

Bottleneck in multiphonon nonradiative transitions

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The nonradiative decay process of rare-earth ions in solids has been considered up to now to be independent of excitation intensity. In this paper we show that the multiphonon nonradiative decay probabilities of rare-earth ions in a germanate glass are reduced at high excitation state densities for the larger energy gaps. The classical exponential energy gap law is shown to “rotate” at higher excitation around the 3.2-phonon point. The observed effect is described in terms of a spatial saturation of the accepting mode term with an effective diffusion length ranging between 45 and 20 Å for excited state density from 2×10^{17} to $8 \times 10^{18} \text{ cm}^{-3}$ at an active ion concentration of $2.5 \times 10^{19} \text{ cm}^{-3}$. [S0163-1829(97)05518-5]

As well known for many years, the multiphonon nonradiative decay of transition metals (TM's) and rare-earth (RE) ions can be described by two types of approaches: either through an N th-order development of the dynamic crystal field at the ion site,¹⁻⁴ which would apply to the quasizero electron-phonon Huang-Rhys coupling parameter (S_0), or through the use of the nonadiabatic Hamiltonian, in a Condon⁴⁻⁷ or non-Condon⁸ approach, which rather corresponds to nonzero S_0 . Both methods were compared many years ago.^{4,7} The second type of approach shows that a nonradiative transition can be described besides an electronic matrix element, by the product of two terms: a “promoting mode” term usually considered as a scaling factor experimentally determined and an “accepting mode” term.^{4,7,8} It was shown that the accepting mode term can be given in a statistical way whatever the details of the physical approach.⁴ Recently, a theory attempted to reconcile both methods,^{9,10} in fact expressing the promoting term through the dynamical crystal field including nonlinear terms.

All the above theories have in common that they consider each ion as individually coupled to an effective mode of the phonon distribution density of states. This, even though nonlinear coupling terms have been introduced,⁹ provides nonradiative decay probabilities which are excitation density independent.

In this paper, we present an experimental demonstration and theoretical hypothesis for an intensity-dependent bottleneck effect in multiphonon nonradiative relaxation rates; here, as an example we shall present the results for Er^{3+} , Tm^{3+} , and Nd^{3+} excited states in a germanate glass. The concentration of RE ions has been kept to a rather low level (0.2% in weight, i.e., $2.5 \times 10^{19} \text{ cm}^{-3}$) in order to avoid any important up-conversion effect by energy transfer¹¹ which could reduce the lifetimes measured at high excitation intensity. The determination of the nonradiative probability is based on a comparison between radiative decays and experimental lifetimes.³ As in Ref. 3, pulsed emission, here of 7 ns duration, from a Nd-YAG laser with frequency doubling is used as well as pulsed Ti-sapphire laser emissions in order to reach, by focusing, a maximum of 15 J/cm^2 of incident excitation. The glass host has the same composition in weight

percentage: GeO_2 66%, K_2O 17%, and BaO 17% as in Ref. 12. The highest phonon frequency ($\hbar\omega_M$) for such a glass is at about 900 cm^{-1} .¹²

Experimentally, it is well known that nonradiative relaxation rates of RE ions behave exponentially with the energy gap separating the considered excited state from the next lower electronic state.^{3,13} This behavior is linked to the accepting modes term.^{4,7} Taking into account some of the promoting mode features shows that the electronic gap should be reduced by about $2.6\hbar\omega_M$,^{3,14} where $\hbar\omega_M$ is the highest phonon energy of the considered host material. The so-called energy gap law for the nonradiative transition W_{nr} is then written

$$W_{\text{nr}} = W_0 \exp[-\alpha(\Delta E - 2.6\hbar\omega_M)], \quad (1)$$

where ΔE is the energy gap to the next lower level and α is given by

$$\alpha = \hbar\omega_M^{-1} \left[\ln \left(\frac{N}{S_0(\bar{n}+1)} \right) - 1 \right], \quad (2)$$

where N is the multiphonon order, S_0 the Huang-Rhys coupling parameter at 0 K, and \bar{n} the phonon occupation number at temperature T . The experimental nonradiative decay probabilities (W_{nr}) have been determined by the usual method,³ that is by measuring experimental decays (τ) from directly excited levels of the considered RE ion and calculating the radiative ones (τ_0) from absorption measurements and application of Judd's theory.¹⁵ The nonradiative decay probability is given by

$$W_{\text{nr}} = \tau^{-1} - \tau_0^{-1}. \quad (3)$$

As an example, the general behavior observed for nonradiative decay rates versus excitation density for $\Delta E > 3\hbar\omega_M$ (ΔE given in terms of the multiphonon order N) is presented in Fig. 1. The excited ions density has been calculated from the incident excitation density, the concentration of the rare earth and the absorption cross sections of the transitions. A decrease by a factor of 5 in the nonradiative probability from level ${}^4F_{3/2}$ of Nd^{3+} is clearly observed, with a saturation in the decrease reflecting the absorption saturation at

