

Thermodynamic assessment of the LiF-NiF₂, NaF-NiF₂ and KF-NiF₂ systems

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DOI

[10.1016/j.jct.2018.01.023](https://doi.org/10.1016/j.jct.2018.01.023)

Publication date

2018

Document Version

Accepted author manuscript

Published in

Journal of Chemical Thermodynamics

Citation (APA)

Ocadiz-Flores, J. A., Capelli, E., Raison, P. E., Konings, R. J. M., & Smith, A. L. (2018). Thermodynamic assessment of the LiF-NiF₂, NaF-NiF₂ and KF-NiF₂ systems. *Journal of Chemical Thermodynamics*, 121, 17-26. <https://doi.org/10.1016/j.jct.2018.01.023>

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PII: S0022-2313(17)32119-1
DOI: <https://doi.org/10.1016/j.jlumin.2018.01.013>
Reference: LUMIN15298

To appear in: *Journal of Luminescence*

Received date: 6 December 2017
Revised date: 9 January 2018
Accepted date: 10 January 2018

Cite this article as: Pieter Dorenbos, The hole picture as alternative for the common electron picture to describe hole trapping and luminescence quenching, *Journal of Luminescence*, <https://doi.org/10.1016/j.jlumin.2018.01.013>

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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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(Dated: January 11, 2018)

Abstract

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 $\text{Tb}^{3+} \ ^5D_4$ emissions by electron ionization and the quenching of the $\text{Eu}^{3+} \ ^5D_0$ emissions by hole ionization are compared.

I. INTRODUCTION

An electronic level scheme is a scheme that shows the level energies of a luminescence centre 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:Fe³⁺ [1] or ZnS:Cu⁺;Fe³⁺ [2]. We will apply the hole picture to describe the quenching of Eu³⁺ emission via the charge transfer state, and to describe charge transfer luminescence involving Yb³⁺. The problems using the electron picture vanish when using the hole picture. Finally, we will compare the quenching temperature of the ⁵D₄ emissions of Tb³⁺ due to electron ionization with the quenching temperature of ⁵D₀ emissions of Eu³⁺ due to hole ionization in compounds.

II. THE ELECTRON PICTURE

Figure 1 shows the level locations of Ce³⁺, Sm²⁺, Eu²⁺, and Tb³⁺ in YPO₄ 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 $4f \rightarrow 5d$ 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 (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 $\text{Y}_2\text{O}_2\text{S}:\text{Eu}^{3+}$ [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 $\text{VB} \rightarrow \text{Eu}^{3+}$ 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.

III. 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. Figure 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 electron picture of Figure 1. The trapping of a hole from the VB by Eu^{2+} in the electron picture creates Eu^{3+} . The Eu^{2+} ground state electron level location in the electron picture is then equivalent to the Eu^{3+} ground state hole level location in the hole picture. The familiar zigzag

curve labelled a) in Fig. 3 connects, in the electron picture, the ground state electron levels of the divalent lanthanides. In the hole picture, however, the same zigzag curve connects the ground state levels of the holes in the trivalent lanthanides. The curve and the states can therefore be labelled as $\text{Ln}^{2+/3+}$. Such notation is quite common in semi-conductor physics when dealing with electron donor and electron acceptor states. Donor ionization is then the same as the electron transfer to the CB and acceptor ionization is the hole transfer to the VB.

Returning to the question how to illustrate excited hole states of Eu^{3+} within the hole picture, we have to use the up-side-down Dieke diagram of $4f^n$ energy levels. This means that the excited electron state levels of Eu^{3+} from the familiar Dieke diagram should be turned up-side down with the ground state at the $\text{Eu}^{2+/3+}$ level location in the band gap. In Figure 3 we have applied this to Eu^{3+} and Yb^{3+} . It is now immediately clear how a hole is being trapped from the valence band by Eu^{2+} . The ionized hole first enters excited hole states of Eu^{3+} (arrows 2) and then moves further upwards to the Eu^{3+} ground state (arrow 3). The transitions between the 5D_0 excited state and 7F_J lower energy states can then be radiative. Figure 3 also illustrates the CCD in the hole picture. Now all parabolas must be facing downwards. The $\text{VB} \rightarrow \text{Eu}^{3+}$ charge transfer is equivalent to the photo-ionization of a hole from Eu^{3+} to the VB. Upon photo-ionizing there is a strong lattice relaxation leading to an offset CCD parabola. From there the hole may relax to the 5D_0 level to generate red Eu^{3+} emission (arrow 3) but it may also relax to one of the 7F_J levels (arrow 4) and then emission will be quenched.

