuclei, for each microcrystal orientation $0$ the ENDOR spectrum at each (super)hyperfine transition should be calculated and given the appropriate weight factor of the (super)hyperfine transition in the EPR spectrum $w_{m}(\theta)$ (see equation 6.6). Discussing the most general case of orientation selection for nuclei with $l > \frac{1}{2}$ giving rise to resolved (super)hyperfine structure is beyond the scope of this work. We will restrict ourselves to the case we encounter in practice: the axial Cl' interaction for Rh$^{2+}$ centres in AgCl. In this specific case a number of approximations are introduced in order to reduce the calculation time for the powder ENDOR spectra, which will now be discussed. In a first approximation, we again assume the $^{35}$Cl isotope to be 100% abundant in calculating the powder EPR spectrum and determining the weight factors. Although this is a nearly perfect approximation for the calculation of ENDOR spectra for nuclei
of the first category, here the approximation is worse, because the ENDOR spectra recorded at superhyperfine transitions of $^{35}\text{Cl}-^{35}\text{Cl}$ pairs differs from that recorded at $^{35}\text{Cl}-^{37}\text{Cl}$ or $^{37}\text{Cl}-^{37}\text{Cl}$ pairs. Second, the ENDOR transition frequencies are calculated to second order in the single nucleus approximation. All interactions between nuclei are thus neglected. In § 3.3.1 it has been shown that for $^{35}\text{Cl}-^{35}\text{Cl}$ pairs, this may not be a very good approximation, especially in the $g_c-g_f$ region of the spectrum (see § 5.3). As intensity for each ENDOR transition at a given EPR superhyperfine transition, the zero order transition probability is taken, assuming that all ENDOR transitions split by second order interaction terms between equivalent nuclei coincide. This gives rise to the set of intensities given in table 6.2. Finally, the weight factors $w_m(t)$ for the $^{37}\text{Cl}$ isotope are assumed to be identical to those of $^{35}\text{Cl}$ and the calculated $^{35}\text{Cl}$ and $^{37}\text{Cl}$ spectra are added in ratios 3:1. In figure 6.9b, the calculated weight factors functions for the various ENDOR transitions (indicated in figure 6.9a) of the axial $^{35}\text{Cl}$ interaction for R6 at X-band are shown for a static magnetic field position in the centre of the EPR powder envelope. The resulting powder ENDOR spectrum is shown in figure 6.9c.

**Table 6.2**: Intensities of the six ENDOR transitions (calculated to first order, columns) of an interaction with one Cl nucleus at the seven superhyperfine EPR transitions (calculated to first order, rows) due to the interaction with two equivalent Cl nuclei. $H_A = A/2$, $H_N = g_n\mu_B B_0$, $H_Q = 3Q$, $B_0 = \nu_{mw}(g\mu_B)$ and $\Delta B_A = A/(g\mu_B)$ and $A$, $g$ and $g_n$ are assumed to be positive.

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<td>6</td>
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<td>8</td>
<td>0</td>
<td>0</td>
<td>8</td>
<td>12</td>
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<tr>
<td>3. $B_0 - \Delta B_A$</td>
<td>12</td>
<td>16</td>
<td>6</td>
<td>6</td>
<td>16</td>
<td>12</td>
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<tr>
<td>4. $B_0$</td>
<td>12</td>
<td>16</td>
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<tr>
<td>5. $B_0 + \Delta B_A$</td>
<td>6</td>
<td>16</td>
<td>12</td>
<td>12</td>
<td>16</td>
<td>6</td>
</tr>
<tr>
<td>6. $B_0 + 2\Delta B_A$</td>
<td>0</td>
<td>8</td>
<td>12</td>
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<td>7. $B_0 + 3\Delta B_A$</td>
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We also want to point out some advantages of recording powder ENDOR spectra at higher microwave frequencies, i.e. Q-band. Due to the higher $g$ factor resolution, the distribution of microcrystal orientations contributing to the powder ENDOR spectrum is narrower at higher microwave frequencies. This is illustrated in figure 6.10a, in which the calculated $w(t)$ functions of the R6 centre for a nucleus with $I = \frac{1}{2}$ are shown for three magnetic field positions in the powder EPR envelope. As a direct result of the higher orientation selectivity as compared to X-band, Q-band powder ENDOR spectra are more single crystal like than the corresponding X-band spectra, as can be clearly seen by comparing the figures 6.10b and 6.7b. In the Q-band powder ENDOR spectra recorded in the centre of the powder EPR envelope and near $g_{||}$, the superhyperfine like structure on the ENDOR transitions
Figure 6.9: (a) microcrystal ENDOR spectrum ($\theta = 41^\circ$), (b) orientation selection at X-band (9.5 GHz) for the axial Cl interaction of the R6 centre (spin Hamiltonian parameters in tables 6.1 and 6.4) for a static magnetic field value of 310 mT (c) calculated powder ENDOR spectrum ($\Gamma_{\text{ENDOR}} = 0.1$ MHz and $R = 2$).

is no longer resolved, although $w(i)$ still clearly shows several maxima. The microcrystal orientations corresponding to these maxima lie, however, very close to one another as a result of which their ENDOR spectra overlap. Also for nuclei with $I > \frac{1}{2}$ powder ENDOR spectra recorded at Q-band are more single crystal like than the corresponding X-band spectra. An additional advantage of recording ENDOR spectra at higher microwave frequencies is the suppression of higher order effects, like the indirect interaction between equivalent nuclei. The only disadvantage of powder ENDOR at higher microwave frequencies is the much lower spectrum intensity as compared with X-band. Indeed, due to the higher orientation selectivity, the number of microcrystal orientations contributing to the high frequency powder ENDOR spectrum is much lower than at X-band. As a result, most of the interactions detected at X-band for the Rh$^{2+}$ complexes in AgCl could no longer be detected at Q-band. Q-band ENDOR spectra could only be recorded for the axial Cl$^-$ interaction for the R5, R6 and R6$'$ centres in the $g_x-g_y$ region of the EPR spectrum. Nonetheless, these additional spectra allow us to determine the $x$ and $y$ components of the superhyperfine and quadrupole tensors for these interactions very accurately.
Figure 6.10: (a) Selection of microcrystal orientations at Q-band (34 GHz) for a centre with axial symmetry and resolved superhyperfine structure of two equivalent nuclei with $I = 3/2$ (spin Hamiltonian parameters of the R6 centre in AgCl, $g_{||} = 0.6$ mT). (b) Simulated powder ENDOR spectra for a nucleus with $I = 1/2$, $g_{||} = 0.3$ and a strongly anisotropic superhyperfine tensor ($A_{||} = 10$ MHz, $A_{\perp} = 20$ MHz) ($g_{\text{endo}} = 50$ kHz, $R = 2$).

In principle, there are no problems with extending the discussion given above to nuclei for which the $\tilde{A}$ and $\tilde{Q}$ tensors are not axial around the main symmetry axis of the centre, and to centres with rhombic (orthorhombic, monoclinic or triclinic) symmetry. Weight factors and ENDOR spectra should
then be calculated as a function of two angular coordinates \((\theta, \phi)\). A two dimensional representation of the \(w(\theta)\) or \(w(\phi)\) functions, as in figures 6.7a, 6.9a and 6.10a is then no longer possible. In the case of rhombic centres, single crystal like spectra can only be recorded when the magnetic field is set to the extremities of the powder EPR envelope. In the case of Rh\(^{2+}\) centres in AgCl these correspond to the \(g_x\) and \(g_y\) components.

Simulation programs have been written (FORTRAN77) for the analysis of powder ENDOR spectra of nuclei with \(I = \frac{1}{2}\) and of interactions with two axial Cl nuclei, in the case of an axial centre with resolved hyperfine and superhyperfine structure (like R4) and in the case of a rhombic centre with resolved superhyperfine structure (like R5) (R4ENDPO, R4CLENDPO, R5ENDPO and R5CLENDPO).

6.4.3. The R6' centre as a test case

Our powder ENDOR simulation programs can be tested by simulating the spectra of heated emulsion microcrystals (which mainly contain the R6' centre) with the single crystal ENDOR data of the \([\text{RhCl}(\text{I})^+\].1Vac centre in AgCl. The experimental spectra were recorded by Moens [MOEN96] at 20 K, 9.52 GHz, and 20 mW microwave power. The single crystal ENDOR parameters for this centre are given in table 5.1. It should be noted that the test case is not ideal. The simulated powder ENDOR spectra are expected to deviate from the experimental ones due to the presence R6 signals in the latter, be it with much lower intensities than the R6' transitions. Moreover, the single crystal ENDOR analysis for this centre is not complete: not all ENDOR transitions in the spectra could be assigned [OLM88]. However, the three most intense interactions which have been identified in the single crystal ENDOR spectra are expected to give rise to intense powder ENDOR patterns. The simulation of powder ENDOR spectra for these interactions should at least give an indication of the accuracy with which the programs we developed are able to reproduce experimental powder ENDOR spectra.

In figure 6.11 the low frequency part (1.5 – 9.0 MHz) of the “angular” variation of the experimental powder ENDOR spectrum with the magnetic field position in the EPR powder envelope is shown. Simulations using the EPR spin Hamiltonian parameters in table 6.1 and ENDOR spin Hamiltonian parameters in table 5.1 for the fourth shell Ag\(^{+}\) ions of R6' (indicated in green \((^{107}\text{Ag})\) and red \((^{109}\text{Ag})\), \(\Gamma_{\text{ENDOR}} = 65\) kHz, \(R = 2\)) show that the most intense ENDOR transitions in the spectra recorded at low fields (\(g_i\) region) are due to this interaction. The agreement between experimental and simulated spectra is very good for this interaction, also for spectra recorded at higher magnetic fields (near \(g_i\)) where the transitions are much less intense. Another set of intense lines at low fields is very well simulated by the \(^{103}\text{Rh}\) interaction of R6' (indicated in blue, \(\Gamma_{\text{ENDOR}} = 50\) kHz, \(R = 2\)). At higher magnetic field values, the agreement between experimental and simulated spectra for this interaction appears to be worse. This is most probably due to the fact that the Rh transitions have very low intensity and start to overlap with the \(^{107}\text{Ag}\) transitions. Certain ENDOR transition in the low frequency part of the spectra cannot be attributed to fourth shell Ag nuclei or to the central Rh nucleus of R6'. They are either due to the R6 centre or to other magnetic nuclei around the R6' complex. The intense broad lines at the low frequency end of the spectra in figure 6.11 are most probably due to a large number of Cl nuclei with slightly different spin Hamiltonian parameters (first shell equatorial, third shell, further shells,...).
Figure 6.11: Low frequency part of the X-band ENDOR spectrum of R6 as a function of the magnetic field position in the EPR powder envelope. Black lines represent experimental spectra. The simulations with the spin Hamiltonian parameters in tables 6.1 and 5.1 for the axial fourth shell Ag nuclei are shown in red (\(^{199}\text{Ag}\)) and green (\(^{107}\text{Ag}\)) and for the \(^{103}\text{Rh}\) nucleus in blue.

Figure 6.12: High frequency part of the X-band ENDOR spectrum of R6 as a function of the magnetic field position in the EPR powder envelope. Black lines represent experimental spectra. The simulations with the spin Hamiltonian parameters in tables 6.1 and 5.1 for the axial Cl nuclei (both isotopes) are shown in red.

Figure 6.12 shows the "angular" variation of the ENDOR spectrum of heated emulsion microcrystals in the frequency region where the axial Cl transition are expected. Simulated spectra using the EPR spin Hamiltonian parameters in table 6.1 and the ENDOR parameters in table 5.1 are shown in red (\(\Gamma_{\text{ENDOR}} = 150\) kHz, \(R = 2\)). The agreement between the experimental and simulated spectra is very good, especially if one considers that the second order splitting of the \(^{35}\text{Cl}\) ENDOR transitions was neglected in the simulations. In the spectra recorded in the \(g_x - g_y\) region, it is clearly seen that some of the ENDOR transitions are split. The simulated transitions agree with the centre of the split lines. The spectra recorded at high magnetic field values have a low signal to noise ratio. But even for these spectra (292.2 – 325.0 mT) the simulations seem to reproduce the structure in the experimental powder ENDOR spectra very well. In the simulations presented in the figure, the experimentally observed tilting of the superhyperfine tensor (see § 5.4.1) was neglected. We checked that its influence on the simulated X-band spectra is negligible.
We may conclude that the programs we developed for the simulation of powder ENDOR spectra can reproduce experimental spectra very well. They will enable us to analyse the spectra of the centres for which no single crystal data are available and to determine the spin Hamiltonian parameters for the various nuclear interactions in these complexes quite accurately. Relatively small tilting angles for the superhyperfine and quadrupole tensors are, however, not expected to be detectable.

6.4.4. The R4 centre

The experimental spectra for this centre were recorded on cubic AgCl emulsion microcrystals doped with approximately 100 ppm Rh\(^{3+}\) dissolved in a 1 M NaCl solution, immediately after X-ray irradiation at room temperature for approximately 1 h. The spectra were recorded at 15 K, 9.54 GHz, with 8 mW microwave power. In figure 6.13, the ENDOR spectrum recorded at \(g_\perp\) of the R4 centre is shown. The most intense transitions in this spectrum can be attributed to the central \(^{103}\)Rh nucleus, one set of axial \(^{35/37}\)Cl nuclei, one set of \(^{107/109}\)Ag nuclei and one set of \(^1\)H nuclei. The assignation to Rh and Cl nuclei is straightforward: the frequency range for these transitions can be predicted from the observed hyperfine and superhyperfine splittings in the EPR spectrum.

The assignation to Ag nuclei is based on arguments given in § 3.3.2. The assignation to \(^1\)H could only be made by observing the "angular" dependence of the corresponding transitions, which are centred on the proton Larmor frequency. For the Ag and proton interactions, the "angular" variation of the powder ENDOR spectrum turns out to be single crystal like and can easily be compressed into a transition frequency versus magnetic field plot. For the other two interactions, experimental and simulated spectra should be directly compared. A few ENDOR transitions with low intensity in the spectrum of figure 6.13 could not be assigned. They are indicated with question marks. Their "angular" dependence could not be followed.

In none of the samples at our disposal, the R4 centre appeared as an isolated species. It was always accompanied by the R5 species. As already mentioned, the difference in thermal stability of these two centres (the R4 centre partly decays at room temperature) presents in principle an easy way of separating their ENDOR spectra in the magnetic field region where their EPR spectra overlap. The R4 axial Cl\(^-\) spectrum is, however, much weaker than that of R5. Moreover, both Cl\(^-\) spectra strongly overlap. As a result, the ENDOR spectrum only gives information on the perpendicular components of the axial Cl\(^-\) interaction parameters of R4. It will be shown that \(A_\parallel (^{35}\text{Cl})\) can be estimated from a simulation of the \(^{103}\)Rh spectra. For all powder ENDOR simulations, the microcrystal R4 EPR
transitions were assumed to have an isotropic line width of 0.9 mT (\( \Gamma_{\text{ENDOR}} = 0.45 \) mT). It is easily seen that the intensity for the \( M_S = -\frac{1}{2} \) and \( M_S = \frac{1}{2} \) ENDOR transitions is different. Intensity ratios of \( R = 2 - 3 \) were used in the simulations. The spin Hamiltonian parameters which could be determined by fitting the simulated to the experimental spectra for all these interactions are listed in table 6.3. Through more accurate powder ENDOR spectrum simulation, some of the ENDOR data given in this table are slightly different from those given in [VRIE99].

Table 6.3: Spin Hamiltonian parameters for the various nuclear interactions of the R4 centre, given in MHz (error given as a subscript). The principal z axis is assumed to be along the \(<001>\) \( g_z \) direction. The principal axes in the equatorial plane cannot be determined experimentally.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>( A_x )</th>
<th>( A_y )</th>
<th>( A_z )</th>
<th>( Q_x )</th>
<th>( Q_y )</th>
<th>( Q_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{109})Ag (4th shell axial)</td>
<td>-12.78_3</td>
<td>-12.78_3</td>
<td>-15.6_1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^1)H (equatorial ?)</td>
<td>-6.35_5_5</td>
<td>4_?</td>
<td>-3.55_5_5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(^{35})Cl (1st shell axial)</td>
<td>37.4_4_4</td>
<td>37.4_4_4</td>
<td>75_5_5</td>
<td>0.11_3_3</td>
<td>0.11_3_3</td>
<td>-0.22_5_5</td>
</tr>
<tr>
<td>(^{103})Rh (central)</td>
<td>-61.34_10_0</td>
<td>-59.90_10_0</td>
<td>-43.40_20_0</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{107/109}\)Ag and \(^1\)H interactions

![Graph](image)

Figure 6.14: "Angular" variation of the low frequency part of the R4 ENDOR spectrum. Filled circles represent experimental data points. The full lines are the results of simulations for the axial 4th shell Ag interaction (\(^{109}\)Ag in red, \(^{107}\)Ag in green) and for the interaction with a set of equivalent protons (magenta). The simulations are carried out using the spin Hamiltonian parameters in table 6.3. The angular variation of interactions assigned to R5 is indicated in dashed lines.

