Intervalence Charge Transfer Luminescence: Interplay between anomalous and $5d-4f$ emissions in Yb-doped fluoride-type crystals.

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(Dated: November 24, 2014)

In this paper we report the existence of intervalence charge transfer (IVCT) luminescence in Yb-doped fluoride-type crystals associated with Yb$^{3+}$–Yb$^{3+}$ mixed valence pairs. By means of embedded cluster, wave function theory $ab$ initio calculations, we show that the widely studied, very broad band, anomalous emission of Yb$^{3+}$-doped CaF$_2$ and SrF$_2$, usually associated with impurity-trapped excitons, is, rather, an IVCT luminescence associated with Yb$^{3+}$–Yb$^{3+}$ mixed valence pairs. The IVCT luminescence is very efficiently excited by a two-photon upconversion mechanism where each photon provokes the same strong 4$f^{14}$-$\text{L}A_{1g}$$\rightarrow$$4f^{13}(\text{F}_{7/2})5\text{d}e_g$-$1\text{I}_{1u}$ absorption in the Yb$^{2+}$ part of the pair: the first one, from the pair ground state; the second one, from an excited state of the pair whose Yb$^{3+}$ moiety is in the higher 4$f^{13}(\text{F}_{5/2})$ multiplet. The Yb$^{3+}$–Yb$^{3+}$ $\rightarrow$ Yb$^{3+}$–Yb$^{3+}$ IVCT emission consists of an Yb$^{3+}$ 5$\text{d}e_g$ $\rightarrow$ Yb$^{3+}$ 4$f_{5/2}$ charge transfer accompanied by a 4$f_{7/2}$$\rightarrow$ 4$f_{5/2}$ deexcitation within the Yb$^{3+}$ 4$f^{13}$ subshell: [2$\text{F}_{5/2}$5$\text{d}e_g$,$\text{F}_{7/2}$] $\rightarrow$ [2$\text{F}_{5/2}$4$\text{f}^{14}$]. The IVCT vertical transition leaves the oxidized and reduced moieties of the pair after electron transfer very far from their equilibrium structures; this explains the unexpectedly large band width of the emission band and its low peak energy, because the large reorganization energies are subtracted from the normal emission. The IVCT energy diagrams resulting from the quantum mechanical calculations explain the different luminescent properties of Yb-doped CaF$_2$, SrF$_2$, BaF$_2$, and SrCl$_2$: the presence of IVCT luminescence in Yb-doped CaF$_2$ and SrF$_2$; its coexistence with regular 5$\text{d}$-$4f$ emission in SrF$_2$; its absence in BaF$_2$ and SrCl$_2$: the quenching of all emissions in BaF$_2$; and the presence of additional 5$\text{d}$-$4f$ emissions in SrCl$_2$ which are absent in SrF$_2$. They also allow to interpret and reproduce recent experiments on transient photoluminescence enhancement in Yb$^{3+}$-doped CaF$_2$ and SrF$_2$, the appearance of Yb$^{3+}$ 4$f^{3/2}$ absorption bands in the excitation spectra of the IR Yb$^{3+}$ emission in partly reduced CaF$_2$:Yb$^{3+}$ samples, and to identify the broad band observed in the excitation spectrum of the so far called anomalous emission of SrF$_2$:Yb$^{3+}$ as an IVCT absorption, which corresponds to an Yb$^{3+}$ 4$f_{5/2}$$\rightarrow$ Yb$^{3+}$ 4$f_{5/2}$ electron transfer.

Keywords: $ab$ initio, IVCT, electron transfer, Yb$^{3+}$, Yb$^{3+}$, fluorites, anomalous emission, luminescence

1. INTRODUCTION

The capability of lanthanide ion dopants to luminesce from their 4$\text{f}^{n}$ and/or 4$\text{f}^{n-1}5\text{d}$ excited states has granted them a prominent role as activators in solid state lighting, lasers, fiber amplifiers, and medical imaging devices[18]. Frequently, however, their applicability is compromised by quenching or by replacement of the expected luminescence by an anomalous emission. Detailed understanding of these mechanisms is important in the search for new interesting phosphor and scintillating materials based on lanthanide ion activators.

The anomalous emission of Yb$^{2+}$ in Yb-doped materials is a prototypical case (for a review on the anomalous emission of Yb$^{3+}$ and Eu$^{2+}$-doped crystals, see Ref. [5]). The interplay between anomalous and 5$d$-$4f$ emissions in Yb$^{2+}$-doped fluoride-type crystals results in a complex electronic spectroscopy, which has been the focus of investigations for decades[25,26]. The adjective anomalous has been used to reflect the irregular, unexpected, very large Stokes shift of the emission observed, with respect to the 4$f^{14}$$\rightarrow$ 4$f^{13}5\text{d}$ excitation, which makes the red shifted emission band extremely broad. When Yb$^{2+}$ is doped in CaF$_2$, the anomalous emission prevails[25,26] but also occurs in SrF$_2$, where both, anomalous emission and regular 4$f^{13}5\text{d}$$\rightarrow$ 4$f^{14}$ luminescence have been detected together[25,26] and no emission whatsoever occurs in BaF$_2$ up to 1.5$\mu$m[31,32]. Changing the ligand, as in the SrF$_2$ and SrCl$_2$ series, also affects the interplay. The dual character of the luminescence of Yb in SrF$_2$ disappears in the SrCl$_2$ host, where the anomalous emission is not observed; only regular 5$d$-$4f$ emission bands have been assigned in this case showing a complex temperature behaviour[19,20]. Analyses of spectroscopic data have suggested that the anomalous emission observed in Yb$^{3+}$-doped CaF$_2$ and SrF$_2$ is associated with an excited state which has a “radically different” (smaller) radiative rate compared with that of higher lying levels. This characteristic has allowed the application of a two-frequency UV + IR transient photoluminescence enhancement technique which ultimately produces the IR excited state absorption spectrum (ESA) from the lowest anomalous state to close lying energy levels[19,20]. The anomalous emission of Yb has also been observed in Yb$^{3+}$-doped CaF$_2$ after application of reducing conditions[22].

Analogous competitions between regular 5$d$-$4f$ (as well as 4$f-$4$f$) and anomalous emissions have been reported involving other commonly used lanthanide ion activators: Ce$^{3+}$, Pr$^{3+}$, and Eu$^{3+}$[8,9,17,19]. For all of them (including Yb$^{3+}$), it is recognized that it is difficult to prevent the coexistence of another different valence state[19,20,22] which means that the formation of mixed valence pairs, that is, pairs between two metal sites differing only in oxidation
state, is very likely. In this way, occurrence of Ce\(^{3+}\)–Ce\(^{4+}\), Pr\(^{3+}\)–Pr\(^{4+}\), Eu\(^{2+}\)–Eu\(^{3+}\), and Yb\(^{2+}\)–Yb\(^{3+}\) mixed valence pairs should be expected, to some extent. In this paper we show that the study of the electronic structure of Yb\(^{2+}\)–Yb\(^{3+}\) mixed valence pairs is crucial to understand anomalous emission and its interplay with regular emissions in Yb-doped fluoride-type crystals. The same is true for Ce\(^{3+}\)–Ce\(^{4+}\) pairs, as we show in an analogous study of the anomalous emission in Ce\(^{3+}\)-doped Cs\(_2\)LiLuF\(_6\) elpasolite.\(^{23}\)

Since mixed valence pairs (for lanthanides: Ln\(^{n+}\)–Ln\(^{(n+1)+}\)) constitute a donor–acceptor (DA) redox system, electron transfer between the donor and acceptor sites, Ln\(^{n+}\) + Ln\(^{(n+1)+}\) → Ln\(^{(n+1)+}\) + Ln\(^{n+}\), may occur, and the process can be referred to as an intervalence charge transfer (IVCT)\(^{23}\) in analogy with the IVCT processes that have been investigated involving mostly mixed valence transition metal compounds\(^{23,43,44}\) and, scarcely, lanthanide ions.\(^{23,24}\) Although most IVCT studies refer to thermally and radiatively induced electron transfer between the ground states of the donor and acceptor sites, we show here that the D + A → A + D reaction can involve many of the excited electronic states of the mixed valence pair and lead to a variety of non-radiative and radiative IVCT processes.

The goal of this paper is to show that all of the spectral features we have summarized above for Yb\(^{2+}\)-doped CaF\(_2\), SrF\(_2\), BaF\(_2\), and SrCl\(_2\) hosts can be explained if the existence of Yb\(^{2+}\)–Yb\(^{3+}\) mixed valence pairs is assumed, \textit{ab initio} multielectronic wavefunction-based diabatic potential energy surfaces of the ground and excited states of the embedded Yb\(^{2+}\)–Yb\(^{3+}\) active pairs are calculated, and quantitative energy diagrams for the Yb\(^{2+}\) + Yb\(^{3+}\) → Yb\(^{3+}\) + Yb\(^{2+}\) electron transfer reaction, along well defined reaction coordinates, are produced. In this framework, the anomalous emission of Yb-doped fluoride-type crystals is interpreted as an Yb\(^{2+}\)–Yb\(^{3+}\) → Yb\(^{3+}\)–Yb\(^{2+}\) IVCT emission, in which an Yb\(^{2+}\) 5d\(_e\) → Yb\(^{3+}\) 4f\(_{5/2}\) electron transfer and a 4f\(_{5/2}\) → 4f\(_{5/2}\) deexcitation within the Yb\(^{2+}\) 4f\(^{13}\) subshell take place: \([2\,4f_{5/2} 5d_{e}\rightarrow 2\,4f_{7/2}]\rightarrow [2\,4f_{7/2} 4f_{14}^{14}]\). So, the bielectronic character of this IVCT luminescence explains the very slow radiative decay rate of the so far called anomalous emission. Its very large band width comes from the large change in the electron transfer reaction coordinate accompanying the electronic transition: \(|\Delta Q_{DA}| = 0.49 \text{ Å (CaF}_2\text{),} 0.60 \text{ Å (SrF}_2\text{)}\). Its occurrence and temperature quenching in CaF\(_2\) and SrF\(_2\), including its coexistence with regular 5d–4f emission in SrF\(_2\) below 140 K, or its absence in BaF\(_2\) and SrCl\(_2\), including the absence of any emission in BaF\(_2\), can be understood on the basis of changes in the topology of the diabatic IVCT energy diagrams of the Yb\(^{2+}\) – Yb\(^{3+}\) intravalence pairs in the different hosts. The IR ESA spectra measured in CaF\(_2\) and SrF\(_2\) are also reproduced, showing a close, upper lying state, which may contribute a much faster monoionoctic Yb\(^{2+}\) 5d\(_e\) → Yb\(^{3+}\) 4f\(_{5/2}\) IVCT emission, plus a number of other close lying upper levels which contribute to the transient photoluminescence enhancement.

In parallel to this work, we are presenting analogous studies on the nature of the anomalous luminescence of Ce-doped Cs\(_2\)LiLuCl\(_4\) and its interplay with regular emissions.\(^{23}\) There, the fast anomalous emission of Ce is identified as a monoionoctic Ce\(^{3+}\) 5d\(_e\) → Ce\(^{3+}\) 4f IVCT luminescence, which is observed and calculated to be above the lowest, regular 5d\(_e\) → 4f emission of the Ce\(^{3+}\) active center. That work and the present paper are part of an effort focused on assessing and showing the relevance of intervalence charge transfer processes in the optical properties of very common lanthanide ions activators. Both works show that IVCT luminescence has been observed experimentally, but has not been identified as such, neither in Yb\(^{2+}\)-doped nor in Ce\(^{3+}\)-doped crystals. The same is true for other IVCT processes which are predicted and have not been identified or observed (i.e. transient IVCT photoluminescence enhancement, other IVCT absorptions, emissions, and non-radiative energy transfers). Altogether, the results presented so far suggest that the theoretical effort should continue and cover other common hosts and activators like those mentioned above; they also suggest that incorporating quantitative IVCT energy diagrams to experimental analyses should be useful.\(^{23}\)

This paper is organized as follows: In Sec. II we describe the \textit{ab initio} calculation of intervalence charge transfer potential energy surfaces of Yb\(^{2+}\)–Yb\(^{3+}\) pairs in fluoride-type crystals and the corresponding IVCT configuration coordinate diagrams. In Sec. III we interpret the anomalous luminescence of CaF\(_2\)–Yb\(^{3+}\) as an IVCT luminescence, we explain its mechanism and we discuss the involvement of IVCT states in transient photoluminescence enhancement experiments and in the excitation of the IR Yb\(^{3+}\) emission by Yb\(^{2+}\) 4f–5d absorptions. Finally, in Sec. IV we show that changes in the topology of the IVCT energy diagrams account for the interplay between IVCT and regular 5d–4f emissions in the chemical series of fluoride-type crystals CaF\(_2\), SrF\(_2\), BaF\(_2\) (Sec. [VA]) and SrF\(_2\), SrCl\(_2\) (Sec. [VB]). The conclusions are summarized in Sec. V.

II. POTENTIAL ENERGY SURFACES OF YB\(^{2+}\)–YB\(^{3+}\) ACTIVE PAIRS IN FLUORITE-TYPE CRYSTALS

In this Section we describe how the diabatic potential energy surfaces of the ground and excited states of Yb\(^{2+}\)–Yb\(^{3+}\) mixed valence active pairs can be calculated in the CaF\(_2\), SrF\(_2\), BaF\(_2\), and SrCl\(_2\) (MX\(_2\)) hosts using the potential energy surfaces obtained from independent Yb\(^{2+}\) and Yb\(^{3+}\) embedded cluster calculations as building blocks. From them, quantitative IVCT energy diagrams can be built in terms of normal electron transfer reaction coordinates which involve concerted vibrational breathing modes of the donor (YbX\(_3\))\(^{6+}\) and acceptor (YbX\(_3\))\(^{5+}\) sites. The approximations involved in this procedure are outlined; their accuracy is expected to be sufficient to achieve the goals of this work, which have been stated in the Introduction.
A. Yb\(^{2+}\)–Yb\(^{3+}\) diabatic potential energy surfaces

A convenient definition for the diabatic wavefunctions and energies of the Yb\(^{2+}\)–Yb\(^{3+}\) mixed valence pairs can be set up using generalized antisymmetric product functions, resulting from the combination of the \(n_D\) states of the donor \(D\) and \(n_A\) states of the acceptor \(A\) states, which in this work are the states of the 4f\(^{14}\), 4f\(^{13}5d_{x^2}\), 4f\(^{13}5d_{12}\), and 4f\(^{13}\)\(^{1}S\) manifolds of the donor (YbX\(_6\))\(^{6-}\) and those of the 4f\(^{13}\) manifold of the acceptor (YbX\(_6\))\(^{5-}\) separated embedded clusters, respectively. So, from the combination of the state \(i\) of \(D\), \(\Phi_{Di}\), and the state \(j\) of \(A\), \(\Phi_{Aj}\), two diabatic wavefunctions are obtained: one for the \(ij\) state of \(DA\), \(M\(\Phi_{Di}\Phi_{Aj}\)) and one for the \(ji\) state of \(AD\), \(M\(\Phi_{Ai}\Phi_{Dj}\)) (\(M\) is a normalization constant and \(A\) is the inter-group antisymmetrization operator:\(^{24}\))

\[
E_{Di Aj}^{\text{diab}} = M\left(\Phi_{Di}\Phi_{Aj}\right) [\hat{H}] M\left(\Phi_{Aj}\Phi_{Di}\right),
\]

\[
E_{Aj Di}^{\text{diab}} = M\left(\Phi_{Aj}\Phi_{Di}\right) [\hat{H}] M\left(\Phi_{Di}\Phi_{Aj}\right).
\]

Given that the electronic spectroscopic transitions are dominated by the totally symmetric vibrational coordinates, the breathing modes of the donor (YbX\(_6\))\(^{6-}\) and acceptor (YbX\(_6\))\(^{5-}\) sites are the only vibrational degrees of freedom we will consider, which results in the parametric dependence of the diabatic potential energy surfaces on the Yb–X distance in the left and right components of the \(DA\) and \(AD\) pairs, \(d_L\) and \(d_R\). \(E_{Di Aj}^{\text{diab}}(d_L, d_R)\) and \(E_{Aj Di}^{\text{diab}}(d_L, d_R)\). Note that \(E_{Di Aj}^{\text{diab}}(x, y) = E_{Aj Di}^{\text{diab}}(y, x)\). The two diabatic potential energy surfaces for the ground state 00 of the Yb\(^{2+}\)–Yb\(^{3+}\) mixed valence pair in Yb-doped CaF\(_2\), \(E_{\text{D0A0}}^{\text{diab}}(d_L, d_R)\) and \(E_{\text{A0D0}}^{\text{diab}}(d_L, d_R)\), can be seen in Fig.\(^{1}\).

