



Excited states dynamics under high pressure in lanthanide-doped solids

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ABSTRACT

Emission related to rare earth ions in solids takes place usually due to $4f^n \rightarrow 4f^n$ and $4f^{n-1}5d^1 \rightarrow 4f^n$ internal transitions. In the case of band to band excitation the effective energy transfer from the host to optically active impurity is required. Among other processes one of the possibilities is capturing of the electron at the excited state and the hole at the ground state of impurity.

The latest results on high pressure investigations of luminescence related to Pr³⁺ and Eu²⁺ in different lattices are briefly reviewed. The influence of pressure on anomalous luminescence and $4f^{n-1}5d^1 \rightarrow 4f^n$ luminescence in BaSrF₂:Eu²⁺ and LiBaF₃:Eu²⁺ systems and Pr³⁺ $4f^n \rightarrow 4f^n$ emission quenching is presented and discussed. A theoretical model describing the impurity-trapped exciton as a system where a hole is localized at the impurity and an electron is captured by Coulomb potential at Rydberg-like states is developed. The results show the importance of local lattice relaxation for the creation of stable impurity-trapped exciton states. The ligands shifts create a potential barrier that controls the effect of mixing between the Rydberg-like electron and localized electron wave functions.

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1. Introduction

Rare earth ions are commonly used as activators in dielectric matrices due to their ability to emit light. Such materials are known as phosphors and are investigated for more than 150 years. Shionoya [1] in the introduction to Phosphor Handbook has mentioned about the first synthesis of ZnS-based phosphor done by T. Sidot in 1866. Since this time phosphors and especially dielectric crystals doped with lanthanide ions (Ln^{α+} ions) have found many applications as light sources in fluorescence lamps, display devices, X-ray detector and scintillators, luminescence paints and laser materials [1].

The most effective excitation of the Ln^{α+} takes place due to $4f^n \rightarrow 4f^{n-1}5d^1$ absorption or due to energy transfer from the host lattice to the impurity ion. After excitation of the Ln^{α+} the system can relax radiatively emitting photons due to internal transitions yielding sharp lines related to parity-forbidden $4f^n \rightarrow 4f^n$ transitions or broad band luminescence related to parity-allowed $4f^{n-1}5d^1 \rightarrow 4f^n$ transition. At band-to-band excitation Ln^{α+} ions capture the free carriers: electron at the excited and hole at the ground state, and then decay radiatively in the same way as upon local excitation. Doping with Ln^{α+} ions usually quenches the lattice emission related to self-trapped exciton (STE).

Energy of the lowest state of the excited $4f^{n-1}5d^1$ electronic configuration of Ln^{α+} ion in a given lattice weakly depends on the lanthanide [2–4]. Energy required to excite an electron from the ground state of the $4f^n$ electronic configuration to the lowest state

of the $4f^{n-1}5d^1$ electronic configuration always shows a characteristic pattern with the number of electrons n at the f shell [5,6]. It diminishes with n increasing from 1 to 7 and from 8 to 14, and rapidly decreases between n equal to 7 and 8. The energy of the $4f^{n-1}5d^1$ state of the Ln^{α+} ion in the lattice diminishes with respect to the free ions due to the interaction of the d electron with a host [7,8] by a quantity of depression energy related to lattice polarization and crystal field splitting. One considers that both the contributions are proportional to R^{-n} (R is ion–ligands distance). For polarization case [9] $n=6$ and for crystal field approach [10], $n=5$. The location of the energy of the ground state $4f^n$ and the lowest state of the $4f^{n-1}5d^1$ electronic configurations in the case of Ln³⁺ and Ln²⁺ has been presented in Refs. [3,11].

Crucial effect for the efficiency of luminescence is that the emitting state and the ground state of the dopant may not be degenerated with the conduction band (CB) and valence band (VB). Effective energy transfer from the host to impurity requires an existence of impurity-trapped exciton (ITE) and/or charge transfer (CT) states that cause the localization of electron and hole near the dopant.

