Carrier recombination processes and divalent lanthanide spectroscopy in $YPO_4: Ce^{3+}; L^{3+}$ (L=Sm,Dy,Tm)

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We studied charge carrier trapping, detrapping, and recombination phenomena in Ce^{3+} doped YPO₄, codoped with Sm³⁺, Dy³⁺, or Tm³⁺. Ce ions trap the holes and Sm, Dy, and Tm trap electrons created during x-ray irradiation. By means of red to infrared stimulation, the trapped electrons can be back transferred to Ce leading to shorter wavelength $Ce^{3+} 5d-4f$ luminescence. Excitation spectra for this recombination luminescence were recorded from 10 K to room temperature. It provides information on the excited state energies of divalent Sm, Dy, and Tm with respect to the lanthanide ground state energy and with respect to the mobility edge energy of YPO₄. From the temperature dependence, insight is obtained on the carrier recombination pathways. We will identify temperature independent tunneling recombination, recombination by thermal excitation to the conduction band, and phonon-assisted delocalization of electrons from impurity states within the conduction band.

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I. INTRODUCTION

Detailed knowledge on electron-donor and electronacceptor states of impurities in compounds has always been a challenging issue in materials science. This is so for semiconductors where aspects connected with minority and majority charge carriers and depletion layers are of utmost important for device performance. Electron-donor and electronacceptor states of transition-metal or rare-earth cations control photochromic and photocatalytic behavior,^{1,2} and are also of current interest for development of ferromagnetic semiconductors for spintronic applications.³ Charge carrier trapping in lanthanide impurities is of importance for application in dosimetry, for storage phosphors in medical imaging, and for persistent luminescence phosphors.⁴

Electron donor, electron acceptor or charge carrier trapping properties are intimately linked with the location of the impurity states with respect to the conduction and valence band of the host compound, and much experimental and theoretical research has been devoted to elucidate this.^{5,6} Lanthanide ions doped in insulating compounds are the most commonly applied activators in luminescence phosphors and scintillators,^{7,8} and also here level location is important because the location of the emitting state relative to the conduction band often determines the quantum efficiency of luminescence.⁹

Over the past 10 years we have worked on empirical methods and experimental techniques to better understand the location of the electron donor and electron accepting states of the divalent and the trivalent lanthanides in wide band gap halides and chalcogenides. In the past 2 years we have used YPO₄ as our model host lattice.^{10–13} The results of those studies provided us with the detailed level scheme shown in Fig. 1. The top of the valence band is set at energy zero. E^{ex} at 8.55 eV is the energy needed to excite the phosphate group and its excitation leads to self-trapped exciton

emission that is observe at low temperature. The bottom of the conduction band or the mobility edge is experimentally found at 9.2 eV.¹³ The zigzag curve labeled 4f(3+) connects the $4f^n$ ground state energies for all the trivalent lanthanides in YPO₄ (n=1 for Ce³⁺ and n=14 for Lu³⁺). The energy required to donate an electron to the conduction band is given by the difference between the ground-state energy and the bottom of the conduction band. The energy difference with the top of the valence band relates to the energy released when a hole from the valence band is being trapped, i.e., when an electron jumps from its $4f^n$ state to a hole that has thermalized at the top of the valence band. Clearly Ce³⁺ followed by Tb³⁺ and Pr³⁺ are the most deep hole traps, and Eu³⁺, Gd³⁺, Yb³⁺, and Lu³⁺ cannot trap such hole.

The zigzag curve labeled 4f(2+) connects the lowest energy 4f electron acceptor states of the trivalent lanthanide



FIG. 1. (Color online) Scheme with the location of divalent and trivalent lanthanide electron donor and acceptor states in YPO_4 .

ions. After an electron is trapped the ground state of the divalent lanthanide will be occupied. Clearly Eu^{3+} is the deepest electron trap followed by Yb³⁺, Sm³⁺, Tm³⁺, etc. In Fig. 1 we have added the lowest energy 5*d* states of the trivalent lanthanides connected with the curve labeled 5*d*(3 +). We also added all the excited 4*f*ⁿ states of *L*³⁺ that can be derived from the well-known Dieke diagram of trivalent lanthanide 4*f* levels. The excited 4*f*ⁿ⁺¹ states of the divalent lanthanides are from.¹⁴