It is important to note that in this work the electronic coupling between any two diabatic states \(ij\) of \(D\) and \(kl\) of \(AD\), \(V_{Di Aj, kDl}^{\text{diab}}\), \(M\left(\Phi_{Di}\Phi_{Aj}\right) [\hat{H}] M\left(\Phi_{kD}\Phi_{l}\right)\), will be neglected for all values of the \(d_L\) and \(d_R\) coordinates. As a consequence, there will be no avoided crossings among the diabatic potential energy surfaces nor mixings between the diabatic states. Whereas this approximation can be expected to be a good one away from the intersection regions, it becomes weaker on them, since the diabatic energies at intersections give upperbounds to the energy barriers that would result from avoided crossings should the electronic couplings be considered. We comment further on this issue in the next section where diabatic energy diagrams for the electron transfer reactions will be extracted from the diabatic energy surfaces. As we will show in this work, many spectroscopic features of the mixed valence pairs can be addressed quantitatively or semiquantitatively within the diabatic approximation, using the diabatic energy surfaces only. We describe next how they will be computed in this work.

According to the group function theory used to define the diabatic wavefunctions of the mixed valence pairs, the diabatic pair energies are the sum of the donor and acceptor energies plus their mutual Coulomb and exchange interaction:\(^{24}\) The latter should be almost independent of the donor and acceptor states, in general. Hence, we can write:

\[
E_{Di Aj}^{\text{diab}} = E_{Di} + E_{Aj} + E_{\text{CX}}^{\text{diab}} \approx E_{Di} + E_{Aj} + E_{\text{DA}}^{\text{diab}}.
\]

In Eq.\(^{1}\) \(E_{Di}\) and \(E_{Aj}\) include the embedding interactions of \(D\) and \(A\) with the crystalline environment of the \(DA\) pair in the MX\(_2\) crystal. In this work, we will compute \(E_{\text{CX}}^{\text{diab}}\) using the energy curves obtained from independent donor (YbX\(_6\))\(^{6-}\) and acceptor (YbX\(_6\))\(^{5-}\) clusters embedded in the perfect MX\(_2\) hosts, as building blocks. According to this alternative we will use:

\[
E_{Di Aj}^{\text{diab}}(d_L, d_R) = E_{\text{Di}}^{\text{ec}}(d_L) + E_{\text{Aj}}^{\text{ec}}(d_R) + E_{\text{EC}}^{\text{DA}}(d_{DA}),
\]

\[
E_{Aj Di}^{\text{diab}}(d_L, d_R) = E_{\text{Aj}}^{\text{ec}}(d_L) + E_{\text{Di}}^{\text{ec}}(d_R) + E_{\text{EC}}^{\text{DA}}(d_{DA}),
\]

where \(E_{\text{Di}}^{\text{ec}}(d_L)\) and \(E_{\text{Aj}}^{\text{ec}}(d_R)\) are the independent embedded cluster energy curves of the donor and acceptor obtained as described in Sec.\(^{11}\) and

\[
E_{0}^{\text{ec}}(d_{DA}) = E_{\text{EC}}^{\text{DA}}(d_{DA}) - E_{\text{DM}}^{\text{DA}}(d_{DA}) - E_{\text{AM}}^{\text{DA}}(d_{DA}) \approx (q_D \times q_A - (q_D + q_A) \times q_M)e^2/d_{DA},
\]

with \(E_{\text{EC}}^{\text{DM}}\) (or \(E_{\text{CX}}^{\text{AM}}\)) standing for the Coulomb and exchange interaction energy between the donor (YbX\(_6\))\(^{6-}\) (or acceptor (YbX\(_6\))\(^{5-}\)) cluster and the cluster of the original host cation (MX\(_2\))\(^{6-}\) (\(M\): Ca\(^{2+}\), Sr\(^{2+}\), or Ba\(^{2+}\), in this case). Except for short cation-cation distances, \(-E_{\text{EC}}^{\text{DA}} + E_{\text{EC}}^{\text{AM}} \approx (q_D - q_M) \times q_M + q_M \times q_A)e^2/d_{DA} = (-2 \times 2 - 3 \times 2 + 2 \times 3)e^2/d_{DA} = (-2 \times 2)e^2/d_{DA} = \approx (-2 \times 2)e^2/d_{DA} = \approx (-2 \times 2)e^2/d_{DA}.

In any case, the term \(E_{0}^{\text{ec}}(d_{DA})\) is common to the DA and AD energy surfaces and to all states of both. Its effect is a common shift of all of them and, consequently, it does not contribute to energy differences between them.

In this alternative, the symmetry reductions around \(D\) and \(A\) due to the presence of the other (\(A\) and \(D\), respectively) are not considered. Therefore, the energy splittings driven by symmetry lowering, which are dependent on the distance and relative orientation between \(D\) and \(A\), are not obtained. The most important ones in the present work would be the splittings produced on the (YbX\(_6\))\(^{5-}\) levels by the presence of the Yb\(^{3+}\) substitutional ion. Yet, whereas such site symmetry reductions would add significant computational effort to the embedded cluster calculations, the corresponding splittings would only be responsible for fine structure features of the spectra; they would neither affect the positions nor the number of the main absorption and emission bands. Therefore, the alternative chosen in this work will be able to capture the basics of the energy surfaces of the pairs by means of completely independent calculations on the \(D\) and \(A\) embedded clusters. This is the strength of the present approach.
B. Independent embedded cluster calculations

In this Section we describe the details and summarize the results of the quantum mechanical calculations of the \( E_D(d_{\text{vb}}) \) and \( E_A(d_{\text{vb}}) \) components of the mixed valence pair energies in Eq. [2]. As donor \( D \) and acceptor \( A \) we adopted, respectively, the \((\text{YbX}_6)_\text{b}^–\) and \((\text{YbX}_6)_\text{s}^–\) clusters \((X=\text{F, Cl})\). We performed \textit{ab initio} wave function theory embedded cluster quantum chemical calculations on these clusters embedded in the MX\(_3\) hosts, with the MOLCAS suite of programs.\(^{39}\) The calculations include bonding interactions, static and dynamic electron correlation effects, and scalar and spin-orbit coupling relativistic effects within the clusters, which are treated at a high theoretical level. They also include Coulomb, exchange, and Pauli repulsion interactions between the host and the clusters, which are considered at a lower theoretical level by means of a quantum mechanical embedding potential. Electron correlation effects between the cluster and the host are excluded from these calculations.

1. Details of the quantum mechanical calculations

The calculations presented here assume that \( \text{Yb}^{2+} \) and \( \text{Yb}^{3+} \) ions substitute for \( \text{M}^{2+} \) \((\text{M}^{2+}=\text{Ca}^{2+}, \text{Sr}^{2+}, \text{Ba}^{2+})\) and occupy cubic sites in the perfect fluorite structures.\(^{29}\) Following the embedded-cluster approximation, the imperfect crystals were divided into the defect cluster and the embedding host, which were represented as follows.

The embedded-cluster scalar relativistic second-order Douglas-Kroll-Hess Hamiltonian\(^{27,28}\) and wave functions, comprising the Yb impurity at \((0,0,0)\) and eight \( X \) ligands at variable \((x,x,x)\), included all the electrons of \( \text{Yb}^{2+} \) or \( \text{Yb}^{3+} \) and eight \( \text{X}^– \). The basis sets used to expand the cluster molecular orbitals included all the electron ANO-RCC bases \( \text{Yb} (25s22p15d11f4g2h) \) [98s8p5d4f3g2h], \( \text{F} (14s9p4d3f2g) \) [5s4p3d] or \( \text{Cl} (17s12p5d4f2g) \) [6s5p3d].\(^{29,30}\) In addition, the highest occupied \( s \) and \( p \) orbitals of the embedding \( \text{M}^{2+} \) ions, contracted as \( \text{Ca}^{2+} (20s15p)[1s1p], \text{Sr}^{2+} (23s19p)[1s1p], \text{Ba}^{2+} (27s23p)[1s1p] \), were used as orthogonalization functions at the 12 second neighbour sites \((\frac{1}{2}, \frac{1}{2}, 0)\), to fulfill strong orthogonality, and 5 \( s \)-type Gaussian type functions were used at the six \((\frac{1}{2}, 0, 0)\) interstitial sites surrounding the \( \text{YbX}_6 \) cube in the fluorite structures; their orbital exponents were optimized to give minimal impurity-trapped exciton energy. The embedded-cluster calculations were performed using \( D_{\text{vb}} \) symmetry.

AIMP embedding potentials were used in the embedded-cluster Hamiltonian to represent the host effects due to interactions with the remainder of the crystal ions, which include quantum mechanical embedding effects associated with exchange and Pauli repulsion, in addition to Coulomb electron repulsion and Madelung interactions.\(^{31,32}\) The embedding potentials for all four \( \text{MX}_3 \) hosts were obtained in this work to represent the \( \text{M}^{2+} \) and \( \text{X}^– \) ions located outside the cluster, at their cubic crystal structure sites \((\text{Group 225, Fm}3\text{m}, a_0 = 5.46294 \, \text{Å} (\text{CaF}_2), 5.796 \, \text{Å} (\text{SrF}_2), 6.2001 \, \text{Å} (\text{BaF}_2), 6.9744 \, \text{Å} (\text{SrCl}_2))\).\(^{33}\) The potentials were obtained by performing self-consistent embedded \( \text{M}^{2+} \) and \( \text{F}^– \) ion calculations at the Hartree-Fock level on the perfect host crystal as described in Ref. \( ^{42} \). All ions located in a cube of \( 7 \times 7 \times 7 \) unit cells, centered at the impurity site, were represented by their total ion embedding AIMP; an additional set of 2781 point charges was used to ensure that the Ewald potential is reproduced within the cluster volume. These charges were obtained following the zero multipole method of Gellé and Le Petit.\(^{34}\)

A recent study on radial correlation effects on interconfigurational transitions at the end of the lanthanide series has revealed that \( 4f \) to \( 5f \) double excitations must be included at the variational multiconfigurational self-consistent field step preceding second order perturbation theory calculations.\(^{35}\) Consequently, state-average restricted active space self-consistent field (RASSCF)\(^{36,37}\) calculations were done on the \((\text{YbX}_6)_\text{b}^–\) and \((\text{YbX}_6)_\text{s}^–\) embedded clusters including \( 4f \) to \( 5f \) single and double excitations from the \( 4f_{14} \) and \( 4f_{13} \) reference to calculate the \( 4f_{14} – 1 \Gamma_{\text{av}} \) ground state, and the \( 2 \Gamma_{2u}, \Gamma_{1u} \) and \( 2 \Gamma_{2v} \), \( 2 \Gamma_{2v} \) states of the \( 4f_{13} \) manifold, whereas single excitations from the \( 4f_{14} \) reference to one \( d_{\text{av}} \) shell and to the \( 5d \) shell (which belong to the \( t_{2g} \) and \( e_{\text{g}} \) irreducible representations) were also allowed to provide the minimal configurational space required for the spectroscopy of the \((\text{YbX}_6)_\text{b}^–\) cluster; plus additional single and double excitations from the \( 4f \) shell to the \( 5f \) shell to account for the large change of radial correlation upon \( 4f_{14} \rightarrow 4f_{15} 5d^4 \) electronic transitions. These calculations are referred here as RASSCF(\( 4f \rightarrow 3h/5f / a_{\text{av}} e_{\text{g}} t_{2g} \rightarrow 3e_1 \)), which indicates the maximum number of holes allowed in the \( 4f_{14} \) shell and the maximum number of electrons allowed in the empty \( a_{\text{av}} \) and \( 5d \) shells to calculate the ungerade \( ^{2S+1} \Gamma_{\text{av}} \) states of the \( \Gamma = A_{1u}, A_{2u}, E_u, T_{1u}, T_{2u} \) octahedral irreps.

Once these wave functions are obtained, they become the multireference for multistate second order perturbation theory calculations (MS-RASPT2)\(^{37,38}\) which include dynamic electron correlation, also necessary for getting sufficient precision in the structure and electronic transition data. At this level, all valence electrons of the embedded-cluster were correlated, which amounts to 86 and 85 electrons \((\text{Yb}: 22 \text{ or} 21; \text{eight} \ X: 64)\). We used the standard IPEA parameter value \((0.25 \text{ a.u.) introduced in Ref.} \,^{50}\) as a simple way to correct for systematic underestimations of CASPT2 transition energies from closed-shell ground states to open-shell excited states, also recommended for other cases. An imaginary shift of 0.1 was also used to avoid intruder states.\(^{39}\)

The highly correlated wavefunctions and energies resulting from the previous spin-orbit free step, namely, the eigenvectors (which are transformed RASSCF wave functions) and eigenvalues (MS-RASPT2 energies) of the spin-orbit free effective Hamiltonian computed at the MS-RASPT2 step, were transferred and used in the last step of
spin-orbit coupling calculations, which used the restricted-active-space state interaction method (RASSCF). The transformed RASSCF wave functions were used to compute the spin-orbit coupling matrix resulting from adding the AMFI approximation of the Douglas-Kroll-Hess spin-orbit coupling operator to the scalar relativistic Hamiltonian. Given that \( D_{2h} \) symmetry was used, the MS-RASPT2 energies show slight degeneracy breakings which would spread further throughout the spin-orbit calculation, the spin-free-state-shifting technique was used to substitute them for averaged values which were used in the diagonal elements of the spin-orbit coupling matrix. The calculation and diagonalization of the transformed RASSCF spin-orbit interaction matrix leads to the final results of the \textit{ab initio} calculations on the independent (Yb\(_{X}\)\(_{6}\)\(^{-}\)) and (Yb\(_{X}\)\(_{5}\)) active centers, which can be used in Eq. 2 to compute the diabatic potential energy surfaces of the (Yb\(_{X}\)\(_{6}\)\(^{-}\)–(Yb\(_{X}\)\(_{5}\)) mixed valence active pairs.

