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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 (Ln$^{3+}$ = 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$^{3+}$) 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 CaF$_2$: 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.

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 $4f^7 - 4f^55d^1$ transitions.

Lanthanide ions feature relatively low redox potentials, giving rise to stable divalent and tetravalent ions in addition to the trivalent ones. 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.

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. 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. Recently, radiative decay of an Eu$^{2+}$–Tb$^{3+}$ charge transfer state was reported in CaS and used for broadband infrared LEDs.

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; 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.
II. COMPUTATIONAL METHOD

Diabatic potential energy surfaces for electron transfer states of Eu$^{2+}$/Ln$^{3+}$ pairs in CaF$_2$ (Ln = Ce, Pr, Nd, 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 ion pairs involved.

The electronic structures of the electron donor and acceptor octahedral embedded clusters (LnF$_3$)$_6^{6-}$ and (LnF$_3$)$_5^{5-}$ were obtained with the suite of programs MOLCAS, using $D_{3h}$ symmetry, in two step spin–orbit coupling (SOC) SA-RASSCF/MS-RASPT2/RASSI-SO DKH calculations. First, the spin–orbit–free many-electron relativistic second-order Douglas–Kroll–Hess (DKH) Hamiltonian $^{23,25}$ was used to perform all-electron calculations with the same type of basis set used in the calculations of CaF$_2$:Yb$^{3+}$, Yb$^{3+}$ in Ref. 9; Gaussian atomic natural orbital relativistic basis sets ANO-RCC for the lanthanides$^{45}$ and fluorine, with respective contractions (25s22p15d11f4g2h)/[9s8p5d4f3g2h] (quadruple zeta with polarization quality) and (14s9p4d4f)/[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)/[11s8p5d] and located at the 12 neighbor sites ($\frac{1}{2}, \frac{1}{2}, 0$) on the resulting cluster-host orthogonalization functions$^{39}$ and 5 s-type Gaussian type functions located at the six ($\frac{1}{2}, 0, 0$) interstitial sites surrounding the LnF$_3$ cube in the fluorite structure, whose orbital exponents were optimized to give an minimal impurity-trapped exciton energy in CaF$_2$:Yb$^{3+}$. State-average restricted active-space self-consistent field (SA-RASSCF)$^{27,29}$ calculations were performed, allowing all possible occupations in the Ln 4f shells and up to four electrons in the Ln 5f shells, in order to account for the so-called double-shell effect$^{32,41}$. During the variational calculation, state averaging was performed over all states of equal spin and spatial irreducible representations, 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)$^{27,29}$ calculations allowed us to correlate all cluster valence electrons, except the 4d electrons of the lanthanides. A standard IPEA value of 0.25 a.u. and an imaginary shift of 0.15 a.u. were used.

Second, the atomic mean-field integral (AMFI) approximation of the DKH spin–orbit coupling (SOC) operator was added to the Hamiltonian$^{22}$ and restricted active-space state-interaction spin–orbit (RASSI-SO)$^{27,29}$ 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)$^{37}$ that include Coulomb, exchange, and Pauli repulsion interactions from the CaF$_2$ host lattice obtained in Ref. 9 from self-consistent embedded-ion (SCEI)$^{24}$ Hartree–Fock calculations.

III. RESULTS AND DISCUSSION

Figure 1 displays the calculated MMCT diagrams for all Eu$^{2+}$/Ln$^{3+}$ pairs in CaF$_2$. These diagrams correspond to a one-dimensional cross section in the two-dimensional ($d_d$, $d_s$) configurational space, where $d_d$ and $d_s$ 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.

