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AN EXAMPLE OF CONCENTRATION SENSITIVE ELECTRON–PHONON COUPLING IN $\{(C_4H_9)_4N\}_3$ $Eu_xY_{1-x}(NCS)_6$ AND A NEW HYPOTHESIS FOR SELF-QUENCHING

F. AUZEL
Centre National d'Etudes des Télécommunications 92220 Bagneux, France

G.F. DE SA' and W.M. de AZEVEDO
Dpt. de Fisica, Universidade Federal de Pernambuco, 50000 RECIFE – Pe, Brazil

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The strong vibronic one-phonon side-bands of the $^5D_0 \rightarrow {}^7F_0$ emission of Eu^{3+} in $\{(C_4H_9)_4N\}_3$ $Eu_xY_{1-x}(NCS)_6$ are used to compute the Huang–Rhys electron–phonon coupling factor (S_0) of Eu^{3+} with the mode at 35 cm^{-1}. Increasing concentration from 1 to 100 is found to lead to a doubling of the electron–phonon coupling strength. Generalization of such an effect is proposed as a new hypothesis for part of the self-quenching process of rare-earth ions.

1. Introduction

Vibronic structure in absorption, excitation or emission spectra are characteristic of the strength of the electron–phonon interaction. In general, they may have two causes; either a shift in equilibrium of lattice coordinates: the Huang–Rhys coupling factor S_0 is non-zero, or a phonon-forced electric–dipole transition ($S_0 = 0$), respectively the so-called Δ- and M-process [1]. Recently we have stressed the formal analogy between non-radiative decays and vibronic side-bands [2] showing that side-bands can give information about non-radiative decay. In this paper, we present an example of increase of the electron–phonon coupling with concentration of the active ion as measured by side-bands intensities. This in turn allows us to predict the existence of an increase in non-radiative decay due to ion–ion induced electron–phonon interactions besides any cross-relaxation processes.

2. Experimental

The single crystals of $\{(C_4H_9)_4N\}_3$ $Eu_xY_{1-x}(NCS)_6$ used to obtain the emission and Raman spectra of this study were grown following the method previously described elsewhere [3]. Chemical analyses for Eu^{3+} and $(NCS)^-$ have been performed to ascertain the active ion concentration and formula of the compounds.

Fluorescence and Raman spectra were obtained with a Spex 1702 double monochromator using an Argon laser as excitation source at 4765 and 4880 Å.

3. Results

The fluorescence spectra of $\{(C_4H_9)_4N\}_3\ Eu_xY_{1-x}(NCS)_6$ for $x = 0.01$ and 1 at 300 K are presented in fig. 1 for the $^5D_0 \rightarrow {}^7F_0$ transition. In this compound the Eu^{3+} is N-bonded to six thiocyanates in an octahedral arrangement although the symmetry is distorted when C and S atoms are considered. For instance in the case of Er^{3+} it is known that the Er–N–C–S groups are approximately linear with Er–N–C and N–C–S angles of respectively 174 and 176° [3]. This distortion in the coordination geometry gives rise to the sharp $^5D_0 \rightarrow {}^7F_0$ electronic line observed in fig. 1. A group theoretical analysis of the whole Eu^{3+} spectra has indicated [4] that the site symmetry for the rare-earth was probably a distortion of 0_h belonging to the C_{2v} point-group. The allowed 0-phonon line is surrounded on both sides by two anti-stokes (A-S) and Stokes (S) one-phonon lines at 35 and 130 cm^{-1} corresponding to the two strongest Raman lines region of fig. 2. Dilution with Yttrium gives a strong increase to the 0-phonon line reflecting a reduction in self-quenching and also a decrease in the relative intensities of the one-phonon side-bands.

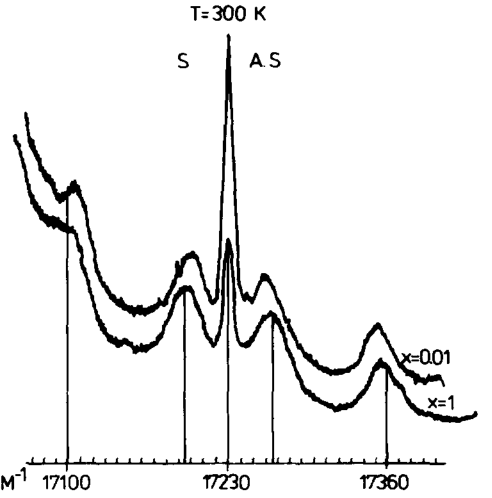

Fig. 1. Emission spectra for the $^5D_0 \rightarrow {}^7F_0$ electronic line with its two one-phonon anti-Stokes (A-S) and Stokes (S) side-bands at 35 and 130 cm^{-1} for two Eu^{3+} concentrations ($x = 0.01$ and $x = 1$).

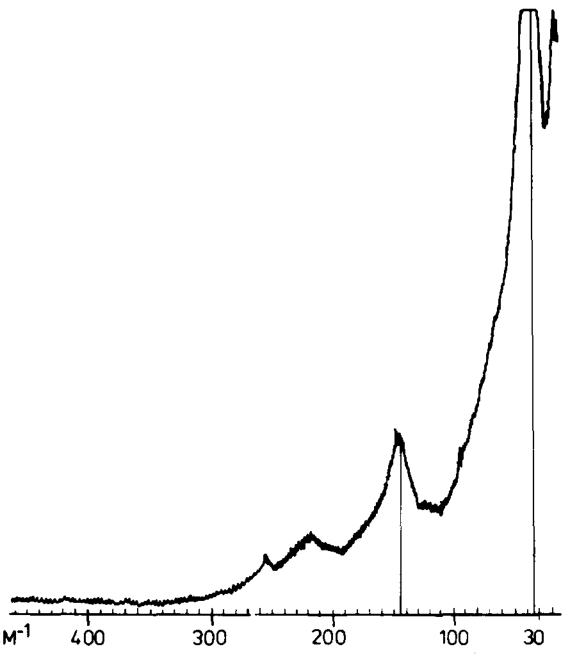

Fig. 2. Raman spectra in the 20–400 cm^{-1} region for the $x = 1$ compound at 300 K.