In figure 6.14, the experimental and simulated low frequency part of the R4 ENDOR spectrum is shown. The filled circles in this plot represent experimental ENDOR transition frequencies. The
simulated "angular" dependences were obtained by simulating powder ENDOR spectra for the various interactions (using the EPR parameters in table 6.1 and ENDOR spin Hamiltonian parameters in table 6.3) for a large number of static magnetic field positions, determining the frequency position (maximum in the non-derivative spectrum) of the single crystal like spectra and connecting the positions corresponding to the same $M_S$ multiplet for each nucleus (with $I = \frac{1}{2}$). The agreement between the experimental and simulated "angular" variations is very good. In the $g_\perp$ magnetic field region, except for a small number of weak lines for which the "angular" variation cannot be followed, the whole low frequency spectrum (0 – 10 MHz, see figure 6.13) can be reproduced by the simulation of an interaction with one set of equivalent Ag nuclei and one set of equivalent protons. For magnetic field values from 270 mT onwards, additional transitions appear in the spectra, which can be attributed to the R5 centre (see § 6.4.5). For almost all magnetic field positions, these are clearly separated from the R4 transitions.

The interaction with the set of Ag nuclei is characterised by an axial (within experimental error) superhyperfine tensor (see table 6.3). An intensity ratio between the $M_S = -\frac{1}{2}$ and $M_S = \frac{1}{2}$ transitions (R) of about 3 is observed for this interaction. From this ratio, it can be deduced that the $\tilde{A}$ tensor components for the Ag interaction should have the same sign as $g_N$, i.e. negative. For the proton interaction, only two transitions are observed for each magnetic field value. The asymmetrical line shape of the powder ENDOR spectrum recorded at $g_x$ for this interaction, however, indicates that it is characterised by a rhombic rather than an axial $\tilde{A}$ tensor. We did not succeed in determining the $A_y$ component, though. At magnetic field positions up to 290 mT the experimental position of the high frequency proton transition cannot be accurately determined, due to overlap with the axial Cl ENDOR spectrum. Near $g_L$, both proton ENDOR transitions can be clearly observed. The low frequency line has the largest intensity, which indicates that for this interaction the sign of $A_x$ and $A_z$ is opposite to that of $g_N$ (which is positive).

Interaction with the first shell axial Cl nuclei

Figure 6.15 shows the axial Cl ENDOR spectrum for R4 recorded (black lines) at the magnetic field positions corresponding to different superhyperfine transitions in the EPR spectrum (indicated with arrows) and simulated (red lines, $\Gamma_{\text{ENDOR}} = 150$ kHz) using the spin Hamiltonian parameters in table 6.3. For $B_0 > 271$ mT, this interaction can no longer be correctly analysed due to the presence of the intense axial Cl spectrum of R5. At magnetic field positions $a$ and $b$, the agreement between experimental and simulated spectra is very good. For higher magnetic field positions, the agreement is not so good, especially for the transitions at the high frequency end of the spectrum, due to the $^{35}$Cl isotope. For the low frequency transitions ($^{37}$Cl isotope) the agreement is still rather good. We therefore believe that the difference between experimental and simulated spectra is mainly due to the second order splitting of the $^{35}$Cl ENDOR lines. This splitting can be estimated if the $A_y$ value for the interaction is known. Estimating this value at 75 MHz (which will be substantiated below), one can estimate the splitting of the $^{35}$Cl transitions at

$$\Delta_{2^{nd}_{\text{order},x}} = \frac{A_y^2 + A_z^2}{2\hbar v_{MW}}$$

(6.8)
which corresponds to 370 kHz at 9.54 GHz. This value is of the same order of magnitude as the quadrupole splitting ($Q_z = 330$ kHz). Deviations between experimental and simulated ENDOR transition frequencies of the order of the observed quadrupole splitting could thus possibly be explained by second order effects. Neglecting the effect of second order splitting would lead to the conclusion that the $\tilde{A}$ and $\tilde{Q}$ tensors for this interaction are rhombic [VRIE99, PAWL98], but the simulations do not significantly improve taking rhombicity into account. We also checked that a tilting of the $\tilde{A}$ tensor up to a few degrees and/or a tilting of the $\tilde{Q}$ tensor up to $10^\circ$ do not improve the simulations significantly. We therefore conclude that these tensors are, within experimental error, axial around the $g_{ii}$ direction. A better agreement between experimental and simulated spectra would be expected at Q-band microwave frequencies, but we did not succeed in recording Q-band ENDOR spectra for the R4 centre.

**Interaction with the central Rh nucleus**

The experimental (black) and simulated (red, using the ENDOR parameters in table 6.3 and $\Gamma_{\text{ENDOR}} = 90$ kHz) "angular" variation of the $^{103}$Rh transitions of R4 are shown in figure 6.16. If the hyperfine tensor were to be axial, only two transitions should be observed in the spectrum recorded at $g_L$. The fact that experimentally three transitions are observed, indicates that the hyperfine tensor has rhombic symmetry, with the difference between $A_x$ and $A_y$ approximately equal to twice the $^{103}$Rh Larmor frequency. The $M_S = \frac{1}{2}$ transition of the $x$ component then approximately coincides with the $M_S = -\frac{1}{2}$ transition of the $y$ component. As the $M_S = -\frac{1}{2}$ transitions (highest intensity) occur at higher frequencies than the $M_S = \frac{1}{2}$ transitions, the hyperfine values are negative (same sign as $g_{ii}$).
For higher magnetic field values the transitions broaden and from (approximately) $B_0 = 290$ mT onwards, a superhyperfine like structure emerges on the transitions. In the magnetic field range 290 – 310 mT the $^{103}$Rh spectrum partly overlaps the axial Cl spectrum of R5 (and R4). The resolved "superhyperfine" structure in the ENDOR spectra recorded near $g_z$ is well reproduced by the simulations. This structure is mainly determined by the $A_z$ value of the axial $^{35}$Cl interaction, which could thus be determined with an accuracy estimated at 5 MHz.

**Figure 6.16**: "Angular" variation of the $^{103}$Rh interaction of the R4 centre. Experimental spectra are shown in black and simulated spectra, using the spin Hamiltonian parameters in table 6.3 in red.

6.4.5. The R5 centre

In figure 6.17, the X-band ENDOR spectrum recorded with the magnetic field set to $g_z$ of R5 is shown. The spectrum was measured using the same sample and in the same experimental conditions as for the measurements of R4, but after storage at room temperature for three months. By this anneal, the concentration of R4 centres in the sample is largely reduced. Nevertheless, the silver and rhodium interactions of the latter centre are still observed in the spectrum. For the R5 centre, again four types of interactions can be identified in the spectrum. The interaction with the two equivalent first shell axial Cl nuclei is found in the frequency range expected from the observed superhyperfine splitting in the EPR spectrum. A set of four intense lines is again attributed to Ag nuclei. Compared to the analogous interaction for R4, the Ag ENDOR transitions for R5 are shifted towards lower frequencies. Very close to the proton transitions for R4 similar ENDOR transitions are found in the R5 spectrum, which are consequently also assigned to $^1$H nuclei. The assignment of a set of two transitions to the $^{103}$Rh interaction is not so obvious. The following arguments lead to its identification:
1. We checked that these transitions could not be assigned to an interaction with a single set of Ag or H nuclei.

2. The splitting between the two lines agrees very well with twice the $^{103}$Rh Larmor frequency at $g_x$.

3. The "angular" dependence of the transitions can be simulated assuming they are due to $^{103}$Rh (see below).

4. For a Rh centred complex, such an interaction is expected and no other transitions in the spectrum could be assigned to this interaction.

The optimised spin Hamiltonian parameters for the various interactions are shown in Table 6.4. For the $^{109/107}$Ag, $^1$H and $^{103}$Rh interactions, the ENDOR spectra are single crystal like and the analysis of their "angular" dependence will again be presented in a single crystal like fashion.

For the axial $^{35}$Cl interaction, a direct comparison between experimental and simulated spectra is necessary in order to evaluate the quality of the fitting. For all powder ENDOR simulations, the microcrystal R5 EPR transitions were assumed to have an isotropic line width of 1.4 mT ($\Gamma_{\text{ENDOR}} = 0.7$ mT). The intensity for the $M_S = -\frac{1}{2}$ and $M_S = \frac{1}{2}$ ENDOR transitions again clearly differs, which allows to determine the sign of the (super)hyperfine parameters. Intensity ratios of $R = 2 \sim 3$ were used.

Table 6.4: Spin Hamiltonian parameters for the various nuclear interactions of the R5 centre, given in MHz (error given as a subscript). The principal axes of the interaction tensors are along the principal $g$ axes.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>$Q_x$</th>
<th>$Q_y$</th>
<th>$Q_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{109}$Ag (4th shell axial)</td>
<td>-11.47$_3$</td>
<td>-11.47$_3$</td>
<td>-14.4$_1$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1$H (equatorial ?)</td>
<td></td>
<td>?</td>
<td>-6.5$_1$</td>
<td></td>
<td></td>
<td>-3.0$_1$</td>
</tr>
<tr>
<td>$^{35}$Cl (1st shell axial)</td>
<td>38.52$_{20}$</td>
<td>38.75$_{20}$</td>
<td>73.4$_3$</td>
<td>0.267$_{20}$</td>
<td>0.315$_{20}$</td>
<td>-0.582$_{30}$</td>
</tr>
<tr>
<td>$^{103}$Rh (central)</td>
<td>-14.3$_1$</td>
<td></td>
<td>-18.0$_1$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ag, Rh and H interactions

Figure 6.18 shows the "angular" dependence of the low frequency part of the ENDOR spectrum. For the 4th axial Ag interaction (simulations in red and green for $^{109}$Ag and $^{107}$Ag, respectively) all transitions are observed for all magnetic field positions in the R5 EPR powder envelope and a perfect
agreement between experimental and simulated spectra is obtained, using the spin Hamiltonian parameters in table 6.4. For the $^{103}\text{Rh}$ hyperfine interaction, only the $M_S = -\frac{1}{2}$ could be followed in the complete magnetic field range. The $M_S = \frac{1}{2}$ transition, which has lower intensity, overlaps with a $^{109}\text{Ag}$ transition of the R4 centre in the high magnetic field range of the "angular" variation. For all magnetic field values, no more than two transitions could be assigned to Rh. This might suggest that the $\bar{A}$ tensor for this interaction is (nearly) axial. On the other hand, one would expect the hyperfine tensor to be clearly rhombic for this rhombic centre. Other $^{103}\text{Rh}$ transitions might be hidden under the more intense Ag transitions. We are thus unable to determine the $y$ component of the hyperfine tensor from our experimental results.

![Figure 6.18: "Angular" variation of the low frequency part of the R5 ENDOR spectrum. Filled and open circles represent experimental data points assigned to R5 and R4, respectively. The full lines are the results of simulations using the spin Hamiltonian parameters in table 6.4 for the 4th shell Ag interaction ($^{109}\text{Ag}$ in red, $^{107}\text{Ag}$ in green), the central $^{103}\text{Rh}$ interaction (blue) and a proton interaction (magenta).](image)

Also for the proton interaction, only two transitions are observed for each magnetic field position. As a result, again only two principal superhyperfine values can be determined for this interaction. The intensity variation of the low frequency proton line suggests that the principal superhyperfine value which can be determined from the low field part of the "angular" variation ($A_y$) is directed along $g_y$. The principal $A_x$ value cannot be determined from our spectra. At low magnetic fields, the high frequency proton transition overlaps the $^{37}\text{Cl}$ transitions, which are more intense, as a result of which its position cannot be determined. At the high magnetic field end of the "angular" variation, both proton transitions are separated from interactions with other nuclei, but still partly overlap the R4 proton ENDOR transitions. The "angular" variation of the R5 proton transitions are very well reproduced by the simulation using the parameters in table 6.4.
Axial Cl interaction

A correct analysis of the X-band powder ENDOR spectra of R5 is difficult, because the $g_x$ and $g_y$ components of the EPR spectrum overlap and because the $^{35}$Cl ENDOR transitions exhibit second order splitting. The latter effect already made the analysis of the Cl spectrum of R4 difficult. Both problems are overcome by recording the ENDOR spectra at Q-band.

![Graph showing ENDOR spectra](image)

**Figure 6.19**: Experimental (black) and simulated (red) Q-band (34.020 GHz) ENDOR spectra of the R5 axial Cl interaction at (a) $g_x$ and (b) $g_y$. The simulated spectra are calculated using the ENDOR data in Table 6.5.

The Q-band Cl ENDOR spectra recorded at $g_x$ and $g_y$ of R5 are shown in figure 6.19. These spectra are single crystal like and can be analysed very easily. From the upper triplet of lines in the $g_x$ and $g_y$ spectrum ($M_S = -\frac{1}{2}$ multiplet of the $^{35}$Cl isotope) a first estimate for the $x$ and $y$ components, respectively, of the $\tilde{A}$ and $\tilde{Q}$ tensors can be calculated, using the first order expressions for the transition frequencies (equation 3.53). These parameters can be further optimised by fitting the simulated to the experimental spectra. First, the $g_x$ spectrum is optimised, because this should in principle resemble the single crystal spectrum recorded at $g_x$ very well. The experimental and simulated $g_y$ spectra already show powder characteristics (asymmetrical line shape). For magnetic field values larger than that corresponding to $g_y$, the intensity of the spectrum decreases spectacularly, as a result of which the "angular" dependence of the spectrum cannot be recorded over the complete powder EPR envelope.

If we accept the fact that powder ENDOR shows insufficient resolution to allow a determination of the tilting angles of the superhyperfine and quadrupole tensors, only one more parameter should be determined for this interaction: $A_x$. This parameter can be deduced from the "angular" dependence of the X-band spectrum, shown in figure 6.20. In general, the agreement between experimental and simulated spectra is very good. In the spectra recorded in the $g_x$-$g_y$ region (275 – 280 mT) small deviations from the simulated spectra can be observed due to the second order splitting of the $^{35}$Cl transitions. The spectra recorded in the 305 – 325 mT range of the EPR envelope are very noisy. It is not obvious to judge the quality of the simulated spectra in this magnetic field range. In the spectra recorded in the magnetic field range near $g_h$, the ENDOR signal can again be clearly distinguished from the noise. Also for these spectra, the agreement between experiment and simulations is very good. The spin Hamiltonian parameters for this interaction are thus determined very accurately (table 6.4).
Figure 6.20: Experimental (black) and simulated (red) "angular variation" of the ENDOR spectrum of the axial Cl ions of the R5 centre. The simulations were performed using the spin Hamiltonian parameters in table 6.4.

6.4.6. The R6 centre

The ENDOR analysis for the R6 centre is not obvious, because it is very difficult to isolate its spectra. In melt-grown single crystals, its EPR spectrum strongly overlaps that of R6'. Even at Q-band, the R6
EPR and ENDOR spectra can only be recorded in a limited angular range near $\vec{B}_0 \parallel (100)$ ($g_z$ region) and only axial CI transitions are observed. In emulsion microcrystals, the R4 and R5 species are in most cases also (and more abundantly) present. Although the latter complexes can be eliminated from the samples by heating them to temperatures above 150°C, this procedure has proven to produce R6' centres in the microcrystals, rendering the analysis of the R6 interactions even more difficult.

In a sample, ideal for the study of R6, this centre should be produced by X-ray irradiation in a high concentration, without formation of R4 and R5 complexes. We had no such ideal samples at our disposal. An "angular" variation of the ENDOR spectrum has been recorded for two nearly ideal samples: a powder prepared from emulsions doped with nominally 100 ppm Cs₂RhCl₆(CH₃CN) dissolved in a 4 M NaCl solution (sample 1) and a powder prepared from emulsions doped with nominally 1000 ppm Na₃RhCl₆·12H₂O (sample 2). The Q-band EPR spectra for these samples after X-ray irradiation at room temperature are shown in figure 6.21. The spectrum of sample 1 is dominated by the R6 signal, whose intensity is nonetheless rather low. A very small trace of R5 centres also seems to be present in this sample. For sample 2, the intensity of the R6 EPR signal, which dominates the spectrum, is much higher, but also other components are present. The most abundant additional species in this sample is R5. Small concentrations of R4 and R6' also appear to be present. The spin Hamiltonian parameters for the interactions which could be identified in the ENDOR spectra of R6 are listed in table 6.5. In the simulation of the spectra, the single crystal EPR transitions were assumed to have a line width of 1.2 mT ($\Gamma_{\text{EPR}} = 0.6$ mT) and $R = 2$.