In this contribution the high pressure spectroscopy of the Ln^{α+} ions that include influence of pressure on $4f^{n-1}5d^1 \rightarrow 4f^n$, CT and ITE transitions is presented. The model that describes the CT states as well as the ITE states is presented in a consistent way. It is shown that for phosphor performance the physical nature of the ITE states is crucial. The model was then used for the analysis of the influence of hydrostatic pressure on luminescence of Ce³⁺, Pr³⁺ in oxides and Eu²⁺ in fluorides. Specifically the arguments for the delocalization of an electron at the ITE states similar to the case of shallow donor states in semiconductors are presented.

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2. Model of CT and ionization processes

The CT and ionization processes as well as internal transitions and band-to-band excitation are presented in Fig. 1a. One should notice that the diagram represents the occupation of the levels in the ground state of the system, where the VB and the localized level labeled $\text{Ln}^{\alpha+}$, representing the ground state of $\text{Ln}^{\alpha+}$, are occupied whereas the CB and the level labeled $(\text{Ln}^{\alpha+})^*$, representing $\text{Ln}^{\alpha+}$ ion in the excited state, are empty. Thus energies E_g and E_1 represent the real energy of the transition between the band and localized states whereas E_2 and E_3 represent the positions of the localized level of the ion $\text{Ln}^{\alpha+}$ with respect to the band edges in the diagram and are not equal to the ionization and CT transition energies, respectively.

To consider the transitions representing the CT and ionization processes one should consider the final states in both cases. The CT transition is defined as the excitation of an electron from a VB to ground states of $\text{Ln}^{\alpha+}$, resulting in the localization of an electron and creation of an $\text{Ln}^{(\alpha-1)+}$ ion in the ground state, and creation of a hole in the VB. As a result of the localization additional electrons at the impurity ion and the energy of the $\text{Ln}^{(\alpha-1)+}$ system in the ground state increase with respect to the $\text{Ln}^{\alpha+}$ system by quantity ΔE . The energy of CT transition is then equal to

$$E_{\text{CT}} = E_3 + \Delta E. \quad (1)$$

The ionization of the $\text{Ln}^{\alpha+}$ ion takes place when an electron is excited from the $\text{Ln}^{\alpha+}$ to the conduction band. As a result, $\text{Ln}^{(\alpha+1)+}$ and the electron in CB are created. Delocalization of the electron causes decrease in energy of the system by quantity ΔE (energy needed for localization of an electron). The ionization energy is then equal to

$$E_{\text{JON}} = E_2 - \Delta E. \quad (2)$$

In the model of ITE [12,13], energy related to the localization of one electron at the impurity has been related to the space occupied by $\text{Ln}^{\alpha+}$ ion as follows:

$$\Delta E = U_1 = \frac{C}{R^m} \quad (3)$$

where R is the distance between impurity and ligand, constant C is related to fundamental quantities and exponent m depends on the model that describes the interaction of the localized electron with ligands. Relation (3) shows that ΔE does not depend on the number

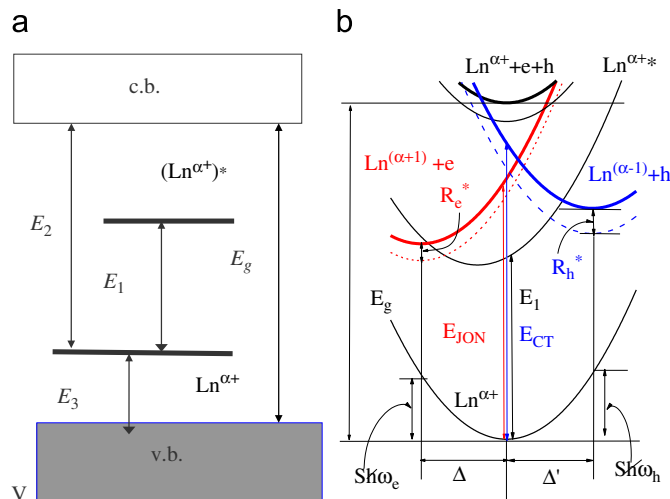


Fig. 1. (a) Diagram of occupation of the $\text{Ln}^{\alpha+}$ lattice system in the ground state and (b) configurational coordinate diagram describing the energetic structure and transitions in the $\text{Ln}^{\alpha+}$ ion and ITE and CT states.

of 4f electrons, n (type of ion) but since it depends on R it can be different in different lattices. Actually this rule is broken when the electron number changes between 7 and 8 [4].