**Table I. Lowest free-ion and $O_h$ terms.**

<table>
<thead>
<tr>
<th>Ln$^{3+}$</th>
<th>Ln$^{3+}$</th>
<th>Free-ion term</th>
<th>$O_h$ terms</th>
</tr>
</thead>
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<tr>
<td>Ce$^{3+}$</td>
<td>4f$^1$</td>
<td>$^2F'$</td>
<td>$^2A_{2u}$, $^2T_{1u}$ and $^2T_{2u}$</td>
</tr>
<tr>
<td>Ce$^{3+}$</td>
<td>4f$^2$</td>
<td>$^3H$</td>
<td>$^2E_g$, $^2T_{1g}$ and $^3T_{2g}$</td>
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<tr>
<td>Pr$^{3+}$</td>
<td>4f$^3$</td>
<td>$^4I$</td>
<td>$^4A_{1u}$, $^4A_{2u}$, $^4E_u$, $^4T_{1u}$, and $^4T_{2u}$</td>
</tr>
<tr>
<td>Pr$^{3+}$</td>
<td>4f$^4$</td>
<td>$^5I$</td>
<td>$^5A_{1g}$, $^5A_{2g}$, $^5E_g$, $^5T_{1g}$, and $^5T_{2g}$</td>
</tr>
<tr>
<td>Nd$^{3+}$</td>
<td>4f$^5$</td>
<td>$^6H$</td>
<td>$^6E_u$, $^6T_{1u}$, and $^6T_{2u}$</td>
</tr>
<tr>
<td>Sm$^{3+}$</td>
<td>4f$^6$</td>
<td>$^7F$</td>
<td>$^7A_{2g}$, $^7T_{1g}$, and $^7T_{2g}$</td>
</tr>
<tr>
<td>Eu$^{3+}$</td>
<td>4f$^7$</td>
<td>$^8S$</td>
<td>$^8A_{1u}$</td>
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<tr>
<td>Gd$^{3+}$</td>
<td>4f$^8$</td>
<td>$^9F$</td>
<td>$^9A_{2g}$, $^9T_{1g}$, and $^9T_{2g}$</td>
</tr>
<tr>
<td>Tb$^{3+}$</td>
<td>4f$^9$</td>
<td>$^{10}I$</td>
<td>$^{10}A_{1g}$, $^{10}A_{2g}$, $^{10}E_g$, $^{10}T_{1g}$, and $^{10}T_{2g}$</td>
</tr>
<tr>
<td>Dy$^{3+}$</td>
<td>4f$^{10}$</td>
<td>$^{11}I$</td>
<td>$^{11}A_{1g}$, $^{11}A_{2g}$, $^{11}E_g$, $^{11}T_{1g}$, and $^{11}T_{2g}$</td>
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<tr>
<td>Ho$^{3+}$</td>
<td>4f$^{11}$</td>
<td>$^{12}I$</td>
<td>$^{12}A_{1g}$, $^{12}A_{2g}$, $^{12}E_g$, $^{12}T_{1g}$, and $^{12}T_{2g}$</td>
</tr>
<tr>
<td>Er$^{3+}$</td>
<td>4f$^{12}$</td>
<td>$^{13}I$</td>
<td>$^{13}A_{1g}$, $^{13}A_{2g}$, $^{13}E_g$, $^{13}T_{1g}$, and $^{13}T_{2g}$</td>
</tr>
<tr>
<td>Tm$^{3+}$</td>
<td>4f$^{13}$</td>
<td>$^{14}I$</td>
<td>$^{14}A_{1g}$, $^{14}A_{2g}$, $^{14}E_g$, $^{14}T_{1g}$, and $^{14}T_{2g}$</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>4f$^{14}$</td>
<td>$^{15}I$</td>
<td>$^{15}A_{1g}$</td>
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</tbody>
</table>

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FIG. 1. (a)–(m) Metal-to-metal charge transfer (MMCT) configuration coordinate many-electron energy diagrams of Eu$^{2+}$/Ln$^{3+}$ pairs in CaF$_2$. (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). It is obtained from

$$Q_{et} = \frac{1}{\sqrt{1 + m^2}} \left[ \sqrt{\eta} (d_A - d_{A_0}) + m \sqrt{\eta} (d_D - d_{D_0}) \right],$$