Table 6.5: Spin Hamiltonian parameters for the various nuclear interactions of the R6 centre, given in MHz (error given as a subscript). The principal z axis of the interaction tensors is along the principal $g_z$ axis. The principal directions in the plane perpendicular to $g_z$ cannot be determined.

<table>
<thead>
<tr>
<th>nucleus</th>
<th>$A_x$</th>
<th>$A_y$</th>
<th>$A_z$</th>
<th>$Q_x$</th>
<th>$Q_y$</th>
<th>$Q_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{109}\text{Ag}$ (4th shell axial)</td>
<td>-9.41₃</td>
<td>-9.41₃</td>
<td>-12.6₁</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{35}\text{Cl}$ (1st shell axial)</td>
<td>38.9₂</td>
<td>38.9₂</td>
<td>79.2₆</td>
<td>0.3₄₂</td>
<td>0.3₄₂</td>
<td>-0.6₈₄</td>
</tr>
</tbody>
</table>
Analysis of the low frequency part of the ENDOR spectrum

In figure 6.22, the X-band ENDOR spectrum of sample 1, recorded at 20 K, 9.57 GHz and 20 mW microwave power with the magnetic field set to $g_z$ is shown. In the 12 – 25 MHz part of the spectrum, the axial Cl transitions occur. In the 1 – 10 MHz frequency range, interactions with the central Rh nucleus and the fourth shell Ag nuclei are expected. One set of lines in this spectrum can be assigned to Ag. This assignment is further confirmed by comparing the spectrum of sample 1 with that of other samples which contain the R6 complex in an appreciable concentration. A comparison with the low frequency part of the spectrum of sample 2 (containing R5 and R6) and of heated emulsion microcrystals (containing R6 and R6'), presented in figure 6.23, shows that also in these samples, the Ag transitions of R6 can be identified. The Ag interaction of R6 is weaker than that for R5 and also slightly weaker than that for R6'.

![Figure 6.22: X-band (9.57 GHz) ENDOR spectrum of sample 1, recorded at $g_z$ ($B_0 = 284$ mT) of R6. Transitions assigned to Cl and Ag are indicated in red and green, respectively. The most intense transition in the low frequency part of the spectrum is marked with a full line arrow in blue. The possible positions of the other $M_z$ lines, assuming the transition is due to $^{103}$Rh, are indicated with dashed line arrows.](image1)

![Figure 6.23: Detail of the X-band ENDOR spectrum in the 2 - 7 MHz range of (a) heated emulsion microcrystals, (b) sample 1 and (c) sample 2. The Ag transitions of R6 are marked with solid green lines. The Ag transitions of R5 and R6' are marked with dashed lines in blue and red, respectively.](image2)

The most intense transition in the low frequency part of the spectrum of sample 1 (figure 6.22) is not included in the set of four Ag lines. It would be quite obvious to assign this to the $M_S = -\frac{1}{2}$ transition of the interaction with the central Rh nucleus. However, no second Rh line (belonging to the other $M_S$ multiplet) can be identified in the spectrum, neither if $A_L$ is assumed to be positive, nor if it is negative. For $A_L < 0$, the second transition could, of course, overlap the Ag transitions. In the spectra of other R6 containing samples (figure 6.23) this "Rh" line overlaps with more intense transitions of the Ag interactions of R5 or R6'. An assignment of the most intense line in the low frequency spectrum of sample 1 to $^{103}$Rh is thus certainly not conclusive.
The experimental and simulated (using the parameters in table 6.5) "angular" dependence of the Ag lines are shown in figure 6.24. The agreement between both is very good. The intensity of the transitions is rather low, especially in the high magnetic field range of the EPR powder envelope, where it becomes difficult to determine the exact position of the transitions. The estimated error on $A_{ij}$ for this interaction is thus rather large. The experimental "angular" dependence of the transition which might be due to the interaction with the central $^{103}$Rh nucleus is also shown in figure 6.24. In view of the ambiguity of this assignation, no simulations were performed for this interaction and no hyperfine parameters were determined.

**Figure 6.24**: Experimental (filled circles) and simulated X-band (9.57 GHz) "angular" dependence of the R6 Ag ENDOR transitions ($^{107}$Ag: red, $^{109}$Ag: green) using the data in table 6.5. The angular dependence of an intense transition which could not be assigned to the Ag interaction of R6 is also shown (marked with a dashed line).

**Figure 6.25**: Experimental (black) and simulated (red, parameters in table 6.5) "angular" dependence of the R6 Cl ENDOR spectrum.

Figure 6.25 presents the "angular" dependence of the axial Cl spectrum of sample 1. The simulations using the R6 spin Hamiltonian parameters in table 6.5 agree very well with the experimental spectra, which, however, have a low signal to noise ratio. For magnetic field positions in the EPR envelope higher than 320 mT, the ENDOR signals can no longer be discerned from the noise. From the partial "angular" dependence of this spectrum, the $A_j$ component of the superhyperfine tensor cannot be determined very accurately. In sample 2, the concentration of R6 centres is appreciably higher than in sample 1, as a result of which also the signal to noise ratio of the spectra is higher. Even in the $g_j$ range, ENDOR transitions can be clearly distinguished from the noise, as can be seen in figure 6.26. In order to obtain a good simulation for this spectrum, the concentration of R5 centres in this sample should not be neglected. For the simulation in figure 6.26, the R5 and R6 complexes were assumed
to be equally abundantly present in the sample. The high frequency end of the spectrum is nicely reproduced by the simulation of the CI transitions of R6. A further test for the spin Hamiltonian parameters determined from the powder ENDOR analysis is simulating the partial single crystal ENDOR angular variation, which could be recorded on melt-grown AgCl:Rh$^{2+}$ at Q-band and is shown in figure 6.27a. Finally, also the Q-band powder ENDOR spectrum recorded at $g_z$ of irradiated emulsion microcrystals, presented in figure 6.27b, can be simulated in a satisfactory way using the spin Hamiltonian parameters in table 6.5. The good agreement between simulated and experimental axial CI spectra of R6 recorded for various samples in which this complex is present, guarantees that the spin Hamiltonian parameters for this interaction are determined very accurately.

![Figure 6.26](image)

*Figure 6.26 : Experimental (black) and simulated X-band (9.52 GHz) ENDOR spectrum of sample 2 in the axial CI frequency range, recorded at $g_z$ of R6 ($B_0 = 338 mT$).*

![Figure 6.27](image)

*Figure 6.27 : Q-band single crystal (a) and powder (b) axial CI ENDOR spectra of R6.*

6.5. Comparison with the magnetic resonance results by Pawlik et al.

Pawlik et al. studied paramagnetic Rh$^{2+}$ centres produced by irradiation or heat treatment of AgCl emulsion microcrystals, doped with 250 ppm Na$_3$RhCly, dissolved in an aqueous (H$_2$O) NaCl solution using X and Q-band EPR and X-band ENDOR [PAWL98]. The spin Hamiltonian parameters obtained in their study are listed in Table 6.6.

Pawlik et al. identified three centres in their samples. Their labeling of these centres is inspired by the thermal stability of the centres. Although there seems to be no perfect match of $g$ values (cfr. table 6.1), the centres which they label the low temperature centre and the medium temperature centre, undoubtedly correspond to R4 and R5, respectively. The shift between the $g$ values appears to be systematic. For the third centre, which Pawlik et al. consider to be identical to the complex identified in melt-grown single crystals and which they label high temperature centre, a similar systematic shift
(\(= 0.01\)) of the \(g\) values is found compared with the single crystal data by Olm et al. The low temperature centre was investigated in samples illuminated with band gap light at room temperature, without subsequent heat treatment. In order to investigate the medium temperature centre, the latter samples were subsequently heated to 110°C. For the study of the high temperature centre, samples were prepared taking extreme care to prevent the aquation of [RhCl\(_6\)]\(^5\) complexes in the dopant solution. In order to eliminate small concentrations of low and medium temperature centres from these samples, they were heated to 150°C after illumination with band gap light at room temperature. The concentration of Rh\(^{2+}\) complexes in the samples studied by Pawlik et al. appears to be considerably higher than in ours. In addition, their samples seemed not to be contaminated with Mn\(^{2+}\). As a result, they were able to record the \(g_{ll}\) range of the various Rh\(^{2+}\) spectra at Q-band.

Measurements were also performed on samples for which the dopant salt was dissolved in a D\(_2\)O solution, which allows to identify the \(^1\)H interactions in an unambiguous way. Pawlik et al. were able to obtain all three principal components of the proton superhyperfine interactions for the low and medium temperature centres. On the other hand, Pawlik et al. did not have the facility of recording ENDOR spectra at Q-band, which facilitates the analysis of the axial Cl interactions considerably. For the analysis of [RhCl\(_6\)]\(^5\) complexes, they did not directly compare the powder spectra with single crystal spectra.

**Table 6.6**: Spin Hamiltonian results from the powder EPR and ENDOR study of pure and aquated RhCl\(_6\) complexes in AgCl emulsion microcrystals by Pawlik et al. [PAWL98]. Superhyperfine and quadrupole parameters are given in MHz. The error is given as a subscript. (-) indicates that the sign was not determined, but should be negative.

<table>
<thead>
<tr>
<th>Low temperature centre (R4)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>(g) tensor</td>
<td>(^{109})Ag</td>
<td>(^{35})Cl</td>
<td>(^{103})Rh</td>
</tr>
<tr>
<td>(g_x = 2.548_{5})</td>
<td>(A_x = (-) 12.8_{1})</td>
<td>(A_x = 37.8_{2})</td>
<td>(Q_x = -0.20_{2})</td>
</tr>
<tr>
<td>(g_y = 2.538_{5})</td>
<td>(A_y = (-) 12.8_{1})</td>
<td>(A_y = 36.2_{2})</td>
<td>(Q_y = -0.20_{2})</td>
</tr>
<tr>
<td>(g_z = 1.986_{5})</td>
<td>(A_z = (-) 15.5_{1})</td>
<td>(A_z = 68.5_{2})</td>
<td>(Q_z = 0.40_{2})</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Medium temperature centre (R5)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>(g) tensor</td>
<td>(^{109})Ag</td>
<td>(^{35})Cl</td>
<td>(^{103})Rh</td>
</tr>
<tr>
<td>(g_x = 2.492_{5})</td>
<td>(A_x = (-) 11.5_{1})</td>
<td>(A_x = 40.4_{2})</td>
<td>(Q_x = -0.28_{2})</td>
</tr>
<tr>
<td>(g_y = 2.442_{5})</td>
<td>(A_y = (-) 11.5_{1})</td>
<td>(A_y = 39.0_{2})</td>
<td>(Q_y = -0.34_{2})</td>
</tr>
<tr>
<td>(g_z = 2.018_{5})</td>
<td>(A_z = (-) 14.2_{1})</td>
<td>(A_z = 72.2_{2})</td>
<td>(Q_z = 0.62_{2})</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>High temperature centre (R6+R6*)</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(g) tensor</td>
<td>(^{109})Ag</td>
<td>(^{35})Cl</td>
<td>(^{103})Rh</td>
</tr>
<tr>
<td>(g_x = 2.436_{5})</td>
<td>(A_x = (-) 9.7_{1})</td>
<td>(A_x = 41.6_{2})</td>
<td>(Q_x = -0.35_{2})</td>
</tr>
<tr>
<td>(g_y = 2.406_{5})</td>
<td>(A_y = (-) 9.7_{1})</td>
<td>(A_y = 39.7_{2})</td>
<td>(Q_y = -0.47_{2})</td>
</tr>
<tr>
<td>(g_z = 2.018_{5})</td>
<td>(A_z = (-) 12.7_{1})</td>
<td>(A_z = 77.5_{2})</td>
<td>(Q_z = 0.82_{2})</td>
</tr>
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</table>
In general, there seems to be a reasonably good agreement between the ENDOR spin Hamiltonian parameters obtained by Pawlik et al. and those we determined (compare table 6.6 with tables 6.3-5). Pawlik et al. did not determine the sign of the Ag and Rh hyperfine values. Our choice for the signs of these parameters is explained in § 6.4.4-6. Where necessary in table 6.6, a minus sign was added between brackets for these spin Hamiltonian parameters. In the following, some discrepancies between the two studies for each of the centres will be discussed.

6.5.1. The R4 or low temperature centre

Apart from any systematical shift in the values, qualitative differences in the \( \vec{g} \) tensor obtained in the two studies are found. Pawlik et al. found the \( \vec{g} \) tensor to be rhombic (although technically speaking, \( g_x \) and \( g_y \) are within experimental error equal). From the analysis of the X-band EPR spectrum alone, one might indeed conclude that the R4 has a rhombic \( \vec{g} \) tensor, as concluded by Vercammen et al. [VERC98c]. However, the X-band ENDOR results already indicate that the observed splitting in the EPR spectrum corresponds to a hyperfine splitting. This is confirmed by the simulation of the \( g_i \) component of the powder EPR spectrum (see figure 6.2). The comparison of the X and Q-band EPR spectra directly demonstrates that within the experimental error of Q-band EPR resolution, the \( \vec{g} \) tensor is axial. Pawlik et al. were able to record the \( g_i \) EPR component of R4 and found that its value is significantly lower than that of the other Rh\(^{2+}\) centres. In spite of a careful search, we were unable to confirm this result for our samples. This is most probably due to the lower concentration of Rh\(^{2+}\) centres in our samples and the contamination with Mn\(^{2+}\), which obscures the \( g_i \) region of the spectrum. The evidence presented by Pawlik et al. for their experimental result is very convincing.

The agreement between the superhyperfine parameters for the Ag interaction in both studies is very good. For the axial Cl interaction, the agreement is much worse. A few reasons may be found to explain this discrepancy. Pawlik et al. analysed the Cl spectra in a single crystal like way (cfr. the explanation of the orientation selection principle for powder ENDOR in § 2.5.6). They thus neglected the influence of the resolved superhyperfine structure in the EPR spectrum. Furthermore, they did not take the second order splitting of the \(^{35}\)Cl transitions into account in their analysis. They determined the \( z \) component of the \(^{35}\)Cl superhyperfine tensor from X-band ENDOR spectra recorded in the \( g_i \) region of R4 using samples which also contain R5 complexes. One might wonder whether under these conditions the \( A_z \) value can be determined with the stated accuracy. A remark should also be made concerning the sign of the quadrupole values. These were explicitly mentioned in the article by Pawlik et al. via the definition of the quadrupole parameters \( q \) and \( q' (Q_x = -q + q'; Q_y = -q - q' \) and \( Q_z = 2q \)). For all Rh\(^{2+}\) centres, the sign of \( q \) given by Pawlik et al. does not agree with the literature data for Rh\(^{2+}\) complexes in NaCl and AgCl, where it is negative. The sign of \( q \) can in the case of the R4 centre easily be checked by recording the Cl ENDOR spectra at the different superhyperfine transitions at \( g_i \), as shown in figure 6.15. Our choice of sign for the quadrupole parameters is in agreement with the literature data and the powder ENDOR simulations for R4 (which explicitly take into account the sign of the quadrupole parameters) reproduce the variation of the spectra recorded at the different EPR superhyperfine transitions very well.
In principle, the hyperfine values for the $^{103}$Rh interaction determined by Pawlik et al. do not agree with ours, within experimental error. The discrepancy is not large, but the errors given for the parameters are small. The reason for the discrepancy is most probably the single crystal like analysis of the powder ENDOR spectra by Pawlik et al. They may erroneously have interpreted "superhyperfine" ENDOR transitions as single crystal like spectra, resulting in a value for $A_z$ significantly larger than the one we obtained by powder ENDOR spectrum simulation.

As a result of the higher dopant concentration and of a comparison between the spectra of hydrated and deuterated RhCl$_6$ complexes, Pawlik et al. were able to determine all three superhyperfine values for the proton interaction. In spite of a very careful search, even with the knowledge of the value, we were unable to determine the $A_y$ component ($A_x$ according to Pawlik et al.). The evidence presented by Pawlik et al. is nonetheless convincing. The third component of the superhyperfine tensor is large and positive, as a result of which the isotropic superhyperfine constant is very small (small spin density on the proton) and the anisotropic part of the tensor is large. Assuming that the anisotropic superhyperfine interaction is due to a point dipole interaction, the Rh – H distance can be estimated at 0.255 nm. As the largest superhyperfine component is found along a $g_x$ direction, the interacting proton is most probably situated in the horizontal plane of the complex.