Depending on the location of the lanthanide ground-state energy with respect to the Fermi energy, the lanthanides enter inorganic wide band-gap compounds either in the divalent, trivalent, or the tetravalent charge state.¹⁵ In some compounds Ce⁴⁺, Tb⁴⁺, and Pr⁴⁺ can be formed when synthesis is under oxidizing conditions. The trivalent charge state is most common and it can be adopted by all the lanthanides. The 2+ charge state is common for Eu located on divalent cation sites. Also Yb, Sm, and Tm can in some compounds adopt the divalent state when synthesis is under appropriate reducing conditions. The absorption, excitation, and luminescence properties of these four divalent lanthanides are well established.¹⁶ For the other lanthanides, to our information, the divalent charge state in wide band-gap compounds cannot be stabilized during synthesis. Occasionally divalent lanthanides can however be formed employing photoreduction techniques. For example, x-ray or γ irradiation of alkaline earth fluorides (CaF₂, SrF₂, and BaF₂) doped with trivalent lanthanide ions produce a significant fraction of divalent lanthanides. The ionizing radiation creates free electrons that are trapped by the trivalent lanthanide dopants. The thus created divalent lanthanides can then be studied by optical absorption.¹⁷ It are those type of studies that have provided us with the sparse sources of data on the spectroscopy of many of the divalent lanthanide ions.¹⁴

In this work we have studied $YPO_4: Ce^{3+}; L^{3+}$ (L =Sm,Tm,Dy) by means of optical stimulated luminescence (OSL) spectroscopy. Figure 1 shows that Sm^{3+} , Dy^{3+} , and Tm^{3+} form 1–2 eV deep electron traps. Ce³⁺ is a 3.9 eV deep hole trap. By utilizing x-rays, electrons are excited to the conduction band. Part of them are trapped by the trivalent lanthanide codopant and the hole in the valence band is trapped by Ce^{3+} ; thus a significant fraction of L^{2+} and Ce^{4+} defect pairs are formed. In other words both a photoreduction and a photo-oxidation process is induced by the x-rays. Next, electrons from L^{2+} defects are excited by monochromatic light to higher energy states leading to ionization and eventually recombination with the hole on a Ce⁴⁺ defect. By monitoring the 340 nm $Ce^{3+} 5d-4f$ recombination emission intensity as a function of the L^{2+} excitation wavelength, one obtains the OSL-excitation spectrum. The OSL-excitation spectrum is actually the product of the divalent lanthanide absorption spectrum with the probability for ionization and recombination. Studies have been performed as function of temperature from 10 K to RT, and this provides us with detailed insight into the ionization and delocalization processes of electrons from the lanthanide traps. This work will evidence that Sm²⁺, Dy²⁺, and Tm²⁺ can be created in YPO₄ by means of x-ray photoreduction, and that we can study the spectroscopy of those divalent lanthanides and its photoionization properties by means of OSL techniques. We will show that the level scheme of Fig. 1 explains why and how electrons can be transferred from one lanthanide ion to another. In this work it is demonstrated for electron transfer between Ce and Sm, Dy, and Tm in YPO_4 but the ideas should equally well apply for any other combination of two lanthanides in any other compound.

II. EXPERIMENTAL METHODS

Powder samples of YPO₄ were synthesized by solid-state reaction as described previously.¹⁰ The lanthanide concentrations in the melt were 0.5 at. % for both Ce³⁺ and codopant Sm³⁺, Dy³⁺, or Tm³⁺. With powder x-ray diffraction we verified that the samples are of single phase.