Yb^{3+} with one hole in the $4f$ orbital has a more simple energy level structure than Eu^{3+} does. There is the $^7F_{7/2}$ ground state with $^2F_{5/2}$ as the only $4f^{13}$ excited state. Contrary to Eu^{3+} an ionized hole may return to Yb^{2+} by photon emission which is also known as charge transfer luminescence [11, 12]. The hole picture for Yb^{3+} explains very nicely in one diagram the occurrence of such CT-luminescence. On ionization of the hole from Yb^{3+} to the VB (arrow 4), a radiative hole transition to the $^2F_{7/2}$ Yb^{3+} ground state (arrow 5) or to the $^2F_{5/2}$ excited state (arrow 6) occurs. It leads to two wide CT-luminescence bands separated by about 1.25 eV. The CT-emission to the $^2F_{5/2}$ excited state is followed by ≈ 980 nm (1.25 eV) narrow band $\text{Yb}^{3+} \ ^2F_{5/2} \rightarrow ^2F_{7/2}$ emissions (arrow 7).

The hole picture now solves all problems raised with the electron picture. The need to illustrate the $\text{VB} \rightarrow \text{Eu}^{3+}$ CT excitation separate from the emission of Eu^{3+} in Fig. 2 has

disappeared. The CC-diagram of the Struck and Fonger model that cannot be used to follow the path of the electron makes perfect sense in the hole picture. All transitions and parabolas should refer to hole states instead of electron states, and then one may follow the path of the hole during excitation, relaxation, emission or quenching. The description of hole trapping from the valence band in the hole picture is entirely similar to the description of electron trapping from the conduction band in the electron picture. Also the route of the electron in the CCD when describing quenching via thermal ionization to the CB in the electron picture is entirely similar to that of the hole in the hole picture.

IV. LUMINESCENCE QUENCHING BY ELECTRON OR BY HOLE IONIZATION

Generally the thermal quenching of luminescence intensity $I(T)$ with temperature T can be expressed by

$$I(T) = \frac{I(0)}{1 + \frac{\Gamma_0}{\Gamma_\nu} \exp\left(\frac{-\Delta E}{k_B T}\right)} \quad (1)$$

where Γ_ν is the radiative decay rate, Γ_0 is the attempt rate for thermal quenching, k_B is the Boltzmann constant, and ΔE is the energy barrier for thermal quenching. The attempt rate Γ_0 has similar magnitude as the maximum phonon frequency in compounds. It is typically $1-3 \times 10^{13}$ Hz corresponding with phonon energies of 330 to 1000 cm^{-1} .

We will use the $4f^8[{}^5D_4]$ emissions of Tb^{3+} to illustrate quenching by electron ionization. The VRBE in the 5D_4 state of Tb^{3+} is in many oxides, like in Fig. 1 for YPO_4 , found near -5 eV. Then, when the CB-bottom is below about -3 eV and also below the lowest Tb^{3+} 5d-level, thermal quenching of 5D_4 emission may proceed by electron ionization. Figure 4 shows the quenching temperature $T_{0.5}$ for the Tb^{3+} 5D_4 emission against the energy difference between the Tb^{3+} 7F_6 g.s. and the CB-bottom. Most of the data on transition metal based compounds is from [7], and data from literature on other compounds were added [14–16]. To establish the VRBE at the CB-bottom, we used the latest set of parameter values for VRBE construction as proposed in [17]. By using a typical radiative decay rate of 500 Hz (2 ms) for the 5D_4 emissions and Eq. (1), the quenching temperature $T_{0.5}$ is predicted to change with about 475K/eV. The dashed line in Fig. 4 was constructed with that slope, and indeed data tend to scatter around that line. The intercept with the horizontal axis is near 3.95 eV which is 0.4 eV above the emitting 5D_4 level. This energy can be regarded as

a measure for the energy lost in lattice relaxation. The energy difference $\Delta E(^7F_6\text{-CB})$ is actually the energy of the IVCT band that can be observed in excitation spectra of Tb^{3+} emission[13].

To illustrate quenching via hole ionization one may use data on the quenching of $\text{Eu}^{3+}[^5D_0]$ emissions. Figure 5 shows the onset temperature T_k for thermal quenching of Eu^{3+} emission against the energy of the CT-band as was presented in [17]. The typical radiative rate for the Eu^{3+} emission is, like for $\text{Tb}^{3+}[^5D_4]$ emissions, 500 Hz (2 ms), and when we assume that the onset of thermal quenching corresponds with the temperature $T_{0.1}$ where emission intensity has dropped by 10% we predict with Eq. (1) that $T_{0.1}$ will change with 430 K/eV. In Fig. 5 a line with such slope has been constructed, and indeed data tend to scatter around such line with an intercept on the horizontal axis about 0.6 eV above the energy of the 5D_0 level. Note that 0.6 eV is also the typical width of the Eu^{3+} CT-band [18] and it is indicative for the amount of energy that is lost in lattice relaxation.