6.5.2. The R5 or medium temperature centre

Apart from a systematic shift, the $g$ values determined for this centre in both studies agree very well. For the Ag interaction, the agreement of the superhyperfine values is again nearly perfect. The correspondence for the axial Cl interaction is again not very good. As we determined the superhyperfine and quadrupole parameters for this interaction by simulating both X and Q-band ENDOR spectra, we believe that our results are much more accurate than those of Pawlik et al. The $^{103}$Rh parameters determined by Pawlik et al. do not agree at all with our results. Different sets of transitions were assigned to Rh in the two studies. As already mentioned in § 6.3.5, the identification of Rh transitions is not unambiguous. In the spectra we recorded, we did not observe the transitions which Pawlik et al. assigned to Rh. In the spectra they present, the transitions we assigned to the hyperfine interaction are clearly seen, and remain, to our knowledge, unassigned. Therefore we prefer our assignment. As far as the proton interaction is concerned, we again failed to identify the third component of the superhyperfine tensor ($A_z$) in the X-band spectra. We also tried to record the ENDOR spectrum of the proton interaction at Q-band, where the $^1$H transitions are expected to be well separated from all other spectral components for magnetic field values in the $g_x$ – $g_y$ region. Unfortunately, no proton transitions were observed in the spectra, most probably due to their low intensity as a result of the strongly anisotropic superhyperfine tensor. Using the superhyperfine parameters by Pawlik et al. the Rh – H distance can be calculated to be very similar to that in the case of R4.

6.5.3. [RhCl$_4$]$^{+}$ centres

The preparation of the samples on which Pawlik et al. performed their study of the high temperature centre (irradiation with band gap light and subsequent heating to 150°C) suggests that both R6 and
R6' centres could be produced. We experimentally checked that this is indeed the case. Moreover, in the Q-band EPR spectrum of the sample Pawlik et al. used for the study of the high temperature centre (figure 6.28c), an intense spectral component is observed between the positions which the authors indicate as $g_x$ and $g_y$. The latter two components correspond to R6', whereas the central component corresponds to $g_z$ of R6.

![Figure 6.28: Experimental Q-band EPR spectra of the samples studied by Pawlik et al. (copy of the original figure 2 of reference [PAWL98]). Sample (a) was used for the study of the low temperature centre, (b) for the medium temperature centre and (c) for the high temperature centre. The principal g components of the dominant centre in each sample are indicated.](image)

Although the central component appears to have the highest intensity, R6' is probably predominantly present in the sample. This is explained in figure 6.29, in which the simulated Q-band (35.35 GHz) EPR spectra of R6 (a) and R6' (b) are shown. Due to the rhombicity of the $\bar{g}$ tensor for R6', its EPR spectrum has lower amplitude than that of the axial R6 centre. The powder EPR pattern observed by Pawlik et al. is well reproduced assuming that the concentration of R6' centres is three times as high as that of R6. It may thus be easily understood that in the X-band ENDOR spectra, primarily the interactions of the R6' centre have been observed. Hence, Pawlik et al. identified the high temperature centre as being identical to the primary centre in melt-grown AgCl microcrystals, i.e. [RhCl$_4$]$^{3-}$:1Vac. We have demonstrated, by comparing the Q-band EPR spectra of irradiated and heated emulsion microcrystals, ground and large melt-grown AgCl single crystals (see figure 6.4) that

![Figure 6.29: Simulated Q-band (35.35 GHz) powder EPR spectra of (a) R6 and (b) R6' using the EPR parameters in table 6.1. The spectrum (c) is the result of adding spectra (a) and (b) in intensity ratios 1:3.](image)
the [RhCl₆]⁺ centre produced in emulsion microcrystals by X-ray or UV irradiation is different from the primary centre in melt-grown AgCl single crystals.

6.6. Microscopic models for the centres

The EPR and ENDOR results may now be used to construct a detailed microscopic model for each of the centres. As the R6' has already been identified as a [RhCl₆]⁺:1Vac complex, only for the R4, R5 and R6 centres models should be proposed. The EPR and ENDOR data alone present insufficient evidence to derive the complete microscopic model for all these centres in an unambiguous way. However, additional information can be used to fill in the missing pieces of the puzzle. The X-band EPR study by Vercammen et al. [VERC98c] demonstrated the correlation between hydrated [RhCl₆]⁺ complexes in the dopant flow and the intensity of the Rn (n = 4, 5 and 6) spectra in irradiated emulsion microcrystals, strongly suggesting that the R4, R5 and R6 complex have two, one and no Cl⁻ ligands exchanged for solvent molecules (H₂O or OH⁻), respectively. For what concerns the charge compensation of the centres, our knowledge of the single crystal studies of [RhCl₆]⁺ complexes in NaCl and AgCl may be used. In these studies, it has been demonstrated that the charge compensation may be preserved by cation vacancies in NNN positions in the plane perpendicular to the gₓ axis of the complex. It was also shown that undercompensated or overcompensated complexes may have a high stability, dependent on the growth conditions of the crystals (solution or melt-grown).

In the following, for each of the three centres a microscopic model will be proposed and it will be compared to the model of Pawlik et al., who performed quantum chemical calculations (Hartree Fock) in order to determine the position of the charge compensating vacancies of the complexes. They further only considered completely locally compensated centres to be thermally stable. All models are shown in figure 6.30.

6.6.1. The R4 centre

The observation of a strongly anisotropic interaction with a proton situated in the equatorial plane of the complex at a distance from the Rh²⁺ ion comparable to the anion – cation distance in AgCl strongly indicates that one or more equatorial ligands in the [RhCl₆]⁺ complex have been exchanged by proton containing molecules or ions of the solvent. The axial ̅g tensor (within experimental accuracy of Q-band EPR) puts severe restrictions on the possible models for this centre. In a cubic crystal, a centre with (nearly) axial symmetry either has (nearly) tetragonal (D₄h or C₄ᵥ) or (nearly) trigonal (D₃d, D₃h, or C₃ᵥ) symmetry. In view of the strong interaction with two equivalent Cl⁻ and two equivalent Ag⁺ ions along the gₓ axis of the complex, trigonal symmetry can be ruled out. Only complexes with all four equatorial ligands exchanged or with two equatorial hetero ligands in a cis-configuration can give rise to a (nearly) axial ̅g tensor. In view of the stability of [RhCl₆(H₂O)₆:ν]³⁻ complexes in the dopant solution, a complex with four hetero ligands can be excluded. Moreover, the ¹⁰⁵Rh hyperfine interaction reveals that the symmetry is not accurately axial, but shows a small rhombic distortion, expected for a cis-[RhCl₆X₂]²⁻(2ν⁻) complex (ν = 0 if X = OH⁻ and ν = 1 if X = H₂O). This model is presented in figure 6.30a. It has orthorhombic I (C₃ᵥ) symmetry.
Figure 6.30: Models for the R4 ((a) and (b)), R5 ((c) and (d)), R6 (e) and R6’ (f) centres in AgCl microcrystals. The models (b), (d) and (f) are proposed by Pawlik et al. [PAWL98] for the low, medium and high temperature centres, respectively. Large red circles represent Cl ions, small gray circles Ag⁺ ions. Vacancies are indicated in purple. Large blue circles indicate hetero ligands (H₂O or OH). In the models (a) and (c) the small blue circles represent a Ag⁺ ion if the hetero ligand is OH and a vacancy if the hetero ligand is H₂O. In the models (b) and (d) the hetero ligands are assumed to be H₂O.
It is important to know the exact nature of the hetero ligands of the complex. From the ENDOR spectra, the difference between an interaction with a proton in a OH\(^-\) ion or with two equivalent protons in a H\(_2\)O molecule is not easily observed. In the case of a H\(_2\)O ligand, in principle the interaction between the two equivalent protons should be observed. Two types of interactions may be distinguished: the indirect interaction via the electron spin, which is in this case smaller than 7 kHz, and the direct dipolar interaction between the protons, which can be estimated at 35 kHz. The latter value is calculated assuming that the interaction between the \(^1\)H nuclei is a point dipole interaction, approximating the distance between the nuclei by the equilibrium value for the free H\(_2\)O molecule.

The ENDOR line width for this interaction is of the order of 50 kHz, as a result of which splittings due to the interaction between the nuclei are not expected to be resolved. Calculating the line width of the EPR spectrum from the hyperfine interactions identified in the ENDOR spectrum presents another possibility of making the distinction between H\(_2\)O or OH\(^-\) ligands. From the simulation of the EPR spectrum, a line width of 0.9 mT was derived for the R4 microcrystal spectrum. If one assumes that the hetero ligands are H\(_2\)O, this line width is produced by a hyperfine splitting due to two equivalent Ag nuclei with splitting \(A_i\) (\(^{107}/^{109}\)Ag), to two equivalent protons with splitting \(A_p\) (\(^1\)H) and two equivalent protons with splitting \(A_p\) (\(^1\)H). In the case of OH\(^-\) ligands, only two protons interact with the unpaired electron (one with splitting \(A_p\) (\(^1\)H) and the other with splitting \(A_p\) (\(^1\)H)). If in the case of H\(_2\)O ligands, the calculated line width is larger than the experimentally observed value of 0.9 mT, this case can be ruled out. If not, both types of ligands remain possible. For the case of H\(_2\)O ligands, the line width is calculated at 0.75 mT and in the case of OH\(^-\) ligands it is 0.70 mT. Also these calculations do not present us a possibility of making the distinction between the two possible types of ligands. An experimental way of determining the nature of the hetero ligands would be observing the vibrational spectra of the complexes (IR or Raman spectra). The vibrational spectra of H\(_2\)O and OH\(^-\) are indeed strongly different. It is, however, not straightforward to prepare from AgCl emulsion microcrystals a sample which is suitable for IR or Raman measurements. Therefore, such measurements have not been performed. The model presented in figure 6.30a considers both possibilities for the hetero ligands.

The extra charge introduced by the R4 complex in the AgCl crystal is of course also dependent of the nature of the exchanged ligands. In the case of H\(_2\)O ligands, the extra charge is +3e and in the case of OH\(^-\) ligands, it is +e. From the study of [RhCl\(_4\)]\(^6\) complexes in AgCl and NaCl we know that the charge compensation for this type of complexes may be preserved by cation vacancies in NNN positions. No cation vacancies had been found in nearest neighbour (NN) positions in the model system studies. For the R4 complex, the position of nearby vacancies should not disturb the (nearly) tetragonal \(\tilde{g}\) tensor symmetry of the complex. Only configurations with four, two (in a \(\text{cis}\)-configuration) or no nearby cation vacancies preserve the symmetry of the complex. This implies that the complex cannot be completely locally charge compensated by cation vacancies. In the case of H\(_2\)O ligands, the extra charge of +3e is very likely to be partially compensated by cation vacancies. With four nearby vacancies, the complex has a net charge of \(-e\) and with only two vacancies, the net charge is +e. The probability for a complex having four NNN cation vacancies in one plane is
expected to be very low. Moreover, for the [RhCl$_6$]$^{3+}$ complexes in solution-grown NaCl it has been observed that cation vacancies which overcompensate the complex tend to migrate away at temperatures at which they become mobile (cfr. the transformation of [RhCl$_6$]$^{3+}$.2Vac into [RhCl$_6$]$^{3+}$.1Vac at T > 220 K). For these two reasons, a configuration with four cation vacancies is considered improbable. In the model proposed in figure 6.30a, the two vacancies are proposed to be in the NNN cation positions closest to the H$_2$O ligands, which from the electrostatic point of view seem to be favoured over the other NNN positions in the equatorial plane. If the hetero ligands are OH$, the net charge of the complex is $-e$ if two vacancies are near the complex or $+e$ if no local charge compensating vacancies are present. As vacancies which are not required for the charge compensation are expected to migrate away from the complex, we prefer a model with no nearby vacancies in this case.

The model proposed by Pawlik et al. for the R4 complex is shown in figure 6.30b. In this model, the hetero ligands are considered to be H$_2$O. It differs from the model in figure 6.30a only in the number and the position of the cation vacancies. The model 6.30b is supported by Hartree Fock calculations, which indicate that this vacancy configuration is the most stable. Nonetheless, we believe this model may be ruled out for two reasons. First, in cases where the vacancy configuration could be determined in an unambiguous way ([RhCl$_6$]$^{3+}$ complexes in AgCl and NaCl), no configurations involving NN cation vacancies have ever been observed, although calculations tend to predict that these configurations are more stable than those involving NNN cation vacancies [OLM88]. Second, the model has orthorhombic I symmetry ($C_{2v}$), but is not expected to have an axial $\tilde{g}$ tensor. The degree of orthorhombicity for this centre is expected to be at least of the order of that for the [RhCl$_6$]$^{3+}$.1Vac centre in AgCl, because in both cases, one more vacancy is found on one of the perpendicular principal $\tilde{g}$ axes, and in the figure 6.30b, this vacancy is closer to the Rh$^{3+}$ ion than in the R6$^6$ complex. In the complex in figure 6.30a, the $d_{z^2}$ and $d_{x^2}$ orbitals are accidentally degenerate, if the axis between the Rh – hetero ligand bonds is exactly 90°, giving rise to a perfectly axial $\tilde{g}$ tensor.

6.6.2. The R5 centre

The R5 centre has a rhombic $\tilde{g}$ tensor. In view of the large interaction with two equivalent Cl$^-$ and Ag$^+$ ions on the $g_z$ axis of the complex, this axis is approximately directed along an $\langle 001 \rangle$ axis. If we assume that the $g_z$ axis coincides with $\langle 001 \rangle$, the complex may have orthorhombic I, orthorhombic II or monoclinic II symmetry (see table 2.1). The observed proton interaction suggests ligand exchange along the $g_x$ axis. In principle, both trans-[RhCl$_6$X$_2$]$^{4+}$$^\gamma$ and [RhCl$_6$X]$^{4+}$$^\gamma$ complexes are compatible with the symmetry of the centre. However, based on the correlation between singly hydrated complexes in the dopant solution and R5 centres in irradiated microcrystals demonstrated by Vercammen et al., we rule out the former possibility. Symmetry does not impose any restrictions to the number and positions of charge compensating cation vacancies for this complex. We still expect only to find cation vacancies in NNN positions in the equatorial plane. The vacancy configuration for R5 (shown in figure 6.30c) is proposed by analogy with the structural models for R4. These models
have orthorhombic II symmetry. Again, two cases are considered. If the hetero ligand is assumed to be a \(\text{H}_2\text{O}\) molecule, we assume it is accompanied by a cation vacancy, whereas a complex with an \(\text{OH}^-\) ligand is assumed to be non-locally charge compensated.

The model proposed by Pawlik et al. for the R5 complex is shown in figure 6.30d. It, again, only considers the possibility of a \(\text{H}_2\text{O}\) hetero ligand and differs from our model in the number and position of the charge compensating cation vacancies. This model cannot be ruled out based on the observed symmetry of the centre. As it involves cation vacancies in NN positions, we consider it to be improbable.

6.6.3. The R6 centre

No proton interactions have been observed for the R6 centre, indicating that no ligand exchange has taken place in the [RhCl\(_6\)]\(^{2+}\) complex. Additional indications for this fact are the correlation between the concentration of [RhCl\(_6\)]\(^{2+}\) complexes in the dopant solution and the intensity of the R6 centre after irradiation of AgCl emulsion microcrystals, and the principal \(g\) values of this centre, being very close to those of the R6' centre which also has a [RhCl\(_6\)]\(^{2+}\) core. Only the vacancy configuration of the complex should be determined, in order to obtain a complete structural model for this centre. A model with two NNN vacancies in a cis-configuration and a non-locally charge compensated centre are both in agreement with the observed \(\bar{g}\) tensor symmetry. Using the same arguments as for the R4 and R5 complexes, the non-locally charge compensated model (shown in figure 6.20e) is preferred. However, in this case the vacancy configuration can be determined in a less ambiguous way by observing the temperature dependence of the EPR spectrum. This can be explained as follows. If the centre has no nearby vacancies, its true symmetry is cubic (\(O_h\)). Due to the orbital degeneracy of its ground state electronic configuration, it undergoes a Jahn-Teller elongation along a \(\langle 001\rangle\) direction at low temperature. As a result, a centre with tetragonal symmetry is observed (\(D_{4h}\)) : the true symmetry is hidden. However, at sufficiently high temperature, the elongation axis of the centre may hop between the physically equivalent \(\langle 001\rangle\) axes. If this hopping rate is sufficiently high, an averaged spectrum is expected to be observed : the true cubic symmetry is effectively restored. Thus, for a centre with no nearby vacancies, one expects to observe a transition from tetragonal to cubic \(\bar{g}\) tensor symmetry, when the temperature is raised. A similar transition from orthorhombic II (\(C_{2v}\)) to tetragonal (\(C_{4v}\)) symmetry has been observed for the [RhCl\(_6\)]\(^{2+}\).1Vac centres in AgCl [OLM88] and NaCl [VERC98a, SABB98a]. For a cis-[RhCl\(_6\)]\(^{2+}\).2Vac centre on the other hand, the electronic ground state configuration shows no orbital degeneracy. No Jahn-Teller effect is expected : the observed symmetry at low temperature is the true symmetry of the centre (orthorhombic I, \(C_{2v}\)). No changes in the symmetry of the centre are expected as a function of temperature.

