

Parameters and mechanism of elementary interaction of the electronic excitation of rare-earth ions with the local impurity oscillations

V. P. Gapontsev, Yu. E. Sverchkov, A. K. Gromov, A. A. Izyneev, and V. B. Kravchenko

Institute of Radio Engineering and Electronics, USSR Academy of Sciences

(Submitted 12 January 1979)

Pis'ma Zh. Eksp. Teor. Fiz. **29**, No. 4, 234–238 (20 February 1979)

The parameters of elementary nonradiative energy transfer of the electronic excitation of rare-earth ions to the local impurity oscillations of the hydroxyl groups in inorganic glass dielectrics were determined by accurately measuring the kinetics of luminescence in a wide dynamic range of intensities. An anomalous temperature dependence of the transfer probability was observed. It is shown that the theory of ion-ion energy transfer can be used to describe quantitatively the observed effects of ion-vibrational transfer.

PACS numbers: 77.90. + k, 78.60. – b

At present, in spite of a large number of experimental and theoretical publications,¹¹⁻⁴⁾ the mechanisms of elementary electron-vibrational interactions, which produce nonradiative multiphonon relaxation (MPR) of the rare-earth impurity ions (RII) from the excited states of the crystal and inorganic glass dielectrics, have not been determined. In this paper, we determine experimentally the parameters of this type of elementary interaction apparently for the first time. For the experiment we chose a case in which the vibrating quench oscillators with an impurity are distributed in the matrix in a statistically homogeneous way. This enabled us to determine the parameters of the elementary event from the kinetics of luminescence decay of the rare-earth impurity ions after photoexcitation by the δ pulse. For the local quenching in the multipole approximation of the interaction, the indicated kinetics can be generally described by an expression analogous to that used in the theory of the ion-ion multipole resonance energy transfer¹⁵⁾:

$$I(t) = I(0)R(t)\exp\left\{-\frac{4\pi}{3}N\Gamma\left(1-\frac{3}{m}\right)C_{e,K}^{3/m}t^{3/m}\right\}, \quad (1)$$

where N is the concentration of the vibrating oscillators, $R(t)$ is the law of luminescence decay of the rare-earth impurity ions in the absence of quenchers in the matrix, $\Gamma(x)$ is the γ function, m is the parameter of the multipole interaction, and $C_e = W_e r^m$ is the parameter characterizing the probability of the elementary ion-vibrational energy transfer W_e at a distance r . If the elementary multiphonon relaxation is the result of coherent interactions of the electronic excitation with the vibrating oscillators and/or the exchange interactions predominate, then the kinetics of luminescence apparently will differ greatly from those described by expression (1). Thus, if N and $R(t)$ are known, then we can draw definite conclusions about the mechanism of multiphonon relaxation from the $I(t)$ curve, which was measured in a sufficiently wide dynamic range of intensities, and the parameters m and C_e can be determined if it can be confirmed experimentally that expression (1) can describe this process.

We investigated experimentally the kinetics of luminescence of the most promising, for laser applications, rare-earth impurity ions Nd^{3+} , Yb^{3+} , and Er^{3+} from the metastable states ${}^4F_{3/2}$, ${}^2F_{5/2}$, and ${}^4I_{13/2}$, respectively, in phosphate glass of the $\text{Ba}_3\text{Al}(\text{PO}_3)_9$ compound with different composition of hydroxyl groups (OH^-). The effect of quenching of these groups on the luminescence of the rare-earth ions in the activated glass was reported in Ref. 6. The quenching process is a multiphonon process, since the frequencies of the main valence vibrations of the HO groups are $2800\text{--}3000\text{ cm}^{-1}$, which is much lower than the frequencies of the electronic transitions of the indicated ions ($\sim 5300, 6500, \text{ and } 10000\text{ cm}^{-1}$, respectively). The concentration of the