(1)
The vertical offset $E_{\text{MMCT},0}$ (equilibrium energy of the lowest level of the Eu$^{2+}$–Ln$^{3+}$ 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. Long-range Coulomb repulsion between both lanthanide centers remains approximately the same after MMCT transition due to the conjugate 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 diabatic low-lying states are obtained by combining the Eu$^{2+}$ 4$f^6(5$S$_{1/2}$) state with the lowest Ln$^{3+}$ LS (or 5$S_{1/2}$L) term (see Table I), which is split into LSJ (or 5$S_{1/2}$L) 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 Eu$^{2+}$–Ln$^{3+}$ states are displayed in black.

For completeness, the levels of the excited Eu$^{2+}$ 4$f^65d^1$ 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 Eu$^{2+}$ 4$f^65d^1$ level, respectively. The Eu$^{2+}$ 4$f^6 \leftrightarrow 4f^55d^1$ 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 Eu$^{2+}$–Ln$^{3+}$ 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

Table II. Properties of MMCT configuration coordinate diagrams of Eu$^{2+}$–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$^{3+}$ 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. $E_{\text{MMCT},\text{back}}$ is the Franck–Condon absorption energy from the lowest MMCT state toward the structurally stressed electronic ground state. $Q_{\text{rel},0}$, $Q_{\text{rel},c}$, and $Q_{\text{rel},e}$ 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.

<table>
<thead>
<tr>
<th>Pair</th>
<th>$N$</th>
<th>$E_{\text{MMCT},0}$</th>
<th>$E_{\text{MMCT},\text{abs}}$</th>
<th>$E_{\text{MMCT},\text{back}}$</th>
<th>$Q_{\text{rel},0}$</th>
<th>$Q_{\text{rel},c}$</th>
<th>$Q_{\text{rel},e}$</th>
<th>Potential decay after MMCT absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu$^{2+}$/Ce$^{3+}$</td>
<td>1</td>
<td>37 550</td>
<td>51 760</td>
<td>−23 050</td>
<td>0.495</td>
<td>0.891</td>
<td>0.817</td>
<td>Eu$^{2+}$ d–f emission</td>
</tr>
<tr>
<td>Eu$^{2+}$/Pr$^{3+}$</td>
<td>2</td>
<td>25 430</td>
<td>40 000</td>
<td>−10 710</td>
<td>0.498</td>
<td>0.679</td>
<td>0.586</td>
<td>Quenching</td>
</tr>
<tr>
<td>Eu$^{2+}$/Nd$^{3+}$</td>
<td>3</td>
<td>22 810</td>
<td>37 450</td>
<td>−8 090</td>
<td>0.500</td>
<td>0.633</td>
<td>0.506</td>
<td>Quenching</td>
</tr>
<tr>
<td>Eu$^{2+}$/Sm$^{3+}$</td>
<td>4</td>
<td>20 560</td>
<td>35 310</td>
<td>−5 830</td>
<td>0.500</td>
<td>0.596</td>
<td>0.458</td>
<td>Quenching</td>
</tr>
<tr>
<td>Eu$^{2+}$/Eu$^{3+}$</td>
<td>5</td>
<td>11 930</td>
<td>26 450</td>
<td>+2 680</td>
<td>0.495</td>
<td>0.451</td>
<td>0.323</td>
<td>e$^-$ trapping</td>
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<tr>
<td>Eu$^{2+}$/Gd$^{3+}$</td>
<td>6</td>
<td>9 530</td>
<td>0</td>
<td>+15 250</td>
<td>0.508</td>
<td>0.254</td>
<td>0.164</td>
<td>Quenching</td>
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<tr>
<td>Eu$^{2+}$/ Tb$^{3+}$</td>
<td>7</td>
<td>42 400</td>
<td>57 020</td>
<td>−27 780</td>
<td>0.500</td>
<td>0.966</td>
<td>0.966</td>
<td>Eu$^{2+}$ d–f emission</td>
</tr>
<tr>
<td>Eu$^{2+}$/Tb$^{3+}$</td>
<td>8</td>
<td>29 640</td>
<td>44 260</td>
<td>−14 780</td>
<td>0.502</td>
<td>0.749</td>
<td>0.644</td>
<td>MMCT emission</td>
</tr>
<tr>
<td>Eu$^{2+}$/Dy$^{3+}$</td>
<td>9</td>
<td>21 260</td>
<td>36 020</td>
<td>−6 360</td>
<td>0.504</td>
<td>0.609</td>
<td>0.428</td>
<td>Quenching</td>
</tr>
<tr>
<td>Eu$^{2+}$/Ho$^{3+}$</td>
<td>10</td>
<td>23 230</td>
<td>38 050</td>
<td>−8 300</td>
<td>0.506</td>
<td>0.640</td>
<td>0.388</td>
<td>Ln$^{3+}$ f–f emission</td>
</tr>
<tr>
<td>Eu$^{2+}$/Er$^{3+}$</td>
<td>11</td>
<td>24 660</td>
<td>39 420</td>
<td>−9 680</td>
<td>0.506</td>
<td>0.666</td>
<td>0.396</td>
<td>Ln$^{3+}$ f–f emission</td>
</tr>
<tr>
<td>Eu$^{2+}$/Tm$^{3+}$</td>
<td>12</td>
<td>17 730</td>
<td>32 430</td>
<td>−2 840</td>
<td>0.504</td>
<td>0.551</td>
<td>0.309</td>
<td>Quenching</td>
</tr>
<tr>
<td>Eu$^{2+}$/Yb$^{3+}$</td>
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<td>7 950</td>
<td>23 020</td>
<td>+7 290</td>
<td>0.512</td>
<td>0.387</td>
<td>0.202</td>
<td>e$^-$ trapping</td>
</tr>
</tbody>
</table>
oxidation numbers (2+ and 3+ vs 3+ and 2+) and is assumed to be state-independent. Therefore, Ln3+/2+ 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 configurations. For Eu2+/3+−Eu3+/2+, 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) and is discussed at length elsewhere for mixed-valence lanthanide pairs in CaF2 and other hosts.