Figure 6.31a shows the temperature dependence of the single crystal EPR spectrum (at Q-band, 34.00 GHz) of melt-grown Rh doped AgCl, recorded with the magnetic field along a \(\langle 001\rangle\) direction. In figure 6.4, we already illustrated that both R6 and R6' centres are present in melt-grown AgCl single crystals. The well-known changes in the symmetry of the R6' centre as a function of temperature are clearly observed. From 80 K onwards, the \(g_r\) and \(g_z\) components gradually disappear (at 100 K they
have completely disappeared), while the \( g_z \) component, which becomes the \( g_j \) component of the averaged centre, remains visible.

![Diagram showing temperature dependence of the Q-band EPR spectrum](image)

**Figure 6.31:**
(a) Temperature dependence of the Q-band (34.00 GHz) EPR spectrum of a Rh doped melt-grown AgCl single crystal, recorded with the magnetic field along a \(<001>\) direction and room temperature powder EPR spectrum of irradiated AgCl microcrystals doped with 1000 ppm Rh\(^{3+}\). The spectral components of R6' are indicated in red, those of R6 in green.
(b) Angular variation of the Q-band (34.04 GHz) EPR spectrum of Rh\(^{3+}\) complexes in a melt-grown AgCl single crystal, recorded at room temperature. Experimental data points are indicated with filled circles, the full lines are simulations (R6' (red) : \( g_j = 2.438 \), \( g_z = 2.219 \), R6 (green) : \( g = 2.293 \)).

Only near room temperature, the \( g_j \) component of the averaged centre is clearly visible. At temperatures below 100 K, the intensity of the \( g_j \) component of R6 remains unchanged. In fact, it is better observed as the intensity of the overlapping \( g_y \) component of R6' decreases. At 120 K, the intensity of the R6 spectrum has already decreased and at 170 K it is no longer observed. In the room temperature spectrum, a component at \( g = 2.293 \) is observed, approximately equal to the average value of the low temperature principal \( g \) values. Recording the angular dependence of the spectrum (shown in figure 6.31b) has shown that this component is isotropic. It is also observed in the room temperature powder EPR spectrum of AgCl microcrystals with a high concentration of R6 centres. This is illustrated in the lower trace in figure 6.31a, which shows the spectrum for AgCl emulsion microcrystals doped with nominally 1000 ppm Rh\(^{3+}\), after irradiation at room temperature (the corresponding low temperature spectrum is shown in figure 6.21b). Therefore, we identify this isotropic component as the high temperature spectrum of R6. This implies that the centre has no nearby vacancies (model shown in figure 6.30e). Note that this assignment is consistent with the observation that the R6 centre appears to be more stable in irradiated emulsion microcrystals than in heated microcrystals or melt-grown single crystals. In NaCl a similar phenomenon has been
observed: the \([\text{RhCl}_6]^{4-}\) \(0.0\) Vac complex is the most stable centre in X-ray irradiated solution-grown crystals, whereas \([\text{RhCl}_6]^{4+}\) \(1.0\) Vac is dominant in heated or melt-grown crystals.

Olm et al. [OLM88] explained the presence of an isotropic spectral component in the room temperature spectra of Rh doped melt-grown AgCl single crystals by a reversible migration of the cation vacancy near room temperature. The migration was proposed to be reversible, because at low temperature only an orthorhombic Rh\(^{2+}\) centre had been observed. A similar transformation from the high temperature tetragonal to a cubic centre had not been observed in melt-grown NaCl single crystals [SABB98a]. The dominant centres in both crystals have the same structure, though. The present identification of \([\text{RhCl}_6]^{4+}\) centres in AgCl offers another possibility of explaining these results.

In melt-grown AgCl, both R6 and R6' centres are abundantly present. R6' undergoes a transformation from orthorhombic II to tetragonal symmetry and R6 from tetragonal to cubic. These transformations occur at different temperatures, which may give the impression that, as a function of temperature, three forms of the same centre are observed, especially when due to insufficient g factor resolution at X-band, the low temperature form of the R6 centre cannot be detected. In melt-grown NaCl single crystals, only very low concentrations of \([\text{RhCl}_6]^{4-}\) \(0\) Vac centres have been observed. \([\text{RhCl}_6]^{4+}\) \(1\) Vac and \([\text{RhCl}_6]^{4+}\) \(2\) Vac are the dominant Rh\(^{2+}\) centres in these crystals. The former only undergoes a transformation from orthorhombic II to tetragonal symmetry, whereas the latter undergoes no Jahn-Teller transformation. Therefore, at room temperature, and even above, no isotropic Rh\(^{2+}\) related spectrum could be detected.

**Table 6.7**: Absolute values of the superhyperfine parameters (given in MHz) for the fourth shell cation interaction of \([\text{RhCl}_6]^{4+}\) and \([\text{IrCl}_6]^{4+}\) in AgCl and NaCl. The values for the one-vacancy centres in NaCl have been made axial \((A_z = (A_x + A_y)/2)\).

<table>
<thead>
<tr>
<th>Complex / host lattice</th>
<th>Value (A_z)</th>
<th>Number of vacancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{RhCl}_6]^{4+}) in AgCl [this work]</td>
<td>9.41</td>
<td>0.0 (0) Vac</td>
</tr>
<tr>
<td>([\text{RhCl}_6]^{4+}) in NaCl [ZDRA97,CALL98,SABB98a]</td>
<td>12.6</td>
<td>0.0 (0) Vac</td>
</tr>
<tr>
<td>([\text{IrCl}_6]^{4+}) in NaCl [ZDRA99,SABB00b]</td>
<td>2.88</td>
<td>0.0 (0) Vac</td>
</tr>
<tr>
<td>([\text{IrCl}_6]^{4+}) in AgCl [SABB00a]</td>
<td>6.29</td>
<td>0.0 (0) Vac</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Complex / host lattice</th>
<th>Value (A_z)</th>
<th>Number of vacancies</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{RhCl}_6]^{4+}) in AgCl [this work]</td>
<td>4.29</td>
<td>0.0 (0) Vac</td>
</tr>
<tr>
<td>([\text{IrCl}_6]^{4+}) in NaCl [ZDRA97,CALL98,SABB98a]</td>
<td>4.90</td>
<td>0.0 (0) Vac</td>
</tr>
<tr>
<td>([\text{IrCl}_6]^{4+}) in AgCl [SABB00a]</td>
<td>17.27</td>
<td>0.0 (0) Vac</td>
</tr>
</tbody>
</table>

If the spin Hamiltonian parameters for the R6 and R6' centres are compared, a small but significant and well-detectable shift in the superhyperfine values for the interaction with the fourth shell axial Ag nuclei is observed: \(|A^{Ag}\) (R6)\(| < |A^{Ag}\) (R6')\(|. These values are given in Table 6.7, along with those for
the fourth shell axial cation interactions for [RhCl₆]³⁺ and [IrCl₆]³⁺ complexes and NaCl. All results in this table seem to indicate that the spin density on the fourth shell axial ions (through overlap or covalency), increases as the number of vacancies near the complex increases.

Sabbie et al. [SABB00] investigated the formation of Ir²⁺ centres in AgCl emulsion microcrystals. They observed the transformation of a primary centre with rhombic symmetry, produced after X-ray irradiation at low temperature, into a second centre with axial symmetry at a temperature (170 K) markedly higher than that at which the vacancies become mobile in AgCl (120 K). They identified these two centres as [RhCl₆]³⁺.1Vac and [RhCl₆]³⁺.0Vac, respectively. The observed shift in the superhyperfine (see table 6.7) value for the fourth shell Ag interaction was used as an argument in favour of this hypothesis. The present results for [RhCl₆]³⁺.nVac centres in AgCl confirm that the transformation might be related with vacancy migration. The shift in the Ag superhyperfine values for the Rh³⁺ and Ir²⁺ complexes is of the same order of magnitude.

Although this shift in the fourth shell superhyperfine values does not give any direct (symmetry related) indication about the number and position of cation vacancies, it appears to be very systematic, independent of the exact nature of the central ion and the host lattice. It may be worth trying to find out its physical significance through quantum chemical calculations.

6.6.4. Comparison of the models for R4, R5 and R6 with those for the [RhCl₆]³⁺.nVac centres in NaCl

The models we propose for the R4, R5 and R6 centres, produced by UV or X-ray irradiation of Rh³⁺ doped AgCl emulsion microcrystals only differ by the number of equatorial [Cl⁻ - Ag⁺] pairs along (100) directions being exchanged by [H₂O - Vac] or [OH⁻ - Ag⁺] (indicated in blue in figures 6.31a and c). The following relations between the spin Hamiltonian parameters for these centres are striking:

\[ g_\uparrow (R4) > g_\downarrow (R5) > g_\perp (R6) \]  \hspace{1cm} (6.9)

\[ A^{CI}_C (R4) < A^{CI}_C (R5) < A^{CI}_C (R6) \]  \hspace{1cm} (6.10)

\[ q^{CI}_C (R4) < q^{CI}_C (R5) < q^{CI}_C (R6) \]  \hspace{1cm} (6.10)

\[ A^{AO}_{\infty \infty} (R4) > A^{AO}_{\infty \infty} (R5) > A^{AO}_{\infty \infty} (R6) \]  \hspace{1cm} (6.11)

In these relations \( T_\perp = (T_x + T_y) / 2 \) for a rhombic tensor \( \tilde{T} \) and \( T_{\infty \infty} = (T_x + T_y + T_z) / 3 \). For the hyperfine interaction, the following relation would be expected

\[ A^{Rh}_{\infty \infty} (R4) > A^{Rh}_{\infty \infty} (R5) > A^{Rh}_{\infty \infty} (R6) \]  \hspace{1cm} (6.12)

Unfortunately, we were unable to identify the Rh interaction for the R6 centre in an unambiguous way. Similar relations have been found for the [RhCl₆]³⁺.nVac complexes in NaCl, for which a similar set of models, only differing in the number of NNN cation vacancies in the equatorial plane, has been proposed (the number of vacancies is given between brackets)

\[ g_\uparrow (2) > g_\downarrow (1) > g_\perp (0) \]  \hspace{1cm} (6.13)

\[ A^{CI}_C (2) < A^{CI}_C (1) < A^{CI}_C (0) \]  \hspace{1cm} (6.14)

\[ q^{CI}_C (2) < q^{CI}_C (1) < q^{CI}_C (0) \]  \hspace{1cm} (6.14)

\[ A^{AO}_{\infty \infty} (2) > A^{AO}_{\infty \infty} (1) > A^{AO}_{\infty \infty} (0) \]  \hspace{1cm} (6.15)
\[ A_{\text{iso}}^{m} (2) > A_{\text{iso}}^{m} (1) > A_{\text{iso}}^{m} (0) \] (6.16)

These relations seem to reflect some kind of continuous variation in the structure of the centres involved. They do not serve as a proof for the proposed structural models, but seem to be indicative for a monotonous change in the spin density distribution over these series of complexes. It would be very interesting to find out whether quantum chemical calculations reproduce these trends in the spin Hamiltonian parameters and provide a deeper insight into their physical significance.

6.7. Conclusions

Four stable Rh\(^{5+}\) complexes have been identified in AgCl emulsion microcrystals doped with Na\(_3\)RhCl\(_6\).12H\(_2\)O, dissolved in an aqueous NaCl solution. Three of these (labeled R4, R5 and R6) centres are produced by UV or X-ray irradiation of the microcrystals at room temperature. The fourth centre is only produced in measurable concentrations after heat treatment. The EPR study at X and Q-band microwave frequencies demonstrated that the R4 and R6 centres are characterised by an axial \(\tilde{g}\) tensor, whereas the R5 and R6' centres have rhombic \(\tilde{g}\) symmetry.

In the X-band ENDOR spectra of R4 and R5, interactions with nearby protons could be identified, most probably due to ligand exchange (Cl\(^-\) exchanged by H\(_2\)O or OH\(^-\)) in the plane perpendicular to the \(g_z\) axis of the corresponding complexes. ENDOR further demonstrated that the R4 complex shows a small rhombic distortion. Based on the spectroscopic results and the knowledge acquired from the study of single crystal model systems, two possible models were proposed for this centre: \([\text{RhCl}_4(\text{H}_2\text{O})_2]\)^{2+}, associated with two NNN cation vacancies next to the hetero ligands, or non-locally charge compensated \([\text{RhCl}_4(\text{OH})_2]\)^{4+}. The structure of the R5 centre cannot be determined equally accurately from the spectroscopic results. By analogy with the R4 centre, \([\text{RhCl}_6\text{H}_2\text{O}]\)^{3+} with one NNN vacancy next to the hetero ligand, and non-locally charge compensated \([\text{RhCl}_6\text{OH}]\)^{4+} are proposed as possible structures for this centre.

The R6 and R6' centres are also present in melt-grown AgCl single crystals. They are identified as \([\text{RhCl}_6]\)^{4+}.0Vac and \([\text{RhCl}_6]\)^{4+}.1Vac complexes, respectively. These models are consistent with the observed temperature behaviour of the EPR spectrum for the centres. Both centres exhibit a Jahn-Teller elongation, which is static at low temperature (T < 120 K, T < 80 K, respectively). Hence, the R6 complex has \(D_{4h}\) tetragonal symmetry, and the R6' centre has \(C_{2v}\) orthorhombic II symmetry. At room temperature a thermally assised hopping of the elongation axis between physically equivalent orientations takes place, as a result of which the centres are observed to have \(O_h\) and \(C_{2v}\) symmetry, respectively.

In addition to the identification of the observed centres, much attention has been paid to the simulation of powder ENDOR spectra. Available powder ENDOR simulation programs [VAND95] have been modified to take into account the effect of resolved hyperfine and superhyperfine structure in the EPR spectrum. A superhyperfine like structure on the \(^{103}\)Rh ENDOR spectra of the R4 centre, predicted by simulations, has been experimentally observed. Also in the ENDOR spectra of the first shell axial Cl\(^-\) ions, superhyperfine effects are observed and simulated. Correct simulations for the latter spectra are complicated by isotopic effects, the high nuclear spin of the magnetic isotopes and the interaction between the equivalent Cl nuclei. In spite of these difficulties, the "angular" variation of the Cl ENDOR
spectra, as a function of the magnetic field position within the EPR powder envelope, could be very well simulated.
Chapter 7: Summary and conclusions

7.1 Introduction

In chapter 1, an introduction to the problem of Rh doping in AgCl emulsion microcrystals and AgCl and NaCl single crystal model systems was given. It has been explained that the problem is of fundamental physical interest, but also attracts the attention of photographic industry.

Mainly in the beginning of this research project, the collaboration with the Research and Development Laboratory of Agfa-Gevaert has been intense. With the increasing importance of digital imaging and the consequently decreasing market for AgX consumer photography (X = Cl, Br), the industrial relevance of this fundamental research has decreased. Nonetheless, AgX photography still takes an important position in the consumer market and in medical and industrial imaging applications. Recent publications by other research groups, like the Eastman Kodak group at Rochester (see e.g. [PAWL98], [EACH99], [EACH00a], [PAWL00] and [EACH00b]), show that photographic industry is still interested in fundamental research of AgX photographic systems and processes.

From the fundamental side, on the other hand, quantum chemical tools for calculating the structure of point defects in solids become increasingly powerful, up to the point where they are able to predict the optical, vibrational and magnetic properties of such defects in a reliable way. Focusing on magnetic resonance properties, e.g., recently (super)hyperfine constants have been calculated very reliably for radicals in organic solids like alanine [LAHO99a], steroids [LAHO99b] and sugars [LAHO99c], for the F centre in LiF [MALL01] and OH impurities in alkaline-earth oxides [LICH00]. Ab initio calculations of $\tilde{g}$ tensors for $d^1$ transition metal ions have also been reported [PATC99]. Because of the large amount of experimental data on rhodium centres in AgCl and NaCl, made available by this study, these complexes present a challenging research field for computational physicists or chemists. Presently, the first density functional calculations (DFT) on Rh$^{2+}$ centres in NaCl are being performed by the research group of professor M. Moreno (Cantabria University, Santander, Spain).