Actual experimental data that are measured for CT and ionization energies are defined by Eqs. (1) and (2). It is interesting to note that for the materials in which both transitions are observed in the same ion the sum of ionization and CT energies does not depend on ΔE and is equal E_g .

Quantity ΔE has been actually estimated by Dorenbos [4] who considered differences between ground state energies of Ln^{2+} and Ln^{3+} ions in a particular lattice. He has shown that ΔE does not depend on the number of 4f, n , except for Gd [4], which is in agreement with predictions of our model.

3. Configurational coordinate model for excited states

To consider the dependence of energy of CT and ionization transitions on lattice and to analyze the ITE effect we have applied perturbation theory, where impurity ion potential is a perturbation of the ideal crystal. Such a model, called effective mass approximation (EMA), has been successfully used in semiconductors for describing the donor and acceptor states [14]. The EMA describes the bound states of carriers captured by infinite Coulomb potential of ionized impurity screened by static dielectric constant of the crystal as hydrogen-like states appear below/above each minimum/maximum of the lattice band. By analogy to atomic physics we call these states the Rydberg states, understanding that the similarity is related only to the spatial extension of the wave function and small ionization energies since atomic Rydberg states are characterized by much larger main quantum numbers [15]. Such an approach has been used for formulation of ITE concept [12,13,16] where the following Hamiltonian was proposed:

$$H = \frac{-\hbar^2 \nabla^2}{2m} + V_{\text{cr}}(\mathbf{r})|_{r>R} + V_{\text{Ln}}(\mathbf{r})|_{r<R} - \frac{e^2}{\epsilon r} + V_{\text{latt}}(\Delta, \mathbf{r}) \quad (4)$$

where V_{Ln} is the local potential of the $\text{Ln}^{(\alpha \pm 1)+}$ ion and V_{cr} is the lattice periodic potential. Subscripts $r > R$ and $r < R$ denote the potential outside and inside the first coordination sphere, respectively, while R is the average distance between the $\text{Ln}^{\alpha+}$ ion and the ligands, $e^2/\epsilon r$ is a long-range Coulomb potential of $\text{Ln}^{(\alpha \pm 1)+}$, e is the electron charge and ϵ is the static dielectric constant of the material. Δ is the shift of the ligands, which is a response of lattice on the localization–delocalization of electron.

Hamiltonian (4) yields two types of states: the localized states related to the local potential V_{Ln} of $\text{Ln}^{(\alpha \pm 1)+}$ described by functions $\varphi_c(\mathbf{r})$, which are in fact the states of $\text{Ln}^{\alpha+}$, and the delocalized states with carriers bound by Coulomb potential (the Rydberg states) represented by functions $F_{nlm}(\mathbf{r})$. Obviously $\varphi_c(\mathbf{r})$ and $F_{nlm}(\mathbf{r})$ are orthogonal functions.

In the EMA [14], the Rydberg states create the hydrogen-like structure with the ground state energy equal to $Ry_{e(h)}^* = \pm Ry m_{e(h)}^*/\epsilon^2$, $+$ is for hole bounding with respect to VB and is for bounded electron with respect to CB. Here, Ry is the Rydberg constant and $m_{e(h)}^*$ is the electron (hole) effective mass. The Rydberg states are delocalized since the electrons (hole) spread from the $\text{Ln}^{(\alpha \pm 1)+}$ ion on distances larger than the lattice constant.

$V_{\text{latt}}(\Delta, \mathbf{r})$ describes the lattice reaction to the transition of $\text{Ln}^{\alpha+}$ into $\text{Ln}^{(\alpha \pm 1)+}$ and includes the electronic energy related to the localization–delocalization of the electron U_1 , and the lattice-relaxation energy. It has been shown [12] that the decrease and increase in the electron number causes compression and expansion of the lattice (negative and positive Δ). In the adiabatic approximation $V_{\text{latt}}(\Delta, \mathbf{r})$ is considered as a sum of two components: $V_{\text{latt}}'(\Delta)$ and $V_{\text{latt}}''(\Delta, \mathbf{r})$ where $V_{\text{latt}}'(\Delta) = \pm U_1 - Sh\omega$, where $Sh\omega$ is the lattice-relaxation energy.

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