Luminescence excitation and emission spectra were recorded on beamline 3.2 (4-40 eV) at Daresbury synchrotron radiation source (SRS) in the United Kingdom using the mobile optical luminescence end station (MOLES) instrument.¹⁸ This instrument is comprised of a variable temperature closed-cycle cryostat with ports for ultraviolet (UV), vacuum-UV, or x-ray irradiation, photon stimulation, and luminescence detection. The instrument can also be coupled to a laboratory x-ray source. In this case a 50 W Oxford Instruments XTF5011 x-ray tube with copper target, producing bremsstrahlung radiation up to 30 kV and Cu $K\alpha$ emission at 8 keV. OSL excitation spectra were measured after first irradiating the sample at room temperature with x-rays during 1 h and then cooling it down to 10 K. This treatment is meant to produce a significant concentration of metastable Ce⁴⁺ and L^{2+} defects. At 10 K the sample was scanned with photons in the range from 430 nm (2.88 eV) to 1260 nm (0.984 eV) by a 19 cm Jobin-Yvon Triax scanning spectrometer coupled to a 20 W tungsten lamp. Long-pass 455 nm, 420 nm, and 500 nm filters were used to suppress second order diffracted light for the measurements with the codopants Sm, Tm, and Dy, respectively. A 6 mm Schott UG11 filter provides a detection window centered at 340 nm (FWHM \approx 40 nm) which covers the characteristic $5d \rightarrow 4f$ emission doublet of Ce³⁺ at 338 nm (3.20 eV) and 352 nm (3.52 eV). The filtered Ce³⁺ luminescence is detected with a blue/green sensitive photomultiplier with bialkali photocathode operating in photoncounting mode. Next the sample is raised in temperature (in steps of 10 or 20 K) and the scan is repeated at each temperature. The recorded luminescence is corrected for differences in photon fluxes at different wavelengths and also for the decrease of trapped charge after each scan which is typically $\approx 1\%$ per scan due to the very low excitation power densities used in the experiments.

III. RESULTS

Figure 2 shows the excitation spectrum of both Ce^{3+} and Sm^{3+} emission in YPO₄; Ce^{3+} ; Sm^{3+} . Both spectra reveal the exciton creation band at 8.55 eV. The excitation to the first 5*d* state of Ce^{3+} at 3.83 eV is below the range of the synchrotron beam line but the four higher energy 5*d* excitations at 4.96, 5.21, 5.51, and 6.11 eV can all be identified. $Sm^{3+} 4f$ -5*d* excitation bands at 7.10 and 7.24 eV appear as dips in the excitation spectrum of Ce^{3+} emission. The broad



FIG. 2. (Color online) Luminescence excitation spectra of (a) 3.5 eV Ce³⁺ emission and (b) 2.0 eV Sm³⁺ emission in YPO₄ at 6 K. Characteristic features are indicated.

excitation band at 6.8 eV is assigned to electron transfer from the top of the valence band to Sm³⁺. The energies for electron transfer to other lanthanides such as Eu³⁺, Tm³⁺, and Yb³⁺ in YPO₄ are also well established,¹⁹⁻²¹ and the curve labeled 4f(2+) in Fig. 1 connects the energies of those electron acceptor states.

OSL-excitation spectra for YPO₄:Ce³⁺;Sm³⁺ were recorded for temperatures between 10 and 300 K with 10 K intervals. Figure 3 shows a subset of those spectra. One observes broad OSL-excitation bands revealing strong temperature dependence between 1.6 and 2.1 eV that we will attribute to $4f^6 \rightarrow 4f^55d_1$ transitions involving the first 5d state $(5d_1)$ of Sm²⁺. One also observes a narrow excitation band at 1.83 eV. This band becomes most pronounced at the lowest temperature of 10 K and we will attribute it to the $4f^6 \rightarrow$ $-4f^{6} {}^7F_0 \rightarrow {}^5D_0$ transition of Sm²⁺. Another set of broad bands is seen between 2.4 and 2.8 eV. They will be attributed



300K

100



[LS]5d

FIG. 4. (Color online) OSL-excitation spectrum of divalent Dy in $YPO_4: Ce^{3+}; Dy^{3+}$ as function of temperature. Spectra (a), (b), (c), and (d) are at 10 K, 40 K, 80 K, and 120 K, respectively. Between 120 and 300 K spectra are shown measured at 20 K intervals.

to excitation of Sm²⁺ to higher energy $4f^55d_2$ states. The OSL-excitation spectra do not reveal a significant temperature dependence between 10 K (spectrum a) and 160 K (spectrum b), however, a strongly increasing intensity is observed with temperature from 160 to 300 K. The thermal dependence is strongest when the optical excitation energy is lowest. Apparently after optical excitation to the low energy $4f^6 \rightarrow 4f^55d_1$ states of Sm²⁺ more thermal energy is required to delocalize the electron in order to recombine with Ce⁴⁺ than when exciting in the higher energy $4f^6 \rightarrow 4f^55d_2$ states.

