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A fundamental self-generated quenching center for lanthanide-doped high-purity solids

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Abstract

An intrinsic self-generated quenching center for lanthanide-doped high-purity solids is presented for transitions, which cannot be quenched by cross-relaxation. This center, in fact a cluster-like pair of active centers, is shown to come from a particular multiphonon-assisted energy transfer between them. Being due to the vibronic properties of the host it cannot be suppressed. Its role in lanthanide first excited states self-quenching is analyzed and a simple mathematical expression is derived. This law is compared with experimental results for self-quenching in Er-doped fluorophosphate glasses.

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1. Introduction

Self-quenching, the fact that quantum efficiency is reduced when active ion concentration is increased, is a pervading effect for any luminescent center. In the case of lanthanide first excited states, because of the considered level positions, it cannot be due to cross-relaxation between various excited states and it has been mainly considered as due to diffusion towards unidentified impurities or "poisonous non-radiative centers". However, we have proposed to consider that an increase of active ion equivalently leads to an effective increase in the electron–phonon coupling [1–3] so creating selfgenerated quenching centers, but the increase of electron–phonon coupling with active ion concentration has been disputed [2,4] and the details of

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the electron-phonon increase mechanism had not been presented. The purpose of the present work is to give details on the mechanism for such a selfgenerated dissipative step which, as we shall see, constitutes a fundamental limit for self-quenching of lanthanide first excited state in high-purity matrix.

This would particularly apply to the cooperative luminescence case of Yb^{3+} as first observed by Nakazawa and Shionoya in $YbPO_4$ [5]. In such a case, non-radiative processes at the virtual emitting state should be rather weak, whereas the essential of the non-radiative process would come from the reduction of the Yb^{3+} first excited state lifetime at high concentrations through selfquenching and the self-generated quenching process described below.

In the following, we consider the special case of multiphonon-assisted energy transfer described schematically in Fig. 1. One excited ion transfers



Fig. 1. Energy scheme for the proposed self-generated multiphonon-assisted process W_{12} ; wavy lines indicate non-radiative transitions; W_r and W_{nr} are one-ion radiative and non-radiative decay probabilities.

the quasi-totality of its excitation energy to an empty ground state Stark level (except the lowest one) of its identical neighbor preceded by an eventual diffusion step. In such phonon-assisted energy transfer, we consider that most of the energy is lost through the multiphonon step and that the remaining transferred electronic energy is also subsequently lost through onephonon decay down the ground state Stark level ladder of the acceptor ion. In the following, we shall compare the magnitude of this newly considered effect with non-radiative and radiative decays within one ion.

2. Multiphonon non-radiative decay versus multiphonon-assisted energy transfer at the microscopic level

Miyakawa and Dexter have presented long time ago a common treatment for both multiphononnon-radiative decay and for multiphonon-assisted energy transfer processes [6]. It has been shown that both processes essentially differ by two aspects [7–9]:

(i) Non-radiative decay implies a promoting term which equivalently comes out as a reduction in the energy gap by about the energy of two phonons [8–10]. The probability for non-radiative relaxation can be expressed as [9]

$$W_{\rm nr}(\Delta E) = W_{\rm nr}(2\hbar\omega) \exp[-\alpha(\Delta E - 2\hbar\omega)]$$
(1)

with $\alpha = (\hbar\omega)^{-1}[\ln(N/es(n+1))]$, where *n* is the phonon occupation number at a considered temperature, e = 2.718, ..., N the multiphonon order, and *s* the Huang–Rhys electron–phonon coupling parameter for the considered active ion. It has been shown that $W_{nr}(2\hbar\omega)$ is about a constant for any material with a value of order $2 \times 10^6 \text{ s}^{-1}$ [8,9]; *N/s* has also been shown to have an average value of 82 [11] for both crystalline and glassy materials.