In this final chapter and at the end of our experimental study of paramagnetic Rh impurities in AgCl and NaCl, we shall summarise the most important conclusions of this study and this work. The experimental work to which the conclusions refer was carried out by Dr. P. Moens, Dr. M. Zdravkova, Dr. H. Vercammen (U.I.A.), Dr. K. Sabbe and ourselves. The availability of EPR at X, Q and W-band and ENDOR at X and Q-band at the two research groups involved in this research project (Magnetic Resonance Group, Ghent University and EPR group, University of Antwerp (U.I.A.)) has been crucial. The relevance of these results to practical photographic systems and to the general understanding of the paramagnetic properties of transition metal ion complexes in ionic solids will be discussed. Finally, the most important fundamental questions remaining unanswered after this study will be pointed out.

7.2 Summary of the results and their relevance to photographic systems

In order to obtain information about the structure of Rh impurities in photographic emulsions, a series of model systems has been studied. The relation between the various model systems is once more given in figure 7.1 (see also figure 1.5).
The model systems most closely related to real photographic emulsions are the AgCl emulsion microcrystals. Single crystal model systems were studied because the information one can obtain from single crystals is much more detailed than that obtainable from microcrystal powders. As large single crystals of AgCl can only be grown from the melt, also NaCl single crystals, which are structurally very similar and which can be grown both from the melt and from aqueous solution, were used as model systems. By studying solution-grown NaCl, it was hoped that solvent effects (Cl⁻ ligand exchange by H₂O or OH⁻) could be studied in a single crystal environment. NaCl single crystals grown from the melt were investigated in order to obtain information about the differences between melt-grown and solution-grown crystals. For all single crystal model systems, also the corresponding microcrystal powder system (ground crystals) has been studied, in order to check the feasibility of powder magnetic resonance studies of Rh centres in these environments. The study of ground NaCl crystals grown from the melt [SCHW97] and from aqueous solution [SABB98c] were not discussed in detail in this work, because they did not reveal any new results and did not contribute significantly to the general understanding of powder EPR and ENDOR spectra for these systems.

In the review of results on Rh centres in AgCl emulsion microcrystals and model systems, a clear difference should be made between what should be regarded as experimental facts, and the interpretations which have been given to these experimental facts. The experimental facts one obtains from a magnetic resonance study are the information on the ground state electronic properties...
and the symmetry of paramagnetic centres and on the presence of nearby magnetic nuclei. Microscopic models for paramagnetic centres constructed from the magnetic resonance data are usually merely interpretations of these facts. The experimental evidence supporting a certain microscopic model (or set of models) may, however, be so convincing that the model itself acquires the status of a fact.

7.2.1 The study of [RhCl₆]⁺ complexes

As a result of the model system studies, the microscopic models of the [RhCl₆]⁺ complexes in AgCl and NaCl have acquired the status of facts. By studying the angular dependence of the Q-band ENDOR spectrum of the axial Cl⁻ ions, the symmetry of the various centres could be determined in an unambiguous way (chapter 5). The annealing properties of these centres in solution-grown NaCl demonstrated that their interconversion involves the migration of cation vacancies [VERC98a]. The [RhCl₆]⁺.nVac models proposed for these centres are the only possible models which are in agreement with the above-mentioned experimental results and the static Jahn-Teller effect observed for two of these centres (with n = 1 [OLM88, VERC98a, SABB98a] and 0 (chapter 6)). From the formation conditions and stability of these complexes in various single crystal systems, two more general conclusions (facts) can be drawn. First, the charge of Rh complexes in AgCl and NaCl is not necessarily completely locally compensated: depending on the crystal preparation, overcompensated [SABB98a] and undercompensated complexes [ZDRA97, VERC98c, VRIE00] may be stable. Vacancies appear to be more tightly bound to the [RhCl₆]⁺ complexes in melt-grown than to complexes produced by irradiation in solution-grown (micro-)crystals ([SABB98a] and chapter 6). A second very important conclusion is the fact that all charge compensating vacancies near RhCl₆ complexes in NaCl and AgCl have been found in NNN positions [OLM88, CALL98, VERC98a].

7.2.2 Evaluation of NaCl as a model system

In spite of some important differences, NaCl has thus proven to be a very good model system for the study of [RhCl₆]⁺ complexes in AgCl. Unfortunately, the concentration of hydrated Rh²⁺ complexes in solution-grown NaCl turned out to be too low to allow a detailed single crystal study (chapter 4). Two types of Rh-related centres have been observed in NaCl, which could not be identified in AgCl. They point to the differences between the NaCl and AgCl host lattices. The first type is the Rh⁺ centre in NaCl (chapter 4). It has been demonstrated that the [RhCl₆]⁺.1 Vac and [RhCl₆]⁺.0 Vac centres in NaCl act as electron traps. The fact that no Rh⁺ centres were observed in AgCl is most probably a consequence of the narrower band gap of the latter host lattice. The second type is a Rh²⁺ dimer centre in melt-grown NaCl [VERC98b]. The exact structure of this centre is apparently still under discussion [SABB00]. The absence of such type of centre in AgCl and solution-grown NaCl points to the fact that the aggregation properties of Rh ions in the various model systems might be different.

7.2.3 The study of hydrated Rh²⁺ complexes in AgCl emulsion microcrystals

Mainly due to the lack of a detailed single crystal study, the models for the hydrated Rh²⁺ complexes in AgCl (R4, R5) emulsion microcrystals, as presented by Pawlik et al. [PAWL98] or by ourselves (see
chapter 6, figure 6.30) are not yet as well established as those for the non-hydrated complexes. They are merely interpretations of the following experimental facts:

1. The correlation between the concentration of $[^\text{RhCl}_n(\text{H}_2\text{O})_{6-n}]^{(n-3)^-}$ (n = 4, 5 and 6) complexes in aqueous solutions and the decrease in sensitivity of photographic emulsions doped with these solutions [ENDO90].

Endo et al. attributed the reduced desensitisation to the incorporation of hydrated Rh$^{2+}$ complexes in the AgCl microcrystals (interpretation).

2. The correlation between the $[^\text{RhCl}_n(\text{H}_2\text{O})_{6-n}]^{(n-3)^-}$ concentration in the dopant solution and the intensity of the R4, R5 and R6 spectra in irradiated AgCl emulsion microcrystals (doped with approximately 100 ppm Rh$^{3+}$), and the difference in thermal stability for these centres [VERC96, VERC98c].

These results supported the hypothesis of Endo et al. Vercammen et al. interpreted the R4, R5 and R6 centres as $[^\text{RhCl}_6]^{4+}$ complexes in which two, one and none of the Cl$^-$ ligands have been replaced by H$_2$O molecules, respectively.

3. The observation with X-band ENDOR that the Rh$^{2+}$ ion in the R4 and R5 complexes is closely associated with one or several equivalent protons ([PAWL98] and chapter 6). A powder ENDOR analysis does in principle not allow to determine the exact position of the proton(s) in these complexes. The relative magnitude of the principal superhyperfine values indicate that they are situated in the equatorial plane and the calculated Rh – H distance is comparable to the equilibrium Ag – Cl distance in the crystal. These results strongly indicate that in the R4 and R5 complexes Cl$^-$ ligands have been exchanged by H$_2$O, thus confirming the hypotheses of Endo et al. and Vercammen et al., although OH$^-$ substitution cannot be excluded. The powder EPR and ENDOR analyses do certainly not allow to determine the number and position of charge compensating vacancies near these complexes in an unambiguous way. For the R4 centre, the axial $\tilde{g}$ tensor symmetry suggests that the number of charge compensating vacancies is even and that they are in NNN positions. For the R5 centre, even this type of symmetry information is not available.

7.2.4 Direct relevance to practical photographic systems

AgCl emulsion microcrystals most closely resemble the actual photographic environment of the Rh dopant and should thus provide the most directly applicable results to practical systems. Nonetheless, the relevance of this model system study to real photographic emulsions may still be questioned. First, the centres which have been investigated in this work are paramagnetic trapped electron Rh$^{2+}$ complexes. Those present in the emulsion microcrystals (practical systems or model systems) before exposure are the diamagnetic precursor Rh$^{3+}$ complexes. It is of course the structure of the latter centres which determines the trapping depth and efficiency of the Rh dopant in AgCl microcrystals, and thus its effect on the contrast and sensitivity of emulsions. The structure of the former determines the thermal stability of the trapped electron centres.

One might wonder to which extent the results obtained for the Rh$^{2+}$ complexes apply to the precursor Rh$^{3+}$ centres. It should be noted that the Rh$^{2+}$ centres are produced by UV or X-ray irradiation at room temperature. The irradiation is not expected to change the ligand structure of the Rh complexes. The
trapping of an electron after irradiation may however induce lattice distortions around the Rh ion (e.g. as a result of the Jahn-Teller effect or reduced electrostatic interactions between the central ion and its nearest shells of anions and cations). Moreover, at room temperature Ag⁺ vacancies, which may preserve the charge compensation of the Rh³⁺ complexes, are mobile. The vacancy configuration of the trapped electron centre may thus also differ from that of the precursor. In this respect, it should be noted that Vercammen et al. [VER98c] also performed X-band EPR measurements on in situ UV irradiated emulsion microcrystals at 20 K. At this temperature, the vacancies and Ag⁺ interstitials in AgCl are frozen in. They report no differences between the spectra after in situ irradiation at 20 K and those after room temperature irradiation. Detecting the changes in the EPR spectrum due to differences in the vacancy configuration might, however, be rather difficult at X-band. Unfortunately, we were unable to repeat the experiments of Vercammen et al. at Q-band or using X-band ENDOR, because our spectrometers do not offer the possibility of in situ irradiation.

Relying on the X-band EPR results, one would conclude that the structure of the Rh³⁺ precursor centres is identical to that of the investigated Rh²⁺ trapped electron centres, except for possible lattice relaxations. If the models we proposed for the R4, R5 and R6 centres (or those by Pawlik et al.) correctly describe their charge compensation, the diamagnetic Rh³⁺ precursor centres are non-locally charge compensated with an extra charge of +2e (or +e). This may, in view of the long range Coulomb interaction with conduction band electrons, explain the high trapping efficiency of Rh³⁺ ions in AgCl emulsion microcrystals.

One might further criticise the relevance of the present work to real photographic systems by noting that the Rh concentration in the investigated microcrystals is much higher than that used in commercial emulsions. In view of the possible influence of aliovalent cation impurities on the Frenkel equilibrium in AgCl, one might expect that the charge compensation by cation vacancies may be dependent of the concentration of aliovalent impurities in the microcrystal [HAM88]. The conclusions drawn about the charge compensation of the complexes in the model systems do not necessarily apply to practical photographic emulsions.

In the discussion about the relevance of the model systems study to real photographic systems, the following should be kept in mind. One might consider investigating realistic photographic emulsion microcrystals or even photographic films, but it might turn out to be fairly difficult. Rh concentrations in such systems are very low (in the ppb range) and one cannot use electron magnetic resonance techniques to investigate the structure of Rh³⁺ complexes, because these are not paramagnetic. Other spectroscopic techniques, like optical absorption or vibrational spectroscopy, do not provide equally direct structural information. If one, on the other hand, decides to investigate model systems, as we did in this study, one should be aware that even very realistic model systems are never exactly identical to the practically relevant system.

7.3 Relevance as fundamental research

The most directly relevant result to the fundamental understanding of the behaviour of transition metal ion complexes in ionic solids is of course the information on the microstructure for the various complexes identified in the course of this study: the Rh⁺ complexes in NaCl (chapter 4),
[RhCl₆]⁺nVac complexes in NaCl and AgCl [ZDRA97, CALL98, VERC98b] and Rn complexes in AgCl emulsion microcrystals (chapter 6). Some other theoretical and experimental results of this work, which may be of general importance in the EPR and ENDOR spectroscopic research of such complexes will be summarised in the following.

In chapter 3, first order calculations of the $\tilde{g}$ tensor of low spin $d^6$ ions in a tetragonally distorted octahedral crystal field have been given and the mechanisms, discussed in the literature in order to explain the deviations of $g_{||}$ from $g_e$ for elongated complexes, have been reviewed. In chapter 4, the $\tilde{g}$ (first order) and $\tilde{D}$ (second order) tensors for a $d^6$ ion in a tetragonally distorted octahedral crystal field have been deduced. The calculations of $g$ values and zero field splitting parameters illustrate how spin Hamiltonian parameters may be derived from real (but approximated) Hamiltonian properties using perturbation theory.

In chapters 2 and 3, the splitting of ENDOR transitions due to the indirect interaction between equivalent nuclei via the electron spin has been evaluated in the case of nuclei with $I = 1/2$ and $I = 3/2$, respectively. The X-band ENDOR spectrum for the interaction with two equivalent $^{35}$Cl nuclei for Rh$^{2+}$ complexes in AgCl and NaCl has been used to illustrate this effect. It has been demonstrated (both theoretically and experimentally) how this second order splitting is largely reduced by recording the ENDOR spectra at higher microwave frequencies, e.g. Q-band (see chapter 5). As a second advantage of Q-band ENDOR, its higher orientation and species selectivity, both for single crystals (chapter 5) and powders (chapter 6) has been illustrated.

In chapter 5, it has been explained how the symmetry of low spin elongated $d^6$ ions in a distorted octahedral crystal field can be deduced unambiguously from the ENDOR analysis of the interaction of the unpaired electron with the first shell anions along the elongation axis. This method has been applied to determine the number and position of charge compensating cation vacancies near [RhCl₆]⁺ complexes in NaCl and AgCl. For these purposes, the ENDOR analyses had to be performed at Q-band.

In chapter 6, some effects of resolved (super)hyperfine structure in the EPR spectrum on powder ENDOR spectra have been demonstrated. Both experimentally and through simulations, it has been shown that the powder ENDOR transitions may exhibit a superhyperfine like structure. This structure was experimentally most clearly observed for the $^{103}$Rh interaction of the R4 centre. Also the spectra of the first shell axial Cl nuclei exhibit such a structure. The spectrum simulations for the latter nuclei, with $I > 1/2$ and for which the ENDOR spectra recorded at different EPR superhyperfine transitions of a certain microcrystal orientation are fundamentally different, are very complicated. The approximations used for the simulations of these spectra, which have been explained in chapter 6 and seem to produce very satisfying simulations, may be inspiring for later powder ENDOR analyses.

7.4 Questions raised by the study of Rh complexes in AgCl and NaCl

In this study of Rh impurities in NaCl and AgCl, we have focussed on the fundamental question how these impurities are incorporated in the crystalline hosts. The answer(s) to this question have raised
new and even more fundamental questions, the most important (in our opinion) of which are listed in the following.

Why are charge compensating cation vacancies near RhCl₆ complexes in NaCl and AgCl only found in NNN positions [ZDRA97, CALL98, VERC98a]?

What causes the stability of \([\text{RhCl}_6]^{4+}\) complexes to be different in solution-grown and melt-grown single crystals [SABB98a]?

How should the tilting angles of the superhyperfine and quadrupole tensors of the first shell axial anions in low spin elongated \(d^7\) complexes be physically interpreted and how do they depend on the specific vacancy configuration ([VRIE01a, VRIE01b], chapter 5)?

How should the observed monotonous trends observed in the spin Hamiltonian parameters of the \([\text{RhCl}_6]^{4+}.n\text{Vac} (n = 0, 1, 2)\) centres in NaCl and for the Rn (\(n = 4, 5, 6\)) centres in AgCl be physically interpreted ([VRIE00], chapter 6)?

Why can the Rh\(^{1+}\) complex in NaCl, associated with a NNN cation vacancy, not be observed with EPR or ENDOR at X and Q-band (chapter 4)?

The answers to at least some of these questions are expected to be found from quantum chemical calculations of Rh complexes in AgCl and NaCl, which should provide information on the geometry of the complexes and on the distribution of the unpaired electron(s) over the complexes. The results of such calculations might in return give new impulses to further experimental research of Rh complexes in AgCl, NaCl or other ionic crystal lattices.
Appendix 1: Character tables of $O_h$ and $D_{4h}$ [ALTM94, BOES94b]

### Table A1: Character table of $O_h$

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>E</th>
<th>$3C_{2x&lt;100^v}$</th>
<th>$8C_{3x&lt;111^v}$</th>
<th>$6C_{2x&lt;110^v}$</th>
<th>$6C_{4x&lt;100^v}$</th>
<th>i</th>
<th>$3O_{(100)}$</th>
<th>$8S_{6x&lt;111^v}$</th>
<th>$6O_{(110)}$</th>
<th>$6S_{4x&lt;100^v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$E_g$</td>
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<td>2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$T_{1g}$</td>
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<td>0</td>
<td>1</td>
<td>3</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$T_{2g}$</td>
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<td>0</td>
<td>1</td>
<td>-1</td>
<td>3</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_u$</td>
<td>2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>-2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-3</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$T_{2u}$</td>
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<td>0</td>
<td>1</td>
<td>-3</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table A2: Transformation properties of central metal and ligand orbitals (sixfold coordination) in $O_h$ symmetry. The ligand numbering is defined in figure A.1.