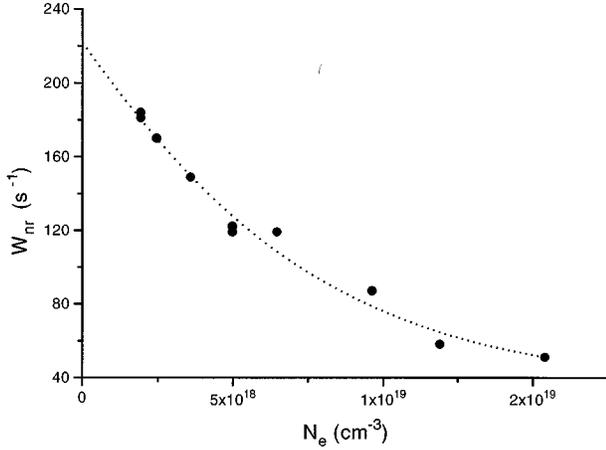


FIG. 1. Nonradiative decay probability (W_{nr}) of the ${}^4F_{3/2}$ level of Nd^{3+} ($2.5 \times 10^{19} \text{ cm}^{-3}$) in a germanate glass at room temperature versus excited state density (N_e).

$1.25 \times 10^{19} \text{ cm}^{-3}$. The quantum efficiency for this state is found to increase from 92% to 98% within our excitation range. The results obtained for Er^{3+} , Tm^{3+} , and Nd^{3+} are given in Fig. 2, which shows that the exponential gap law is followed with an α parameter (here the slope on the semi-logarithmic plot), increasing with the absorbed excitation intensity, i.e., with the excited ions density (N_e). Interestingly, the nonradiative decay is independent of excitation for gaps corresponding to $3.2\hbar\omega_M$; this value is about the predicted $2.6\hbar\omega_M$ one for the promoting mode contribution⁴ found in Eq. (1); below this value, the nonradiative decay rate increases. It can be noted that the scattering of the experimental points because of the excitation normalized plot is much reduced in comparison with unnormalized ones.³ The observed increase for the α parameter of the studied germanate glass for room-temperature experiments is a general trend since a systematic study, to be published elsewhere, has show it for glasses with different compositions and maximum phonon frequencies. This demonstrates that contrary to

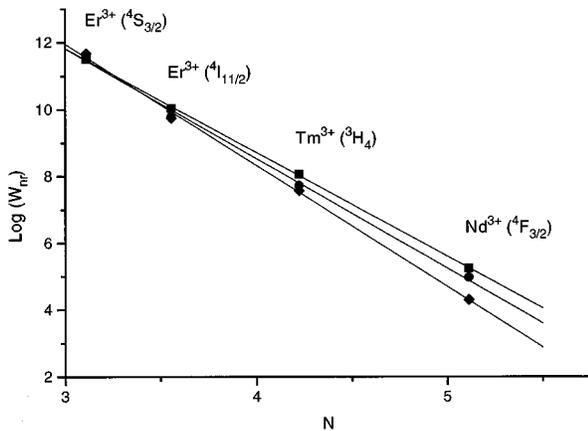


FIG. 2. Variation of the exponential gap law versus the multiphonon order N , for three excitation densities: (■) $N_e = 10^{17} \text{ cm}^{-3}$ ($l_c = 54 \text{ \AA}$), (●) $N_e = 4 \times 10^{18} \text{ cm}^{-3}$ ($l_c = 22 \text{ \AA}$), and (◆) $N_e = 10^{19} \text{ cm}^{-3}$ ($l_c = 20 \text{ \AA}$), solid lines are the fits obtained from Eq. (8).

what has been believed up to now, one should specify excitation levels in an α parameter determination, especially when high peak excitation powers are used. However, we think that some part of this discrepancy can still be attributed to the τ_0 determination as pointed out in Ref. 3. Besides this, our observed decrease in the nonradiative relaxation rate with increasing pump intensity could explain why the threshold can be reached in the laser effect observation in hydrated neodymium chloride powder,¹⁶ which has the very low quantum efficiency of 10^{-4} .

To our knowledge, there has been no experimental investigation of the influence of excitation density on multiphonon nonradiative decay.⁷ The existing theoretical consideration of an intensity dependence would predict, on the opposite, an increase of the nonradiative decay rate through a proposed ‘‘supernonradiant’’ effect.¹⁷

In order to explain our experimental observations, we shall consider a microscopic process, involving only the accepting term readily described by the energetical behavior of experiments and which is known to bear a simple statistical meaning: This term leads to the usually observed ‘‘exponential gap law’’ given by Eq. (1),⁷ which is a reasonable approximation of the statistical term for accepting modes in the weak electron-phonon coupling approximation.⁴ This approach is justified by the observed ‘‘rotation’’ of the experimental curves of Fig. 2 around the point $N = 3.2$. It shows that the promoting term, as given here by the $N = 3.2$ ordinate, is not modified by the excitation intensity, and each excited ion then individually contributes to the promoting term.