The program MOLCAS was used for all calculations. All AIMP data (for embedding and/or for cores) and interstitial basis set can be found in Ref. 54.

2. Energy curves of Yb\(^{2+}\) and Yb\(^{3+}\) independent active centers

The results of the quantum mechanical calculations on the donor (Yb\(_{X}\)\(_{6}\)) and acceptor (Yb\(_{X}\)\(_{5}\)) cubic clusters embedded in the four MX\(_{2}\) hosts are collected in the Supplementary Material of this paper, where the details of the electronic structure of the ground and excited states of the Yb\(^{2+}\) and Yb\(^{3+}\) active centers are presented. Tables 1 to IV of Ref. 55 include the Yb–X equilibrium bond distance, totally symmetric vibrational frequency, minimum-to-maximum energy differences relative to the 4f\(^{14}\)–1A\(_{1g}\) ground state, and analyses of the spin-orbit wavefunctions of all 7 A\(_{1u}\), 7 A\(_{2u}\), 14 E\(_{u}\), 21 T\(_{1u}\), and 21 T\(_{2u}\) spin-orbit levels calculated. They also include the results for the electronic states of the 4f\(^{13}\) configuration of the Yb\(^{2+}\) active centers. Plots of their energy curves vs. the Yb–X bond distance at different levels of methodology (RASSCF, MS-RASPT2, and RASSI-SO) and the calculated absorption spectra are also presented in Figures 1 to 5 of Ref. 55. The data of only the lowest levels (14 of Yb\(^{2+}\) and 5 of Yb\(^{3+}\)) in CaF\(_{2}\) are presented here in Table 5 selected energy curves are presented in the left graph of Fig. 3, all the energy curves are presented in the left graph of Fig. 5.

The excited states of Yb\(^{2+}\) in the four hosts appear to be grouped in four manifolds of impurity states (see Table 3 and left graph of Fig. 3 for CaF\(_{2}\)): 4f\(^{13}\)(7/2)5d\(_{e}\), 4f\(^{13}\)(5/2)5d\(_{e}\), 4f\(^{13}\)(7/2)5d\(_{t}\), and 4f\(^{13}\)(5/2)5d\(_{t}\) which, in some cases, show significant configurational interaction. The more delocalized ITE states, whose electronic structure shows the same characteristics as those found in previous quantum mechanical studies on U\(^{4+}\)-doped Cs\(_{2}\)GeF\(_{6}\) and Yb\(^{3+}\)-doped SrCl\(_{2}\) appear above the lowest 4f\(^{13}\)(7/2)5d\(_{e}\) impurity manifold in all four hosts. The lowest excited states of Yb\(^{2+}\) are, in all cases, the 4f\(^{13}\)(7/2)5d\(_{e}\) electric dipole forbidden 1E\(_{u}\)–1T\(_{2u}\), and the electric dipole allowed 1T\(_{1u}\) states. (In all figures, blue and green colours have been used for the energy curves of the 4f\(^{13}\)5d\(_{e}\) and 4f\(^{13}\)5d\(_{t}\) manifolds, respectively; maroon has been used when they interact among themselves or with ITE states. Black has been used for the Yb\(^{2+}\) ground state and for the lowest 4f\(^{13}\)(7/2) manifold of Yb\(^{3+}\); red is used for the higher 4f\(^{13}\)(7/2) components.)

The present \textit{ab initio} results and those of calculations presented elsewhere (58) especially designed to allow the wavefunctions of excited states to spread electron density beyond first neighbors, over the twelve next Ca\(^{2+}\) or Sr\(^{2+}\) ions, as proposed by McClure and Pédrini for impurity-trapped excitons allows us to conclude that none of the electronic states of the Yb\(^{2+}\) active centers can be considered responsible for the anomalous emission observed in the CaF\(_{2}\) and SrF\(_{2}\) hosts. Therefore, the hypothesis of the impurity-trapped excitons being responsible for the anomalous emission is not supported by the \textit{ab initio} quantum mechanical calculations. Impurity-trapped excitons show up in the calculations, but at much higher energies than those that would allow them to play a role in the anomalous emission. As we show in Sec. III and IV, intercalation charge transfer within the Yb\(^{2+}\)–Yb\(^{3+}\) active pairs has to be invoked instead.

C. Quantitative energy diagrams for Yb\(^{2+}\)–Yb\(^{3+}\) intercalation charge transfer reaction

Even though the calculation of the two diabatic potential energy surfaces \( E_{\text{Diab}}^{\text{Di}}(d_{i}, d_{k}) \) and \( E_{\text{Diab}}^{\text{Ad}}(d_{i}, d_{k}) \) associated with each \( ij \) state of the embedded pair before and after electron transfer is necessary for the obtaining of the structural and energetic results discussed in this paper (note that any of the MX\(_{2}\):Yb\(^{2+}\)–Yb\(^{3+}\) excited states lead to two energy surfaces like those for the ground state presented in Fig. 1 which would make their joint plot extremely crowded and cumbersome), the extraction of the minimal energy electron transfer reaction path from them is a very important step leading to quantitative IVCT energy diagrams which will be actually used to discuss IVCT luminescence and other radiative and non-radiative IVCT processes in Sec. III and IV. In this Section we explain how these diagrams are built: In a first step, the normal electron transfer reaction coordinate \( Q_{et} \) for the ground state of the mixed valence pair, \( Q_{et}^{(0)} \), will be defined from the topology of the \( E_{\text{Diab}}^{\text{Di}}(d_{i}, d_{k}) \) and \( E_{\text{Diab}}^{\text{Ad}}(d_{i}, d_{k}) \) energy surfaces, in terms of concerted vibrational breathing modes of the donor \( D \) and acceptor \( A \) sites, which leads to the diabatic \( E_{\text{Diab}}^{\text{Di}}(Q_{et}^{(0)}) \) and \( E_{\text{Diab}}^{\text{Ad}}(Q_{et}^{(0)}) \) branches for the reaction. In a second step, the energy curves of the excited states of the mixed valence pairs will be evaluated at the \( d_{i}, d_{k} \) coordinate values which correspond to the \( Q_{et}^{(0)} \) axis, leading to \( E_{\text{Diab}}^{\text{Di}}(Q_{et}^{(0)}) \) and \( E_{\text{Diab}}^{\text{Ad}}(Q_{et}^{(0)}) \) branches for all states of interest and, hence, to the final quantitative IVCT diagram. The same procedure would be applicable to any
other two \( E_{DA}^{\text{diab}} (d_L, d_R) \) and \( E_{AD}^{\text{diab}} (d_L, d_R) \) diabatic surfaces, which would lead to analogous energy diagrams along corresponding \( Q_L \), reaction coordinates.

1. Electron transfer reaction coordinate

Within the diabatic approximation, the two symmetric diabatic energy surfaces involved in the electron transfer reaction between the \( D \) and \( A \) ground states, \( E_{DA}^{\text{diab}} (d_L, d_R) \) and \( E_{AD}^{\text{diab}} (d_L, d_R) \), do intersect, without avoiding crossing, at all \( d_L = d_R \) points (see Fig. 1), where they are degenerate, while the corresponding pair wavefunctions \( MA(\Phi \Phi) \) and \( MA(\Phi \Phi \Phi \Phi) \) never mix, but keep their pure character. In this way, the electron transfer reaction path (see Fig. 1) connects the energy minimum of the \( DA \) (YbX\(_8\))\(^{5-}\)-(YbX\(_8\))\(^{5-}\) pair, \( E_{00}^{DA} = E_{00}^{AD} (d_{DA}, d_{AC}) \), for which the (YbX\(_8\))\(^{5-}\) and (YbX\(_8\))\(^{5-}\) clusters are at their Yb-X equilibrium distance, \( d_L = d_R \), and \( d_{DA} = d_{AC} \), with that of the symmetrical minimum of the \( AD \) (YbX\(_8\))\(^{5-}\)-(YbX\(_8\))\(^{5-}\) pair, \( E_{00}^{AD} = E_{00}^{DA} (d_{DA}, d_{AC}) \), at the \( d_L = d_{DA}, d_R = d_{AC} \) point, crossing from the \( DA \) to the \( AD \) surface through the activated complex, which is the crossing point with minimal energy, equal sharing of the transferred electron, and equal Yb-X bond distance for the left and right clusters of the \( DA \) and \( AD \) pairs, \( d_L = d_R = d_{DA} \). The diabatic electron transfer activation energy: 

\[
Q_{et} = E_{00}^{DA} - E_{00}^{AD} = E_{00}^{AD} - E_{00}^{DA} = E_{00}^{DA} - E_{00}^{AD} = E_{00}^{DA} - E_{00}^{AD} = E_{00}^{DA} - E_{00}^{AD}
\]

which have been expressed in terms of the displacements \( \delta_{X_{\text{et}}} \) and \( \delta_{X_{\text{et}}} \) of the X ligand atoms in the left and right YbX\(_8\) moieties away from their respective Yb atoms, starting from the positions they occupy in the activated complex. A graphical representation of the X displacements along \( Q_{et} \) is shown in Fig. 1 (bottom graph). Since the left and right cluster breathings imply \( \delta_{X_{\text{et}}} = \delta_{X_{\text{et}}} = \ldots = d_L - d_{ac} \) and \( \delta_{X_{\text{et}}} = \delta_{X_{\text{et}}} = \ldots = d_R - d_{ac} \), we can write

\[
Q_{et} = \sqrt{8} (d_L - d_{ac}),
\]

\[
Q_{et} = \sqrt{8} (d_R - d_{ac}),
\]

and

\[
Q_{et} = \sqrt{8} (1 + m^2) (d_L - d_{ac})/m.
\]

We may mention the relationship of this reaction coordinate and the one of the vibronic model of Pielbo et al.\(^{39} \)

The latter corresponds to \( d_{ac} = (d_{ac} + d_{ac})/2 \), which implies \( m = -1 \) and gives 

\[
Q_{et} = \sqrt{8} (Q_R - Q_L) = 2 (d_R - d_L).
\]

2. Quantitative Yb\(^{3+}\)-Yb\(^{3+}\) IVCT energy diagrams

According to Eq. 2 and Eqs. 4-8, quantitative IVCT energy diagrams for the embedded Yb\(^{3+}\)-Yb\(^{3+}\) active pairs can be obtained using the energy curves resulting from the independent embedded cluster calculations of the electronic states of the donor (YbX\(_8\))\(^{5-}\) and acceptor (YbX\(_8\))\(^{5-}\) active centers described in Sec. 2B. We illustrate here how this is done using the energy curves of only two electronic states for the donor and acceptor clusters embedded in CaF\(_2\), \( (n_D = 2, n_A = 2) \): the ground state and one excited state, which have been plotted in the left graph of Fig. 2. The IVCT energy diagram resulting from these, which includes \( 2n_D n_A = 8 \) diabatic mixed valence pair states, is plotted in the right graph of Fig. 2 and is described next. The much more dense IVCT energy diagrams used below in this paper result from obvious extensions which use the
complete manifold of excited states calculated for the separated active centers.

Using the energy curves of the 1A1g and 1Γg ground states of the Yb²⁺ and Yb³⁺ doped CaF₂ (see Table 1), the diabatic potential energy surfaces \( E^{\text{diab}}(d_{1}, d_{2}) \) and \( E^{\text{diab}}(d_{1}, d_{2}) \), for the pair before \((\text{Yb}X_{A})^{6−}(\text{Yb}X_{B})^{5−}\) [1A1g, 1Γg] and after \((\text{Yb}X_{A})^{5−}(\text{Yb}X_{B})^{6−}[1\Gamma_{7u}, 1\Lambda_{1g}] \) electron transfer, are obtained from Eq. 2. From any of them, the activated complex structure, \( d_{A}=2.261 \, \text{Å} \), is obtained searching for the minimal energy along the \( d_{1}=d_{B} \) axis. Using this value, plus the Yb–F equilibrium distances of the independent embedded cluster ground states, \( d_{A}=2.329 \, \text{Å} \) (1A1g) and \( d_{A}=2.201 \, \text{Å} \) (1Γg), respectively, the diabatic electron transfer reaction coordinate for the ground state of the mixed valence pair is defined from Eqs. 4 and 5, and the two mixed valence pair ground state branches [1A1g,1Γg] and [1Γg,1A1g] are obtained; they are plotted in black in the right graph of Fig. 2. The two diabatic energy curves cross at the activated complex structure \( (Q_{et} = 0 \, \text{Å}; d_{1} = d_{2} = 2.261 \, \text{Å}; E^{\text{diab}} = 3774 \, \text{cm}^{-1}) \). In the structures of the pairs around the minimum of the DA state [1A1g,1Γg] \( (Q_{et} = -0.256 \, \text{Å}; d_{1} = d_{B} = 2.329, d_{A} = 2.201 \, \text{Å}) \), the complementary AD state \( [1\Gamma_{7u}, 1\Lambda_{1g}] \) has a much higher energy because the oxidized and reduced moieties, A and D, are under strong structural stress. The opposite is true around the minimum of the AD state \( [1\Gamma_{7u}, 1\Lambda_{1g}] \). We indicate this in the energy diagram by representing the energy of a given mixed valence pair state with full lines when it is around its minimum, and with dashed lines when it is under strong stress. Computing the energies of the excited states of the pairs at the \( d_{1}, d_{B} \) values corresponding to the ground state electron transfer coordinate we obtained the energy curves of the DA states [1A1g,2Γg] (red), [1Eg,1Γg] (blue), and [1Eg,2Γg] (orange), plus their IVCT AD counterparts. They are plotted in the right graph of Fig. 2 using the above definition of solid and dashed lines.

The quantitative IVCT diagram shown in Fig. 2 can be used to read different types of processes.

The \( D_{A0}→A_{0}D_{0} \) thermally induced ground state inter-valence electron transfer reaction, Yb²⁺→Yb³⁺ [1A1g,1Γg] → Yb³⁺→Yb²⁺ [1Γg,1A1g], with an upperbound activation energy barrier of 3774 cm⁻¹ (black, solid line connecting the two equivalent ground state minima through the activated complex).

Vertical absorptions of the independent active centers, which occur at their (fixed) ground state structure, such as: the Yb³⁺ 4f→4f absorption 1Γg → 2Γg at a Yb³⁺–F distance 2.201 Å \( (D_{A0}→D_{A1}, \text{arrow 1}) \), and the Yb²⁺ 4f→5d absorption 1A1g → 1Eg at a Yb²⁺–F distance 2.329 Å \( (D_{A0}→D_{A2}, \text{arrow 2}) \). These transitions are the same read in the energy curves of the independent active centers in the left graph of Fig. 2.

Vertical IVCT absorptions from the pair ground state, at fixed \( Q_{et} = -0.256 \, \text{Å} \), which means a left Yb-F distance 2.329 Å and a right Yb-F distance 2.201 Å. The initial pair \((\text{Yb}X_{A})^{6−}(\text{Yb}X_{B})^{5−}\) is relaxed and, after the radiatively induced electron transfer, the final pair \((\text{Yb}X_{A})^{5−}(\text{Yb}X_{B})^{6−}\) is very stressed and far from equilibrium. These absorption bands are very wide. There is a lowest IVCT absorption \( (D_{A0}→A_{0}D_{0}, \text{arrow 3}) \), which leads to the photoinduced ground state electron transfer reaction after non-radiative decay, and higher lying IVCT absorptions, like \( D_{A0}→A_{1}D_{1} \) (arrow 4).

