Charge transfer from Eu^{2+} to trivalent lanthanide co-dopants: Systematic behavior across the series

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Jonas J. Joos,^{1,a)} Ivo Neeffjes,² Luis Seijo,³ and Zoila Barandiarán^{3,b)}

AFFILIATIONS

¹LumiLab, Department of Solid State Sciences, Ghent University, B-9000 Gent, Belgium

²Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

³Departamento de Química, Instituto Universitario de Ciencia de Materiales Nicolás Cabrera, and Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049 Madrid, Spain

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^{a)}Author to whom correspondence should be addressed: jonas.joos@UGent.be

^{b)}zoila.barandiaran@uam.es

ABSTRACT

Electron transfer processes between lanthanide activators are crucial for the functional behavior and performance of luminescent materials. Here, a multiconfigurational *ab initio* study reveals how direct metal-to-metal charge transfer (MMCT) between the Eu^{2+} luminescence activator and a Ln^{3+} co-dopant ($\text{Ln}^{3+} = \text{Ce}^{3+}, \text{Pr}^{3+}, \text{Nd}^{3+}, \text{Pm}^{3+}, \text{Sm}^{3+}, \text{Eu}^{3+}, \text{Gd}^{3+}, \text{Tb}^{3+}, \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}, \text{Tm}^{3+}, \text{and Yb}^{3+}$) systematically dictates the luminescence and optical properties of CaF_2 . The combination of the structures and energies of the electronic manifolds, the vibrational force constants, and the structural properties of the donor and acceptor in the host determines the predictions of five different behaviors of $\text{CaF}_2:\text{Eu}^{2+}$, Ln^{3+} co-doped materials after MMCT absorption: formation of stable traps, MMCT emission, emission quenching, Ln^{3+} emission, and Eu^{2+} emission.

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I. INTRODUCTION

Lanthanide ions are popular activators for luminescence and have been proposed for various applications. Specifically, divalent europium, Eu^{2+} , has attracted considerable attention thanks to its efficient and color-tunable luminescence, originating from parity and spin-allowed $4f^7 - 4f^65d^1$ transitions.^{1–6}

Lanthanide ions feature relatively low redox potentials, giving rise to stable divalent and tetravalent ions in addition to the trivalent ones.⁷ In mixed-valence compounds, intervalence charge transfer (IVCT) transitions can strongly alter the luminescence dynamics by quenching existing radiative decay channels or by introducing new ones.^{8–11}

The multivalent nature of lanthanide ions can be exploited further to introduce new functional behavior. In storage or

long-afterglow phosphors, a trivalent co-dopant is typically added to the Eu^{2+} activator, introducing a metastable metal-to-metal charge transfer (MMCT) state.¹² In Ce^{3+} -doped garnet scintillators, Ce^{4+} is intentionally added to accelerate the decay and, hence, improve the time response of the radiation detector.^{13,14} Recently, radiative decay of an $\text{Eu}^{2+}\text{-Tb}^{3+}$ charge transfer state was reported in CaS and used for broadband infrared LEDs.¹⁵

To date, the quest for suitable host–dopant–co-dopant combinations is largely based on exploring the considerable parameter space via an inefficient trial-and-error strategy. Empirical rules that aspire to predict the properties of lanthanide pairs are popular,^{16–18} yet, their accuracy is low and physical foundation is questionable, partly because they only account for electronic energies and ignore vibrational effects and geometrical changes

during the electron transfer.^{19,20} Improved models and accurate theory are, hence, required.

During the last few years, multiconfigurational *ab initio* embedded cluster calculations have explored the $4f^N$ and $4f^{N-1}5d^1$ excited states of lanthanide ions doped in solid hosts.^{21–27} In addition, it has been shown that diabatic combinations of such calculations on isolated ions in different oxidation states can successfully describe the optical spectra and other relevant features of IVCT and MMCT states.^{8–11,15,28–30} Here, this calculation method is systematically applied to study MMCT states of the co-doped materials $\text{CaF}_2:\text{Eu}^{2+}$, Ln^{3+} ($\text{Ln}^{3+} = \text{Ce}^{3+}$, Pr^{3+} , Nd^{3+} , Pm^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , and Yb^{3+}). After consideration of the effect of local vibrations and geometry changes upon electron transfer, systematic variations are found that predict distinct functional behaviors of co-doped materials.

II. COMPUTATIONAL METHOD

Diabatic potential energy surfaces for electron transfer states of $\text{Eu}^{2+}/\text{Ln}^{3+}$ pairs in CaF_2 ($\text{Ln} = \text{Ce}$, Pr , Nd , Pm , Sm , Eu , Gd , Tb , Dy , Ho , Er , Tm , and Yb) and the corresponding MMCT configuration coordinate many-electron energy level diagrams were calculated here following the procedure in Refs. 8 and 28, using the results of independent embedded cluster calculations from Ref. 30. They are aimed at describing spectroscopically relevant forward and backward electron transfers between Eu_{Ca} and Ln_{Ca} substitutional defects with non-local charge compensations. This level of calculation means a first step forward toward the understanding of electron transfer processes involving lanthanide impurities. More accurate configuration coordinate diagrams and oscillator strengths require much more computationally demanding adiabatic potential energy surfaces, which will have to be computed individually for each of the 13 lanthanide ionic pairs involved.