Figure 4 shows the OSL-excitation spectra of YPO₄:Ce³⁺;Dy³⁺. We again observe a broad strongly temperature dependent band with a maximum that slightly red shifts from 1.33 eV at 10 K to 1.27 eV at 300 K that we will attribute to the first spin allowed $4f^{10} \rightarrow 4f^{9}5d_1$ excitation of Dy²⁺. At energies higher than 1.5 eV strong OSL-excitation bands are observed that even at the lowest temperature of 10 K remain intense. Sharp band features are observed at 1.56 eV (795 nm), 1.63 eV (762 nm), and 1.66 eV (746 nm).

Figure 5 shows the OSL-excitation spectra of YPO₄:Ce³⁺;Tm³⁺. Like for Sm and Dy a broad strongly temperature-dependent OSL excitation band is observed slightly redshifting from 1.99 at 10 K to 1.96 eV at 300 K. This band will be attributed to the first spin allowed $4f^{13}$ $\rightarrow 4f^{12}5d_1$ excitation of Tm²⁺. At the lowest temperature of 12 K the band is still observed. Apparently without further thermal stimulation the excited electron manages to escape from Tm²⁺ and recombine with Ce⁴⁺. Other strong and broad OSL excitation bands are observed at 2.62 and 2.88 eV. Narrow band OSL-excitation features are not observed.

IV. DISCUSSION

FIG. 3. (Color online) OSL-excitation spectra of divalent Sm in $YPO_4: Ce^{3+}; Sm^{3+}$ as function of temperature. Spectrum (a) is at 10 K and spectra (b) through (i) are from 160 to 300K with 20 K interval.

The OSL excitation spectra of divalent Sm, Dy, and Tm are the product of optical absorption and the probability for the excited electron to delocalize leading to radiative recombination at Ce⁴⁺. Figure 6 illustrates possible recombination



FIG. 5. (Color online) OSL-excitation spectrum of divalent Tm in YPO_4 : Ce³⁺; Tm³⁺ as function of temperature. Spectra (a) and (b) are at 12 and 40 K. Between 40 and 300 K spectra are shown measured at 20 K intervals.

routes. In (a) the trapped electron is excited to a state located above the mobility edge. The electron may delocalize via conduction band states with a rate Γ_d to recombine radia-



FIG. 6. (Color online) Plausible recombination pathways during OSL (a) via the conduction band, (b) tunneling recombination and thermally excited recombination via the conduction band, and (c) tunneling recombination and thermally excited subband-gap barrier recombination.



FIG. 7. (Color online) The divalent lanthanide states in YPO₄. Curve 4f(CT), 4f ground-state location derived from electron transfer data. * denotes 4f ground-state location derived from thermoluminescence glow curve analysis of YPO₄: Ce³⁺; L^{3+} . Curve 4f(TL), 4f ground-state location derived from thermoluminescence. Curve 5d(2+), the location of the lowest energy $4f^{n}5d$ states of the divalent lanthanides. $4f^{n+1}$ and $4f^{n}5d$ excited state levels of L^{2+} are indicated by horizontal bars. The gray vertical bars indicate what states are reached during OSL.

tively via the 5*d* states with the hole on Ce⁴⁺. The electron may also radiatively or nonradiatively fall back with a retrapping rate Γ_r to its parent trap. Below we will conclude that the ratio Γ_d/Γ_r increases with temperature and with the energy of the stimulating photon.

When the trapped electron is excited to a level below the mobility edge of YPO₄ then either the electron has to be thermally stimulated to the conduction band or the electron has to recombine by means of a subband recombination pathway. Subband recombination inevitably requires that we deal with close pairs of Ce⁴⁺ and L^{2+} defects. Figure 6(b) illustrates that recombination may proceed by tunneling through the barrier between the two configurational coordinate parabola's belonging to the electron donor and electron acceptor states with a rate Γ_t . The tunneling rate will depend strongly on the barrier width which likely decreases when higher vibrational levels are occupied, i.e., when temperature increases. When the temperature is sufficiently high the electron may be excited to the conduction band. The recombination rate Γ_{th} will be strongly thermally activated. Figure 6(c) shows a situation where subband-gap recombination is possible by thermal excitation across the barrier between the two parabola's. Tunneling and subband-gap pathways are only possible when the distance between Ce^{3+} and L^{2+} is not too large. Pathway (a) is the only recombination route for distant pairs.