The onset of the MMCT radiative absorption $E_{\text{MMCT}}^{\text{abs}}$, i.e., the photon energy that corresponds to a vertical (Frank–Condon) Eu2+/3+−Ln3+/2+ CT absorption, shows a similar zigzag shape, with an approximately constant difference of 14715 ± 240 cm$^{-1}$ across the series. This is the relaxation or reorganization energy after radiative electron transfer, basically due to the ligand contraction around Eu3+ after the electron is gone from Eu2+. The crossings of the branches of the low-lying Eu2+/3+−Ln3+/2+ MMCT absorption bands are expected due to such important reorganizations, which are quantified by the large horizontal offsets between both minima, $Q_{\text{et}}$, (difference between the values of the electron transfer coordination coordinate in the Eu3+/2+−Ln3+/2+ and Eu2+/3+−Ln3+/2+ 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.

The crossings of the branches of the low-lying Eu2+/3+−Ln3+/2+ states with the MMCT configuration Eu3+/2+−Ln3+/2+ are essential for understanding the properties of Eu2+/3+−Ln3+/2+ pairs and consequently for assessing the possibility of adding functionality to an Eu2+/3+−Ln3+/2+ pair, which could act as an energy storage or electron trap and get involved in trapping/detrappping phenomena, and cases of potential metastability of the Eu3+/2+−Ln3+/2+ MMCT configuration that could radiatively decay, which would yield Ln3+/2+−Eu3+/2+ 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 Eu3+ or of the Ln3+ co-dopant is accessed. Let us now discuss all these possibilities.