The electronic structures of the electron donor and acceptor octahedral embedded clusters $(\text{LnF}_8)^{6-}$ and $(\text{LnF}_8)^{5-}$ were obtained with the suite of programs MOLCAS,³¹ using D_{2h} symmetry, in two step spin-orbit coupling (SOC) SA-RASSCF/MS-RASPT2/RASSI-SO DKH calculations.³⁰ First, the spin-orbit-free many-electron relativistic second-order Douglas-Kroll-Hess (DKH) Hamiltonian^{32,33} was used to perform all-electron calculations with the same type of basis set used in the calculations of $\text{CaF}_2:\text{Yb}^{2+}$, Yb^{3+} in Ref. 9: Gaussian atomic natural orbital relativistic basis sets ANO-RCC for the lanthanides³⁴ and fluorine,³⁵ with respective contractions $(25s22p15d11f4g2h)/[9s8p5d4f3g2h]$ (quadruple zeta with polarization quality) and $(14s9p4d)/[5s4p3d]$ (quadruple zeta with polarization without *f*-function quality); plus the occupied 3s and 3p orbitals of the embedding Ca^{2+} ions, contracted as $(20s15p)/[1s1p]$ and located at the 12 neighbor sites $(\frac{1}{2}, \frac{1}{2}, 0)$, acting as cluster-host orthogonalization functions;³⁶ and 5 s-type Gaussian type functions located at the six $(\frac{1}{2}, 0, 0)$ interstitial sites surrounding the LnF_8 cube in the fluorite structure, whose orbital exponents were optimized to give a minimal impurity-trapped exciton energy in $\text{CaF}_2:\text{Yb}^{2+}$.⁹ State-average restricted active-space self-consistent field (SA-RASSCF)^{37–39} calculations were performed, allowing all possible occupations in

TABLE I. Lowest free-ion and O_h terms.

Ln^{2+}	Ln^{3+}	Config.	Free-ion term	O_h terms
	Ce^{3+}	$4f^1$	$^2F^o$	$^2A_{2u}$, $^2T_{1u}$, and $^2T_{2u}$
Ce^{2+}	Pr^{3+}	$4f^2$	3H	3E_g , 2^3T_{1g} , and $^3T_{2g}$
Pr^{2+}	Nd^{3+}	$4f^3$	$^4I^o$	$^4A_{1u}$, $^4A_{2u}$, 4E_u , $^4T_{1u}$, and 2^4T_{2u}
Nd^{2+}	Pm^{3+}	$4f^4$	5I	$^5A_{1g}$, $^5A_{2g}$, 5E_g , $^5T_{1g}$, and 2^5T_{2g}
Pm^{2+}	Sm^{3+}	$4f^5$	$^6H^o$	6E_u , 2^6T_{1u} , and $^6T_{2u}$
Sm^{2+}	Eu^{3+}	$4f^6$	7F	$^7A_{2g}$, $^7T_{1g}$, and $^7T_{2g}$
Eu^{2+}	Gd^{3+}	$4f^7$	$^8S^o$	$^8A_{1u}$
Gd^{2+}	Tb^{3+}	$4f^8$	7F	$^7A_{2g}$, $^7T_{1g}$, and $^7T_{2g}$
Tb^{2+}	Dy^{3+}	$4f^9$	$^6H^o$	6E_u , 2^6T_{1u} , and $^6T_{2u}$
Dy^{2+}	Ho^{3+}	$4f^{10}$	5I	$^5A_{1g}$, $^5A_{2g}$, 5E_g , $^5T_{1g}$, and 2^5T_{2g}
Ho^{2+}	Er^{3+}	$4f^{11}$	$^4I^o$	$^4A_{1u}$, $^4A_{2u}$, 4E_u , $^4T_{1u}$, and 2^4T_{2u}
Er^{2+}	Tm^{3+}	$4f^{12}$	3H	3E_g , 2^3T_{1g} , and $^3T_{2g}$
Tm^{2+}	Yb^{3+}	$4f^{13}$	$^2F^o$	$^2A_{2u}$, $^2T_{1u}$, and $^2T_{2u}$
Yb^{2+}		$4f^{14}$	1S	$^1A_{1g}$

the Ln 4*f* shells and up to four electrons in the Ln 5*f* shells, in order to account for the so-called double-shell effect.^{40–42} During the variational calculation, state averaging was performed over all states of equal spin and spatial irreducible representation, resulting from the ligand-field splitting of the lowest free-ion lanthanide ion *LS* terms. The accounted states are listed in Table I. Subsequent, multi-state second-order perturbation theory (MS-RASPT2)^{43–46} calculations allowed us to correlate all cluster valence electrons, except the 4*d* electrons of the lanthanides. A standard IPEA value of 0.25 a.u.⁴⁷ and an imaginary shift of 0.15 a.u.⁴⁸ were used.

Second, the atomic mean-field integral (AMFI) approximation of the DKH spin-orbit coupling (SOC) operator was added to the Hamiltonian⁴⁹ and restricted active-space state-interaction spin-orbit (RASSI-SO)^{50,51} calculations were performed where all states of a given cluster computed in the first step were allowed to interact.

In these calculations, the clusters were embedded in *ab initio* model potentials (AIMPs)⁵² that include Coulomb, exchange, and Pauli repulsion interactions from the CaF_2 host lattice obtained in Ref. 9 from self-consistent embedded-ion (SCEI)⁵³ Hartree-Fock calculations.

III. RESULTS AND DISCUSSION

Figure 1 displays the calculated MMCT diagrams for all $\text{Eu}^{2+}/\text{Ln}^{3+}$ pairs in CaF_2 . These diagrams correspond to a one-dimensional cross section in the two-dimensional (d_D , d_A) configurational space, where d_D and d_A denote the donor-ligand (Eu-ligand in current cases) and acceptor-ligand (Ln-ligand in current cases) distances, i.e., the breathing mode normal coordinates

CaF₂ : Eu, Ln

FIG. 1. (a)–(m) Metal-to-metal charge transfer (MMCT) configuration coordinate many-electron energy diagrams of Eu²⁺/Ln³⁺ pairs in CaF₂. (n) Legend for the curves in (a)–(m). The colors of the curves indicate the electron configuration or dominant total spin according to the legends in (n).

of both clusters. The one-dimensional cross section is made along the electron transfer reaction coordinate, Q_{et} , as defined by the piecewise straight line that connects the (d_D , d_A) values of the equilibrium structures of the ground (D_0A_0) and lowest MMCT state