(ii) In the case of multiphonon-assisted energy transfers, the promoting terms are, respectively, the electric dipole for emission at the sensitizer and the electric dipole for absorption at the activator ion, which help to constitute the spectral overlap between multiphonon side-bands at the two interacting ions; the probability for energy transfer is also given by an exponential law [6]:

$$W_{12}(\Delta E) = W_{12}(0) \exp[-\beta \Delta E]$$
⁽²⁾

with $\beta = \alpha - (\hbar \omega)^{-1} \ln(1 + s_1/s_2)$, and s_1 and s_2 being the Huang–Rhys electron–phonon coupling parameters for ions 1 and 2. Eq. (2) can be written as

$$W_{12}(\Delta E) = W_{12}(0) \exp[-((\ln(N/es(n+1) - \ln(1+s_1/s_2))(\hbar\omega)^{-1}\Delta E]]$$

or

$$W_{12}(\Delta E) = W_{12}(0) \exp[-((\ln(N/e(1+s_1/s_2) \times s(n+1))(\hbar\omega)^{-1}\Delta E]].$$
(3)

Eq. (3) shows the important fact that had been overlooked until now, that multiphonon energy transfer for a given energy gap comes out as a factor $(1 + s_1/s_2)$ increase in the Huang–Rhys coupling parameter, *s*, for one-ion non-radiative decay, when two ions are coupled by the Coulomb and the multiphonon interaction.

Though each ion interact with different modes of vibration, these modes may be close to each other in frequency so much the better that the two ions are in our case identical. Then $s_1 = s_2$ and Eq. (2) can be written [6] as

$$W_{12}(\Delta E) = W_{12}(0) \exp[-(\ln(N/e^{2s(n+1))}) \times (\hbar\omega)^{-1} \Delta E].$$
(4)

Such a pair of ions, or cluster, constitutes a fundamental self-generated dissipative non-radiative entity with a Huang–Rhys coupling increased by a factor of order 2. This non-radiative process could indeed be considered as equivalent to a usual non-radiative multiphonon decay within a pair of ions with as stronger electron–phonon coupling. However, it differs from a classical non-radiative decay by the fact that the phonon promoting term is not needed here, being replaced by the Coulomb interaction. The increased electron–phonon coupling comes from the fact that each ion participates in part by their own coupling parameter and their own sidebands to the common overlap integral needed by the considered energy transfer.

A typical value for $W_{12}(0)$ is 10^5 s^{-1} for Y_2O_3 [12]. For the same reasons for which $W_{\rm nr}(2\hbar\omega)$ is about a constant [8,9], we propose here that $W_{12}(0)$ be also considered as a constant, 10^5 s^{-1} , for various hosts: it contains the coulomb interaction matrix element $|\langle H_{S1,S2} \rangle|^2$ between the two lanthanide ions which from their known oscillators strength should not vary much from host to host. Because the promoting term for sidebands is coming from the electronic oscillator strengths in ions S1 and S2, all lines, for various hosts, in a semi-log plot given by Eq. (3) should also cross at the constant value ordinate $W_{12}(0)$ point just as for $W_{\rm nr}(2\hbar\omega)$ when the $2\hbar\omega$ promoting term is taken into account [8,9]. With N/s = 82, it is then possible to propose quasi-universal functions in any materials for non-radiative decays as well as for multiphonon transfers at 0 K (in order to momentarily eliminate $\hbar\omega$ from the formulas):

$$W_{\rm nr}(s^{-1}) = 2 \times 10^6 \exp[-\ln(82/e))(N-2)]$$
 (5)

or

$$W_{\rm nr}(s^{-1}) = 2 \times 10^6 \exp[-3.4(N-2)].$$
 (6)

For transfers at 300 K from Ref. [12], it had been experimentally obtained in Y_2O_3 :

$$W_{12}(s^{-1}) = 10^5 \exp(-2.6 \times 10^{-3} \Delta E)$$

= 10⁵ exp(-1.3N) (7)

with $\hbar\omega$ taken as 500 cm⁻¹ for Y₂O₃.

At 0 K, the exponential parameter has to be corrected for the phonon occupation number n =

0.1, that it contains for 300 K (see inset Fig. 2) or $W_{12}(s^{-1}) = 10^5 \exp[-(1.3 + \ln(1.1))N]$

$$=10^5 \exp(-1.4N).$$
 (8)

Now assuming that N/s keeps the same for nonradiative decay and energy transfer, one can estimate the electron-phonon multiplying factor experimentally found by comparing the exponential parameter in Eqs. (3) (6) and (8). It comes for the exponential parameters at 0 K from W_{nr} and W_{12} :

$$3.4 - \ln(1 + s_1/s_2) = 1.4$$

or $1 + s_1/s_2 = 7.4$ larger than the value 2 estimated for equal phonon coupling in both ions. It could indicate that more than two ions are coupled together or that the average N/s is not the same for transfers and non-radiative decays. Due to the lack of available experimental results in the literature for multiphonon transfers studies, no answer can be given at this point.