Electron transfer non-radiative decays to the ground state or to excited states of the pair can also be visualized in the IVCT energy diagram, like the \( D_{A0}→A_{0}D_{0} \) or the \( D_{AI}→A_{1}D_{1} \) decays. In this case, the IVCT diagram is very helpful identifying the most probable decay mechanisms, the corresponding energy barriers have to be found in the full diabatic potential energy surfaces involved, \( E^{\text{diab}}(d_{1}, d_{B}) \) and \( E^{\text{diab}}(d_{1}, d_{B}) \), because they may occur at \( d_{1}, d_{B} \) points not corresponding to the ground state electron transfer reaction coordinate \( Q_{et} \) axis.

Finally, vertical emissions can also be discussed using the IVCT energy diagrams in analogous terms as we have discussed vertical absorptions above. These can be regular emissions of the independent active centers, like \( A_{1}D_{1}→D_{2}A_{0} \) (arrow 5), and IVCT emissions, like \( A_{1}D_{1}→D_{2}A_{0} \) (arrow 6). Rigorously, the electron transfer reaction coordinate \( Q_{et} \) axis should correspond to the \( ij \) emitting state of the pair. Yet, the IVCT diagram obtained for the \( Q_{et}^{1g} \) and \( Q_{et}^{1f} \) axes are very similar in most cases. Hence, although the transition energies tabulated in this work will be calculated rigorously, we will use the ground state IVCT energy diagram to discuss absorption, decays, and emission processes altogether. Therefore, independent active center emissions and IVCT emissions will be discussed in analogous terms as the independent active center absorptions and IVCT absorptions, with obvious substitutions of the \( Q_{et} \) fixed values involved in the radiative processes and their effects on the emission band lines.

III. IVCT LUMINESCENCE IN CAF₂:YB²⁺

In this Section we present and discuss in detail the IVCT luminescence of CaF₂:Yb²⁺. The manifolds of excited states of Yb²⁺→Yb³⁺ pairs in CaF₂ are introduced in Sec. III A and they are used to interpret the anomalous luminescence of CaF₂:Yb²⁺ as an IVCT luminescence in Sec. III B, where its mechanism is discussed in detail. Additionally, we discuss two experiments that reinforce the involvement of IVCT states: Firstly, in Sec. III C we show that the transient photoluminescence enhancement measured via two-frequency excitation experiments can be interpreted, in detail, as an IVCT photoluminescence enhancement experiment; then, in Sec. III D we show that the IVCT model also explains the excitation of the IR Yb³⁺ emission by Yb²⁺ 4f→5d absorptions.
A. Excited states of Yb$^{2+}$–Yb$^{3+}$ pairs

The full diabatic IVCT energy diagram for the ground and excited states of the Yb$^{2+}$–Yb$^{3+}$ pairs in CaF$_{2}$, along the normal reaction coordinate of the ground state, can be seen in Fig. 5. It has been built using all the parent independent embedded cluster energy curves plotted in the left graph, following the procedure explained in Section II.C.2. The vertical transition energies from the Yb$^{2+}$–Yb$^{3+}$ [1A$_{1g}$,1Γ$_{7u}$] ground state minimum (Q$_{el}$ = −0.256, d$_{el}$,d$_{el}$ = 2.330,2.201 Å; zero energy in the diagram), which can be read directly from the diagram, are also collected in Table II. As indicated in the Table, only the excited states which are relevant for the discussions of this paper have been tabulated; the remaining data is available in Ref. [S5]. Vertical transition energies from the minima of other two electronic states of the Yb$^{2+}$–Yb$^{3+}$ pairs, [1A$_{1g}$,2Γ$_{7u}$] and [2A$_{1u}$,1Γ$_{7u}$], have also been included in Table II. In the [1A$_{1g}$,2Γ$_{7u}$] state the (YbX)$_{5}^{−}$ right moiety of the Yb$^{2+}$–Yb$^{3+}$ pair is excited in the lowest of the 4f$^{13}$(5/2) levels; in the [2A$_{1u}$,1Γ$_{7u}$] state the (YbX)$_{5}^{−}$ left moiety is excited in the lowest of 4f$^{13}$(5/2)5e$_{c}$ levels (cf. symmetry labels and configurational character of the parent independent embedded cluster states in Table II). Vertical absorptions and emissions from their minima will be used in the next subsections; however, their values cannot be read directly from the IVCT diagram of Fig. 3 since their electron transfer reaction coordinate is that of the ground state. Specific IVCT diagrams along the [1A$_{1g}$,2Γ$_{7u}$] and [2A$_{1u}$,1Γ$_{7u}$] reaction coordinates would have to be constructed using Eqs. 4–8 and the procedure outlined in Sec. II.C.2. However, the similarity of all three IVCT diagrams allows to visualize the data from Table II in Fig. 3.

Diabatic energy barriers for the IVCT reaction Yb$^{2+}$–Yb$^{3+}$ → Yb$^{3+}$–Yb$^{2+}$, connecting two different electronic states of the pairs: [D$_{i}$,A$_{j}$] → [A$_{k}$,D$_{l}$], have been included in Table III for the forward and backwards reactions, together with the d$_{el}$,d$_{el}$ coordinates of their activated complex point, since they play an important role in non-radiative decay pathways, as discussed below. The forward/backwards energy barriers have been calculated searching for the activated complex point of the [D$_{i}$,A$_{j}$] → [A$_{k}$,D$_{l}$] reaction directly along the intersection points of the two E$_{Diab}$(d$_{i}$,d$_{R}$) and E$_{Diab}$(d$_{i}$,d$_{R}$) energy surfaces. Again, even though the activated complex d$_{i}$,d$_{R}$ structures gathered in the Table do not necessarily fall in the ground state electron transfer reaction coordinate of Fig. 3, they are not far from the crossing points of their respective E$_{Diab}$(Q$_{el}$) and E$_{Diab}$(Q$_{el}$) branches; so, they can be visualized in Fig. 3.

In the following and for clarity, the IVCT energy diagram of Fig. 3 will be reduced so as to include only the electronic states that have been found to participate in the IVCT luminescence mechanism of Yb-doped CaF$_{2}$ crystals and in the electronic spectroscopy experiments that will be discussed below. The reduced IVCT diagram appears in Fig. 4.

B. IVCT luminescence mechanism

The results of the quantum mechanical calculations described in the preceding sections suggest that the IVCT luminescence, which has been observed experimentally and has been interpreted so far as an anomalous luminescence, occurs according to the following mechanism involving steps I to V. The data which characterize the radiative and non-radiative processes the Yb$^{2+}$–Yb$^{3+}$ pair states undergo, can be found in Table II and Fig. 4. Table II should be useful to clarify the electronic structure of their Yb$^{2+}$ and Yb$^{3+}$ parent states.

1. Step I. First photon absorption.

Step I is the first photon absorption [1A$_{1g}$,1Γ$_{7u}$] → [1T$_{1u}$,1Γ$_{7u}$]. This step is the lowest electric dipole allowed 4f$^{14}$ → 4f$^{13}$5d$e_{c}$ excitation of Yb$^{2+}$: 1A$_{1g}$ → 1T$_{1u}$ temperature dependent (multiphonon) non-radiative decay to the lowest lying state of the 4f$^{13}$5d$e_{c}$ configuration, 1E$_{u}$, can be expected to occur[13,20]. Alternatively, a lower energy photon can excite directly the 1E$_{u}$ state with a less efficient, electric dipole forbidden transition[5,21]. These two states can be labelled as the [1T$_{1u}$,1Γ$_{7u}$] and [1E$_{u}$,1Γ$_{7u}$] states of the Yb$^{2+}$–Yb$^{3+}$ pair, respectively. Comparisons between their calculated vertical transition energies and experimental peak energies[20,24] (Table II) 25706 cm$^{-1}$ and 23576 cm$^{-1}$ vs. 27400 cm$^{-1}$ and 24814 cm$^{-1}$, respectively, suggest similar overestimations of around 1500 cm$^{-1}$.

2. Step II. Non-radiative electron transfer.

Step II is the non-radiative electron transfer [1T$_{1u}$,1Γ$_{7u}$] and/or [1E$_{u}$,1Γ$_{7u}$] → [2Γ$_{7u}$,1A$_{1g}$]. A very small energy barrier (49 cm$^{-1}$) is found for Yb$^{2+}$–Yb$^{3+}$ [1T$_{1u}$,1Γ$_{7u}$] → Yb$^{3+}$–Yb$^{2+}$ [2Γ$_{7u}$,1A$_{1g}$] electron transfer, which suggests that such non-radiative decay is very likely to occur. At the activated complex point of the electron transfer, (d$_{i}$,d$_{R}$)=(2.323 Å, 2.197 Å) the resulting Yb$^{3+}$–Yb$^{2+}$ [2Γ$_{7u}$,1A$_{1g}$] state is so structurally stressed that a profound non-radiative relaxation towards its final equilibrium structure (d$_{i}$,d$_{R}$)=(2.201 Å, 2.330 Å) follows (see step II in Fig. 4). The same is true for the [1E$_{u}$,1Γ$_{7u}$] → [2Γ$_{7u}$,1A$_{1g}$] non-radiative charge transfer for which the energy barrier is found to be even smaller: 14 cm$^{-1}$.

These small energy barriers suggest that step II, which is an Yb$^{2+}$ (2F$^{−}_{7/2}$ 5d$e_{c}$)–Yb$^{3+}$ (2F$^{−}_{7/2}$) → Yb$^{3+}$ (2F$^{−}_{5/2}$)–Yb$^{2+}$ (4f$^{14}$) non-radiative IVCT that leaves Yb$^{3+}$ in its 2F$^{−}_{5/2}$ 2Γ$_{7u}$ excited state, should be an efficient quenching mechanism for regular 4f$^{13}$5d$e_{c}$ → 4f$^{14}$ radiative emissions back to the ground state. This explains that experimental detection of these emissions has never been reported for the CaF$_{2}$ host, as far as we know.
Going into more details, it is worth noting that $[1E_u,1Γ_7u]$ can excite the IVCT directly through non-radiative decay along step II, followed by steps III and IV explained below. $[1T_{1u},1Γ_7u]$, however, can excite it directly through its own step II, but also indirectly through an intermediate decay to $[1E_u,1Γ_7u]$. This explains the difference observed experimentally in the short time part of the intensity decay curves of the anomalous (IVCT) emission; whereas the intensity of the emission shows a risetime when $1T_{1u}$ is excited, the risetime dissipates when $1E_u$ is directly excited instead.

The calculators show branching of the step II non-radiative decays, which could result in quenching of the IVCT luminescence. Besides, the energy barrier for the electron transfer reaction back to the ground state of the $Yb^{2+}$--$Yb^{2+}$ pair after step II, $Yb^{3+}$--$Yb^{3+}$ $[2Γ_7u;1A_{1g}] \rightarrow Yb^{2+}$--$Yb^{2+}$ $[1A_{1g};1Γ_7u]$, is found to be 285 cm$^{-1}$. All this indicate that: (i) both non-radiative decays below the branching should occur, and (ii) the pairs that decay to the $Yb^{3+}$--$Yb^{3+}$ $[2Γ_7u;1A_{1g}]$ minimum (the end of step II) and can yield IVCT luminescence after the next steps, will still face temperature dependent decay to the ground state through the low energy barrier. This is in fact the reason that the final state of the anomalous luminescence of CaF$_2$:Yb$^{2+}$ has been observed at 180 K [11,20]. Also, since the temperature dependence of the non-radiative decay from the $1T_{1u}$ to the $1E_u$ states of Yb$^{2+}$ mentioned in step I, $[1T_{1u};1Γ_7u] \rightarrow [1E_u;1Γ_7u]$, should influence step II as well, right at the initiation of the IVCT emission mechanism, the overall temperature dependence of the IVCT luminescence should be complex; this is further discussed in Section IV A 2.

3. Step III. Second photon absorption.

Step III is the second photon absorption $[2Γ_7u;1A_{1g}] \rightarrow [2Γ_7u;1T_{1u}]$.

This step is equivalent to step I, since Yb$^{2+}$ is excited to its lowest 4f$^{14}$ state and then, 4f$^{12}$--5d$_{6g}$ electric dipole allowed level 1T$_{1u}$ by a second photon of the same wavelength as that of step I. The difference is that now, after step II, the Yb$^{3+}$ component of the pair is in its $2F_{5/2}$ 1Γ$_7u$ excited state instead of its $2F_{7/2}$ 1Γ$_7u$ ground state. As commented in step I, alternatively, the lower lying $[2Γ_7u;1E_u]$ state can be directly excited in this step by a second, lower energy photon.

This step reveals that the excitation of the IVCT luminescence is a two-photon process. Whether excitation of the yellow-green anomalous luminescence is a one- or a two-photon process has not been investigated experimentally, as far as we know.

4. Step IV. Non-radiative decay to the luminescent level.

Step IV is the non-radiative decay to the luminescent level $[2Γ_7u;1T_{1u}] \rightarrow [1Γ_7u,2A_{1u}]$.

The non-radiative relaxation from $[2Γ_7u,1T_{1u}]$ to the lowest $[1Γ_7u,2A_{1u}]$ level in this energy region separated from lower lying states by a large energy gap, is now significantly different from that described in step I after excitation to the $[1T_{1u},1Γ_7u]$ state with the first photon, because the number and nature of the electronic states that are found below the excited level are now different. In effect, the first photon excites to the lowest levels of the Yb$^{2+}$--$Yb^{2+}$ $[2F_{7/2}5d_{eg};2F_{7/2}]$ manifold, in which both the 4f$^{13}$ inner-shell of Yb$^{2+}$ and the 4f$^{13}$ shell of Yb$^{3+}$ are in their $2F_{7/2}$ ground spin-orbit multiplet. However, the second photon excites to a more crowded energy region, where two manifolds of the Yb$^{3+}$--$Yb^{2+}$ pair share the same energy range: $[2F_{7/2}5d_{eg};2F_{7/2}]$ and $[2F_{5/2}2F_{7/2}5d_{eg}]$; these two manifolds have their 4f$^{13}$ inner-shell of Yb$^{2+}$ and 4f$^{13}$ shell of Yb$^{3+}$, respectively, excited into the $2F_{5/2}$ spin-orbit multiplet. As a result, all of these energy levels lie close in energy (cf. Table II) and non-radiative relaxation should not be hindered by energy gaps and it should be fast until the luminescent level $[1Γ_7u,2A_{1u}]$ is reached. This step would be reduced to a minimum when the $[2Γ_7u,1E_u]$ level is directly excited.

5. Step V. IVCT luminescence.

Step V is the IVCT luminescence $[1Γ_7u,2A_{1u}] \rightarrow [1A_{1g},2F_{7/2}]$. In the last step, the IVCT luminescence consists of three vertical Yb$^{3+}$--$Yb^{2+}$ $→ Yb^{2+}$--$Yb^{3+}$ intervalscence charge transfer transitions. They occur from the excited Yb$^{2+}$ $[2F_{7/2},2F_{5/2}5d_{eg}]$ state $[1Γ_7u,2A_{1u}]$ to the three components of the Yb$^{3+}$ $[4f^{14}]+Yb^{3+} [2F_{7/2}]$ ground state: $[1A_{1g},1Γ_{8u}]$ at 19974 cm$^{-1}$, $[1A_{1g},1Γ_{8u}]$ at 19999 cm$^{-1}$, and $[1A_{1g},1Γ_{7u}]$ at 20508 cm$^{-1}$. These leads basically to two wide bands 530 cm$^{-1}$ apart.