($D_0^+A_0^-$) with their saddle point, i.e., the activated complex (ac).^{8,28} It is obtained from

$$Q_{\text{et}} = \frac{1}{\sqrt{1+m^2}} \left[\sqrt{n_A} (d_A - d_{A_c}) + m \sqrt{n_D} (d_D - d_{D_c}) \right], \quad (1)$$

TABLE II. Properties of MMCT configuration coordinate diagrams of $\text{Eu}^{2+}/\text{Ln}^{3+}$ pairs in CaF_2 , as obtained from the diabatic combination of *ab initio* calculations on individual Eu^{2+} , Eu^{3+} , Ln^{3+} , and Ln^{2+} active centers. These properties are defined in Fig. 2: $E_{\text{MMCT},0}$ and $E_{\text{MMCT}}^{\text{abs}}$ represent the vertical offset and Franck–Condon absorption energies between the ground state and the lowest MMCT state, respectively. $E_{\text{MMCT}}^{\text{abs,back}}$ is the Franck–Condon absorption energy from the lowest MMCT state toward the structurally stressed electronic ground state. $Q_{\text{et},0}$, $Q_{\text{et},c}$, and $Q_{\text{et},c'}$ are the values of the electron transfer coordinate in the lowest MMCT state equilibrium structure, the crossing between the ground state and the lowest MMCT state, and the crossing between the highest level of the ground state LS term and the lowest MMCT state. Energies are given in cm^{-1} and distances in Å.

Pair	<i>N</i>	$E_{\text{MMCT},0}$	$E_{\text{MMCT}}^{\text{abs}}$	$E_{\text{MMCT}}^{\text{abs,back}}$	$Q_{\text{et},0}$	$Q_{\text{et},c}$	$Q_{\text{et},c'}$	Potential decay after MMCT absorption
$\text{Eu}^{2+}/\text{Ce}^{3+}$	1	37 550	51 760	−23 050	0.496	0.891	0.817	Eu^{2+} <i>d</i> – <i>f</i> emission
$\text{Eu}^{2+}/\text{Pr}^{3+}$	2	25 430	40 000	−10 710	0.498	0.679	0.586	Quenching
$\text{Eu}^{2+}/\text{Nd}^{3+}$	3	22 810	37 450	−8 090	0.500	0.633	0.506	Quenching
$\text{Eu}^{2+}/\text{Pm}^{3+}$	4	20 560	35 310	−5 830	0.500	0.596	0.458	Quenching
$\text{Eu}^{2+}/\text{Sm}^{3+}$	5	11 930	26 450	+2 680	0.496	0.451	0.323	e^- trapping
$\text{Eu}^{2+}/\text{Eu}^{3+}$	6	0	15 250	+15 250	0.508	0.254	0.164	Quenching
$\text{Eu}^{2+}/\text{Gd}^{3+}$	7	42 400	57 020	−27 780	0.500	0.966	0.966	Eu^{2+} <i>d</i> – <i>f</i> emission
$\text{Eu}^{2+}/\text{Tb}^{3+}$	8	29 640	44 260	−14 780	0.502	0.749	0.644	MMCT emission
$\text{Eu}^{2+}/\text{Dy}^{3+}$	9	21 260	36 020	−6 360	0.504	0.609	0.428	Quenching
$\text{Eu}^{2+}/\text{Ho}^{3+}$	10	23 230	38 050	−8 300	0.506	0.640	0.388	Ln^{3+} <i>f</i> – <i>f</i> emission
$\text{Eu}^{2+}/\text{Er}^{3+}$	11	24 660	39 420	−9 680	0.506	0.666	0.396	Ln^{3+} <i>f</i> – <i>f</i> emission
$\text{Eu}^{2+}/\text{Tm}^{3+}$	12	17 730	32 430	−2 840	0.504	0.551	0.309	Quenching
$\text{Eu}^{2+}/\text{Yb}^{3+}$	13	7 950	23 020	+7 290	0.512	0.387	0.202	e^- trapping

where

$$m = \begin{cases} \frac{d_{\text{D}_{\text{ac}}} - d_{\text{D}_0}}{d_{\text{A}_{\text{ac}}} - d_{\text{A}_0}}, & \text{D}_0\text{A}_0 \rightarrow \text{ac} \\ \frac{d_{\text{D}_0^+} - d_{\text{D}_{\text{ac}}}}{d_{\text{A}_0^-} - d_{\text{A}_{\text{ac}}}}, & \text{ac} \rightarrow \text{D}_0^+\text{A}_0^-, \end{cases} \quad (2)$$

n_{D} and n_{A} represent the coordination numbers of the donor (D) and acceptor (A), and d_{D_e} and d_{A_e} correspond to the equilibrium structures.

The diabatic low-lying states are obtained by combining the $\text{Eu}^{2+} 4f^7 (^8S_{7/2})$ state with the lowest Ln^{3+} LS (or ^{2S+1}L) term (see Table I), which is split into *LSJ* (or $^{2S+1}L_J$) multiplets by spin–orbit coupling. (Note that, for simplicity, we are using a simplified atomic description of the real manifolds of O_h molecular states based on their main character.) These low-lying $\text{Eu}^{2+}\text{–Ln}^{3+}$ states are displayed in black.

For completeness, the levels of the excited $\text{Eu}^{2+} 4f^6 5d_e^1$ manifold, as calculated and discussed in Ref. 27, are added. The associated pair levels are in combination with the Ln^{3+} ground state and are colored in green and red, indicating the dominant high-spin (HS) or low-spin (LS) nature of the corresponding $\text{Eu}^{2+} 4f^6 5d_e^1$ level, respectively. The $\text{Eu}^{2+} 4f^7 \leftrightarrow 4f^6 5d^1$ transitions are responsible for the luminescent properties of Eu^{2+} -doped phosphors, and it is, therefore, important to include these excited states in the discussion on the interaction between the lanthanide dopants.