<table>
<thead>
<tr>
<th>$T_i$</th>
<th>metal orbital</th>
<th>ligand $e_g$ orbital</th>
<th>ligand $p_z$ orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>none</td>
<td>$-s_i - s_j + s_k - s_l + s_m$</td>
<td>$-p_x - p_y + p_z + p_w + p_{3z} - p_{3x}$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$d_{3z^2-r^2}, d_{x^2-y^2}$</td>
<td>$s_i + s_j - s_k - s_l + 2s_m$</td>
<td>$-p_x - p_y + p_z + p_w + 2p_{3z}$</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$d_{x^2}, d_{y^2}, d_{xy}$</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>$E_u$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>none</td>
<td>$s_i - s_j, s_k - s_l, s_m$</td>
<td>$p_x + p_y + p_z + p_w + p_{3z}$</td>
</tr>
<tr>
<td>$T_{2u}$</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
</tbody>
</table>

### Table A3: Character table of $D_{4h}$

<table>
<thead>
<tr>
<th>$D_{4h}$</th>
<th>E</th>
<th>$C_{2(001)}$</th>
<th>$2C_{2&lt;100^v}$</th>
<th>$2C_{2&lt;110^v}$</th>
<th>$2C_{4(001)}$</th>
<th>i</th>
<th>$\sigma_h$</th>
<th>$2\sigma_{y(100)}$</th>
<th>$2\sigma_{y(110)}$</th>
<th>$2S_{4(001)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
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<td>1</td>
<td>1</td>
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<td>1</td>
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</tr>
<tr>
<td>$B_{1g}$</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{2g}$</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_g$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E_u$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table A4: Transformation properties of central metal and ligand orbitals (sixfold coordination) in \( D_{4h} \) symmetry. The ligand numbering is defined in figure A.1.

<table>
<thead>
<tr>
<th>( \Gamma_{l} )</th>
<th>metal ( d ) orbital</th>
<th>ligand ( s ) orbital</th>
<th>ligand ( p_{x} ) orbital</th>
<th>ligand ( p_{y} ) orbital</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>( d_{x^2-r^2} )</td>
<td>( s_{5} + s_{6} )</td>
<td>( -p_{z5} + p_{z6} )</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>( s_{1} + s_{2} + s_{3} + s_{4} )</td>
<td>( -p_{x1} - p_{y2} + p_{x3} + p_{y4} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( B_{1g} )</td>
<td>( d_{x^2-y^2} )</td>
<td>( s_{1} - s_{2} + s_{3} - s_{4} )</td>
<td>( -p_{x1} + p_{y2} + p_{3x} - p_{4y} )</td>
<td>none</td>
</tr>
<tr>
<td>( A_{2g} )</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>( p_{1y} - p_{2x} - p_{3y} + p_{4x} )</td>
</tr>
<tr>
<td>( B_{2g} )</td>
<td>( d_{y} )</td>
<td>none</td>
<td>none</td>
<td>( p_{3y} + p_{2x} - p_{3y} - p_{4x} )</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>( d_{yz}, d_{zx} )</td>
<td>none</td>
<td>none</td>
<td>( p_{1z} - p_{3z}, p_{2z} - p_{4z} )</td>
</tr>
<tr>
<td>( A_{1u} )</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>( B_{1u} )</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>( p_{3x} - p_{4x} )</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>none</td>
<td>( s_{5} - s_{6} )</td>
<td>( p_{5z} + p_{6z} )</td>
<td>( p_{1z} + p_{2z} + p_{3z} + p_{4z} )</td>
</tr>
<tr>
<td>( B_{2u} )</td>
<td>none</td>
<td>none</td>
<td>none</td>
<td>( p_{3z} - p_{4z} + p_{3x} - p_{4x} )</td>
</tr>
<tr>
<td>( E_{u} )</td>
<td>none</td>
<td>( s_{1} - s_{3}, s_{2} - s_{4} )</td>
<td>( p_{1x} + p_{3x}, p_{2y} + p_{4y} )</td>
<td>( p_{3x} + p_{6x}, p_{5y} + p_{5y} )</td>
</tr>
</tbody>
</table>

Table A5: Reduction of \( O_{h} \)'s irreducible representations in \( D_{4h} \).

\[
\begin{array}{|c|c|}
\hline
\text{representation of } O_{h} & \text{reduction in } D_{4h} \\
\hline
A_{1g} & A_{1g} \\
A_{2g} & B_{1g} \\
E_{g} & A_{1g} \oplus B_{1g} \\
T_{1g} & E_{g} \oplus A_{2g} \\
T_{2g} & E_{g} \oplus B_{2g} \\
A_{1u} & A_{1u} \\
A_{2u} & B_{1u} \\
E_{u} & A_{1u} \oplus B_{1u} \\
T_{1u} & E_{g} \oplus A_{2u} \\
T_{2u} & E_{g} \oplus B_{2u} \\
\hline
\end{array}
\]

Figure A1: Transition metal ion in sixfold coordination. The \( p_{x} \) orbitals for all 6 ligands are indicated, defining the sign convention for the orbitals.
Appendix 2: Matrix elements of the one-electron orbital and spin momentum operators

**Table A6**: Wave functions obtained from real atomic orbitals by operating with \( \hat{i}_x, \hat{i}_y \) and \( \hat{i}_z \) [MABB92]

<table>
<thead>
<tr>
<th>Original orbital</th>
<th>( \hat{i}_x )</th>
<th>( \hat{i}_y )</th>
<th>( \hat{i}_z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d_{3z^2-r^2} )</td>
<td>(-i\sqrt{3}d_{yz})</td>
<td>(i\sqrt{3}d_{zx})</td>
<td>0</td>
</tr>
<tr>
<td>( d_{x^2-y^2} )</td>
<td>(-id_{yz})</td>
<td>(-id_{zx})</td>
<td>2id_{xy}</td>
</tr>
<tr>
<td>( d_{xz} )</td>
<td>(id_{x^2-y^2} + i\sqrt{3}d_{3z^2-r^2})</td>
<td>(id_{xy})</td>
<td>(-id_{zx})</td>
</tr>
<tr>
<td>( d_{xy} )</td>
<td>(-id_{xy})</td>
<td>(-i\sqrt{3}d_{3z^2-r^2} + id_{x^2-y^2})</td>
<td>(id_{yz})</td>
</tr>
<tr>
<td>( p_x )</td>
<td>(id_{zx})</td>
<td>(-id_{yz})</td>
<td>(-2id_{x^2-y^2})</td>
</tr>
<tr>
<td>( p_y )</td>
<td>(id_{xy})</td>
<td>(-ip_z)</td>
<td>(ip_y)</td>
</tr>
<tr>
<td>( p_z )</td>
<td>(-ip_y)</td>
<td>(ip_x)</td>
<td>0</td>
</tr>
<tr>
<td>( s )</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Table A7**: Wave functions obtained by operating with the spin momentum operators on the one-electron spin wave functions

| \( |m_s\rangle \) | \( \hat{s}_x \) | \( \hat{s}_y \) | \( \hat{s}_z \) |
|-----------------|----------------|----------------|----------------|
| \( |1/2\rangle \) | \(1/2\,-1/2\rangle \) | \(1/2\,-1/2\rangle \) | \(1/2\,1/2\rangle \) |
| \( |-1/2\rangle \) | \(1/2\,1/2\rangle \) | \(-1/2\,1/2\rangle \) | \(-1/2\,-1/2\rangle \) |
Samenvatting

Situering van het onderzoek

In dit proefschrift wordt de structuur van rhodiumonzuiverven in AgCl en NaCl onderzocht met behulp van de magnetische resonantietechnieken *elektronen paramagnetische resonantie* (EPR) en *elektronen nucleaire dubbele resonantie* (ENDOR). Dit probleem wordt ingeleid in het eerste hoofdstuk. De voornaamste doelstelling van dit onderzoek is te bepalen op welke manier Rh-ionen in het AgCl- en NaCl-gasrooster worden ingebouwd. Wat is hun valentie? Wat is hun ligandstructuur? Hoe wordt de extra lading die zij in het gasrooster introduceren gecompenseerd? EPR en ENDOR vormen een unieke combinatie die toelaat een antwoord te vinden op deze vragen. Ze verschaffen informatie over de symmetrie en de elektronische grondtoestand (valentie) van een paramagnetisch transitiemetaal in een kristallijke omgeving en laten in principe toe de aard en de positie van naburige magnetische kernen te bepalen. Een dergelijke studie kan worden geclasseerd als fundamenteel onderzoek van extrinsieke puntdefecten in ionaire vaste stoffen.

Ondanks zijn fundamentele karakter is dit onderzoek gegroeid vanuit een vraag van de industrie. Rh³⁺ fungeert immers als diepe, permanente elektronenval in AgX (X = Cl of Br) en wordt als intentionele onzuiverheid aan fotografische emulsies toegevoegd om het contrast van films te verhogen of hun gevoeligheid te verlagen. Rh³⁺ is weliswaar diamagnetisch in een gasrooster met de NaCl-kristalstructuur, maar na vangst van een elektron wordt het ion paramagnetisch en kan het met EPR en ENDOR onderzocht worden. Een gedetailleerde kennis van de structuur van deze onzuiverven is niet alleen belangrijk om hun werking als elektronenval te begrijpen, maar kan ook nuttig zijn bij het doelgericht aanvragen van patenten.

Voor de industrie (Agfa-Gevaert) is enkel het onderzoek van Rh-onzuiverven in AgCl-microkristallen in fotografische emulsies van direct belang. Magnetische resonantiestudies op microkristallen (poeders) zijn haalbaar, maar wegens hun oriëntatiegevoeligheid leveren EPR en ENDOR meer gedetailleerde structurele informatie op bij éénkristalstudies. Bijgevolg werd er besloten ook Rh-ionen in éénkristalmodelsystemen voor de AgCl-microkristallen in een fotografische emulsie aan een magnetische resonantiestudie te onderwerpen. Voor de hand liggende modelgasroosters zijn AgCl-éénkristallen. Die men echter niet, zoals voor AgCl-microkristallen in fotografische emulsies wel het geval is, uit waterige oplossing laten groeien. Omdat uit onderzoek van Endo en Saikawa [ENDO90] het vermoeden was gerezen dat Rh-complexen met één of meerdere solventmoleculen (H₂O of OH⁻) als ligand in AgCl-microkristallen kunnen worden ingebouwd en dergelijke effecten niet verwacht worden in kristallen gegroeid vanuit de smelt, werd ook NaCl als modelsysteem in de studie betrokken. NaCl is structureel zeer verwant aan AgCl en laat kristalgroei vanuit waterige oplossing en vanuit de smelt toe. De vergelijking van Rh-complexen in deze twee types NaCl-éénkristallen laten toe de invloed van de kristalgroeimethode op de inbouw van Rh-onzuiverven te onderzoeken, terwijl de vergelijking van AgCl- en NaCl-kristallen gegroeid vanuit de smelt specifieke verschillen tussen de twee gasroosters aan het licht kunnen brengen, die onafhankelijk zijn van de kristalgroeimethode. Onderzoek van Rh-complexen in gemalen AgCl- en NaCl-éénkristallen (microkristallen, poeders) laten enerzijds toe het effect van de kristalgroei op de inbouw van Rh-
ionen te onderzoeken (inbouw aan het oppervlak mogelijk?) en bieden anderzijds een mogelijkheid
tot het op punt stellen van de simulatieprogrammatuur voor poeder-EPR- en -ENDOR-analyses (als in
eénkristallen en poeders dezelfde complexen aanwezig zijn). In figuur 1 worden de modelsystemen,
waarin Rh-onzuiverheden in het kader van dit onderzoek werden bestudeerd, en hun onderlinge
relaties schematisch voorgesteld. Het onderzoek verliep in samenwerking met het Laboratorium voor
Experimentele Vaste-stoffysica van de UIA (Antwerpen) en de onderzoekslaboratoria van Agfa-
Gevaert.

Figuur 1: Overzicht van de modelsystemen voor fotografische emulsies waarin Rh
onzuiverheden in het kader van dit onderzoek werden bestudeerd en hun onderlinge relaties.
De modelsystemen waarvoor de resultaten expliciet in dit proefschrift zijn opgenomen, zijn in
grijs aangeduid. De resultaten van de studie van Rh-complexen in NaCl-poeders zijn niet
essentieel voor dit proefschrift en zijn er bijgevolg ook niet expliciet in opgenomen.
Aangezien men grote AgCl-éénkristallen niet uit waterige oplossing kan laten groeien,
konden Rh onzuiverheden in dergelijke gastkristallen niet onderzocht worden.

De studie van rhodiumonzuiverheden in NaCl en AgCl wordt in dit proefschrift behandeld als
fundamenteel onderzoek. In hoofdstuk 7 worden de implicaties van de resultaten voor praktische
fotografische systemen belicht. Tevens wordt er gewezen op een aantal fundamentele vragen die
deze resultaten oproepen en die verder theoretisch onderzoek vereisen.

Magnetische resonantie spectroscopie
In het tweede hoofdstuk van dit proefschrift worden de basisprincipes van de gebruikte
spectroscopische technieken uiteengezet. Het hoofdstuk vangt aan met een kwantummechanische
beschrijving van een paramagnetisch transitiemetaalion in een diamagnetisch kristalrooster.
Vervolgens wordt het spin-Hamiltonianformalisme, eigen aan EPR en ENDOR, geïntroduceerd. De
spin-Hamiltoniaan is een effectieve Hamiltoniaan, die enkel de energienevenus van het systeem
waartussen EPR- en/of ENDOR-transities plaatsgrijpen correct beschrijft. De fysische interpretatie van de onderscheiden termen in de spin-Hamiltoniaan (Zeemanterm (\(\tilde{g}\) tensor), nulveldsplittingsstermen (\(\tilde{D}\) tensor), (super)hyperfijninteracties (\(\tilde{A}\) tensor) en quadrupoolinteracties (\(\tilde{Q}\) tensor)), relevant voor de beschrijving van de paramagnetische systemen die aan bod komen in deze studie, wordt besproken. 

Daarna worden steady-state EPR- en ENDOR-spectroscopie nader beschreven. EPR is de absorptie van microgolfstraling door een paramagnetisch systeem (bijvoorbeeld een onzuiverheidson met ongepaarde elektronen in een kristal) in de aanwezigheid van een uitwendig magnetisch veld. Een toegelaten EPR-overgang grijpt plaats wanneer het magnetisch elektronenspinkwantumgetal \(M_S\) van het paramagnetisch systeem met effectieve spin \(S\) met één eenheid toe- of afneemt. Meestal wordt hierbij de microgolffrequentie vastgehouden en laat men de intensiteit van het magneetveld variëren.

Een toegelaten nucleaire magnetische resonantie-overgang (NMR-overgang) grijpt plaats wanneer het magnetisch kernspinkwantumgetal \(M_I\) voor een kern met spin \(I\) met één eenheid toe- of afneemt. NMR-overgangen kunnen worden gedetecteerd als veranderingen in de intensiteit van het EPR-spectrum van een paramagnetisch systeem als functie van de frequentie van invallende radiofrequente (RF) straling. Dit fenomeen noemt men ENDOR.

Er wordt aandacht geschonken aan de magnetische resonantiefenomenen (kwantummechanische beschrijving van de absorptie van micro- en RF golven, relaxatie, saturatie) en aan de beschrijving van de gebruikte spectrometers. Er wordt aangehaald hoe de spin-Hamiltoniaanparameters uit de spectra kunnen worden afgeleid en hoe uit deze informatie een model voor het paramagnetische defect kan worden geconstrueerd. Bijzondere aandacht wordt besteed aan het probleem van een ongepaard elektron dat interageert met meerdere equivalente kernen en aan de oriëntatieselectiviteit van ENDOR in het geval van éénkristal- en poederstudies.

