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The hole picture as alternative for the common electron picture to describe hole trapping and luminescence quenching

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A B S T R A C T

Electronic level schemes with the host valence and conduction band together with the level locations of ground and excited states of defects are used to explain and predict luminescence and carrier trapping phenomena. These schemes are always constructed and interpreted by using the electron picture. In this work the alternative hole picture is presented. Such picture is sometimes used in the field of semi-conductors but hardly ever in the field of wide band gap inorganic compounds. We will focus on the lanthanides, and first show where to draw the hole ground state and excited hole states in our scheme. It leads to up-side-down Dieke diagrams and up-side-down configuration coordinate diagrams but for the rest everything is equivalent to the electron picture. With the hole picture, luminescence quenching via hole ionization to the valence band and hole trapping in defects can be illustrated much more conveniently than with the electron picture. As examples the quenching of the Tb^{3+} $^5D_4$ emissions by electron ionization and the quenching of the Eu^{3+} $^5D_0$ emissions by hole ionization are compared.

1. Introduction

An electronic level scheme is a scheme that shows the level energies of a luminescence center or carrier trapping center with respect to the host valence and conduction bands. Such scheme is always constructed from the perspective of the electron, and is then used to illustrate the path of the electron during excitation, ionization, trapping, recombination, emission, tunnelling etc. We are raised with such schemes and so used to it that we also apply it in cases when another type of scheme may be more appropriate. In describing charge carrier trapping in persistent luminescence phosphors we tend to focus on the electron trap and always seem to forget about the hole trap, although its role in the trapping mechanism is of equal importance. Luminescence quenching via electron ionization to the conduction band is well understood and described with a level scheme using the electron picture. Luminescence quenching via hole ionization to the valence band is also a possible quenching route. Such quenching appears difficult to illustrate with the electron picture, yet we frequently tend to use it.

This work first illustrates the electron picture to show what it can be used for. Because there is good information on lanthanide level locations the focus is on that group of elements. The problems that arise with the electron picture when describing how a hole is being trapped and how luminescence is quenched by hole ionization to the valence band is illustrated. Next the alternative hole picture is presented. It is hardly ever used for wide band gap inorganic compounds but is occasionally used to describe luminescence of transition metals in small band-gap semi-conductors like GaN:Fe^{3+} [1] or ZnS:Cu^+;Fe^{3+} [2]. We will apply the hole picture to describe the quenching of Eu^{3+} emission via the charge transfer state, and to describe charge transfer luminescence involving Yb^{3+}. The problems using the electron picture vanish when using the hole picture. Finally, we will compare the quenching temperature of the $^5D_4$ emissions of Tb^{3+} due to electron ionization with the quenching temperature of $^5D_0$ emissions of Eu^{3+} due to hole ionization in compounds.

2. The electron picture

Fig. 1 shows the level locations of Ce^{3+}, Sm^{2+}, Eu^{2+}, and Tb^{3+} in YPO_4 relative to the vacuum level. The methods and parameters used to determine the vacuum referred binding energies (VRBE) can be found elsewhere [3,4]. Upon excitation across the band gap, an electron is promoted from the valence band into the conduction band leaving a hole behind. Such transition is indicated by arrow 1. Arrow 2 represents the 4f → 5d excitation of Ce^{3+}, and arrow 3 represents the thermal ionization of the excited electron to the conduction band (CB). Ce^{3+} is being oxidized and becomes Ce^{4+} and a free electron is created. That electron can be trapped in, for example, a defect like Sm^{3+}. The electron first enters excited Sm^{2+} levels (arrow 4) and then cascades down