The vertical transitions occur at the equilibrium structure of the initial $[1Γ_{7u},2A_{1u}]$ state: $(d_l,d_g)_{e,initial}=(2.201 Å, 2.314 Å)$. This means that the Yb$^{2+}$--Yb$^{3+}$ pair that results from the vertical electron transfer is very much stressed, far away from its own equilibrium structure at $(d_l,d_g)_{e,final}=(2.330 Å, 2.201 Å)$, which defines the offsets on the left and right moieties of the pair as $Δd_l=+0.129 Å$ and $Δd_g=−0.113 Å$, and the offset in the normalized concerted vibrational electron transfer reaction coordinate (the distance between $(d_l,d_g)_{e,final}$ in the $d_l,d_g$ plane) as $[ΔQ_{α1}], = \sqrt{Δd_l^2 + Δd_g^2} = 0.49 Å$. This large offset results in very broad emission bands with full width at half maximum (FWHM) about 5800 cm$^{-1}$, much broader than it could be expected from the regular $2F_{7/2}5d_{eg} → 4f^{14}$ emission, should the latter occur. This is illustrated in Fig. 5 where the simulation of the IVCT band has been produced for the three electronic origins $[1Γ_{7u},2A_{1u}] \rightarrow [1A_{1g},1Γ_{8u},7u,7u]$ using the semiclassical time-dependent approach of Hellec et al. [21,22] with an arbitrary value for the oscillator strengths.
The first reports on the luminescence of CaF$_2$:Yb$^{2+}$ crystals below 200 K describe a broad structureless band in the yellow-green region formed by two overlapping bands peaking at 17600 and 18200 cm$^{-1}$ which suggests that the results of the calculations lead to overestimations of the IVCT luminescence by some 2000 cm$^{-1}$. Values of the FWHM between 3000 and 4000 cm$^{-1}$ have been found experimentally, depending on temperature. The 2000 cm$^{-1}$ overestimation of the calculated peaks of the IVCT bands, together with the 17600 cm$^{-1}$ underestimated formation of the calculated Yb$^{2+}$$^{2}F_{14}^–$A$^{1}g_8$ → $^{2}F_{14}^–$A$^{1}g_8$ transition contribute to a smaller calculated red shift of the IVCT luminescence relative to the Yb$^{2+}$ excitation than observed: it is found to be about 5600 cm$^{-1}$ whereas the experimentally measured red shift is about 10000 cm$^{-1}$. An important characteristic of the level responsible for the IVCT luminescence, [2A$^{1}n$,1Γ$_{7n}$] (or equivalently [1Γ$_{7n}$2A$^{1}n$]), is its very low radiative rate compared with that of upper lying levels. This characteristic is basic for the efficiency of transient photoluminescence enhancement experiments like the ones described next.

### C. Transient IVCT photoluminescence enhancement

Two-frequency transient photoluminescence enhancement measurements on CaF$_2$:Yb$^{2+}$ single crystals at 10 K have been conducted to probe the energy levels lying above the state responsible for the so far called anomalous emission. The experiments are based on the “radically” different radiative decay rates of the lowest emitting state and higher excited states. The sample, excited in the UV at 365 nm (27400 cm$^{-1}$), is irradiated by an IR pulse. The IR excitation induces significant enhancement of the emission because it populates excited states that have significantly higher radiative rates. So, whereas the radiative rate of the lowest emitting level is in the order of 10 ms$^{-1}$, the decay of the transient signal is much faster than 2×10$^2$ μs$^{-1}$. Here we show that these experiments can be interpreted as transient IVCT photoluminescence enhancement experiments.

Even though within the diabatic approximation used here we cannot calculate transition moments between pair states and, hence, radiative rates or emission lifetimes, the analyses of the wavefunctions of the parent Yb$^{2+}$ and Yb$^{3+}$ states can give relevant information on this subject. In this line, the IVCT luminescence can be described as: Yb$^{2+}$$^{2}F_{5/2}$5de$_{g}$→2A$^{1}n$ + Yb$^{3+}$$^{2}F_{7/2}$→1Γ$_{7n}$ → Yb$^{3+}$$^{2}F_{7/2}$→1Γ$_{7n}$ + Yb$^{2+}$$^{2}F_{14}^–$→1A$^{1}g_8$. This indicates that the transition is a double orbital (or spinor) deexcitation, because Yb$^{2+}$ gets its $^{2}F_{14}^–$ subshell deexcited (Yb$^{2+}$→Yb$^{3+}$) at the same time that its 5de$_{g}$ electron is transferred to fill the Yb$^{3+}$ hole (Yb$^{2+}$5de$_{g}$ → Yb$^{3+}$4f$_{5/2}$), which is graphically represented in the scheme labeled double in Fig. 5. Analogue analysis of the emission from the next upper lying level [1E$_{g}$2Γ$_{7n}$] yields the conclusion that its IVCT emission Yb$^{2+}$→Yb$^{3+}$ [1E$_{g}$2Γ$_{7n}$] → Yb$^{3+}$→Yb$^{2+}$ is a single electron transfer Yb$^{2+}$5de$_{g}$ → Yb$^{3+}$4f$_{5/2}$ (see scheme labeled single in Fig. 5). Altogether, it is possible to conclude that the radiative rate of the lowest emission should be much lower than that of the next higher emission, which is in agreement with the lowest emitting state having a long lifetime.

Now, let us discuss the transient photoluminescence enhancement in more detail. Analyses of the transient signals vs. IR wavelength allowed to extract the IR excited state absorption (ESA) spectrum originating in the lowest luminescence level; it consists of two low-intensity sharp peaks at 2260 and 2500 cm$^{-1}$ and a higher intensity broad band from 650 to 950 cm$^{-1}$. Other signals found were assigned to trap liberation processes and atmospheric absorptions of the IR free electron laser (FEL). The calculated vertical IR ESA spectrum originating in the Yb$^{2+}$→Yb$^{3+}$ pair state has been included in Table I. The simulation of the ESA spectrum of Fig. 7, graph (a), has been produced as the superposition of narrow gaussians centered at the energy levels lying below 1700 cm$^{-1}$, using equal values of the oscillator strength for each electronic transition. It also consists of three groups of bands which correlate satisfactorily with the experimental values from Ref. [13] which have also been included in Table I and Fig. 7 for comparisons. As in the previous paragraph, analyses of the pair wavefunctions involved in the calculated IR ESA spectrum in terms of the Yb$^{2+}$ and Yb$^{3+}$ parent states are useful to interpret the IR ESA signals observed, as follows: The sharp experimental peak at 250 cm$^{-1}$ corresponds to an energy transfer from the 4f$^{13}$ shell of Yb$^{2+}$ to the 4f$^{12}$ shell of Yb$^{3+}$:

Yb$^{2+}$→4f$^{13}$[4f$_{7/2}$→4f$_{5/2}$]5de$_{g}$ + Yb$^{3+}$→4f$^{13}$[4f$_{5/2}$→4f$_{7/2}$] + Yb$^{3+}$→4f$^{13}$[4f$_{5/2}$→4f$_{7/2}$] + Yb$^{3+}$→4f$^{13}$[4f$_{5/2}$→4f$_{7/2}$]

or [2F$_{5/2}$5de$_{g}$→2F$_{7/2}$] → [2F$_{5/2}$5de$_{g}$→2F$_{7/2}$] within the pair Yb$^{2+}$→Yb$^{3+}$, which is a 4f→4f emission in Yb$^{2+}$ and a 4f→4f absorption in Yb$^{3+}$. In particular, the two IR ESA bands calculated at 270 and 307 cm$^{-1}$ correspond to [2A$^{1}n$,1Γ$_{7n}$]→[1E$_{g}$2Γ$_{7n}$] and [2A$^{1}n$,1Γ$_{7n}$]→[1Γ$_{7n}$2Γ$_{7n}$]. The sharp experimental peak at 1145 cm$^{-1}$ corresponds to the 2A$^{1}n$→57Γ$_{7n}$ intraconfigurational absorption occurring in the Yb$^{2+}$ center of the pair Yb$^{2+}$→2F$_{5/2}$5de$_{g}$→Yb$^{3+}$→2F$_{5/2}$5de$_{g}$, as it correlates well with the [2A$^{1}n$,1Γ$_{7n}$]→[57Γ$_{7n}$1Γ$_{7n}$] band calculated at 1069 cm$^{-1}$. Finally, the broad band observed from 650 to 950 cm$^{-1}$ is found to correspond to a set of transitions calculated from 686 to 739 cm$^{-1}$, which span a narrower energy interval. Here, higher components of the energy transfer transitions from the 4f$^{13}$ subshell of Yb$^{2+}$ to the 4f$^{13}$ shell of Yb$^{3+}$, like those of the lowest IR ESA band, are found together with a third type of excitations which are intraconfigurational 4f→4f transitions between the Stark components of the Yb$^{2+}$ moiety.

Yb$^{3+}$→4f$_{7/2}$→Yb$^{3+}$4f$_{7/2}$.

In all cases, the electronic transitions involve negligible structural reorganization, which explains why they are very narrow bands.
D. Excitation of the IR Yb$^{3+}$ luminescence

A study of the optical properties of Yb$^{3+}$-doped CaF$_2$ crystals after application of reducing methods such as γ-irradiation and annealing in hydrogen, was conducted in order to investigate the Yb$^{3+}$/Yb$^{2+}$ conversion in the CaF$_2$ host. The study showed the appearance of the 4$f^{14}$→4$f^{13}d^5$ absorption bands characteristic of Yb$^{2+}$-doped CaF$_2$ in the UV absorption spectrum of the treated samples. Two weak overlapping emission bands were observed at room temperature at 565 and 540 nm (17699 and 18519 cm$^{-1}$) which were identified as the yellow-green anomalous emission of Yb$^{2+}$-doped CaF$_2$, which was observable even at room temperature in this case. A reduction on the intensity of the EPR signals associated with Yb$^{3+}$ centers was observed after γ-irradiation at temperatures ranging 10 to 100 K. All of these features were taken as evidences of partial reduction of Yb$^{3+}$ to Yb$^{2+}$ in the CaF$_2$ host.

Since the existence of Yb$^{2+}$–Yb$^{3+}$ mixed valence pairs in these samples appears to be a reasonable hypothesis, the interpretation of the spectral features mentioned can be done in terms of the IVCT diagrams calculated in this work as explained in the previous sections, where the first absorption of Yb$^{3+}$ and the IVCT luminescence mechanism have been described in detail. Yet, the type of samples used in Ref. 12 brings the opportunity to examine the quality of some of the approximations assumed in the IVCT theoretical model used in this paper. In effect, it is worth noticing that departure from cubic site symmetry is far more likely in as-grown CaF$_2$:Yb$^{3+}$ than in CaF$_2$:Yb$^{2+}$ crystals due to necessary charge compensation in the former. Associated with charge compensations, optical absorption signals between 10257 and 10995 cm$^{-1}$ have been found in CaF$_2$:Yb$^{3+}$ crystals (this work, cubic: 10763, 11196 cm$^{-1}$) and have been associated with cubic, tetragonal, trigonal, and rhombic sites; they all correspond to different splittings of the $2F_{5/2}$ excited multiplet. This is also true after the CaF$_2$:Yb$^{3+}$ samples are subjected to reducing treatments. Yet, the shape, number of bands, and peak positions of the IVCT luminescence bands (so far anomalous bands) reported for CaF$_2$:Yb$^{3+}$ reduced samples in Ref. 12 and for CaF$_2$:Yb$^{2+}$ crystals in Ref. 67, are basically identical: two broad, structureless overlapping bands are observed peaking at 17699 and 18519 cm$^{-1}$, and at 17600 and 18200 cm$^{-1}$, respectively. This fact suggests that the diabatic approximation proposed here and the disregard of non-cubic splittings due to local charge compensation and/or mutual interaction between the moieties of the Yb$^{2+}$–Yb$^{3+}$ pairs are reasonable theoretical bases and allow for the quantitative interpretation of the main spectral features of the Yb$^{2+}$–Yb$^{3+}$ mixed valence pairs at the cost of independent embedded cluster calculations.

In the reduced samples of Ref. 12, the 4$f^{14}$→4$f^{13}d^5$ absorption bands of Yb$^{2+}$ were found in the excitation spectrum where the 980 nm (10204 cm$^{-1}$) IR emission of Yb$^{3+}$ was monitored. The IVCT energy diagram (Fig. 4) provides a mechanism for the excitation of the Yb$^{3+}$ emission by the first absorption band of Yb$^{2+}$: a generalization of step I, followed by steps II and III$_{em}$. E.g. the lowest Yb$^{2+}$ 4$f^{14}$→4$f^{13}d^5$ excitation $A_{ig} \rightarrow 1T_{1u}$ is setp I, and the next $A_{ig} \rightarrow 2\rightarrow 4T_{1u}$ excitations will be followed by nonradiative decays to 1T$_{1u}$; the lowest Yb$^{2+}$ 4$f^{14}$→4$f^{13}d^5$ excitation $A_{ig} \rightarrow 5T_{1u}$ (second 4$f^2$→5d band) will be followed by IVCT non-radiative decay [2F$_{7/2}$5d$^5e_1$1G$_{9/2}$ → [117$\nu_7$2F$_{7/2}$5d$^5e_1$1G$_{9/2}$], followed by steps II and III$_{em}$; and similar arguments hold for the higher energy states. Obviously, the Yb$^{3+}$ emission, step III$_{em}$, competes with step III, which excites the IVCT luminescence through a second photon absorption. However, its quenching ability is probably small given than step III$_{em}$ is basically (within the independent embedded cluster approximation) an Yb$^{3+}$ 4$f^2$-electric dipole forbidden transition whereas step III is an electric dipole Yb$^{2+}$ 4$f^2$-5d allowed absorption.

IV. INTERPLAY BETWEEN IVCT AND 5d → 4f EMISSIONS IN CaF$_2$, SrF$_2$, BaF$_2$, AND SrCl$_2$.

As we have discussed, only the very broad yellow-green IVCT luminescence has been detected in CaF$_2$:Yb$^{3+}$ [8,11] in SrF$_2$:Yb$^{3+}$, the equivalent “anomalous” emission has been detected in the red [9] but a second much narrower, blue emission band was also found experimentally and was interpreted as a regular 5d→4f emission from the metastable states 1E$_u$ and 1T$_{2u}$ of Yb$^{2+}$ [10]. And in BaF$_2$:Yb$^{2+}$ there is no emission at all up to 1.5μm after strong laser excitation in the 4f→5d band [11]. The remaining luminescence combination, i.e. that only regular 5d→4f emission is observed, is found in SrCl$_2$:Yb$^{3+}$ [11,16]. The 5d→4f emissions of SrF$_2$:Yb$^{2+}$ and SrCl$_2$:Yb$^{3+}$ are different: an Yb$^{2+}$ electric dipole allowed emission of higher energy, from 1T$_{2u}$, is present in SrCl$_2$:Yb$^{2+}$, which was not found in SrF$_2$:Yb$^{2+}$ from 4.4 K to room temperature [10,15,16]. In this Section we discussed the reasons for such a chemical dependence of the luminescence. Firstly, we discuss the CaF$_2$, SrF$_2$, BaF$_2$ chemical series in Sec. IV.A. Then, we discuss the SrF$_2$, SrCl$_2$ series in Sec. IV.B.