The lowest levels of the $\text{Eu}^{3+}\text{–Ln}^{2+}$ MMCT configurations of the pairs are added in orange and gray as indicated in the legend, Fig. 1(n). They start at an energy $E_{\text{MMCT},0}$ above the ground state (third column in Table II). In the following, systematic variations

of the MMCT properties across the lanthanide series of co-dopants will be discussed by means of a few quantities that are introduced in Fig. 2 and given in Table II.

The vertical offset $E_{\text{MMCT},0}$ (equilibrium energy of the lowest level of the $\text{Eu}^{3+}\text{–Ln}^{2+}$ MMCT configuration) is predominantly determined by the ionization potential (IP) of the Eu^{2+} donor and the electron affinity (EA) of the Ln^{3+} acceptor.⁹ Long-range Coulomb repulsion between both lanthanide centers remains approximately the same after MMCT transition due to the conjugate

FIG. 2. Definitions of the quantities that characterize the MMCT configuration and associated transitions in the case of MMCT electron trapping (a) or MMCT emission (b).

oxidation numbers (2+ and 3+ vs 3+ and 2+) and is assumed to be state-independent. Therefore, Ln^{3+} EA variation across the series determines the variation of the vertical offsets. This is illustrated in Figs. 1(a)–1(m) and 3, where the well-known zigzag curve is found, encompassing the relative stabilities of the $4f^N$ configurations.⁵⁴ For $\text{Eu}^{2+}\text{--}\text{Ln}^{3+}$, the vertical offset is zero due to the indistinguishability of the initial and final states when non-local charge compensation is assumed. This case of homonuclear MMCT is referred to as intervalence charge transfer (IVCT)⁵⁵ and is discussed at length elsewhere for mixed-valence lanthanide pairs in CaF_2 and other hosts.^{11,30}

The onset of the MMCT radiative absorption $E_{\text{MMCT}}^{\text{abs}}$, i.e., the photon energy that corresponds to a vertical (Frank–Condon) $\text{Eu}^{2+}\text{--}\text{Ln}^{3+}$ CT absorption, shows a similar zigzag shape, with an approximately constant difference of $14\,715 \pm 240\text{ cm}^{-1}$ across the series. This is the relaxation or reorganization energy after radiative electron transfer, basically due to the ligand contraction around Eu^{3+} after the electron is gone from Eu^{2+} plus the simultaneous ligand expansion around Ln^{2+} after the electron arrival to Ln^{3+} .

Broad MMCT absorption bands are expected due to such important reorganizations, which are quantified by the large horizontal offsets between both minima, $Q_{\text{et},0}$ (difference between the values of the electron transfer coordination coordinate in the $\text{Eu}^{3+}\text{--}\text{Ln}^{2+}$ and $\text{Eu}^{2+}\text{--}\text{Ln}^{3+}$ configurations), and the numerous electronic origins due to the dense MMCT manifold. Experimental observations of IVCT or MMCT transitions are very scarce due to the small absorption strengths derived from a combination of low MMCT oscillator strengths and the random distributions of lanthanide ions in crystals, but they are, indeed, very broad when observed.^{11,15}

The crossings of the branches of the low-lying $\text{Eu}^{2+}\text{--}\text{Ln}^{3+}$ states with the MMCT configuration $\text{Eu}^{3+}\text{--}\text{Ln}^{2+}$ are essential for understanding the properties of $\text{Eu}^{2+}/\text{Ln}^{3+}$ pairs and consequently for assessing the possibility of adding functionality to a Eu^{2+} -doped phosphor upon Ln^{3+} co-doping.

Of particular importance, due to the obvious impacts on the luminescent properties of the co-doped materials, is to identify cases of potential metastability of the $\text{Eu}^{3+}\text{--}\text{Ln}^{2+}$ MMCT configuration of an $\text{Eu}^{2+}/\text{Ln}^{3+}$ pair, which could act as an energy storage or electron

trap and get involved in trapping/detrapping phenomena, and cases of potential metastability of the $\text{Eu}^{3+}\text{--}\text{Ln}^{2+}$ MMCT configuration that could radiatively decay, which would yield $\text{Ln}^{2+}\text{--}\text{to--Eu}^{3+}$ MMCT emission. Both cases can compete with non-radiative decay of the MMCT state. This may result in luminescence quenching when the ground state is reached (either directly or through intermediate states), but it can also yield other luminescences when a metastable excited state of Eu^{2+} or of the Ln^{3+} co-dopant is accessed. Let us now discuss all these possibilities.

(a) Electron trapping [Fig. 4(a)]. Potentially metastable $\text{Eu}^{3+}\text{--}\text{Ln}^{2+}$ configurations of the pairs allowing for electron trapping are identified when the electron transfer coordinate at the minimum of the lowest MMCT state, $Q_{\text{et},0}$, is significantly longer than that at the crossing point between the ground state and the lowest MMCT state potential energy surfaces, $Q_{\text{et},c}$ ($Q_{\text{et},0} > Q_{\text{et},c}$). Alternatively, they are identified when the energy of an eventual radiative electron back transfer $E_{\text{MMCT}}^{\text{abs,back}}$ is positive (i.e., the Frank–Condon absorption of a photon can transfer the electron back from Ln^{2+} to Eu^{3+}), which is an equivalent condition [see Fig. 4(a)]. This energy is the difference between the structurally stressed ground state in the MMCT equilibrium structure and the MMCT minimum.