Figure 7 shows the location of the $4f^{n+1}$ energy levels of the divalent lanthanides in YPO₄. The zigzag curve labeled 4f(CT) connects the location of the 4f ground-state energies as derived from electron-transfer data. It is the same curve as the one labeled 4f(2+) in Fig. 1. After a lanthanide ion has accepted an electron, substantial lattice relaxation will follow. In Ref. 22 it was suggested that the energy released in lattice relaxation compensates largely for the energy required to dissociate the hole from the transferred electron after electron transfer has taken place. If that is indeed the case then the curve labeled 4f(CT) also connects the ground-state energy locations of the divalent lanthanides in the relaxed lattice configuration. From thermoluminescence studies by Bos et al.¹⁰ the activation energy for electron release from divalent Nd, Sm, Dy, Ho, Er, and Tm in YPO₄ has been derived. Assuming that recombination proceeds via the conduction band that data provides us with the location of the groundstate energy as indicated by the star data symbols in Fig. 7. The zigzag curve labeled 4f(TL) best connects those donor state energies. The 4f(TL) curve is 0.2 eV higher in energy than the 4f(CT) curve. This relatively small difference confirms the equivalence between 4f(CT) and 4f(2+) made in Ref. 22 within a systematic error of several 0.1 eV.

From the energy $E_{fd}(\text{Ce}^{3+})$ of the first $\text{Ce}^{3+} 4f$ -5d excitation band at 3.83 eV the energy $E_{fd}(\text{Eu}^{2+})$ for the lowest energy 4f-5d transition for Eu^{2+} can be predicted.²³ When the 4f-5d energy of Eu^{2+} is predicted the lowest 4f-5d energies for all other divalent lanthanides can be predicted as well by simply adding constant $\Delta E(L^{2+}, \text{Eu}^{2+})$ energy values²⁴

$$E_{fd}(L^{2+}) = (0.64 \pm 0.02)E_{fd}(\text{Ce}^{3+}) + (0.53 \mp 0.06) + \Delta E(L^{2+}, \text{Eu}^{2+}) \text{ eV}$$
(1)

where the $\Delta E(L^{2+}, Eu^{2+})$ values are tabulated in Ref. 24.

Optical absorption spectra of Sm²⁺ or excitation spectra of Sm²⁺ emission usually reveal a weak intensity broad band followed by a band five to ten times stronger at on average 0.15 ± 0.04 eV higher energy.¹⁴ The two bands are due to transitions from the $4f^6[^7F_0]$ Sm²⁺ ground state to $4f^55d_1$ excited states and are known as the SmA and SmB band.^{25,26} The OSL-excitation spectrum in Fig. 3 reveals a weak broad band around 1.72 eV and a main band at 1.90 eV which are finger prints for those SmA and SmB bands. Furthermore Eq. (1) predicts the SmA band at 1.78 ± 0.1 eV which agrees very well with the 1.72 eV band in Fig. 3. We therefore assign the observed bands at 1.72 and 1.90 eV in Fig. 3 to the SmA and SmB bands. The energy separation between the first and second 5d state of Ce^{3+} is 1.13 eV. Because Eq. (1) to first approximation applies also for the higher excited 5dstates²⁷ we expect for the divalent lanthanides a separation of 0.72 eV. We therefore assign the OSL-excitation bands near 2.5 and 2.7 eV in Fig. 3 to $\text{Sm}^{2+} 4f^55d_2$ states. We can now safely conclude that Sm²⁺ has been created in YPO₄ by the x-ray photoreduction treatment and that during OSL excitation an electron is indeed transferred from Sm²⁺ to Ce⁴⁺.