**Paramagnetische eigenschappen van Rh\(^{2+}\)-onzuiverheden in AgCl en NaCl**

Het derde hoofdstuk is gewijd aan magnetische resonantiekarakteristieken van Rh\(^{2+}\)-gecentreerde complexen in NaCl en AgCl. De meest voornaam Rh-onzuiverheden in deze kristallen zijn van dit type. Voor deze wordt de \(\tilde{g}\) tensor voor een ion met een \(d^7\) grondtoestandsconfiguratie in een sterk, tetragonaal geëlongeerd (\(\tilde{A}_{4g}\) grondtoestand) of gecomprimeerd (\(\tilde{B}_{4g}\) grondtoestand), octaëdrisch kristalveld berekend met behulp van eerste orde störgestheorie. Er wordt aangetoond dat de \(g\) factor (hoofdvlak langs de tetragonaal as van het complex) in het geval van elongatie in eerste orde geen afwijking ten opzichte van \(g_e\) (de waarde voor het vrije elektron) vertoont. De belangrijkste mechanismen die in de literatuur worden aangehaald ter verklaring van de experimenteel waargenomen positieve afwijkingen, worden samengevat. Aangezien uit experimentele gegevens blijkt dat Rh\(^{2+}\)-complexen in NaCl en AgCl geëlongeerd zijn, wordt aan het geval van compressie geen verdere aandacht besteed.

Vervolgens worden de ENDOR-spectra voor de voornaamste types van interacties van het ongepaarde elektron met naburige kernen (\(^{103}\)Rh, \(^{107/109}\)Ag, \(^{35/37}\)Cl, \(^{23}\)Na, \(^1\)H) beschreven. Speciale aandacht wordt geschonken aan de interactie van het ongepaarde elektron met de twee equivalenten Cl-ionen langs de elongatie-as. Het ENDOR-spectrum voor deze interactie wordt met behulp van
tweedde orde storingstheorie berekend. Er wordt aangetoond dat, als een gevolg van een indirecte interactie tussen de kernspins van de equivalente ionië via de elektronenspin, de ENDOR-transities, berekend met eerste orde storingstheorie, opspitsen. Voor de beschrijving van de interacties met andere magnetische kernen in het systeem, volstaat een eerste orde behandeling.

Daarna worden de resultaten van het onderzoek naar Rh\(^{2+}\)ionië in AgCl en NaCl, die reeds in een vroeg stadium van dit doctoraatsonderzoek werden behaald (door Dr. P. Moens of in samenwerking met Dr. M. Zdravkova, Dr. H. Vercammen en Dr. K. Sabbe) en niet als persoonlijk experimenteel werk worden gepresenteerd, samengevat. Ook wordt de nomenclatuur voor de onderscheiden Rh-gecentreerde paramagnetische complexen, die verder in het proefschrift wordt gehanteerd, gedefinieerd. De voornaamste resultaten waarop dit doctoraatsonderzoek reeds in een vroeg stadium kon steunen, zijn de identificatie van drie typische Rhodiumhexachloride - vacaturecomplexen in NaCl, aangeduid als [RhCl\(_6\)]\(^{2+}\).nVac (n = 2, 1 en 0, Vac = tweede-dichtste-naburvacature), waarvoor de structuurmodellen als zijnde bekend mochten worden beschouwd [ZDRA97, CALL98, VERC98a], en van drie Rh\(^{2+}\)-gecentreerde complexen in AgCl-microkristallen in fotografische emulsies, aangeduid met Rn (n = 4, 5, 6) [VERC98c], waarvoor de structuurmodellen nog ter discussie stonden. De structuurmodellen van de [RhCl\(_6\)]\(^{2+}\).nVac centra zijn afgebeeld in figuur 2.

Figuur 2: Structuurmodellen voor de [RhCl\(_6\)]\(^{2+}\) complexen in NaCl en AgCl: (a) cis-[RhCl\(_6\)]\(^{2+}\).2Vac, (b) [RhCl\(_6\)]\(^{2+}\).1Vac, (c) [RhCl\(_6\)]\(^{2+}\).0Vac. Het centrale Rh\(^{2+}\) ion wordt voorgesteld door een zwarte streep. Het ongepaarde electron bevindt zich hoofdzakelijk in een d\(_{2g}\) orbital van dit ion. De ionië van het rooster worden voorgesteld door grote (anionen) en kleine sferen (kationen). Kationvacatures worden voorgesteld door blauwe kubussen. In het ENDOR spectrum wordt telkens een sterke interactie waargenomen met de axiale eerste schil anionen (groen) en vierde schil kationen (rood). Voor elk complex zijn de hoofddassen van de g-tensor en de hoofdsymmetriës aangeduid (C\(_5\), of C\(_{3}\)).

Dr. H. Vercammen toonde een correlatie aan tussen de concentratie van [RhCl\(_n\)(H\(_2\)O)\(_{6-n}\)]\(^{n-3}\)-complexen in waterige oplossing en de intensiteit van de EPR-spectra van de Rn centra geproduceerd door bestraling van AgCl-microkristallen gedoteerd uit deze waterige oplossing. Dit resultaat liet vermoeden dat in de R4, R5 en R6 complexen 2, 1 en 0 Cl-liganden zijn uitgewisseld door
solventmoleculen (H₂O of OH). Deze hypothese vroeg echter om verdere experimentele bevestiging (met ENDOR). Voorts kon dit doctoraatsonderzoek steunen op de resultaten van een X-band EPR- en ENDOR-studie van het basisdefect in AgCl:Rh²⁺ éénenkristallen [OLM88], waarvan de structuur identiek is aan dat van het [RhCl₆]⁺.1 Vac centrum in NaCl.

Rh⁺ en het B-centrum
In hoofdstuk 4 worden de EPR- en ENDOR-resultaten voor twee paramagnetische centra in NaCl gepresenteerd.

Het eerste wordt geïdentificeerd als een Rh⁺-ion op een substitutionele kationpositie in het kristalrooster, zonder naburige roosterdefecten. In de grondtoestand heeft Rh⁺ een 4d⁶ elektronenconfiguratie. In een perfect octaëdrisch kristalveld geeft dit aanleiding tot een paramagnetisch centrum met kubische symmetrie en effectieve spin S = 1. De paramagnetische eigenschappen van een dergelijk ion (\(\tilde{g}\) en \(\tilde{D}\) tensor) worden met behulp van storingsrekening afgeleid, waarbij een tetragonale distorsie van het kristalveld wordt toegepast. Eigenaardig genoeg worden bij X-band frequenties de toegelaten EPR-overgangen (\(\Delta M_S = 1\)) niet waargenomen. Er wordt enkel een heel zwakke verboden overgang (\(\Delta M_S = 2\)) bij de dubbele g-waarde gedetecteerd. Het ENDOR-spectrum is zowel bij de toegelaten als bij de verboden overgang detecteerbaar. Bij Q-band frequenties kan het \(\Delta M_S = 1\) EPR-spectrum wel waargenomen. De karakteristieken ervan (verbreding van de "enkele-kwantumtransitie" en het voorkomen van een "dubbele kwantumtransitie") komen overeen met wat in de literatuur beschreven staat voor andere d⁶ ionen in een octaëdrisch kristalveld (bijvoorbeeld Co⁺ of Ni²⁺ in MgO of CaO). Een studie van het vormingsgedrag van dit octaëdrisch Rh⁺-complex in NaCl-kristallen, gegroeid uit waterige oplossing en uit de smelt, toont aan dat het ontstaat wanneer een [RhCl₆]⁺.0Vac centrum een elektron vangt of wanneer een [RhCl₆]⁺.1Vac centrum een elektron vangt en de vacature vervolgens wegmigreert. Dit laatste vormingsmechanisme impliceert het bestaan van een paramagnetisch Rh⁺-centrum in NaCl, geassocieerd met een tweede-dichtste-nabuur vacature, dat bijgevolg tetragonale (C₄ᵥ) symmetrie heeft. Hoewel een dergelijk centrum na vorming door bestraling bij vloeibare stikstoftemperatuur (77 K) stabiel is bij temperaturen onder de 220 K (bij deze temperatuur worden de kationvacatures mobiel in NaCl), werd het niet waargenomen bij X- en Q-band frequenties.

Het tweede paramagnetische centrum dat in dit hoofdstuk behandeld wordt, is het zogenaamde B-centrum. Het X-band EPR-spectrum van dit centrum was reeds voor de aanvang van dit doctoraatsonderzoek bekend [SHOC75]. Het centrum wordt, net zoals [RhCl₆]⁺.0Vac, gevormd in NaCl-kristallen gegroeid uit waterige oplossing en gedoteerd met Rh³⁺, door bestraling met X-stralen bij kamertemperatuur of bij 77 K, gevolgd door opwarming tot kamertemperatuur. Aangezien het niet in kristallen gegroeid uit de smelt voorkomt, werd gesuggereerd dat het Rh²⁺-ion in dit centrum één of meerdere H₂O- of OH-liganden heeft [ZDRA97]. In dit proefschrift worden de eerste resultaten van een EPR- en ENDOR-studie in Q-band gepresenteerd. Met Q-band en W-band [VERCB99b] EPR kan worden aangetoond dat het zogenaamde B-spectrum bijdragen bevat van de [RhCl₆]⁺.2Vac en [RhCl₆]⁺.1Vac centra en van één of meerdere Rh²⁺-centra die hiervan verschillen, en met de term B-achtige centra worden aangeduid. Onderzoek van het Q-band EPR-spectrum onmiddellijk na
bestraling bij 77 K geeft aan dat de Rh$^{3+}$-precursor van de B-achtige centra essentieel verschilt van die van de [RhCl$_6$]$^{3+}$:nVac centra. In het Q-band ENDOR-spectrum van één van de B-achtige centra wordt een interactie met een proton in de nabijheid van het Rh$^{2+}$-ion waargenomen. Deze laatste twee Q-band resultaten zijn in overeenstemming met de hypothese van Zdравkova et al. In B-achtige centra zijn vermoedelijk Cl-liganden uitgewisseld door H$_2$O of OH$^-$. Een meer gedetailleerde studie van B-achtige centra is onmogelijk gebleken door de lage intensiteit van de spectra, die bovendien, zelfs in Q- en W-band, sterk overlappen met die van de [RhCl$_6$]$^{3+}$:nVac centra.

Detectie van kationvacatures
Het vijfde hoofdstuk is gewijd aan de detectie van ladingscompenserende kationvacatures in de nabijheid van transitiemetaalonen met behulp van ENDOR. Een rechtstreekse detectie van dergelijke vacatures is in principe onmogelijk, omdat hun elektronenspin nul is en ze geen kern bevatten (en dus ook geen kernspin hebben). Aangezien kationvacatures een extra negatieve lading in een ionair kristal introduceren, worden ze verwacht een invloed te hebben op de distributie van de ongepaarde elektronen van nabijgelegen paramagnete transitiemetaalonen. Als de vacatureconfiguratie (aantal en posities) een systematische invloed blijkt te hebben op de paramagnete eigenschappen ($\tilde{g}$ tensor, (super) hyperfijn- en quadrupool-interacties) kan dit leiden tot een manier om ze (bijna) rechtstreeks te bepalen. Hiertoe worden in dit hoofdstuk de [RhCl$_6$]$^{3+}$:nVac centra (zie figuur 2) in NaCl (n = 1, 2) en AgCl (n = 1) als modelsysteem gebruikt.

Voor eerst moet de symmetrie van deze centra volledig en ondubbelzinnig kunnen worden bepaald. Een studie van de $\tilde{g}$ tensor alleen laat niet toe te bepalen of het centrum al dan niet inversiesymmetrie bezit. Er wordt aangetoond dat de volledige symmetrie van deze centra kan worden bepaald uit de Q-band ENDOR studie van de interactie van de ongepaarde elektronen met de axiale chloorliganden. Als het centrum inversiesymmetrisch is, moeten de hoofdassen van de $\tilde{A}$ en $\tilde{O}$ tensoren voor deze interactie samenvallen met die van de $\tilde{g}$ tensor. In dat geval moeten de transities van beide Cl-ionen voor alle richtingen van het magneetveld samenvallen. Voor de [RhCl$_6$]$^{3+}$:1Vac en [RhCl$_6$]$^{3+}$:2Vac centra wordt rechtstreeks (op de spectra) aangetoond dat dit niet het geval is. De symmetriepiek van deze centra is bijgevolg C$_{2v}$ en niet D$_{2h}$. De studie laat op ondubbelzinnige wijze toe de C$_2$ symmetrieas van het complex te bepalen en geeft op die manier unieke informatie over de exacte positie van de kationvacatures.

Uit de voorlopig beperkt voor handen zijnde resultaten blijkt de tilthoek tussen de hoofdassen van de $\tilde{A}$ tensor van de axiale chloorkernen en de $\tilde{g}$ tensor van het complex systematisch te worden beïnvloed door de vacatureconfiguratie. Deze tilthoek is mogelijk het gevolg van een verplaatsing van het Rh$^{2+}$-ion naar de vacature(s) toe. Verder onderzoek (quantumcomputationeel en experimenteel) moet uitwijzen of uit deze tilthoek/verplaatsing de vacatureconfiguratie van het complex rechtstreeks kan worden afgeleid. Het bleek noodzakelijk deze studie bij Q-band microgolffrequenties uit te voeren, om de spectra van verschillende oriëntaties van eenzelfde complex en van verschillende complexen goed te kunnen scheiden, en om de opsplitsing van de ENDOR-transities ten gevolge van de indirecte interactie tussen de equivalent chloorkernen te onderdrukken.
Rh-complexen in AgCl-microkristallen

Het zesde hoofdstuk beschrijft de poeder-EPR- en -ENDOR-studie van Rh\(^{2+}\)-complexen in AgCl-microkristallen bij X- en Q-band microgolffrequenties. De Q-band EPR-studie toont aan dat niet drie maar vier Rh\(^{2+}\)-centra gevormd kunnen worden in AgCl-microkristallen. Twee daarvan, R6 en R6\(^{'}\), komen ook in AgCl-éénkristallen voor. Ze worden respectievelijk geïdentificeerd als [RhCl\(_6\)]\(^{4+}\).0Vac (figuur 2c) en [RhCl\(_6\)]\(^{4+}\).1Vac (figuur 2b) complexen. Er wordt aangetoond dat door bestraling (of belichting) van AgCl-microkristallen enkel R6 complexen gevormd worden, terwijl er na verhitting (T > 100°C) zowel R6 als R6\(^{'}\) complexen aanwezig zijn.

![Diagram](a) (b)

**Figuur 3**: Structuurmodellen voor de R4 (a) en R5 (b) centra in AgCl microkristallen in fotografische emulsies. Het centrale Rh\(^{2+}\) ion wordt voorgesteld door een zwarte sfeer. De ionen van het rooster worden voorgesteld door grote (anionen) en kleine sferen (kationen). De grote blauwe sferen stellen heteroliganden (H\(_2\)O of OH\(^{-}\)) voor. In het geval van H\(_2\)O liganden stellen de kleine blauwe sferen kationvakatures voor, bij OH liganden staan ze voor Ag\(^{+}\)-ionen. In het ENDOR spectrum wordt een sterke interactie waargenomen met de axiale eerste schil anionen (groen), de vierde schil kationen (rood) en met één of meerdere equivalente protonen, behorend tot de heteroliganden. Voor elk complex zijn de hoofdassen van de g-tensor aangeduid.

Voor de overige twee, R4 en R5, zijn geen éénkristalgegevens beschikbaar. Uit de vergelijking van X- en Q-band EPR-spectra volgt dat R4 axiale symmetrie heeft en R5 rombisch is. In het ENDOR-spectrum van deze twee centra wordt een interactie met één of meerdere equivalente protonen waargenomen, die hoogstwaarschijnlijk tot de liganden van het Rh\(^{2+}\)-ion behoren. Verder toont ENDOR aan dat het R4 centrum een kleine rombische distorsie vertoont. Rekening houdend met de resultaten van het voorafgaande onderzoek van Dr. H. Vercammen [VERC98c] en met de resultaten van de studies op de modelsystemen, worden voor beide centra telkens twee mogelijke microscopische modellen voorgesteld. Die zijn weergegeven in figuur 3. Onze onderzoekresultaten worden ook uitgebreid vergeleken met die van een parallelle studie door de onderzoeksgroep van Eastman-Kodak [PAWL98].

Naast de identificatie van de Rh\(^{2+}\)-complexen in AgCl-microkristallen, wordt in dit hoofdstuk ook bijzondere aandacht geschonken aan de simulatie van poeder-ENDOR-spectra. Het effect van
geresolveerde superhyperfijnstructuur in het EPR-spectrum op de oriëntatieselectie en op de resulterende poeder ENDOR-spectra wordt uitgebreid besproken. De superhyperfijn-achtige structuren op de ENDOR-transities van de $^{103}$Rh-interactiv van R4, illustreert deze effecten heel goed. Voorts wordt de simulatie van poeder-ENDOR-spectra voor de interactie met de axiale chloorkernen in detail behandeld en worden de gebruikte benaderingen besproken.
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