(a) Electron trapping [Fig. 4(a)]. Potentially metastable Eu2+/3+−Ln3+/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 $E_{\text{abs},\text{back}}^{\text{MMCT}}$ is positive (i.e., the Frank–Condon absorption of a photon can transfer the electron back from Ln3+ to Eu2+), 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.

Broad MMCT absorption bands are expected due to such potentially metastable MMCT states are Eu2+/3+−Sm3+/2+ and Eu2+/3+−Yb3+/2+, which indicates that CaF2:Eu3+/2+, Sm3+ and CaF2:Eu3+/2+, Yb3+ potentially allow temporary energy storage, which is often termed trapping and detrapping from the viewpoint of the transferred electron.26 Interestingly, this phenomenon has been experimentally shown to exist in Eu3+/2+/Sm3+ pairs in CaF2 and not to exist in Eu3+/2+/Tm3+ pairs.27,28

(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 Eu3+/2+−Ln3+/2+ 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 Ln3+ to Eu2+ can be accompanied by a photon emission ($E_{\text{abs},\text{back}}^{\text{MMCT}} > 0$) and potential Ln3+/2+−Eu3+ MMCT emission could occur from the lowest metastable MMCT configuration.

The pairs with such potentially metastable MMCT states in Fig. 1 are Eu2+/3+/Pr3+ and Eu2+/3+/Tb3+. However, a more detailed study of the Pr3+ dopant 4f manifold shows that the lowest SLJ multiplets associated with the 4H, 4F, and 4G free ion terms do interact and overlap.27 As a result, the number and energy spread of excited states right above the Eu2+/3+−Pr3+ 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 Ln3+/2+−Tm3+ co-doped series, where the single-SLJ multiplet simplification is a drawback. Hence, MMCT emission should only be expected from Eu2+/3+/Tb3+ pairs. As a matter of fact, diabatic calculations and experiments have successfully shown the respective presence and absence of MMCT emission of Eu2+/3+/Tb3+ pairs in CaS and SrS.12

(c) Eu2+/3+−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 Ce3+ and Gd3+ co-dopants, where the vertical offset $E_{\text{MMCT}}^{\text{abs}}$ is sufficiently high that the MMCT configuration is resonant with the structurally
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 (\(Q_{et,c} < Q_{et,0} < Q_{et,c}\)) or when it is very similar to one of them. In such cases, small energy barriers for Eu\(^{3+}\) + Ln\(^{2+}\) → Eu\(^{2+}\) + 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 (\(Q_{et,0} \approx Q_{et,c}\)). This appears to be the case of Eu\(^{2+}\)/Tm\(^{3+}\) pairs. But quenching is also possible through crossing with unstable intermediate Eu\(^{3+}\)–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 Eu\(^{2+}\)/Pr\(^{3+}\), Eu\(^{2+}\)/Nd\(^{3+}\), Eu\(^{2+}\)/Pm\(^{3+}\), and Eu\(^{2+}\)/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 Eu\(^{2+}\)/Ho\(^{3+}\) and Eu\(^{2+}\)/Er\(^{3+}\) pairs.

Finally, it is worth mentioning possible detrimental effects of Ln\(^{3+}\) co-doping on the important CaF\(_2\):Eu\(^{2+}\) luminescence: As the vertical offset \(E_{MMCT,0}\) 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 → 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 Eu\(^{2+}\)/Ln\(^{3+}\) pairs in CaF\(_2\) (Ln = Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) were studied using diabatic configuration coordinate diagrams based on multiconfigurational \textit{ab initio} RASSCF/RASPT2/RASSI-SO calculations of isolated lanthanide
active centers. They allow us to systematize and predict the different behaviors of CaF₂:Eu³⁺, Ln³⁺ co-doped materials across the series after MMCT absorption: formation of stable traps, MMCT emission, Eu³⁺ emission, Ln³⁺ 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