The results of the quantum mechanical calculations of the diabatic potential energy surfaces and the full and selected IVCT energy diagrams for the ground and excited states of the Yb$^{2+}$–Yb$^{3+}$ embedded pairs in the CaF$_2$, SrF$_2$, BaF$_2$ hosts are presented in Fig. 6 of Ref. 55 and Fig. 8 in the SrF$_2$, SrCl$_2$ hosts in Fig. 7 of Ref. 55 and Fig. 9. Vertical transition energies and energy barriers for IVCT recombination are given in Tables III and IV respectively (descriptions of their content given in Sec. III.A are valid and readily adaptable to SrF$_2$ and BaF$_2$ results). More data can be found in Ref. 55.

A. Luminescence of Yb$^{2+}$-doped CaF$_2$, SrF$_2$, and BaF$_2$

Probably associated with the increasing lattice volume going from CaF$_2$ (163.0 Å$^3$, 0%) to SrF$_2$ (194.7 Å$^3$, 19%)
to BaF$_2$ (238.3 Å$^2$, 46%), the offset between the Yb–F equilibrium distance of the ground states of the donor Yb$^{2+}$ and acceptor Yb$^{3+}$ independent active centers (1A$_{1g}$ and 1I$_{7u}$, respectively), increases significantly from 0.129 Å (0%) to 0.154 Å (19%), to 0.200 Å (55%), in absolute values.$^{22}$ Other properties change as well (breathing mode vibrational frequencies, ligand field effects, etc.), but their variations in the series are noticeably smaller.$^{23}$ The bond length offsets mentioned determine the values of the normal electron transfer reaction coordinate ($Q_{et}$), at the minimum of the Yb$^{2+}$–Yb$^{3+}$ pair ground state [1A$_{1g}$,1I$_{7u}$] and, therefore, the offsets between the two minima Yb$^{2+}$–Yb$^{3+}$ [1A$_{1g}$,1I$_{7u}$] and Yb$^{3+}$–Yb$^{2+}$ [1I$_{7u}$,1A$_{1g}$] along the $Q_{et}$ axis. In the fluoride series this offset increases as: $|\Delta Q_{et}| = 0.517$ Å (0%, CaF$_2$), 0.616 Å (+19%, SrF$_2$), 0.802 Å (+55%, BaF$_2$), as it can be observed in Fig. 6 of Ref. 55 and Fig. 8. The different luminescent behaviour of Yb in the fluoride series stems from this trend, because the increase in the offset between the two minima in the IVCT configuration diagram provokes a shift of the crossing points between the lowest Yb$^{2+}$–Yb$^{3+}$ [$^2F_{7/2}$, $^5d_{g}$, $^2F_{7/2}$] states and the stressed branches of the Yb$^{3+}$–Yb$^{2+}$ IVCT states [$^5F_{7/2}$, $^4F_{14}$] and [$^7F_{5/2}$, $^4F_{14}$], which act as two different non-radiative decay pathways after the first photon excitation: the first decay yields to the pair ground state, and so, to luminescence quenching; the second, leaves Yb$^{3+}$ in its $^5F_{2}$ excited spin-orbit multiplet, which can ultimately lead to IVCT luminescence. We will see here how the magnitude of the energy barriers for these crossings are responsible for either luminescence quenching, as in BaF$_2$, or interplay between regular 5d–4f and IVCT luminescence, as in CaF$_2$ and SrF$_2$ cases. This is summarized in Fig. 10.

1. **Luminescence quenching in BaF$_2$:Yb$^{2+}$**

The crossing between Yb$^{2+}$–Yb$^{3+}$ [$^2F_{7/2}$, $^5d_{g}$, $^2F_{7/2}$] and Yb$^{3+}$–Yb$^{2+}$ [$^5F_{7/2}$, $^4F_{14}$] that enables quenching of the luminescence (step II$_{quen}$) by direct non-radiative decay to the ground state after the first photon absorption (step I), i.e. from Yb$^{2+}$–Yb$^{3+}$ [1E$_{u}$,1I$_{7u}$] to Yb$^{3+}$–Yb$^{2+}$ [1I$_{7u}$,1A$_{1g}$], varies very strongly in the fluoride series (cf. Table III and Fig. 8): 1680 cm$^{-1}$ (CaF$_2$), 818 cm$^{-1}$ (SrF$_2$), 261 cm$^{-1}$ in BaF$_2$. This result suggests that step II$_{quen}$ should result in appreciable quenching of the luminescence in BaF$_2$ after 4f–5d excitation. This observation holds both for IVCT and 5d–4f luminescence and it is in line with experimental evidences.$^{13}$ Then, we can say that BaF$_2$:Yb$^{2+}$–Yb$^{3+}$ belongs to the case D depicted in Fig. 10.

2. **Interplay between IVCT and 5d–4f emissions in CaF$_2$ and SrF$_2$**

The second important non-radiative pathway following excitation is step II (see Sec. III B), which enables IVCT non-radiative decay to the Yb$^{3+}$–Yb$^{2+}$ [2I$_{7u}$,1A$_{1g}$] excited state and is part of the IVCT luminescence mechanism. The shifts of the energy barriers leading to step II from CaF$_2$ to SrF$_2$ allow to interpret the different luminescent behaviour in these two hosts, as discussed next.

The energy barrier of IVCT crossing from Yb$^{2+}$–Yb$^{3+}$ [1E$_{u}$,1I$_{7u}$] to Yb$^{3+}$–Yb$^{2+}$ [2I$_{7u}$,1A$_{1g}$] increases from CaF$_2$ to SrF$_2$: 14 cm$^{-1}$ (CaF$_2$), 148 cm$^{-1}$ (SrF$_2$). This suggest that [1E$_{u}$,1I$_{7u}$] is more stable in SrF$_2$ than in CaF$_2$. So, regular Yb$^{2+}$ 5d–4f emission from this level should be more likely in SrF$_2$, where, as a matter of fact, it has been observed.$^{10}$ For the same reason, its contribution to exciting the IVCT luminescence through steps II to IV is much less likely in SrF$_2$ than in CaF$_2$, which correlates well with the significantly overall smaller emission lifetime of the IVCT (anomalous) luminescence measured in SrF$_2$ compared with CaF$_2$.$^{13}$ Then, we can say that SrF$_2$:Yb$^{2+}$ and CaF$_2$:Yb$^{2+}$ belong, respectively, to a case intermediate between C and B, and to case D depicted in Fig. 10.

In contrast, the energy barriers for crossing from [1T$_{1u}$,1I$_{7u}$] to [2I$_{7u}$,1A$_{1g}$]: 49 cm$^{-1}$ (CaF$_2$) and 10 cm$^{-1}$ (SrF$_2$), are comparable (although slightly smaller in the latter), which suggests that [1T$_{1u}$,1I$_{7u}$] should contribute significantly to the excitation of the IVCT luminescence in both hosts, especially at very low temperatures, since non-radiative multiphonon decay from this level to the [1E$_{u}$,1I$_{7u}$] should gradually quench this contribution in favour of a build up of the population of [1E$_{u}$,1I$_{7u}$] on a temperature dependent basis.$^{10,29}$ Whereas this temperature dependent build up implies further excitation of the IVCT luminescence in CaF$_2$:Yb$^{2+}$ (because [1E$_{u}$,1I$_{7u}$] preferentially undergoes step II of the IVCT luminescence), it contributes to increasing the intensity of the Yb$^{2+}$ 5d–4f blue emission [1E$_{u}$,1I$_{7u}$]–[1A$_{1g}$,1I$_{7u}$] in SrF$_2$:Yb$^{2+}$ (because 5d–4f emission is the preferred pathway for [1E$_{u}$,1I$_{7u}$] depopulation in this material). Altogether, these results allow to explain the different variation of the IVCT luminescence intensity with temperature in SrF$_2$ compared with CaF$_2$: IVCT luminescence intensity reaches its maximum very sharply in SrF$_2$:Yb$^{2+}$, at very low temperature: 20 K, and quenching already at 140 K; maximum intensity is reached more gradually at 110 K in CaF$_2$ and quenching is observed at 180 K (Ref. 11) (this quenching has been connected with branching to the ground state in Sec. III B). Correspondingly, the intensity of the 5d–4f emission [1E$_{u}$,1I$_{7u}$]–[1A$_{1g}$,1I$_{7u}$] in SrF$_2$ upon excitation in the [1T$_{1u}$,1I$_{7u}$] state (355 nm) is shown to be significantly higher than that measured upon direct excitation in the [1E$_{u}$,1I$_{7u}$] state (370 nm) beyond 140 K, which further reveals the temperature dependent [1T$_{1u}$,1I$_{7u}$]–[1E$_{u}$,1I$_{7u}$] build up at the expense of the [1T$_{1u}$,1I$_{7u}$]–[2I$_{7u}$,1A$_{1g}$] decay and IVCT luminescence.

Beyond step II, which has been discussed so far, the mechanism for IVCT luminescence in SrF$_2$ is the same as in CaF$_2$ and leads to a very broad band consisting of two overlapping bands corresponding to the three Yb$^{2+}$–Yb$^{3+}$ [1I$_{7u}$,2A$_{1g}$] → Yb$^{2+}$–Yb$^{3+}$ [$^4F_{14}$, $^2F_{7/2}$] vertical transitions at 17698, 17716, and 18121 cm$^{-1}$. Its FWHM is about 6000 cm$^{-1}$ as it can be seen in Fig. 5. The peak en-
ergy and FWHM found experimentally are 12670 cm\(^{-1}\) and 4800 cm\(^{-1}\). This indicates that the underestimation of the peak energy found in CaF\(_2\) becomes larger in the SrF\(_2\) host. In SrF\(_2\), the agreement between the calculated IR ESA spectrum and the one deduced from transient photoluminescence enhancement experiments in Ref. [4] is comparable to that in CaF\(_2\). Both the theoretical and experimental spectra can be compared in Table I and Fig. 7. The interpretation of the observed bands is the same as in the CaF\(_2\) case.

3. IVCT absorption in Yb\(^{2+}\)-doped SrF\(_2\)

Finally, we would like to report on the IVCT absorption bands which, according to our interpretation, have been detected in the excitation spectra of Yb\(^{2+}\)-doped SrF\(_2\) (Ref. [11]) even though they have not been identified in the other hosts.

We will try to interpret the excitation spectra of the SrF\(_2\):Yb\(^{2+}\) blue and red emissions\(^{[11]}\) using the calculations presented in this paper. According to them, a large number of close lying states of the Yb\(^{2+}\)-Yb\(^{3+}\) \([2F_{7/2}/5d_{5/2}^{2}F_{7/2}]\) configuration lie above its lowest state, \([1E_{u},1\Gamma_{7u}]\), forming a dense manifold 5500 cm\(^{-1}\) wide. This can be seen in Fig. 6 of Ref. [55] (first manifold of states plotted with solid blue lines); some of the levels are plotted in Fig. 8 and are tabulated in the absorption spectrum from the \([1A_{1g},1\Gamma_{7u}]\) ground state in Table I (see also Ref. [55]). In the vertical absorption spectrum from the \([1A_{1g},1\Gamma_{7u}]\) ground state (Table I), this manifold is crossed by the stressed IVCT \([2F_{5/2}/4f_{14}]\) branches of Yb\(^{3+}\)-Yb\(^{2+}\) \([2\Gamma_{7u},1A_{1g}]\) and \([2\Gamma_{8u},1A_{1g}]\) (dashed red lines in Fig. 6 of Ref. [55] and in Fig. 8) which are found at 28545 and 28809 cm\(^{-1}\) (4070 and 4333 cm\(^{-1}\) above the \([1E_{u},1\Gamma_{7u}]\) state).

Then, according to the mechanism discussed in Sec. III B, IVCT luminescence will be excited if these branches are reached either by crossings (like above) or by direct vertical IVCT absorptions from the ground state (like here, in the excitation spectrum). This explains the differences observed in the experimental excitation spectra: The excitation spectra of the IVCT luminescence consists of one intense and very broad band peaking at about 351 nm (28400 cm\(^{-1}\)) as one can read in Fig. 3 of Ref. [11]. This band can be assigned to the vertical IVCT absorptions Yb\(^{2+}\)-Yb\(^{3+}\) \([1A_{1g},1\Gamma_{7u}]\) \(\rightarrow\) Yb\(^{3+}\)-Yb\(^{2+}\) \([2\Gamma_{7u},1A_{1g}]\), \([2\Gamma_{8u},1A_{1g}]\). The band is broad due to the large offset between the to minima \([1A_{1g},1\Gamma_{7u}]\) and \([2\Gamma_{7u},1A_{1g}]\) along the Q\(_{eff}\) axis (0.616 Å). Interestingly, the broad band indicates a shoulder in its high energy side, which bands that shows non-radiative decay to the IVCT \([2\Gamma_{7u},1A_{1g}]\) branch from states lying above (like the electric dipole allowed \([4T_{1u},1\Gamma_{7u}]\)) could also excite the IVCT luminescence with sufficient efficiency so as to be observed as a shoulder from the main IVCT absorption excitation channel. Correspondingly, the excitation spectrum of the blue \([1E_{u},1\Gamma_{7u}]\) \(\rightarrow\) \([1A_{1g},1\Gamma_{7u}]\) emission shows the electronic structure of the \([2F_{7/2}/5d_{5/2}^{2}F_{7/2}]\) manifold interrupted by a dip, which coincides with the maximum of the intense IVCT absorption band of the IVCT luminescence excitation spectrum. Also, the shoulder of the latter and the fourth and highest intense peak of the former lie very close, which suggests the presence of the electric dipole allowed \([1A_{1g},1\Gamma_{7u}]\) \(\rightarrow\) \([4T_{1u},1\Gamma_{7u}]\) transition. It is interesting to note that in most of the experiments reported for SrF\(_2\):Yb\(^{2+}\) a larger wavelength (typically, 355 nm) has been used to study the luminescent behaviour of the anomalous emission.

The IVCT absorption band we have just assigned can be interpreted as the following one electron transfer: Yb\(^{2+}\) \(4f_{5/2} \rightarrow\) Yb\(^{3+}\) \(4f_{7/2}\). It differs from the commonly observed IVCT absorptions in mixed valence compounds in that the final state of the pair upon electron transfer is not the stressed ground state, but, rather, a stressed excited state. In this case, the Yb\(^{3+}\) part of the pair after electron transfer appears to be in the \(4f_{13}\)(\(2F_{5/2}\)) excited multiplet. This \(4f\rightarrow\)\(4f\) electron transfer is probably weaker than the close lying \(4f\rightarrow\) \(5d\) transitions in the absorption spectrum; however, it is more efficient in exciting the IVCT luminescence, because of its direct decay (step II) not facing an energy barrier, which explains its relative intensity in the excitation spectrum.