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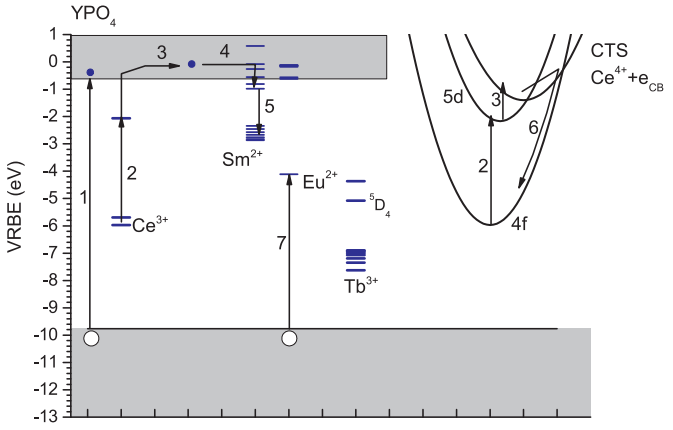

Fig. 1. The electron picture of level energies for Ce^{3+}, Sm^{2+}, Eu^{2+} and Tb^{3+} in YPO^4 with on the right the configuration coordinate diagram illustrating the quenching of Ce^{3+} 5d-4f emission via electron transfer to the CB.

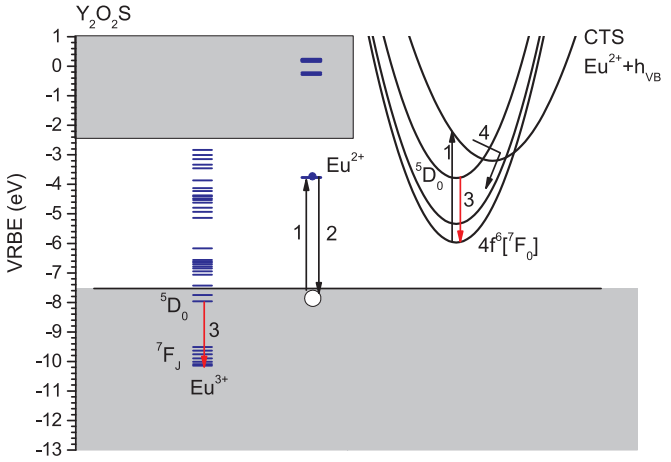

Fig. 2. The electron picture of Eu^{3+} and Eu^{2+} levels in Y_2O_2S with on the right the configuration coordinate diagram illustrating the Struck and Fonger model of quenching of $Eu^{3+}{}^5D_0 \rightarrow {}^7F_J$ emission via the VB → Eu^{3+} charge transfer state.

(arrow 5) to the ground state. During the cascade it may emit a photon or otherwise energy is dissipated in phonon emission [5]. The right hand side of Fig. 1 shows the coordinate configurational diagram (CCD) often used to explain luminescence quenching via the CB. Here it applies to the quenching of the 5d-4f emission of Ce^{3+} in YPO_4 but it equally well applies to the 5d-4f emission of Eu^{2+} [6] or to the emissions from the $^5D_4$ level of Tb^{3+} in compounds with low lying conduction bands [7]. The excited 5d-state parabola is slightly shifted to another configuration coordinate because of lattice relaxation. After or during thermal ionization (arrow 3) of the excited 5d-electron, a much stronger lattice relaxation takes place leading to a more offset CT-parabola. The ionized electron may return radiation less (arrow 6) to the 4f ground state and emission will be quenched. The energy barrier for thermal quenching is then related to the energy difference between the 5d-level location and the CB-bottom. Note that in the level scheme and also in the CC-diagram we follow the path of the electron, and these are therefore illustrations in the electron picture.

Suppose we have the persistent luminescence phosphor $SrAl_2O_4$:Eu^{2+};Dy^{3+}, and by means of β-irradiation holes in the VB and electrons in the CB are created. The electrons will be trapped by Dy^{3+} (or Dy^{3+} associated defects) and the holes will be trapped by Eu^{2+} to create Eu^{3+} [8]. The electron excitation and electron trapping can conveniently be illustrated in the electron picture, but what actually happens during hole trapping is always ignored in literature. Usually an arrow is drawn from the top of the VB to the Eu^{2+} ground state, indicated for YPO_4 by arrow 7 in Fig. 1, as if the hole jumps upwards in a single jump to its final state. Is it a single jump or are other states in between? What are those states and how should that be illustrated? Usually those questions are not asked.