We propose that the observed mechanism is based on the possibility that once an ion has given up its energy to an effective accepting mode, another excited ion nearby finds an already partially filled accepting term which leads to a reduction of the nonradiative decay rate for this ion. Because the number of nearby excited ions depends on the excitation density, the nonradiative decay rate is in turn reduced at higher excitation level.

The nonradiative decay probability, as given by the Fermi golden rule, can be written⁴

$$W_{nr} = \frac{2\pi}{\hbar} |\langle i | H_{int} | j \rangle|^2 R_N \delta(E_j - E_i), \quad (4)$$

where $R_N \delta(E_j - E_i)$, given by the accepting modes term, represents the final density of states; R_N is the function first derived by Huang and Rhys:¹⁸

$$R_N = \exp[-(2\bar{n} + 1)S_0] \left(\frac{\bar{n} + 1}{\bar{n}} \right)^{N/2} I_N(2S_0 \sqrt{\bar{n}(\bar{n} + 1)}), \quad (5)$$

where I_N is the Bessel function of order N with imaginary argument \bar{n} , the phonon occupation number. Including the promoting term, it has been shown^{5,4,8} that in the RE weak-coupling case ($N \gg S_0$), Eq. (5) has to be replaced by

$$R' = e^{-S_0(2\bar{n} + 1)} \frac{S_0^N}{N!} \left(\frac{N_p}{S_0} \right)^2 (\bar{n} + 1)^N, \quad (6)$$

where N_p stands for promoting modes.

Except for the promoting factor $(N_p/S_0)^2$, the other factor (the accepting mode part) of this formula can be also derived by combinatorial analysis,⁴ showing that it only has a statistical content. Using Stirling's approximation, the $N!$ produces the exponential gap behaviour of Eq. (1). The following meaning can be given to the accepting factor in Eq. (6):⁴ It represents the probability to fill simultaneously N of the possible accepting modes of the host from the electronic energy of one ion. Now, if instead of one ion an average of \bar{x} other ions simultaneously contribute to the filling of the common accepting mode set shared with the first considered ion, the filling of the accepting modes shall proceed by $(1 + \bar{x})N$ at a time instead of N . Here \bar{x} is related to the excited state density N_e by

$$\bar{x} = N_e v_l (1 - e^{-N_e v_l}), \quad (7)$$

where $v_l = 4\pi l_c^3/3$ is the volume for phonon diffusion, common at least to two nearby excited ions, and l_c is the phonon diffusion length. \bar{x} represents the probability that a given excited ion can share with another excited ion a common sphere of radius l_c . The effect can be described by simply substituting N by $(1 + \bar{x})N$ in Eq. (6) only for the accepting term and not for the promoting one, assuming them to stay localized. One obtains

$$W_{nr} = W_0 e^{-S_0(2\bar{n}+1)} (\bar{n}+1)^{(1+\bar{x})N} \frac{S_0}{[(1+\bar{x})N]!} \left(\frac{N_p}{S_0}\right)^2. \quad (8)$$

Fitting with l_c as a free parameter, one obtains the solid lines in Fig. 2, in rather good agreement with the experimental points. It shows that Eq. (8) is equivalent to the exponential gap law with an α parameter increasing with excitation density. The l_c calculated values are plotted in Fig. 3. The diffusion length is found to decrease with excitation density down to a saturation value corresponding roughly to the low-frequency acoustic phonon diffusion length of 29 Å, which we have determined from a specific heat estimation of 0.445 cal/cm³ deg, a heat capacity of 1.64 × 10⁻³ cal/cm deg s,¹⁹ and an acoustic velocity of 3.85 × 10⁵ cm/s for a germanate glass,²⁰ l_c being derived from the classical formula for the low-frequency phonon diffusion length:²¹

$$l_c = \frac{3K_c}{V_s c_p}, \quad (9)$$

where K_c is the heat capacity, c_p the specific heat, and V_s the sound velocity.