B. Interplay between IVCT and 5\(d\)\(\rightarrow\)4\(f\) emissions in SrF\(_2\) and SrCl\(_2\)

The dual character of the luminescence of Yb in SrF\(_2\) we have just discussed, disappears in the SrCl\(_2\) host, where the IVCT luminescence is not observed: only regular 5\(d\)\(\rightarrow\)4\(f\) emission bands have been assigned in this case. However, the emission spectrum of SrCl\(_2\):Yb\(^{2+}\) is very complex. This complexity stems precisely from the fact that the IVCT luminescence mechanism cannot occur, hence, 5\(d\)\(\rightarrow\)4\(f\) bands which are not observable in SrF\(_2\):Yb\(^{2+}\), become uncovered in SrCl\(_2\):Yb\(^{2+}\). The purpose of this section is to explain why this is so even if the existence of Yb\(^{2+}\)-Yb\(^{3+}\) mixed valence pairs is likely.\(^{[13],[21],[23]}\) We do not intend to discuss the complex \(4f\rightarrow\)5\(d\) spectroscopy of SrCl\(_2\):Yb\(^{2+}\), which has been the subject of a number of experimental and theoretical studies.\(^{[31],[34],[35],[60]}\)

In the host series SrF\(_2\), SrCl\(_2\), it is the chemical change what leads the variations of the local properties of the Yb\(^{2+}\) and Yb\(^{3+}\) moieties of the Yb\(^{2+}\)-Yb\(^{3+}\) pairs, rather than the structural change. In particular, the energies of the breathing mode of the donor (YbX\(_{3}\))\(^{5+}\) and acceptor (YbX\(_{3}\))\(^{3+}\) embedded clusters clearly show the chemical change, so that the mean values of the ground state vibrational frequencies \(\omega_{vib} = (\omega_{vib}(1A_{1g}) + \omega_{vib}(1\Gamma_{7u})/2\), decrease from 402 cm\(^{-1}\) (0% SrF\(_2\)) to 246 cm\(^{-1}\) (39 % SrCl\(_2\)). These mean values basically determine the curvature of the diabatic potential energy surfaces and the IVCT energy diagrams of the Yb\(^{2+}\)-Yb\(^{3+}\) embedded pairs. The change is very clear in Fig. 7 of Ref. [55] and Fig. 9. As an effect, the crossing points between the lowest Yb\(^{2+}\)-Yb\(^{3+}\) \([2F_{7/2}/5d_{5/2}^{2}F_{7/2}]\) states and the stressed
branches of the Yb\(^{3+}\)-Yb\(^{2+}\) ground and excited configurations \([^2F_{7/2},^4F_{14}]\) and \([^2F_{5/2},^4F_{13}]\) are drastically shifted in SrCl\(_2\) (see Fig. 9 and Table III). And as a consequence, none of the two non-radiative pathways is available in SrCl\(_2\) anymore. We can say that SrCl\(_2\):Yb\(^{3+}\)-Yb\(^{2+}\) belongs to the case A in Fig. 10. Therefore, the first conclusion driven from the SrCl\(_2\):Yb\(^{2+}\)-Yb\(^{3+}\) IVCT energy diagrams is that the IVCT luminescence observed in CaF\(_2\) and SrF\(_2\) cannot occur in this host. The second conclusion is that not only is the [1\(E_u\),1\(\Gamma_{7u}\)] state very stable, but also the higher electric dipole allowed [1\(T_{1u}\),1\(\Gamma_{7u}\)] state is, since it cannot decay through step II, like in CaF\(_2\) and SrF\(_2\). This means that both states can luminesce in a wide range of temperatures (blue arrows in Fig. 9) and that the temperature dependent multiphonon relaxations from [1\(T_{1u}\),1\(\Gamma_{7u}\)] to [1\(E_u\),1\(\Gamma_{7u}\)], which influenced the intensities of the blue and red emissions of SrF\(_2\) discussed above, applies now to the interplay between radiative and non radiative decays from [1\(T_{1u}\),1\(\Gamma_{7u}\)], with the additional complexity arising from the Boltzmann population of close lying states above the 1\(T_{1u}\) before room temperature is reached. All of which results in a complex, but well understood temperature dependence of the relative intensities and lifetimes of the two emission bands.

In addition to the two emission bands from [1\(T_{1u}\),1\(\Gamma_{7u}\)] and [1\(E_u\),1\(\Gamma_{7u}\)], observed peaking at 26500 and 24700 cm\(^{-1}\), respectively (this work: 25500 and 22900 cm\(^{-1}\)), Witzke et al. reported other three emission bands peaking at 19000, 23900, and 25400 cm\(^{-1}\), which were ruled out as internal transitions of the Yb\(^{2+}\) ion and were called defect bands involving, possibly, Yb\(^{3+}\) ions or Yb\(^{3+}\)-Yb\(^{2+}\) pairs. The band peaking at 19000 cm\(^{-1}\) could be associated with the IVCT luminescence Yb\(^{2+}\)-Yb\(^{3+}\) [1\(E_u\),1\(\Gamma_{7u}\)]→ Yb\(^{3+}\)-Yb\(^{2+}\) [1\(\Gamma_{7u}\),1\(A_{1g}\)], calculated as a vertical transition at 17200 cm\(^{-1}\) (see green arrows in Fig. 9).

V. CONCLUSIONS

\textit{Ab initio} quantum mechanical calculations of the electronic structure of Yb\(^{2+}\)-Yb\(^{3+}\) mixed valence pairs in fluorites allow to conclude the existence of two-photon excited IVCT luminescence in Yb-doped CaF\(_2\) and SrF\(_2\). The IVCT emission is found to be a bielectronic deexcitation involving electron transfer from the donor to the acceptor moieties of the Yb\(^{2+}\)-Yb\(^{3+}\) pair, Yb\(^{2+}\) 5d\(e_\text{s}\) → Yb\(^{3+}\) 4\(f\)\(_{7/2}\), and a 4\(f\)\(_{7/2}\) → 4\(f\)\(_{5/2}\) deexcitation within the Yb\(^{2+}\) 4\(f\)\(_{13}\) subshell: Yb\(^{2+}\)-Yb\(^{3+}\) \([^2F_{5/2},5d\(e_\text{s},^2F_{7/2}\)] \→ Yb\(^{3+}\)-Yb\(^{2+}\) \([^2F_{7/2},4F_{14}\)]\). Hence, it is a very slow rate radiative process. It is excited by a very efficient two-photon mechanism where each photon provokes the same strong 4\(f\)\(_{14}\) \→ 1\(A_{1g}\),4\(f\)\(_{14}\) \→ 4\(f\)\(_{13}\)\([^2F_{7/2},5d\(e_\text{s},^1T_{1u}\)]\) absorption in the Yb\(^{2+}\) part of the pair: the first one, from the pair ground state; the second one, from an excited state of the pair whose Yb\(^{3+}\) moiety is in the higher 4\(f\)\(_{14}\)\([^2F_{7/2}\)] spin-orbit multiplet. The band widths of the emissions are very large, in analogy with the wide band widths of well-known IVCT absorptions of transition metal mixed valence compounds.

The calculated IVCT energy diagrams show that two important non-radiative decay pathways may occur after the first photon excitation, which involve non-radiative Yb\(^{2+}\)-Yb\(^{3+}\)-Yb\(^{2+}\)-Yb\(^{3+}\) electron transfer (see graphical conclusion Fig. 10). One, leads to the ground state \([4\(f\)\(_{13}\),^2F\(_{7/2}\)]\), and quenches any emission (black line in Fig. 10), the other, leads to the excited state \([4\(f\)\(_{13}\),^2F\(_{5/2}\)]\), from where the (second-photon) IVCT luminescence excitation takes place (red line in Fig. 10). The structural change in the CaF\(_2\), SrF\(_2\), BaF\(_2\) series and the chemical change in the SrF\(_2\), SrCl\(_2\) series, influence the topology of the calculated IVCT energy diagrams and shift the crossings with both decay pathways making the quenching decay the most likely in BaF\(_2\), the decay towards IVCT luminescence excitation the most likely in CaF\(_2\) and SrF\(_2\), whereas none of the two decays occur in the SrCl\(_2\) case, all of which leads to total quenching of any emission in BaF\(_2\) (case D), IVCT luminescence only in CaF\(_2\) (case B), dual IVCT and 5d→4f emissions in SrF\(_2\) (intermediate case between B and C), and only 5d→4f emissions in SrCl\(_2\) (case A), as experimentally observed.

The electronic structure of the Yb\(^{2+}\)-Yb\(^{3+}\) pairs has been calculated within the diabatic and independent Yb\(^{2+}\) and Yb\(^{3+}\) embedded cluster approximations. The donor (Yb\(_\text{X}_5\)) and acceptor (Yb\(_\text{X}_5\)) \textit{ab initio} wavefunctions and energies have been calculated using high quality, well-established \textit{ab initio} quantum chemical methods, including: extended basis sets, non-dynamic and dynamic electron correlation, relativistic effects up to spin-orbit coupling, and quantum mechanical host embedding, all of them, at the highest levels of methodology compatible with the need to combine them all at once. The two series of hosts chosen to demonstrate the capabilities and limitations of the IVCT model presented span a very complex luminescence scenario for validation. In this context, the overall agreement of the theoretical and experimental results including different types of samples (Yb\(^{2+}\)-doped, Yb\(^{3+}\)-doped) and experimental techniques: emission, excitation, photoluminescence enhancement spectra and their variation with temperature, is very satisfactory and allows to draw the conclusion that the anomalous luminescence of Yb\(^{2+}\) associated so far with impurity-trapped excitons is, rather, an IVCT luminescence associated with Yb\(^{2+}\)-Yb\(^{3+}\) mixed valence pairs. We also conclude that the broad band observed in the excitation spectrum of the so far called anomalous emission of Yb\(^{2+}\)-doped SrF\(_2\) is a broad IVCT absorption band corresponding to the following Yb\(^{2+}\) 4\(f\)\(_{5/2}\) → Yb\(^{3+}\) 4\(f\)\(_{7/2}\) electron transfer.

Acknowledgments

This work was partly supported by a grant from Ministerio de Economía y Competitividad, Spain (Dirección General de Investigación y Gestión del Plan Nacional de I+D+i, MAT2011-24586).
Barandiarán and Seijo IVCT luminescence: Interplay between anomalous and 5d–4f emissions in Yb-doped fluorites

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TABLE I: Spectroscopic constants and analyses of the spin-orbit wave functions of the electronic states of independent Yb$^{3+}$ and Yb$^{2+}$-doped CaF$_2$ cubic defects. Yb–F bond distances, $d$, in Å; totally symmetric vibrational frequencies of the YbF$_{6}$ stretching mode, $\omega_{\text{vib}}$, in cm$^{-1}$; minimum-to-minimum energy differences, $T_{e}$, relative to the ground states, in cm$^{-1}$; $1A_{1g} \rightarrow 1T_{1u}$ absorption oscillator strengths of electric dipole allowed electronic transitions, $f_{i}$, are given relative to that to $1T_{1u}$: $f_{i} = 2.013 \times 10^{-2}$. Manifold averages and mean square deviations of the individual values are indicated. Higher lying excited states of Yb$^{3+}$ can be found in Ref. [35].

| State      | $d_{e}$ | $\omega_{\text{vib}}$ | $T_{e}$ | $f_{i}/f_{1}$ | weights of terms larger than 10% $^{a}$ |
|------------|---------|-----------------------|--------|---------------|-----------------------------------------|
| $1A_{1g}$  | 2.329   | 423                   | 0      | 100.0         | $1^{1}A_{1g}$                            |
| $1E_{g}$   | 2.317   | 423                   | 23510  | 89.21         | $1^{3}T_{1u}$                            |
| $1T_{1u}$  | 2.317   | 423                   | 23548  | 89.94         | $1^{3}T_{1u}$                            |
| $1T_{1u}$  | 2.316   | 423                   | 25636  | 42.33         | $1^{1}T_{1u}$                            |
| $1A_{2u}$  | 2.315   | 424                   | 25704  | 99.57         | $1^{3}T_{2u}$                            |
| $2T_{1u}$  | 2.316   | 424                   | 25730  | 68.39         | $1^{1}T_{2u}$                            |
| $2E_{u}$   | 2.315   | 422                   | 26202  | 48.54         | $1^{1}E_{u}$                            |
| $3T_{2u}$  | 2.314   | 422                   | 26420  | 48.54         | $1^{3}E_{u}$                            |
| $2T_{1u}$  | 2.314   | 423                   | 26533  | 0.160         | $1^{1}E_{u}$                            |
| $1A_{1u}$  | 2.315   | 424                   | 26664  | 96.37         | $1^{3}T_{1u}$                            |
| $3T_{1u}$  | 2.316   | 421                   | 27095  | 0.045         | $1^{3}T_{1u}$                            |
| $3E_{u}$   | 2.315   | 422                   | 28096  | 79.67         | $1^{1}E_{u}$                            |
| $4T_{1u}$  | 2.315   | 423                   | 28327  | 48.35         | $1^{3}T_{1u}$                            |
| $4T_{1u}$  | 2.316   | 421                   | 28344  | 0.001         | $1^{3}T_{1u}$                            |

$^{a}$weights are given in % and correspond to calculations at d(Yb-F) = 2.200 Å and 2.383 Å for Yb$^{3+}$ and Yb$^{2+}$-doped CaF$_2$, respectively.

$^{b}$The Yb$^{2+}$ $1A_{1g} \rightarrow $Yb$^{3+}$ $1\Gamma_{7u}$ minimum-to-minimum energy difference is 6905 cm$^{-1}$. 