The pairs with such potentially metastable MMCT states are $\text{Eu}^{2+}/\text{Sm}^{3+}$ and $\text{Eu}^{2+}/\text{Yb}^{3+}$, which indicates that $\text{CaF}_2\text{:Eu}^{2+}$, Sm^{3+} and $\text{CaF}_2\text{:Eu}^{2+}$, Yb^{3+} potentially allow temporary energy storage, which is often termed trapping and detrapping from the viewpoint of the transferred electron.⁵⁶ Interestingly, this phenomenon has been experimentally shown to exist in $\text{Eu}^{2+}/\text{Sm}^{3+}$ pairs in CaF_2 and not to exist in $\text{Eu}^{2+}/\text{Tm}^{3+}$ pairs.^{57,58}

(b) MMCT emission [Fig. 4(b)]. A second possibility exists when the electron transfer coordinate is significantly shorter at the minimum of the lowest MMCT state than at the crossing points of the MMCT state with the ground state ($Q_{\text{et},0} < Q_{\text{et},c}$) and with the highest of the $\text{Eu}^{2+}\text{--}\text{Ln}^{3+}$ low-lying states ($Q_{\text{et},0} < Q_{\text{et},c'}$). In this case, the MMCT state can be metastable unless it crosses at its minimum with higher excited states (see below). If it is metastable, the radiative electron back transfer from Ln^{2+} to Eu^{3+} can be accompanied by a photon emission ($E_{\text{MMCT}}^{\text{abs,back}} < 0$) and potential $\text{Ln}^{2+}\text{--}\text{to--Eu}^{3+}$ MMCT emission could occur from the lowest metastable MMCT configuration.

The pairs with such potentially metastable MMCT states in Fig. 1 are $\text{Eu}^{2+}/\text{Pr}^{3+}$ and $\text{Eu}^{2+}/\text{Tb}^{3+}$. However, a more detailed study of the Pr^{3+} dopant $4f^2$ manifold shows that the lowest *SLJ* multiplets associated with the 3H , 3F , and 1G free ion terms do interact and overlap.⁵⁹ As a result, the number and energy spread of excited states right above the $\text{Eu}^{2+}\text{--}\text{Pr}^{3+}$ ground state are larger than those in Fig. 1(b), precluding the stability of the lowest MMCT configuration by crossings. This is the only case, in the whole Ln^{3+} co-doped series, where the single-*SLJ* multiplet simplification is a drawback. Hence, MMCT emission should only be expected from $\text{Eu}^{2+}/\text{Tb}^{3+}$ pairs. As a matter of fact, diabatic calculations and experiments have successfully shown the respective presence and absence of MMCT emission of $\text{Eu}^{2+}/\text{Tb}^{3+}$ pairs in CaS and SrS .¹⁵

(c) Eu^{2+} *d-f* emission [Fig. 4(c)]. As we remarked above, when $Q_{\text{et},0} < Q_{\text{et},c'}$, it is still possible that the MMCT crosses at its minimum with a higher excited state. These are the cases of Ce^{3+} and Gd^{3+} co-dopants, where the vertical offset $E_{\text{MMCT},0}$ is sufficiently high that the MMCT configuration is resonant with the structurally

FIG. 3. Evolution of the vertical offset ($E_{\text{MMCT},0}$, green) between the minima of the $\text{Eu}^{2+}\text{--}\text{Ln}^{3+}$ and $\text{Eu}^{3+}\text{--}\text{Ln}^{2+}$ ground states (gs) and the associated Frank–Condon absorption energy ($E_{\text{MMCT}}^{\text{abs}}$, red), for $\text{Eu}^{2+}/\text{Ln}^{3+}$ pairs in CaF_2 as a function of the co-dopant $4f$ shell occupation, N .

FIG. 4. Potential phenomena triggered by MMCT absorption: (a) electron trapping and (b) MMCT emission. Lower row: (c) Eu^{2+} d - f emission, (d) quenching, and (e) Ln^{3+} f - f emission.

stressed Eu^{2+} - Ln^{3+} levels whereby Eu^{2+} is in the excited $4f^6 5d^1$ configuration. In these cases, MMCT absorption can excite Eu^{2+} d - f emission.

Additional possibilities exist when the electron transfer coordinate at the minimum of the lowest MMCT state is intermediate between the crossing points of this state with the lowest and highest Eu^{2+} - Ln^{3+} low-lying states ($Q_{\text{et},c'} < Q_{\text{et},0} < Q_{\text{et},c}$) or when it is very similar to one of them. In such cases, small energy barriers for $\text{Eu}^{3+} + \text{Ln}^{2+} \rightarrow \text{Eu}^{2+} + \text{Ln}^{3+}$ thermal electron back transfer are likely to occur and high probabilities of non-radiative decays that compete with electron trapping and MMCT emission should be expected.^{60–62} These non-radiative decays open two particular possibilities.

(d) Quenching [Fig. 4(d)]. Non-radiative decay from the lowest MMCT state to the ground state is expected when the MMCT state is crossed at its minimum by the ground state ($Q_{\text{et},0} \approx Q_{\text{et},c}$). This appears to be the case of $\text{Eu}^{2+}/\text{Tm}^{3+}$ pairs. But quenching is also possible through crossing with unstable intermediate Eu^{2+} - Ln^{3+} low-lying states that relax further down to the ground state through a crowded set of low-lying states. This is the case of $\text{Eu}^{2+}/\text{Pr}^{3+}$, $\text{Eu}^{2+}/\text{Nd}^{3+}$, $\text{Eu}^{2+}/\text{Pm}^{3+}$, and $\text{Eu}^{2+}/\text{Dy}^{3+}$ pairs.

(e) Ln^{3+} f - f emission [Fig. 4(e)]. When the Ln^{3+} ion has a not so crowded $4f^n$ manifold and metastable low-lying states, it is possible that the MMCT state is crossed at its minimum by a

metastable intermediate Eu^{2+} - Ln^{3+} low-lying state and the non-radiative decay yields Ln^{3+} luminescence. This can be the case of $\text{Eu}^{2+}/\text{Ho}^{3+}$ and $\text{Eu}^{2+}/\text{Er}^{3+}$ pairs.