This shows that the crude one-effective-mode model for nonradiative relaxation rates describes rather well the whole

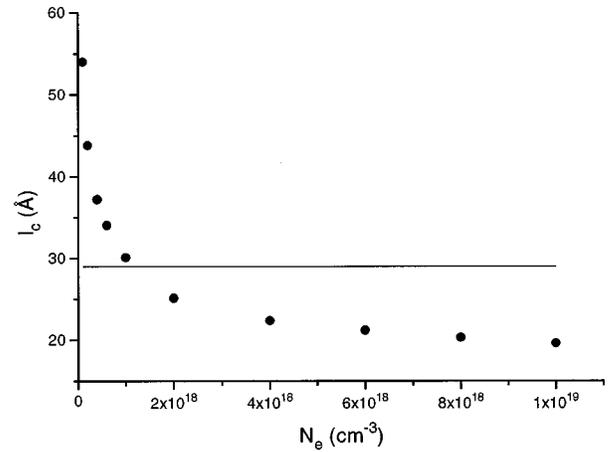


FIG. 3. Phonon diffusion length (l_c) versus excitation density (N_e) derived from nonradiative fits; the value independently derived from sound velocity and thermal properties is given by the horizontal line.

process including the energy dissipation from the 900-cm⁻¹ effective mode towards lower-energy modes. This can be understood in the following way: Since the lower-energy modes are connected with the larger diffusion lengths, the bottleneck we observe contains the slowest step in the energy dissipation. It may take place between the high-energy modes ruling the multiphonon process and the lower-energy ones providing the final heating process. This last type of bottleneck is well documented²² in connection with spin-lattice relaxation and is included here through our effective l_c .

Concluding, we have observed and described theoretically a bottleneck in multiphonon nonradiative decay rates for an excited state density above 1×10^{18} cm⁻³ in a doped germanate glass. Because our approach is statistic, it allows one to predict that such an effect should be very general and could be observed for other multiphonon effects⁴ which can be described by accepting mode terms like Eq. (5). It means that this effect could as well be observed in multiphonon sidebands, multiphonon-assisted energy transfers, and multiphonon infrared absorption. It also gives hints for obtaining laser effects from otherwise nonradiative transitions¹⁵ provided the excitation density is sufficient to allow the coupling between ions through a common phonon diffusion volume.

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¹A. Kiel, in *Quantum Electronics*, edited by P. Grivet and N. Bloembergen (Dunod, Paris, 1964), p. 765.

²W. E. Hagston and J. E. Lowther, *Physica* **70**, 40 (1973).

³C. B. Layne, W. H. Lowdermilk, and M. J. Weber, *Phys. Rev. B* **16**, 10 (1976).

⁴F. Auzel, in *Luminescence of Inorganic Solids*, edited by B. DiBartolo (Plenum, New York, 1978), p. 67.

⁵T. Miyakawa and D. L. Dexter, *Phys. Rev. B* **1**, 2961 (1970).

⁶D. J. Diestler, in *Radiationless Processes in Molecules and Condensed Phases*, edited by F. K. Fong (Springer-Verlag, Berlin, 1976).

⁷R. Englman, *Non-Radiative Decay of Ions and Molecules in Solids* (North-Holland, Amsterdam, 1979).

⁸E. Gutsche, *Phys. Status Solidi B* **109**, 583 (1982).

⁹Y. V. Orlovskii, R. J. Reeves, R. C. Powell, T. T. Basiev, and K. K. Pukhov, *Phys. Rev. B* **49**, 3821 (1994).

- ¹⁰Y. V. Orlovskii, K. K. Pukhov, T. T. Basiev, and T. Tsuboi, *Opt. Mater.* **4**, 583 (1995).
- ¹¹F. Auzel, in *Radiationless Processes*, edited by B. Di Bartolo (Plenum, New York, 1980), p. 213.
- ¹²R. Reisfeld, L. Boehm, Y. Eckstein, and N. Lieblich, *J. Lumin.* **10**, 193 (1975).
- ¹³L. A. Riseberg and H. W. Moos, *Phys. Rev.* **174**, 429 (1968).
- ¹⁴J. M. F. Van Dijk and M. F. H. Schuurmans, *J. Chem. Phys.* **78**, 5317 (1984).
- ¹⁵B. R. Judd, *Phys. Rev.* **127**, 750 (1962).
- ¹⁶C. Gouedard, D. Husson, C. Sauteret, F. Auzel, and A. Migus, *J. Opt. Soc. Am. B* **10**, 2358 (1993).
- ¹⁷M. M. Miller and F. K. Fong, *J. Chem. Phys.* **59**, 1528 (1973).
- ¹⁸K. Huang and A. Rhys, *Proc. R. Soc. London, Ser. A* **204**, 406 (1950).
- ¹⁹E. H. Ratcliffe, *Glass Technol.* **4**, 113 (1963).
- ²⁰M. J. Weber, in *Materials Science and Technology*, edited by R. W. Cahn, P. Haasen, and E. J. Kramer (VCH, New York, 1991), Vol. 9, p.659.
- ²¹C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971), p. 232.
- ²²A. M. Stoneham, *Proc. Phys. Soc. London* **86**, 1163 (1965).