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IVCT luminescence: Interplay between anomalous and 5d–4f emissions in Yb-doped fluorites
TABLE II: Absorption and emission peak positions of the Yb$^{2+}$–Yb$^{3+}$ pair in CaF$_2$ and SrF$_2$ calculated as total energy differences at the equilibrium geometries of the initial state. $d_\text{I}$ and $d_\text{F}$ are the Yb–F distances in the left and right YbF$_6$ moieties. Only data referred in the text are given. For all vertical transitions and data in BaF$_2$:Yb$^{2+}$–Yb$^{3+}$, see Ref. 55. Experimental data are given in squared parentheses. Identification of calculated energy differences with absorption and emission transitions indicated in Figs. 4 and 8 are shown as roman numbers in parentheses. Energies in cm$^{-1}$, distances in Å. See text for details.

| Final state | Yb$^{2+}$–Yb$^{3+}$ [4$f^{14},2F_{7/2}$] | [4$f^{14},2F_{7/2}$] | $[2F_{5/2}5de_{g},2F_{7/2}]$ |
|-------------|---------------------------------|---------------------|------------------|
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 0                  | -10762           |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 686               | -10078           |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 729               | -10055           |
|             | $[4f^{14},2F_{5/2}]$ | [10384]$^a$          | -10035           |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 10763             | -9718            |
|             | $[4f^{14},2F_{5/2}]$ | [$\sim$10794]$^a$ | -9718            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 11196             | -10160           |
| $Yb^{3+}$–Yb$^{3+}$ | $[2F_{5/2},4f^{14}]$ | 15238             | -10762           |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 15728             | -10078           |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 15751             | -10055           |
| $Yb^{3+}$–Yb$^{3+}$ | $[2F_{5/2},5de_{g},2F_{7/2}]$ | $[24814]$ | $[25316]$ |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 23576             | 25316            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 23614             | 24017            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 24263             | 25955            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 24301             | 25907            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 24344             | 25131            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 25706             | 26618            |
| $Yb^{3+}$–Yb$^{3+}$ | $[2F_{5/2},4f^{14}]$ | $[27400]$ | $[27950]$ |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 25922             | 28545            |
|             | $[1\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 26243             | 28809            |
| $Yb^{3+}$–Yb$^{3+}$ | $[2F_{5/2},5de_{g},2F]$ | $[34074]$ | $[35003]$ |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35003             | 23311            |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35194             | 23576            |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35236             | 23614            |
| $Yb^{3+}$–Yb$^{3+}$ | $[2F_{5/2},5de_{g},2F]$ | $[34340]$ | $[35194]$ |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35194             | 23576            |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35236             | 23614            |
| $Yb^{3+}$–Yb$^{3+}$ | $[2F_{5/2},5de_{g},2F]$ | $[34378]$ | $[35236]$ |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35236             | 23614            |
|             | $[2\Gamma_{\text{II}},1\Gamma_{\text{II}}]$ | 35236             | 23614            |

$^a$ Experimental data given in squared parentheses.
Barandiarán and Seijo

IVCT luminescence: Interplay between anomalous and 5d–4f emissions in Yb-doped fluorites

| Multiplet | Energy (cm⁻¹) |
|-----------|---------------|
| [2A₁₃u,1Γ₆u] | 34761 |
| [1E₆u,2Γ₆u] | 34772 |
| [2A₁₃u,1Γ₆u] | 34804 |
| [1T₂₁u,2Γ₆u] | 34810 |
| [5T₁₁u,1Γ₆u] | 35145 |
| [5T₅₁u,1Γ₆u] | 35832 |
| [5T₁₁u,1Γ₆u] | 35874 |
| [5T₂₁u,1Γ₆u] | 36005 |
| [5T₂₁u,1Γ₆u] | 36351 |
| [1Γ₆u,1Γ₆u] | 36470 |
| others g | 36737 |
| [1T₄₁u,2Γ₆u] | 37337 |
| (III) 2nd photon absorption | |

**Notes:**

- **a** Only the absorption line at 10384 cm⁻¹ was assigned to a cubic site in Ref. [54] the splitting of the 4f¹³(²F₅/₂) multiplet was expected to be similar to that found by Kiss (Ref. [67] for the isoelectronic ion CaF₂Tm²⁺: 410 cm⁻¹.
- **b** From Ref. [6] and [7] below 200 K.
- **c** From Ref. [8] at 77 K.
- **d** From Ref. [11] at 4.2 K.
- **e** From Ref. [11] at 4.2 K.
- **f** From absorption spectra from Ref. [6] and [7] at 20°C and Ref. [21] at 77 K.
- **g** From Ref. [55]
- **h** Read from Fig. 2 of Ref. [11] see text for details.
- **i** Experimental data from two frequency transient photoluminescence enhancement spectra at 10 K, from Ref. [13] (CaF₂) and Ref. [14] (SrF₂).
TABLE III: Calculated diabatic energy barriers for the Yb$^{2+}$−Yb$^{3+}$ → Yb$^{3+}$−Yb$^{2+}$ electron transfer reaction within the Yb$^{2+}$−Yb$^{3+}$ active pairs in CaF$_2$, SrF$_2$, BaF$_2$, and SrCl$_2$ fluorite-type crystals. [Di, Aj] and [Ak, Dl] are the electronic states of the pair before and after electron transfer. The energy barrier for crossing in the forward, [Di, Aj] → [Ak, Dl], and backwards, [Ak, Dl] ← [Ak, Dl] reactions are given separated by a semicolon. The values of the Yb–X distances at the activated complex point, $d_i, d_k$, are given: they are, respectively, the Yb-X distances of the left ($L$) and right ($R$) YbX$_4$ moieties. Energy barriers in bold format can be seen in Figures 4, 8, and 9. See text for details.

| (YbX$_4$)$_i^{6-}$ + (YbX$_4$)$_k^{5-}$ | (YbX$_4$)$_i^{4-}$ + (YbX$_4$)$_k^{6-}$ | forward; backwards diabatic energy barriers for IVCT $d_i, d_k$ at the crossing point |
|-----------------|-----------------|-------------------------------|
| Yb$^{2+}$−Yb$^{3+}$ → Yb$^{3+}$−Yb$^{2+}$ | [Di, Aj] → [Ak, Dl] | [4f$^{14}$,4f$^{13}$(7/2)] → [4f$^{13}$(5/2), 4f$^{14}$] |
|                | [1A$_{1g}$,1Γ$_{9u}$] → [2Γ$_{7u}$,1A$_{1g}$] | 11048; **285** 11581; **862** 12390; **1700** 10837; 196 |
|                | 2.220,2.311 2.285,2.377 2.349,2.442 2.711,2.878 |
|                | [4f$^{13}$(7/2)$5d_{e}$,4f$^{13}$(7/2)] → [4f$^{13}$(5/2), 4f$^{14}$] | (II crossing) |
|                | [1E$_u$,1Γ$_{9u}$] → [1Γ$_{7u}$,1A$_{1g}$] | **1680**; 25174 **818**; 25263 **261**; 25775 9416; 32606 |
|                | 2.360,2.159 2.435,2.222 2.501,2.278 2.978,2.612 |
|                | 1701; 25229 819; 25306 266; 25825 9425; 32652 |
|                | 2.364,2.162 2.435,2.222 2.504,2.280 2.978,2.672 |
|                | 2561; 28179 1389; 27976 570; 28256 12846; 38050 |
|                | 2.375,2.154 2.444,2.212 2.510,2.267 3.025,2.612 |
|                | [4f$^{13}$$5d_{e}$,4f$^{13}$] → [4f$^{13}$(7/2), 4f$^{13}$(7/2)$5d_{e}$] | (I$q_{nch}$) quenching |
|                | [2A$_{1u}$,1Γ$_{9u}$] → [1Γ$_{7u}$,1E$_u$] | **76**; 10570 **385**; 10909 **912**; 11470 2838; 13939 |
|                | 2.306,2.209 2.367,2.268 2.433,2.331 2.914,2.675 |
|                | 55.5; 10818 347; 11067 878; 11567 2853; 13494 |
|                | 2.308,2.209 2.369,2.268 2.434,2.331 2.916,2.676 |
|                | [4f$^{13}$$5d_{e}$,4f$^{13}$] → [4f$^{13}$(5/2), 4f$^{14}$] | [4f$^{13}$(5/2), 4f$^{14}$] |
|                | [2A$_{1u}$,1Γ$_{9u}$] → [2Γ$_{7u}$,1A$_{1g}$] | **1650**; 24868 **800**; 25051 **262**; 25646 9491; 32595 |
|                | 2.360,2.160 2.431,2.220 2.503,2.280 2.978,2.612 |
|                | 1774; 25264 861; 25307 277; 25792 9522; 32712 |
|                | 2.365,2.162 2.436,2.222 2.564,2.241 2.979,2.612 |
FIG. 1: Results of quantum mechanical calculations on Yb-doped CaF$_2$ crystals. Top graphs: The two symmetric diabatic potential energy surfaces corresponding to the $[1A_{1g},1\Gamma_{7u}]$ ground state of the Yb$^{2+}$–Yb$^{3+}$ pair before (YbF$_8$)$_6$$^-$–(YbF$_6$)$_5$$^-$ $[1A_{1g},1\Gamma_{7u}]$ (red in right graph) and after (YbF$_8$)$_5$$^-$–(YbF$_6$)$_5$$^-$ $[1\Gamma_{7u},1A_{1g}]$ (blue in right graph) electron transfer are plotted (left graph) and projected (right graph) in the $d_L, d_R$ plane. The Yb–F distances of the left ($d_L$) and right ($d_R$) moieties of the pair are given in Å. Top left graph: Energies are given in cm$^{-1}$ and are referred to the energy of the two equivalent ground state minima. Top right graph: The minimal energy reaction path connecting the two equivalent minima through the activated complex is indicated. Bottom graph: Displacements of the X atoms of the (YbX$_8$)$_L$–(YbX$_8$)$_R$ moieties along the electron transfer reaction coordinate $Q_{et}$. See text for details.
Barandiarán and Seijo

IVCT luminescence: Interplay between anomalous and 5d–4f emissions in Yb-doped fluorites

FIG. 2: Results of quantum mechanical calculations on Yb-doped CaF$_2$ crystals. Left graph: potential energy curves of the ground and one excited state of the independent (YbF$_8$)$_6^–$ and (YbF$_8$)$_5^–$ embedded clusters. Right graph: Diabatic IVCT energy diagram for Yb$^{2+}$–Yb$^{3+}$ embedded pairs. The symmetric (YbF$_8$)$_6^–$–(YbF$_6$)$_5^–$ $D_iA_j$ and (YbF$_8$)$_5^–$–(YbF$_6$)$_5^–$ $A_iD_j$ branches are plotted vs. the normal electron transfer reaction coordinate $Q_{et}$ of the ground state. $D_i$ and $A_j$ refer to the parent independent embedded cluster states. Top right graph: Qualitative representations of the structure of the left and right moieties of the pair for $Q_{et} < 0, = 0$ (activated complex), and $> 0$ are plotted. See text for details.
FIG. 3: Results of quantum mechanical calculations on Yb-doped CaF$_2$ crystals. Left graph: potential energy curves of the ground and excited states of independent donor (YbF$_6$)$^{6-}$ and acceptor (YbF$_6$)$^{5-}$ embedded clusters. Right graph: Diabatic IVCT energy diagram for Yb$^{2+}$–Yb$^{3+}$ embedded pairs. The symmetric (YbF$_6$)$^{5-}$–(YbF$_6$)$^{5-}$ and (YbF$_6$)$^{5-}$–(YbF$_6$)$^{5-}$ branches of the ground and excited states of Yb$^{2+}$–Yb$^{3+}$ pairs are plotted vs. the normal electron transfer reaction coordinate $Q_{et}$ for the pair ground state; the values of the Yb–F distance of the left and right YbF$_6$ moieties, $d_L$ and $d_R$ are indicated. Colors in left graph: black $4f^{14}$ and $4f^{13}(7/2)$; red: $4f^{13}(5/2)$; blue: $4f^{13}5de_e$; maroon: interacting $4f^{13}5d$ and $4f^{13}a_{37}^{13}$ manifolds. Colors in right graph [Yb$^{2+}$, Yb$^{3+}$]: black $[4f^{14}, 4f^{13}(7/2)]$, blue $[4f^{13}5de_e, 4f^{13}(7/2)]$, maroon [interacting $4f^{13}5d$ and $4f^{13}a_{37}^{13}$], green $[4f^{13}5dt_{2g}, 4f^{13}(7/2)]$, the four previous colours become red, orange, grey, and turquoise, when the Yb$^{2+}$ states are combined with the Yb$^{3+}$ $4f^{13}(5/2)$ states, instead.
Barandiarán and Seijo

IVCT luminescence: Interplay between anomalous and 5d–4f emissions in Yb-doped fluorites

FIG. 4: Results of quantum mechanical calculations of the diabatic IVCT energy diagram for Yb$^{2+}$–Yb$^{3+}$ pairs in Yb-doped CaF$_2$ crystals along the ground state normal electron transfer reaction coordinate $Q_{et}$. Mechanism of the IVCT luminescence of Yb-doped CaF$_2$ crystals: steps I to V. Mechanism of the excitation of the IR luminescence of Yb$^{3+}$ through the lowest 4f–5d absorption band of Yb$^{2+}$: steps I, II, III$^{em}$. Energy barriers in cm$^{-1}$ are indicated next to the crossing points between two electronic states of the pairs; see details in Table III. See caption of Fig. 3 and text for details.
FIG. 5: Calculated band profiles of the Yb\(^{2+}\)–Yb\(^{3+}\) [\(2{A}_{1u},{1\Gamma}_{7u}\)] \(\rightarrow\) Yb\(^{3+}\)–Yb\(^{2+}\) [\(1{\Gamma}_{8u,6v,7u,1A}_{1g}\)] intervalence charge transfer luminescence of (YbF\(_8\))\(^{6−}\)–(YbF\(_8\))\(^{5−}\) embedded cluster pairs (magenta) and of the 1\(E_{u}\) \(\rightarrow\) 1\(A_{1g}\) emission band of embedded (YbF\(_8\))\(^{6−}\) (blue) in CaF\(_2\) and SrF\(_2\). Dotted line: not observable emission. Arbitrary values of the oscillator strengths have been used. See text for details.
FIG. 6: Schematic representation of slow and fast IVCT emissions corresponding to a double deexcitation (double) consisting of an Yb$^{2+}$ 5de$_g$ → Yb$^{3+}$ 4f$^{7/2}$ electron transfer accompanied by a 4f$^{7/2}$ → 4f$^{5/2}$ deexcitation within the 4f$^{13}$ subshell of Yb$^{2+}$; and a single deexcitation (single) consisting of an Yb$^{2+}$ 5de$_g$ → Yb$^{3+}$ 4f$^{5/2}$ electron transfer.
FIG. 7: Calculated excited state absorption spectrum of Yb–doped CaF$_2$ (a) and SrF$_2$ (b) originating in the Yb$^{2+}$–Yb$^{3+}$ [2$A_{1u}$,1$Γ_{7u}$] excited state of the (YbF$_8$)$_6$–(YbF$_8$)$_5$ embedded cluster pairs. Transition energies are taken from Table II. All transitions are arbitrarily assigned the same oscillator strength value. Experimental values from Ref. 13 (a) and 14 (b) are indicated with arrows.
FIG. 8: Results of quantum mechanical calculations of the diabatic IVCT energy diagram for Yb$^{3+}$–Yb$^{3+}$ pairs in Yb-doped CaF$_2$, SrF$_2$, and BaF$_2$ crystals along the ground state normal electron transfer reaction coordinate $Q_{et}$. CaF$_2$ and SrF$_2$: IVCT luminescence: steps I to V; excitation of the IR luminescence of Yb$^{3+}$: steps I, II, III$_{em}$. BaF$_2$: quenching of the Yb luminescence: Steps I and II$_{quench}$. Energy barriers in cm$^{-1}$ are indicated next to the crossing points between two electronic states of the pairs; see details in Table III. See caption of Fig. 3 and text for details.
FIG. 9: Results of quantum mechanical calculations of the diabatic IVCT energy diagram for Yb$^{2+}$–Yb$^{3+}$ pairs in Yb-doped SrF$_2$, and SrCl$_2$ crystals along the ground state normal electron transfer reaction coordinate $Q_{et}$. IVCT luminescence in SrF$_2$: steps I to V; excitation of the IR luminescence of Yb$^{3+}$: steps I, II, III$_{em}$; regular 5$d$–4$f$ emission: steps I, I$_{em}$. SrCl$_2$: absorption (black), 5$d$–4$f$ emissions (blue) and IVCT emissions (green) are indicated by arrows. Energy barriers in cm$^{-1}$ are indicated next to the crossing points between two electronic states of the pairs; see details in Table III. See caption of Fig. 3 and text for details.
FIG. 10: Model cases for non-radiative electron transfer decays from Yb$^{2+}$–Yb$^{3+}$ [$^2F_{7/2}\rightarrow^2F_{5/2}$] excited states (blue) in Yb-doped fluorite crystals determining the luminescence properties. Two non-radiative decay pathways leading to IVCT luminescence excitation (red) or to luminescence quenching (black) are emphasized. Yb$^{2+}$-doped CaF$_2$ corresponds to case B, SrF$_2$ to a case between B and C, BaF$_2$, to case D, and SrCl$_2$ to case A.