4. Discussion

In order to avoid problems with deconvolution of the Stokes side bands from a rising background (fig. 1) we shall concentrate upon the A-S and S side-bands at 35 cm^{-1} only.

Having verified that the 0-phonon line was still present at liquid helium temperature and its strength indicating that this normally forbidden line ($J = 0 \leftrightarrow 0$) was allowed by the low site symmetry, we have assumed the one-phonon lines to be of the Δ-process type. This implies the electronic matrix elements to be the same for the 0- and 1-phonon line. Besides this matrix element, the next factor in the transition probability is, for temperature T and an N-phonon band, the well-known function [2]:

$$P(N, T) = e^{-S_0(2\bar{n}+1)} \left(\frac{(\bar{n}+1)}{\bar{n}}\right)^{N/2} \sum_l \frac{(S_0^2\, \bar{n}(\bar{n}+1))^{l+N/2}}{l!(N+l)!}$$

giving:

$$P(0, T)/P(1, T) = 1/S_0(\bar{n}+1)$$

for Stokes emissions. With $\bar{n}$ the occupation number of the considered mode $\hbar\omega$ at temperature $T : \bar{n} = (\exp \hbar\omega/kT - 1)^{-1}$.

In case of absorption or for anti-Stokes emissions, one has by analogy:

$$P(0, T)/P(1, T) = 1/S_0\bar{n} .$$

From the experimentally measured integrated 0-phonon and 1-phonon lines, values of the above ratios are determined giving the values of the Huang–Rhys coupling factor S_0 at 0 K presented in table 1.

The increase in S_0 due to the concentration increase is found to be larger than the experimental error which can be estimated from the discrepancies between the S and A-S lines. Further it can be noted that the S_0 value is larger than usually found for trivalent rare-earth ions ($S_0 \simeq 0.02$–0.1) [2,5,6]; but it is still smaller than the value found for a forbidden $^5D_0 \rightarrow {}^7F_0$ line in WO_4 Ca ($S_0 \simeq 10$) [7]. The fact that our S_0 is less than unity shows that our decision to consider phonon sidebands as caused by a pure Δ-process rather than an M-process or mixed process was well founded. In this latter case, the ratio of the integrated 0-phonon line would involve the ratio of two different electronic matrix elements which should yield an apparent S_0 of the order of unity [1]. Having shown an increase of electron–phonon coupling with concentration, we shall try to estimate the correlative increase in non-radiative decay which can be predicted.

From the simplified form for non-radiative multiphonon decay probability [2]:

$$W_{\mathrm{Mr}}(N) = W_{\mathrm{nR}}(0) \frac{e^{-S_0} S_0^N (\bar{n} + 1)^N}{N!}$$

with N the order of the multiphonon process, $\bar{n}$ the occupancy number for the effective phonon ($\hbar\omega_{\mathrm{m}}$), one obtains:

$$\Delta W_{\mathrm{nR}}(N)/W_{\mathrm{nR}}(R) = \Delta S_0 (N/S_0) - 1$$

for $S_0 < 1$

$$\Delta W_{\mathrm{nR}} = W_{\mathrm{nR}}\, N \Delta S_0/S_0 \ .$$

For a given relative increase of S_0, the correlative increase in non-radiative

Table 1
Values of the Huang–Rhys coupling factor for two concentrations (x = 0.01 and 1)

x Concentration	S_0 for mode $\hbar\omega$ = 35 cm^{-1}	Comments
1%	0.14	From S line
	0.18	From A-S line
100%	025	From S line
	0.32	From A-S line

decay is the highest for the largest energy gaps ($\Delta E = N/\hbar\omega_m$) to the next lower levels. The ideal situation to recognize this effect would be the first excited states of the rare-earth trivalent ions series and $^5D_0(Eu^{3+})$, $^5D_4(Tb^{3+})$. For such levels and others, self-quenching theories up to now have to rely upon unknown sinks or "poisonous" centers [8,9].

Typically for $^5D_0(Eu^{3+})$, one may have $N \simeq 10$ to 40 and for $\Delta S_0/S_0 \simeq 1$, the normally negligible [2] multiphonon decay is found to be multipled by more than one order of magnitude and could still be apparently increased by energy migration in a macroscopic sample. This could explain the self-quenching shown in fig. 1.

We then propose that multiphonon concentration enhanced non-radiative decay be considered as a possibility for self-quenching, through measurement of $S_0(x)$ before calling for the help of diffusion to unknown sinks.

Such a case of concentration sensitive electron–phonon coupling in an organic material is certainly operative also in inorganic hosts as shown by the cooperative side-bands recently discovered [10]. This latter effect also describes an increase in electron–phonon coupling with concentration; the appearance of new lines giving additional paths for lower order multiphonon non-radiative decay provides still another chance for our hypothesis to be operative.

5. Conclusion

A new example of concentration sensitive electron–phonon coupling directly in a luminescence spectrum has been presented. It operates in the same sense as the one demonstrated by cooperative side-bands. We suggest that multiphonon concentration enhanced non-radiative decay should be considered as a new self-quenching process to be taken into account when direct resonant or phonon-assisted energy transfers by cross-relaxation have low probabilities.

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