Since we now know the energy of the first $4f^n5d$ state for Sm^{2+} , the energy of the first $4f^n5d$ states for all other divalent lanthanides in YPO₄ can be predicted.^{14,24} The curve labeled 5d(2+) in Fig. 7 connects those predicted level energies. It is somewhat bumpy which is indicative for the degree of inaccuracy. For (n+1) > 7 the first $4f^n5d$ state has a higher total spin than the $4f^{n+1}$ ground state, and transitions between them are spin forbidden and weak. The first so-called low spin 5*d* state, that we will indicate as [LS]5*d*₁, is usually found at about 0.47 eV higher energy for Dy²⁺ and 0.23 eV

higher energy for Tm^{2+} .¹⁴ We therefore predict the [LS]5 d_1 state for Dy^{2+} at 1.36 eV and for Tm^{2+} at 1.90 eV. These energies agree very well with the observed broad OSLexcitation bands at 1.33-1.27 eV for Dy in Fig. 4 and at 1.96–1.99 eV for Tm in Fig. 5. We regard this as convincing evidence that like for Sm³⁺ also Dy³⁺ and Tm³⁺ can be made divalent in YPO₄ by means of the x-ray photoreduction treatment. Evidently the ground state energies of Sm²⁺, Dy²⁺, and Tm^{2+} are located within the band gap of YPO₄ as predicted by the level scheme of Fig. 1. The spin allowed transitions to the second 5d states are like for Sm^{2+} expected at 0.72 eV higher energy. In the case of Tm the observed band at 2.63 eV in Fig. 5 corresponds with the predicted location. In the case of Dy this cannot be observed in the recorded OSL spectra because of the 500 nm cut-off filter used in the experiment.

We do not expect that the optical absorption strength will depend strongly on temperature and therefore the strong temperature dependence observed in the OSL-excitation spectra must have another cause. We attribute it to temperature dependence of electron delocalization from the excited state of the divalent lanthanide. By adding the energy of the 4f-5d excitation bands found from the OSL-excitation spectra to the 4f(TL) curve in the scheme of Fig. 7, the location of the excited $4f^n5d$ states can be drawn in the same scheme. The SmA and SmB levels appear well below the mobility edge. The Dy²⁺ [HS] $5d_1$ state is just below but the [LS] $5d_1$ state and the [LS] $5d_1$ state are at and well above the mobility edge, respectively.

The gray vertical bars in Fig. 7 illustrate to what range of electronic states electrons are excited during the OSLexcitation experiments of Figs. 3-5. Excitation is often to states that are located above the mobility edge. However, this does not imply that automatically electron delocalization takes place. If that were the case we cannot explain the strong increase of OSL-excitation intensity with temperature. We conclude that the electron has two options; it may delocalize but it has also a high probability of falling back into its parent trap. This is the mechanism as illustrated in Fig. 6(a). We conclude that electron-phonon interaction increases the delocalization rate Γ_d . Two other clear trends are observed; (1) the (isothermal) OSL-excitation intensity tends to increase with higher photon stimulation energy and (2) the (isoexcitation energy) thermal dependence decreases with higher excitation energy. In other words when the electron is excited higher into the conduction band the probability of delocalization increases and becomes less dependent on temperature.

The OSL-excitation spectra and its thermal dependence provide information that is complementary to what can be obtained from photoconductivity studies. For example Ce^{3+} -doped silicate and aluminate compounds reveal strong temperature dependence of the photocurrent^{28,29} upon excitation in the $Ce^{3+} 5d$ states. Clear differences are observed in the temperature dependence when excitation is to levels below the conduction band as compared to levels inside the conduction band.

Figure 8 shows an Arrhenius plot of the intensity of the SmB band, of the [LS] $5d_1$ band of Dy²⁺, and of the [LS] $5d_1$



FIG. 8. (Color online) Arrhenius plots of OSL-excitation intensity. (a) At the maximum of the $\text{Sm}^{2+} 5d_1$ [SmB] excitation band, (b) at the maximum of the Dy^{2+} [LS] $5d_1$ band, and (c) at the maximum of the Tm²⁺ [LS] $5d_1$ band. The slopes of line segments through part of the data are indicated in electron volt.