Finally, it is worth mentioning possible detrimental effects of Ln^{3+} co-doping on the important $\text{CaF}_2:\text{Eu}^{2+}$ luminescence: As the vertical offset $E_{\text{MMCT},0}$ goes down in energy toward the Sm^{3+} co-dopant and, again, toward the Tm^{3+} and Yb^{3+} heavier co-dopants, the corresponding stressed branches of the lowest MMCT states may serve as non-radiative channels to depopulate the Eu^{2+} $4f^6 5d^1$ emitting state through crossings with no or small energy barriers. In the latter case, the thermal quenching of the $5d \rightarrow 4f$ luminescence of Eu^{2+} ions that are coupled to a Ln^{3+} co-dopant could be affected. The diagram in Fig. 1(f) shows that the presence of Eu^{3+} can also quench the luminescence of Eu^{2+} as explained in Ref. 11.

IV. CONCLUSIONS

Metal-to-metal charge transfer (MMCT) states of $\text{Eu}^{2+}/\text{Ln}^{3+}$ pairs in CaF_2 ($\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}, \text{Pm}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}, \text{and Yb}$) were studied using diabatic configuration coordinate diagrams based on multiconfigurational *ab initio* RASSCF/RASPT2/RASSI-SO calculations of isolated lanthanide

active centers. They allow us to systematize and predict the different behaviors of $\text{CaF}_2\text{:Eu}^{2+}$, Ln^{3+} co-doped materials across the series after MMCT absorption: formation of stable traps, MMCT emission, Eu^{2+} emission, Ln^{3+} emission, and emission quenching. This work shows the potential of accurate multiconfigurational calculations in the quest for host–dopant–co-dopant combinations capable of inducing different functional behaviors of interest in luminescent materials.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- P. Pust, V. Weiler, C. Hecht, A. Tücks, A. S. Wochnik, A.-K. Henß, D. Wiechert, C. Scheu, P. J. Schmidt, and W. Schnick, "Narrow-band red-emitting $\text{Sr}[\text{LiAl}_3\text{N}_4]\text{:Eu}^{2+}$ as a next-generation LED-phosphor material," *Nat. Mater.* **13**, 891–896 (2014).
- X. Qin, X. Liu, W. Huang, M. Bettinelli, and X. Liu, "Lanthanide-activated phosphors based on $4f-5d$ optical transitions: Theoretical and experimental aspects," *Chem. Rev.* **117**, 4488–4527 (2017).
- J. Qiao, M. Amachraa, M. Molokeev, Y.-C. Chuang, S. P. Ong, Q. Zhang, and Z. Xia, "Engineering of $\text{K}_3\text{YSi}_2\text{O}_7$ to tune photoluminescence with selected activators and site occupancy," *Chem. Mater.* **31**, 7770–7778 (2019).
- J. Qiao, G. Zhou, Y. Zhou, Q. Zhang, and Z. Xia, "Divalent europium-doped near-infrared-emitting phosphor for light-emitting diodes," *Nat. Commun.* **10**, 5267 (2019).
- M. Zhao, H. X. Liao, M. S. Molokeev, Y. Zhou, Q. Zhang, Q. Liu, and Z. Xia, "Emerging ultra-narrow-band cyan-emitting phosphor for white LEDs with enhanced color rendition," *Light: Sci. Appl.* **8**, 38 (2019).
- T. Wylezich, A. D. Sontakke, V. Castaing, M. Suta, B. Viana, A. Meijerink, and N. Kunkel, "One ion, many facets: Efficient, structurally and thermally sensitive luminescence of Eu^{2+} in binary and ternary strontium borohydride chlorides," *Chem. Mater.* **31**, 8957–8968 (2019).
- M. Suta and C. Wickleder, "Synthesis, spectroscopic properties and applications of divalent lanthanides apart from Eu^{2+} ," *J. Lumin.* **210**, 210–238 (2019).
- L. Seijo and Z. Barandiarán, "Intervalence charge transfer luminescence: The anomalous luminescence of cerium-doped $\text{Cs}_2\text{LiLuCl}_6$ elpasolite," *J. Chem. Phys.* **141**, 214706 (2014).
- Z. Barandiarán and L. Seijo, "Intervalence charge transfer luminescence: Interplay between anomalous and $5d-4f$ emissions in Yb-doped fluorite-type crystals," *J. Chem. Phys.* **141**, 234704 (2014).
- R. B. Hughes-Currie, K. V. Ivanovskikh, J.-P. R. Wells, M. F. Reid, R. A. Gordon, L. Seijo, and Z. Barandiarán, "X-ray excitation triggers ytterbium anomalous emission in $\text{CaF}_2\text{:Yb}$ but not in $\text{SrF}_2\text{:Yb}$," *J. Phys. Chem. Lett.* **8**, 1175–1178 (2017).
- J. J. Joos, L. Seijo, and Z. Barandiarán, "Direct evidence of intervalence charge-transfer states of Eu-doped luminescent materials," *J. Phys. Chem. Lett.* **10**, 1581–1586 (2019).
- J. J. Joos, K. Korthout, L. Amidani, P. Glatzel, D. Poelman, and P. F. Smet, "Identification of $\text{Dy}^{3+}/\text{Dy}^{2+}$ as electron trap in persistent phosphors," *Phys. Rev. Lett.* **125**, 033001 (2020).