We have seen that the two considered ions, contributing both as shown above by their electron-phonon coupling as described by Eq. (3), are equivalent to a defect center with an increased electron-phonon coupling strength. This is the fundamental self-generated dissipative step which appears when the concentration of active centers is increased to the point where phonon-assisted energy transfer may take place.

Plotting, Fig. 2, on the same graph Eqs. (5) and (8) as average universal functions (for T = 0 K and/or for $\hbar \omega > 1000$ cm⁻¹; for other T and $\hbar \omega$ values, the *n* values displayed in insert have to be included into α , using the average constants given above, shows that, W_{12} , the new quenching process crosses W_{nr} and shall be larger than it in the region where lies most of the radiative probability of lanthanide first excited states. The condition is simply $\Delta E > 5\hbar\omega$.

This condition is the same as the one generally considered to be the breakeven point ($\Delta E = 5\hbar\omega$) where radiative transitions equal non-radiative ones in lanthanide-doped systems [9]. Fig. 2 also shows detailed breakeven points for typical radiative probability for ions and transitions, which cannot be quenched by cross-relaxation (emission from first excited states). It shows that



Fig. 2. Comparison between typical probabilities at 0 K for one-ion radiative decays, W_r (horizontal lines), one-ion non-radiative decay W_{nr} , and the multiphonon quenching process, W_{12} , versus energy gap below the considered level, expressed in phonon number N. Inset shows (n + 1) versus temperature for three values of $\hbar\omega(300, 500, 1000 \text{ cm}^{-1})$.

the new self-quenching process is very general and has to be considered for any radiative transition, with sizeable quantum efficiency at lower concentration, with gaps of the order 5–8 phonons.

It also shows that the "self-generated multiphonon-assisted defect center with increased electron–phonon coupling" should be particularly effective in the case of emitters such as Er^{3+} , for ${}^{4}I_{13/2}-{}^{4}I_{15/2}$ laser and amplifier transition, Yb^{3+} for ${}^{2}F_{5/2}-{}^{2}F_{7/2}$ laser transition and cooperative luminescence excitation [5]. It should also be considered for the $Ho^{3+}{}^{5}I_{7}$ and the $Dy^{3+}{}^{5}I_{6}$ states of interest for IR lasers. Finally, the $Tb^{3+}{}^{5}D_{4}$ and $Eu^{3+}{}^{5}D_{0}$ states often involved in organic systems, being cross-relaxation free, are relevant of the same quenching process in host with high-energy vibrators such as C–H and O–H. For the Eu^{3+} case, the transfer final state could be a vibronic sideband state.

This demonstrates that there is no hope to completely avoid self-quenching for such transitions even in highly purified hosts, the "poisonous centers" being intrinsically created by the electron–phonon coupling itself.

3. Macroscopic calculation for self-quenching by the considered process

The considered transitions being of the resonant type, the recent approach [13] taking into account self-trapping has to be used when the experimental geometry for lifetime measurement does not avoid photon trapping. However, we know that such photon trapping can be experimentally avoided by using optically very thin samples and back excitation geometry [13]. In the following, for the sake of simplicity, we assume that photon trapping is experimentally avoided.

Though the defect center is of the same origin as the center used for diffusion, the limited diffusion case cannot apply as in Ref. [13] because the diffusion steps are resonant and the quenching step being multiphonon assisted is slower by the factor representing the ratio of its multiphonon spectral overlap to the resonant overlap. By definition it is [6]: $\exp(-\beta \Delta E) < 1$. In such a case of "fast diffusion or super-migration", generally corresponding to the weak quenching case, we know [14,15] that the quenching rate, R_Q , is proportional to, c, the active ion concentration:

$$R_{\rm O} = 1/\tau(c) - 1/\tau_{\rm w} = Kc,$$
(9)

where τ_w is the active ion lifetime at low concentration, $\tau(c)$ the measured lifetime at concentration *c*.

From Refs. [14,16], it can be shown that

$$R_{\rm Q} = 6.1 C_{12}^{1/4} C_{\rm SS}^{3/4} \frac{c}{R_{\rm min}^3},\tag{10}$$

were R_{\min} is the minimum distance between sensitizer ions in the considered host; C_{12} and C_{ss} are respectively, the sensitizer to quencher and the sensitizer to sensitizer transfer constant, as given by Dexter theory [17], for dipole–dipole transfer probability

$$P_{ij} = (R_{0ij}/R)^6 / \tau_{\rm s} = C_{ij}/R^6, \tag{11}$$

for an assumed dipole–dipole interaction; τ_s is the sensitizer lifetime in absence of interaction; R_{0ij} is the critical transfer distance linked to the critical concentration by $R_{0ij} = (3/4\pi N_{0ij})^{1/3}$.