V. SUMMARY AND CONCLUSIONS

This work demonstrates that the difficulties that arise to describe VB hole trapping, Yb^{3+} CT-luminescence, and luminescence quenching of Eu^{3+} emission when using the electron picture vanish when using the hole picture. The hole ground state of a trivalent lanthanide should be placed at the same location as the electron ground state of the corresponding divalent lanthanide. Quenching by hole ionization to the VB in the hole picture then appears a mirror image to quenching by electron ionization to the CB in the electron picture. Excited hole states are given by the up-side-down Dieke diagrams, and the quenching is described by up-side-down configuration coordinate diagrams. Lowering the conduction band decreases the quenching temperature of $\text{Tb}^{3+} ^5D_4$ emission due to electron ionization at a rate of 475K/eV. A similar rate applies for the decrease of quenching temperature of $\text{Eu}^{3+} ^5D_0$ emission due to hole ionization when the valence band is raised in energy.

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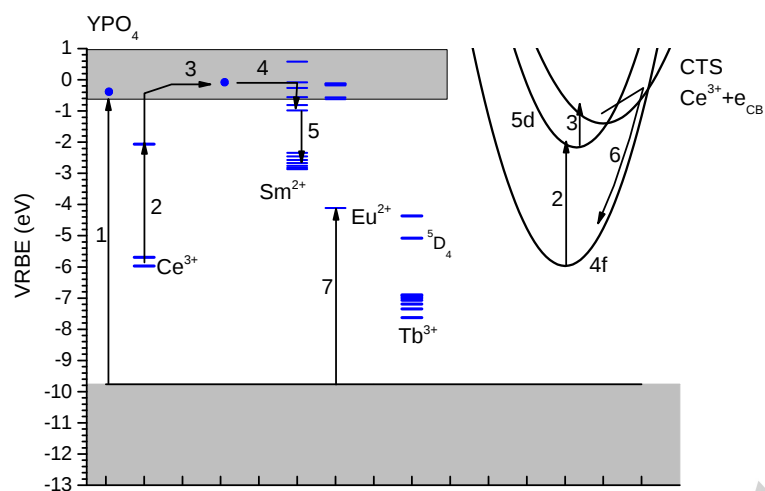


FIG. 1: The electron picture of level energies for Ce^{3+} , Sm^{2+} , Eu^{2+} and Tb^{3+} in YPO_4 with on the right the configuration coordinate diagram illustrating the quenching of Ce^{3+} 5d-4f emission via electron transfer to the CB.

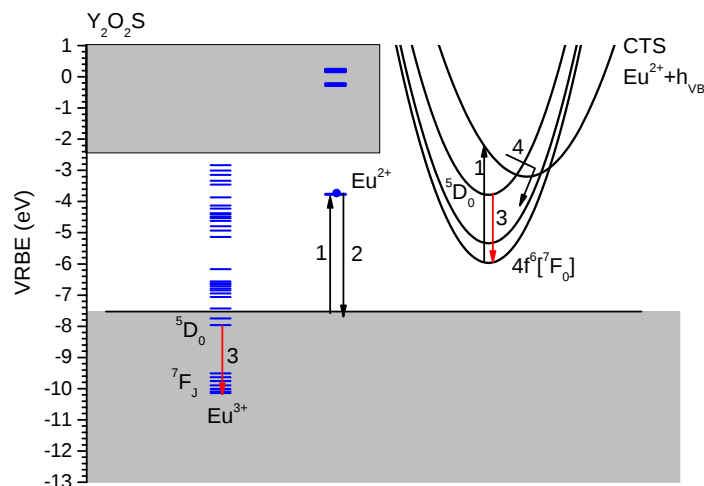


FIG. 2: The electron picture of Eu^{3+} and Eu^{2+} levels in $\text{Y}_2\text{O}_2\text{S}$ with on the right the configuration coordinate diagram illustrating the Struck and Fonger model of quenching of $\text{Eu}^{3+} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_J$ emission via the $\text{VB} \rightarrow \text{Eu}^{3+}$ charge transfer state.