band of Tm²⁺ in the OSL-excitation spectra. The OSL intensity of the SmB band shows a steep decrease with a slope of 0.18 eV when going from room temperature to 160 K. Since the electronic states of the SmB are located below the conduction band of YPO₄ additional thermal energy is needed for the electron to escape from Sm. We therefore attribute the 0.18 eV activation energy to the thermal energy needed to excite an electron from the Sm 5d state into the conduction band. Below 160 K the SmB band intensity in the OSL spectrum in Fig. 3 becomes temperature invariant. Since now the temperature is too low to excite the electron into the conduction band, there must be another recombination pathway in operation. We propose the following; the electron tunnels from the excited Sm^{2+} state to one of the Ce³⁺ 5d states which is then followed by $Ce^{3+} 5d-4f$ emission as illustrated in Fig. 6(b). Above 160 K Γ_{th} becomes larger than Γ_t and the thermally activated pathway dominates. The narrow excitation band at 1.83 eV in Fig. 3 is attributed to the Sm²⁺ $^{7}F_{0}$ $\rightarrow {}^{5}D_{1}$ transition. The band gains intensity relative to the SmB band when the temperature decreases. Most likely this is related with the long radiative life time of the 4f levels resulting in a relatively small retrapping rate Γ_r .

The Arrhenius plots for the 5*d* bands of Dy^{2+} and Tm^{2+} in Fig. 8 show at around 200 K a slope of 0.038 eV and 0.018 eV, respectively. These slopes are much smaller than observed for Sm^{2+} at 200 K. We have an entirely different situation because in the case of Dy and Tm, the electron is excited to an electronic state that is located within the conduction band. A more complicated situation arises for several reasons. For example, there can be spontaneous or phonon stimulated (thermal) delocalization of the electron from this state to conduction band states with a rate Γ_d . Alternatively, the electron may relax all the way down to the ground state

of the parent trap with a rate $\Gamma_r(T)$ as illustrated in Fig. 6(a). Our data demonstrate (1) that the ratio Γ_d/Γ_r increases with increasing temperature and (2) that the ratio increases when optical excitation is to electronic states located increasingly higher into the conduction band. Unfortunately we do not yet have a physical model that explains how and why the rates Γ_r and Γ_d depend on temperature and excitation energy. We do expect that with complementary data such as, e.g., optical absorption spectra and excitation spectra of divalent Sm, Dy, and Tm emission in YPO₄ valuable new insights will be obtained on electron delocalization processes.

V. SUMMARY AND CONCLUSIONS

In this work we have studied the recombination processes in double lanthanide-doped YPO₄. We selected the dopant Ce³⁺ to provide a 3.9 eV deep hole trap and the codopants Sm^{3+} , Dy^{3+} , and Tm^{3+} to provide 1–2 eV deep electron traps. The electron and hole recombination pathways were studied by means of OSL-excitation spectroscopy. The observed bands in the spectra were identified as 4f-5d transitions in Sm²⁺, Dy²⁺, and Tm²⁺, and the energy of the bands correspond very well with predicted values. The recombination processes show often a strong temperature dependence that is connected with the precise location of the relevant electronic state with respect to the conduction band bottom. We have identified that tunneling recombination takes place between Sm²⁺ and Ce⁴⁺ centers at low temperature but recombination through the conduction band dominates at temperatures above 160 K. Excitation to levels located within the conduction band may lead to spontaneous electron delocalization. However, also for those cases increasing the temperature augments the delocalization rate. Evidently lattice vibrations couple with the electronic states. This work has shown that the level scheme of Fig. 1 developed during the past years provides us with the correct energies required to transfer an electron between two lanthanide ions and between lanthanide ions and host energy levels. We demonstrated this for electron transfer between Ce^{3+} and Sm, Dy, or Tm, but the same ideas and scheme should apply equally well for other combinations of lanthanide ions in YPO₄.

There is much more to learn from the double lanthanidedoped YPO₄ system. One may select Pr^{3+} or Tb^{3+} as a hole trapping center and other codopants can be selected as electron trapping centers. The spectroscopy of divalent lanthanides can then be further studied; information that is hard to obtain otherwise. The energy of electron donating levels and accepting levels can be predicted from the level scheme for YPO₄. This may be exploited to select a combination of lanthanides to study tunneling recombination and related afterglow phenomena in detail.

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