Since here, the sensitizer as well as the quenchers are created by the same type of ions but for different considered levels and transfers, one has the following relationship by definition of the considered overlap integrals [6]:

$$C_{12} = C_{\rm ss} \exp(-\beta \,\Delta E). \tag{12}$$

Here, it has been assumed that the electric dipole elements in both ions S1 and S2 have the same order of magnitude (except for a J = 0 state). This is the same assumption as the one behind the energy gap law (7).

Combining, Eqs. (10)-(12), one obtains

$$K = 1.45 \frac{\exp(-\beta \Delta E/4)}{\tau_{\rm s} c_{\rm 0ss}} \tag{13}$$

with c_{0ss} being a critical concentration defined by $c_{0ss} = N_{0ss}^2/N_{max}$ with $N_{max} = 3/4\pi R_{min}^3$.

Assuming that the ion lifetime at low concentration is the same as the sensitizer lifetime when isolated, one gets from Eqs. (9) and (13) the simple proposed relationship

$$\tau(c) = \frac{\tau_{\rm w}}{(1 + 1.45(c/c_{\rm 0ss})\exp(-\beta\,\Delta E/4))}.$$
 (14)

Using Eq. (7) at 300 K it can be practically written as

$$\tau(c) = \frac{\tau_{\rm w}}{(1 + 1.45(c/c_{\rm 0ss})\exp(-N/3))}.$$
 (15)

It is the quasi-universal quenching curve we propose for multiphonon self-quenching of first lanthanide excited states in high-purity host.

4. Comparison with experiments

In Ref. [18], we had been studying the selfquenching of $Er^{3+}({}^{4}I_{13/2})$ in fluorophosphate glasses with an introduction of the doping by precursors differing by their crystalline Er-Er shortest distances. Fluorophosphate glasses have the advantage over other phosphate glasses to have a reduced water content [18]; this allows to consider the vibration energy as coming essentially from the P–O vibration and we can take $\hbar\omega =$ 1100 cm^{-1} . With a gap of 6490 cm⁻¹ for the ${\rm Er}^4 {\rm I}_{13/2} {-}^4 {\rm I}_{15/2}$ transition, it becomes N = 5.9which is introduced into Eq. (15). Taking c_0 as the only free parameter, a rather good simulation for both experimental results is obtained as shown in Fig. 3, with $c_{0ss} = 2.2 \times 10^{18}$ and $5.6 \times$ 10^{18} cm⁻³, respectively, for Er₂O₃ and the ErP₅O₁₄ doping precursors with respective minimum distances of 0.35 and 0.52 nm. The memory of the minimum distances within a cluster of Er ions is thought to be kept during the glass-making process [18]. Here this hypothesis is rather well verified by comparing the obtained c_{0ss} . Having $c_{0ss \propto} R_{\min}^3$, it is found that $(0.52/0.35)^3 = 3.2$ not too far from the ratio of the critical concentration 5.6/2.2 = 2.54. On the other hand, the slight difference in observed τ_w , respectively, 9.5 versus 8.9 ms for the two series of glasses, may be due to a difference in the water content of the doping precursors: ErP₂O₅ is known to easily contain water which is not the case for Er_2O_3 .



Fig. 3. Measured lifetimes of $\mathrm{Er}^4 I_{13/2}$ at 300 K versus Er concentrations in two series of fluorophosphate glasses of identical composition with Er introduced by two different precursors, from Ref. [18], comparison with Eq. (15) is given by the continuous curves.

5. Conclusion

We have proposed a new intrinsic quenching center for lanthanide first excited states and derived a quasi-universal law to describe the corresponding self-quenching process. We show that, being due to the vibronic properties of the host, such process cannot be suppressed whatever the host purity. It solves the old problem to know where the energy is lost in the self-quenching process of the lanthanide first excited states without having to advocate mysterious "poisonous centers" nor "uncontrolled impurities". We have also shown that the vibronic coupling of two active ions in a cluster-like pair may come out as an increase in the Huang–Rhys electron–phonon coupling parameter just as shown by the wellknown theory of Miyakawa and Dexter [6].

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