- S. Liu, J. A. Mares, X. Feng, A. Vedda, M. Fasoli, Y. Shi, H. Kou, A. Beitelrova, L. Wu, C. D'Ambrosio, Y. Pan, and M. Nikl, "Towards bright and fast $\text{Lu}_3\text{Al}_5\text{O}_{12}\text{:Ce,Mg}$ optical ceramics scintillators," *Adv. Opt. Mater.* **4**, 731–739 (2016).
- G. Dantelle, G. Boulon, Y. Guyot, D. Testemale, M. Guzik, S. Kurosawa, K. Kamada, and A. Yoshikawa, "Research on efficient fast scintillators: Evidence and X-ray absorption near edge spectroscopy characterization of Ce^{4+} in Ce^{3+} , Mg^{2+} -Co-doped $\text{Gd}_3\text{Al}_2\text{Ga}_3\text{O}_{12}$ garnet crystal," *Phys. Status Solidi B* **257**, 1900510 (2020).
- J. J. Joos, D. Van der Heggen, L. I. D. J. Martin, L. Amidani, P. F. Smet, Z. Barandiarán, and L. Seijo, "Broadband infrared LEDs based on europium-to-terbium charge transfer luminescence," *Nat. Commun.* **11**, 3647 (2020).
- P. Dorenbos, "Modeling the chemical shift of lanthanide $4f$ electron binding energies," *Phys. Rev. B* **85**, 165107 (2012).
- P. Dorenbos, "A review on how lanthanide impurity levels change with Chemistry and structure of inorganic compounds," *ECS J. Solid State Sci. Technol.* **2**, R3001 (2013).
- P. Dorenbos, A. J. J. Bos, N. R. J. Poolton, and F. You, "Photon controlled electron juggling between lanthanides in compounds," *J. Lumin.* **133**, 45–50 (2013).
- A. Zych, J. Ogieglo, C. Ronda, C. D. Mello Donegá, and A. Meijerink, "Analysis of the shift of zero-phonon lines for $f-d$ luminescence of lanthanides in relation to the Dorenbos model," *J. Lumin.* **134**, 174–179 (2013).
- J. J. Joos, D. Poelman, and P. F. Smet, "Energy level modeling of lanthanide materials: Review and uncertainty analysis," *Phys. Chem. Chem. Phys.* **17**, 19058–19078 (2015).
- G. Sánchez-Sanz, L. Seijo, and Z. Barandiarán, "Electronic spectra of Yb^{2+} -doped SrCl_2 ," *J. Chem. Phys.* **133**, 114506 (2010).
- G. Sánchez-Sanz, L. Seijo, and Z. Barandiarán, " Yb^{2+} -doped SrCl_2 : Electronic structure of impurity states and impurity-trapped excitons," *J. Chem. Phys.* **133**, 114509 (2010).
- L. Seijo and Z. Barandiarán, "Host effects on the optically active $4f$ and $5d$ levels of Ce^{3+} in garnets," *Phys. Chem. Chem. Phys.* **15**, 19221–19231 (2013).
- M. Krośnicki, A. Kędziorowski, L. Seijo, and Z. Barandiarán, "Ab initio theoretical study on the $4f(2)$ and $4f5d$ electronic manifolds of cubic defects in $\text{CaF}_2\text{:Pr}^{3+}$," *J. Phys. Chem. A* **118**, 358–368 (2014).
- J. L. Pascual, Z. Barandiarán, and L. Seijo, "Ab initio theoretical study of the $4f^6$ and $4f^7 5d$ manifolds of Tb^{3+} -doped BaF_2 cubic sites," *J. Lumin.* **145**, 808–817 (2014).
- M. de Jong, A. Meijerink, L. Seijo, and Z. Barandiarán, "Energy level structure and multiple $4f^{12}5d^1$ emission bands for Tm^{2+} in halide perovskites: Theory and experiment," *J. Phys. Chem. C* **121**, 10095–10101 (2017).
- J. J. Joos, P. F. Smet, L. Seijo, and Z. Barandiarán, "Insights into the complexity of the excited states of Eu-doped luminescent materials," *Inorg. Chem. Front.* **7**, 871–888 (2020).
- Z. Barandiarán and L. Seijo, "Metal-to-metal charge transfer between dopant and host ions: Photoconductivity of Yb-doped CaF_2 and SrF_2 crystals," *J. Chem. Phys.* **143**, 144702 (2015).
- Z. Barandiarán, A. Meijerink, and L. Seijo, "Configuration coordinate energy level diagrams of intervalence and metal-to-metal charge transfer states of dopant pairs in solids," *Phys. Chem. Chem. Phys.* **17**, 19874–19884 (2015).
- I. Neefjes, J. J. Joos, Z. Barandiarán, and L. Seijo, "Mixed-valence lanthanide-activated phosphors: Invariance of the intervalence charge transfer (IVCT) absorption onset across the series," *J. Phys. Chem. C* **124**, 2619–2626 (2020).
- G. Karlström, R. Lindh, P.-Å. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Schimmelpfennig, P. Neogrady, and L. Seijo, "Molcas: A program package for computational Chemistry," *Comput. Mater. Sci.* **28**, 222–239 (2003).
- M. Douglas and N. M. Kroll, "Quantum electrodynamical corrections to the fine structure of helium," *Ann. Phys.* **82**, 89–155 (1974).
- B. A. Hess, "Relativistic electronic-structure calculations employing a two-component No-pair formalism with external-field projection operators," *Phys. Rev. A* **33**, 3742–3748 (1986).