Also describing the thermal quenching of Eu^{3+} red emission from the $^5D_0$ level by the charge transfer state provides us with difficulties in the electron picture. During charge transfer, an electron is transferred from the top of the valence band, i.e., a nearest neighbour anion, to Eu^{3+} to create the ground state of Eu^{2+} leaving a hole in the valence band. This is illustrated by arrow 1 in Fig. 2 that pertains to Y_2O_2S:Eu^{3+} [9]. The electron rapidly returns to the hole in the valence band (arrow 2) leaving Eu^{3+} in an excited state that is followed by the red emission from the $^5D_0$ level (arrow 3). In the electron picture we have to draw the Eu^{3+} transitions separate from the CT transition even though everything relates to the same Eu atom. What happens in between excitation and emission cannot be illustrated in this picture. The configuration coordinate diagram on the right of Fig. 2 illustrates the Struck and Fonger model from 1970, that is still used today, of quenching of Eu^{3+} emission via the CT-state [10]. Struck and Fonger consistently write in terms of excitations and states, and although they never even use the word electron or electron excitation we often tend to interpret the CCD in the electron picture. It shows the $^7F_0$ ground state and $^5D_0$ excited state parabolas together with the VB → Eu^{3+} CT-state. The later one shows a large configurational coordinate offset due to strong lattice relaxation after electron transfer. Thermal quenching is explained by the thermally activated transfer from the $^5D_0$ state to the CT-state and the system then returns radiationless to the ground state parabola. In the electron picture the CCD suggests that an electron is excited from the Eu^{3+} ground state to the CTS which clearly is not the case. Eu^{4+} is definitely not created but an electron is excited from an anion. In the electron picture the drawn CCD is somewhat misleading, i.e., it cannot be used to follow the path of the electron.

3. The hole picture

The above problems of illustrating and describing hole capture, excitation of Eu^{3+} emission via the CT-state, and the quenching of its emission via that same state can all be solved by changing the electron picture for the hole picture. Fig. 3 is a level scheme using such hole picture. Here, a hole (or missing electron) moves upward in a diagram to lower its energy. Across band gap excitation is then represented by a downward pointing arrow from the completely hole filled CB to the hole empty VB as illustrated by the downward pointing arrow 1. This transition is equivalent with the upward pointing arrow 1 in the

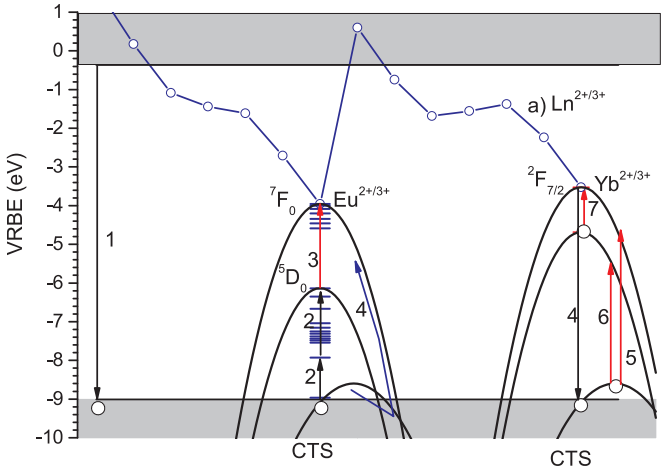

Fig. 3. The hole picture of hole level ground and excited states of Eu^{3+} and Yb^{3+}. The zigzag line a) connects the hole ground state level locations of the trivalent lanthanides. The configuration coordinate diagrams illustrate Eu^{3+} excitation and emission quenching and Yb^{3+} charge transfer luminescence in the hole picture.