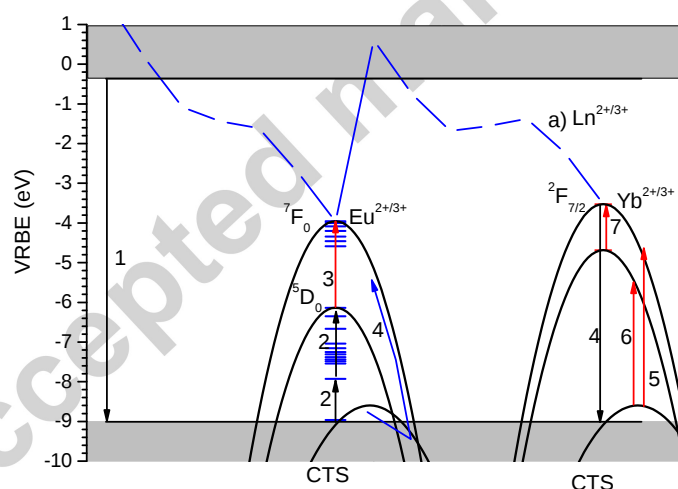


FIG. 3: The hole picture of hole level ground and excited states of Eu^{3+} and Yb^{3+} . The zigzag line a) connects the hole ground state level locations of the trivalent lanthanides. The configuration coordinate diagrams illustrate Eu^{3+} excitation and emission quenching and Yb^{3+} charge transfer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

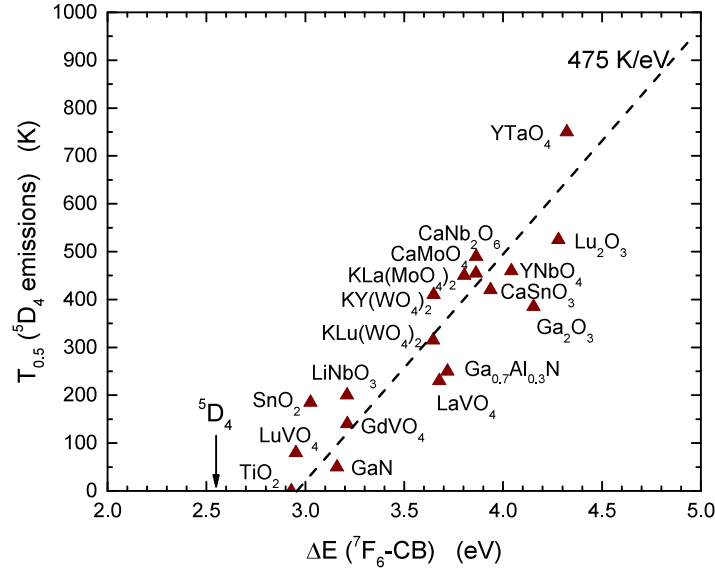


FIG. 4: Thermal quenching temperature of the 5D_4 emission of Tb^{3+} as function of the energy difference between the ground state and the CB-bottom. The solid line drawn to guide the eye has a slope of 475K/eV.

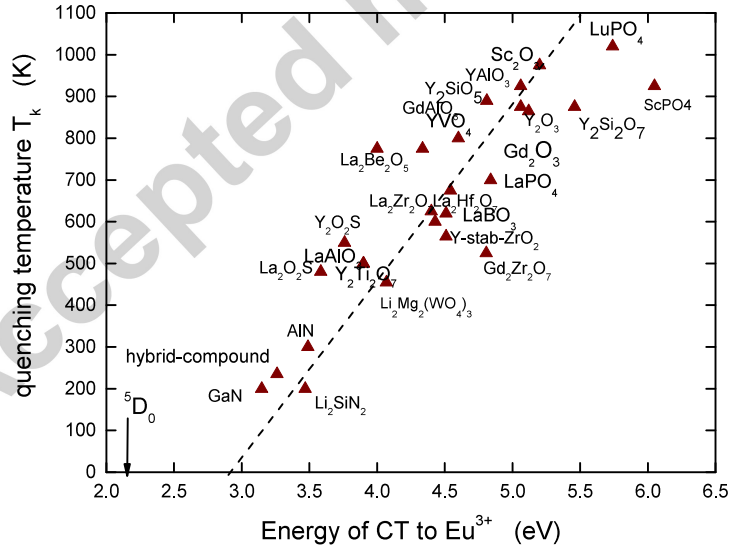


FIG. 5: The onset T_k of thermal quenching of the $^5D_0 \rightarrow ^7F_J$ Eu^{3+} emission as function of CT-band energy. The dashed line drawn to guide the eye has a slope of 430K/eV