- ³⁴B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, P.-O. Widmark, and A. C. Borin, "New relativistic atomic natural orbital basis sets for lanthanide atoms with applications to the Ce diatom and LuF₃," *J. Phys. Chem. A* **112**, 11431–11435 (2008).
- ³⁵B. O. Roos, R. Lindh, P.-Å. Malmqvist, V. Veryazov, and P.-O. Widmark, "Main group Atoms and dimers studied with a new relativistic ANO basis set," *J. Phys. Chem. A* **108**, 2851–2858 (2004).
- ³⁶J. L. Pascual, L. Seijo, and Z. Barandiarán, "Ab Initio model potential study of environmental effects on the Jahn–Teller parameters of Cu²⁺ and Ag²⁺ impurities in MgO, CaO, and SrO hosts," *J. Chem. Phys.* **98**, 9715–9724 (1993).
- ³⁷B. O. Roos, P. R. Taylor, and P. E. M. Siegbahn, "A complete active space SCF method (CASSCF) using a density-matrix formulated super-CI approach," *Chem. Phys.* **48**, 157–173 (1980).
- ³⁸P. Siegbahn, A. Heiberg, B. Roos, and B. Levy, "Comparison of the super-CI and the Newton-raphson scheme in the complete active space SCF method," *Phys. Scr.* **21**, 323–327 (1980).
- ³⁹P. E. M. Siegbahn, J. Almlöf, A. Heiberg, and B. O. Roos, "The complete active space SCF (CASSCF) method in a Newton-raphson formulation with application to the HNO molecule," *J. Chem. Phys.* **74**, 2384–2396 (1981).
- ⁴⁰C. F. Fischer, "Oscillator strengths for ²S–²P transitions in the copper sequence," *J. Phys. B* **10**, 1241–1251 (1977).
- ⁴¹T. H. Dunning, B. H. Botch, and J. F. Harrison, "On the orbital description of the 4s3dⁿ⁺¹ states of the transition-metal atoms," *J. Chem. Phys.* **72**, 3419–3420 (1980).
- ⁴²Z. Barandiarán and L. Seijo, "Radial correlation effects on interconfigurational excitations at the end of the lanthanide series: A restricted active space second order perturbation study of Yb²⁺ and SrCl₂:Yb²⁺," *J. Chem. Phys.* **138**, 074102 (2013).
- ⁴³K. Andersson, P. A. Malmqvist, B. O. Roos, A. J. Sadlej, and K. Wolinski, "Second-order perturbation theory with a CASSCF reference function," *J. Phys. Chem.* **94**, 5483–5488 (1990).
- ⁴⁴K. Andersson, P. Å. Malmqvist, and B. O. Roos, "Second-order perturbation theory with a complete active space self-consistent field reference function," *J. Chem. Phys.* **96**, 1218–1226 (1992).
- ⁴⁵A. Zaitsevskii and J.-P. Malrieu, "Multi-partitioning quasidegenerate perturbation theory. A new approach to multireference möller-Plesset perturbation theory," *Chem. Phys. Lett.* **233**, 597–604 (1995).
- ⁴⁶J. Finley, P.-Å. Malmqvist, B. O. Roos, and L. Serrano-Andrés, "The multi-state CASPT2 method," *Chem. Phys. Lett.* **288**, 299–306 (1998).
- ⁴⁷G. Ghigo, B. O. Roos, and P.-Å. Malmqvist, "A modified definition of the zeroth-order Hamiltonian in multiconfigurational perturbation theory (CASPT2)," *Chem. Phys. Lett.* **396**, 142 (2004).
- ⁴⁸N. Forsberg and P.-Å. Malmqvist, "Multiconfiguration perturbation theory with imaginary level shift," *Chem. Phys. Lett.* **274**, 196–204 (1997).
- ⁴⁹B. A. Heß, C. M. Marian, U. Wahlgren, and O. Gropen, "A mean-field spin-orbit method applicable to correlated wavefunctions," *Chem. Phys. Lett.* **251**, 365–371 (1996).
- ⁵⁰R. Llusar, M. Casarrubios, Z. Barandiarán, and L. Seijo, "Ab initio model potential calculations on the electronic spectrum of Ni²⁺-doped MgO including correlation, spin-orbit and embedding effects," *J. Chem. Phys.* **105**, 5321–5330 (1996).
- ⁵¹P. Å. Malmqvist, B. O. Roos, and B. Schimmelpfennig, "The RASSI approach with spin-orbit coupling," *Chem. Phys. Lett.* **357**, 230–240 (2002).
- ⁵²Z. Barandiarán and L. Seijo, "The ab initio model potential representation of the crystalline environment. Theoretical study of the local distortion on NaCl:Cu⁺," *J. Chem. Phys.* **89**, 5739–5746 (1988).
- ⁵³L. Seijo and Z. Barandiarán, "Ab initio model potential study of local distortions around Cr⁺ and Cr³⁺," *J. Chem. Phys.* **94**, 8158 (1991).
- ⁵⁴L. R. Morss, "Thermochemical properties of yttrium, lanthanum, and the lanthanide elements and ions," *Chem. Rev.* **76**, 827–841 (1976).
- ⁵⁵J. W. Verhoeven, "Glossary of terms used in photochemistry," *Pure Appl. Chem.* **68**, 2223–2286 (1996).
- ⁵⁶A. J. J. Bos, "Theory of thermoluminescence," *Radiat. Meas.* **41**, S45–S56 (2006).
- ⁵⁷B. Welber, "Reversible phototransfer of electrons between rare-earth ions in CaF₂," *J. Chem. Phys.* **42**, 4262–4264 (1965).
- ⁵⁸P. P. Feofilov, "Electron phototransfer in single crystals MeF₂ doped with Eu and Sm," *Opt. Spectrosc.* **12**, 531–533 (1962).
- ⁵⁹Z. Barandiarán, M. Bettinelli, and L. Seijo, "Color control of Pr³⁺ luminescence by electron-hole recombination energy transfer in CaTiO₃ and CaZrO₃," *J. Phys. Chem. Lett.* **8**, 3095–3100 (2017).
- ⁶⁰C. W. Struck and W. H. Fonger, "Unified model of temperature quenching of narrow-line and broad-band emissions," *J. Lumin.* **10**, 1–30 (1975).
- ⁶¹C. W. Struck and W. H. Fonger, "Temperature quenching of luminescence for linear and derivative nuclear operators," *J. Lumin.* **14**, 253–279 (1976).
- ⁶²M. Grinberg, A. Mandelis, and K. Fjeldsted, "Theory of interconfigurational nonradiative transitions in transition-metal ions in solids and application to the Ti³⁺ Al₂O₃ system," *Phys. Rev. B* **48**, 5935–5944 (1993).