



Photon controlled electron juggling between lanthanides in compounds

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ABSTRACT

The energy for electron transfer between a lanthanide dopant and the valence and conduction band of its hosting inorganic compound provides essential information on the position of lanthanide acceptor and lanthanide donor states within the band gap. The many different types of transfer are reviewed, and it is illustrated how they can be utilized to create 4f-electron binding energy schemes of the electrons in any of the 4fⁿ states of each divalent and each trivalent lanthanide in a compound. When both an electron acceptor and electron donor lanthanide are present in the same compound electrons can be transferred between them in a controlled fashion by photon manipulation or by heat. Such electron juggling will be demonstrated in double lanthanide doped in YPO₄ and Y₃Al₅O₁₂.

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1. Introduction

Past years witnessed an increased activity in the research of compounds activated with more than one type of lanthanide ion. In persistent phosphors like SrAl₂O₄:Eu²⁺;Dy³⁺, Eu²⁺ act as luminescence center and electron donor and Dy³⁺ plays a role in the electron trapping. Many studies appear in the field of persistent luminescence with other lanthanide ion pairs [1]. Another topic is solar conversion phosphors where one lanthanide acts as sensitizer for the blue part of the solar spectrum and another, i.e., Yb³⁺, as infra-red emitting center. Co-activation is also employed to reduce unwanted afterglow in X-ray phosphors. The ability to trap a charge carrier (electron from the conduction band or hole from the valence band) by a lanthanide ion and the ability for electron transfer between two different lanthanides is determined by the binding energy of 4f-electrons with respect to that of electrons in the conduction and valence band [2–4]. Past decade phenomenological models have been developed that predict those binding energies for all types of lanthanides (divalent and trivalent) in compounds [5–8].

By means of UV-irradiation, X-ray irradiation, or beta-exposure, lanthanides like Ce³⁺, Pr³⁺, Tb³⁺ can be oxidized to the tetravalent charge state by removal of an electron. Those lanthanides then donate an electron from the 4f-shell to the conduction band. Other lanthanides like Dy³⁺, Sm³⁺, Eu³⁺, Tm³⁺, Yb³⁺ can be reduced to the divalent charge by addition of an electron to the 4f-shell. Those lanthanides then accept an electron from the

conduction band. By doping both types of lanthanide ions in the same compound one may transfer electrons from one lanthanide to the other in a controlled fashion by means of photon excitation or by means of heat. The reversed process Ln⁴⁺ + Ln²⁺ → Ln³⁺ + Ln³⁺ can also be accomplished by photon or thermal stimulation, or it can occur by an electron tunneling process. Recently we studied and identified all these electron transfer or electron juggling processes in YPO₄ and Y₃Al₅O₁₂ [3,4,10–12,14]. Observations appear in excellent agreement with predictions made from 4f-electron binding energy schemes.

In this work we will first review the various types of electron transfer (ET) that can be observed in lanthanide doped compounds. It will be demonstrated how the energy needed for ET can be used to construct binding energy schemes of compounds showing the 4f-electron binding energy in the ground and excited states of each divalent and each trivalent lanthanide relative to the binding energy at the top of the valence band and bottom of the conduction band. The other way around, using the level scheme to predict electron transfer processes is also addressed. In the end, less common ET processes like electron tunneling from one lanthanide to another are discussed.

2. Electron transfer processes

Lanthanides in compounds can adopt the tetravalent [Xe]4fⁿ⁻¹ configuration (like Ce⁴⁺, Pr⁴⁺, Tb⁴⁺), the trivalent [Xe]4fⁿ configuration (all lanthanides), or the divalent [Xe]4fⁿ⁺¹ configuration (like Eu²⁺, Yb²⁺, Sm²⁺, Tm²⁺). In this paper we will use the letter *n* to denote the number of electrons in the 4f-shell of the trivalent lanthanide ion. The different types of electron transfer

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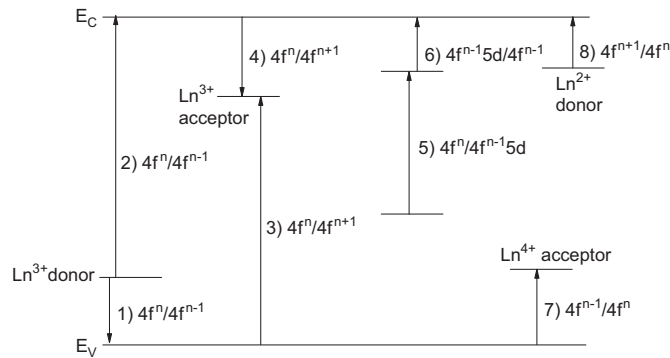


Fig. 1. Illustration of possible electron transfers between lanthanide donor and acceptor states and the host bands. The electron configuration before/after the transition is denoted with $4f^m/4f^{m\pm 1}$ notation.

that are possible in lanthanide doped compounds are illustrated in Fig. 1. The horizontal lines denote the binding energy of electrons in the $4f^m$ ($m=n$, $m=n-1$, or $m=n+1$) ground state levels of lanthanide ions above the top of the valence band at energy E_V and the bottom of the conduction band (mobility edge) at energy E_C . When the $4f^m$ ground state is within the band gap, the 4f-shell may trap a hole from the valence band which is equivalent to donating an electron from that 4f-shell to the valence band hole. The electron transfer is indicated by arrow (1) in Fig. 1. The same lanthanide can also donate an electron from the 4f shell to the conduction band (arrow 2). Ce^{3+} , Pr^{3+} , and Tb^{3+} often play such role in compounds. After the transition the lanthanides become tetravalent. Hole trapping by Ce^{3+} is regarded an important first step in the scintillation process of many Ce^{3+} activated scintillation materials [13].

Arrow (3) indicates ET from the valence band to the 4f-shell of a trivalent lanthanide ion. This is possible whenever the binding energy of electrons in the divalent $4f^{m+1}$ ground state is below E_C . Such transfer is commonly known as charge transfer (CT) and appears as the familiar CT-band in trivalent lanthanide doped compounds. The best examples are found for Eu^{3+} doped inorganic phosphors. In oxides the CT-band is located near 250 nm and it acts as an excellent sensitizer for the 254 nm Hg line emission in tube lighting. Arrow (4) indicates ET from the conduction band to the same trivalent lanthanide ion; this transfer is known as electron trapping or electron capture. After a lanthanide has accepted an electron, its valence has changed and the lanthanide converts to an electron donor defect. By optical or thermal stimulation, a 4f-electron can be excited back into the conduction band; this is illustrated by arrow (8).

Two step ET from a lanthanide to a host band is illustrated by arrows (5) and (6). First a lanthanide is excited to the lowest 5d-state and from there the electron can be excited to the conduction band. This is an important mechanism in the thermal quenching of luminescence. The Arrhenius behavior of such quenching may provide the energy difference E_{dc} between the emitting 5d state and E_C . Finally, arrow (7) illustrates the ET from the valence band to a tetravalent lanthanide.

In principle each of the ETs in Fig. 1 can be observed by monitoring the photon emission or they can be stimulated by photon absorption or thermal excitation. The ET indicated by arrows (3), (7), and (5) are between localized states and dipole allowed; they usually appear as intense, though broad, bands in absorption and excitation spectra. A direct transition from a $4f^m$ ground state to a delocalized conduction band state has small oscillator strength and will be weak. Usually such transition is fully masked by much more intense 4f–5d transitions. An exception is formed by Pr^{3+} and Tb^{3+} doped transition metal (TM)

based compounds. In vanadates, niobates, titanates, the 4f ground state of Pr^{3+} and Tb^{3+} is within the forbidden band and the lowest 5d-state is above E_C . In those case ET from Pr^{3+} and Tb^{3+} to the conduction band can be observed in luminescence excitation spectra. These transitions are known as Intervalence Charge Transfer (IVCT) [9,16–19].

2.1. Utilizing ET to generate level schemes

From now on we will use the naming *4f-level energy* to express the binding energy of the electrons in the 4f-shell in the ground state or an excited state of the $4f^m$ electron configuration. Empirical methods have been developed to place the lanthanide 4f-ground state level relative to the host bands [5–8]. These methods have evolved over the years and by now become more and more reliable in predicting and explaining performance of lanthanide activated compounds. Fig. 2 shows as example [3,12] the lanthanide level location of the divalent and trivalent lanthanides in YPO_4 . We observe the familiar double zigzag curves that connect the 4f ground state energies of the divalent lanthanides (upper curve) and the trivalent lanthanides (lower curve). To good first approximation the shape of these curves is invariant with type of inorganic compound [9]. Once the ground state energies are known, all excited $4f^m$ states can be placed as well.

To construct a scheme as in Fig. 2 relatively few information is required. One needs the energy E_C of the host compound and the energy of ET to a trivalent lanthanide to construct the double zigzag curve for the divalent lanthanides. Fig. 3 shows as example the excitation spectrum of Eu^{3+} emission in the compound $LiYP_4O_{12}$ from [15]. The broad band near 200 nm is the CT band of Eu^{3+} , see arrow (3) in Fig. 1. The band at 8.5 eV is identified as the first $4f^6 \rightarrow 4f^5 5d$ transition in Eu^{3+} , and the discontinuity in the falling slope at 8.6 eV occurs at the energy E^{ex} needed to create an exciton. As a rule of thumb the mobility edge E_C is assumed at 1.08 times higher energy. By studying also the spectroscopy of other trivalent lanthanides in $LiYP_4O_{12}$ the bandgap energy and location of the divalent zigzag curve can be firmly based [15]. For YPO_4 and other compounds similar data can be extracted from the archival literature.

To place the trivalent lanthanide states in the band gap of compounds one needs to establish the location of one trivalent

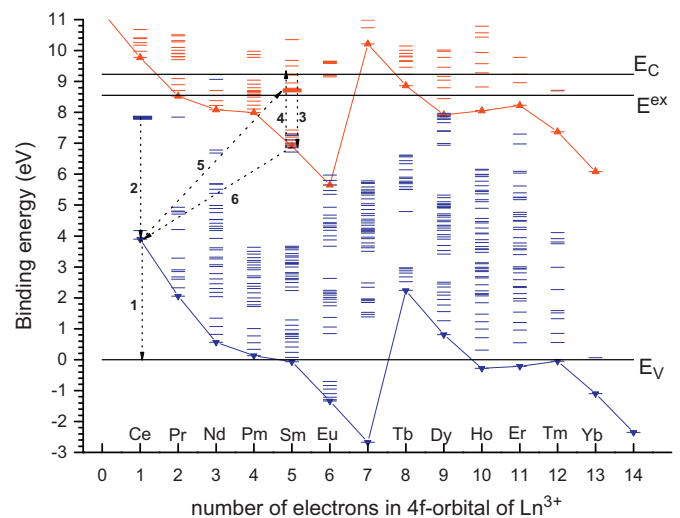


Fig. 2. Divalent lanthanide $4f^{m+1}$ (upper curve and horizontal bars) and trivalent lanthanide $4f^m$ (lower curve and horizontal bars) level location with respect to the top of the valence band at E_V in YPO_4 . E^{ex} and E_C indicate the energy of exciton creation and the mobility edge in YPO_4 . Arrows (1) to (6) indicate observed transitions involving Ce and Sm dopants.

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