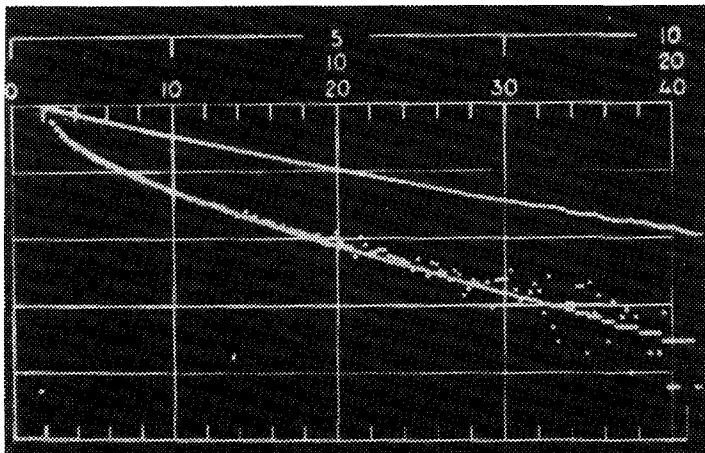


FIG. 1. Experimental curves for the luminescence decay of Nd^{3+} ions ($1 \times 10^{19}\text{ cm}^{-3}$) in $\text{Ba}_3\text{Al}(\text{PO}_3)_9$ glass (top, for $N = 2 \times 10^{19}\text{ cm}^{-3}$; bottom, for $N = 3.4 \times 10^{20}\text{ cm}^{-3}$) and the theoretical dependence for $m = 6$, $C_e = 1.2 \times 10^{-39}\text{ cm}^6\text{-sec}^{-1}$, $N = 3.4 \times 10^{20}\text{ cm}^{-3}$. Scale: Y axis-logarithmic scale; the horizontal lines represent the order of intensity; X axis-0.7 msec/division.

TABLE I.

Ion	Transition	T, K	m	C_e^{exp} $10^{-40}\text{cm}^6\text{-sec}^{-1}$	C_e^{calc} $10^{-40}\text{cm}^6\text{-sec}^{-1}$
Nd ³⁺	${}^4F_{3/2} \rightarrow {}^4I_{15/2}$	300	6 ± 0.1	4.6	3.5
		4.2	6 ± 0.1	12	11
Yb ³⁺	${}^2F_{3/2} \rightarrow {}^2F_{7/2}$	300	6 ∓ 0.1	0.24	0.16
		4.2	6 ± 0.1	0.17	0.14
Er ³⁺	${}^4I_{13/2} \rightarrow {}^4F_{15/2}$	300	6 ∓ 0.2	1.2	1.7
		4.2	6 ± 0.2	1.3	1.7

OH groups in the samples was determined from the absorption level in the 3000 cm^{-1} region relative to the standard sample, which was calibrated with an accuracy of $\pm 20\%$ by melting in a vacuum and collecting the water vapor in a nitrogen trap. It varied from 1×10^{18} to $5 \times 10^{20}\text{ cm}^{-3}$, depending on the technology of preparation of the glass. The concentration of the rare-earth impurity ions was $1 \times 10^{19}\text{ cm}^{-3}$, which almost excluded the possibility of migration of the excitation energy through them.

The kinetics of luminescence of the Nd³⁺ and Yb³⁺ ions were measured in the dynamic range of 60 to 70 dB by counting the photons on an automatic multichannel analyzer described in Ref. 7. The luminescence decay of the Er³⁺ ions ($\lambda \cong 1.54\text{ }\mu\text{m}$) was recorded in the range of intensities of 40 to 45 dB, using an MDR-2 monochromator situated at the exit slit, with cooled FSG-223A photoresistive cells whose signal, after preliminary amplification, was normalized to $I(0)$ and averaged in a two-channel PAR-162/164 gate integrator and then was fed to the memory bank of a minicomputer through a matching device. The latter was used to approximate the obtained curves with the help of expression (1) and the results were displayed on the screen of the ORTEC 6240A multichannel analyzer. An LTI PCh8-type YAG:Nd³⁺ laser (second harmonic) or an ISSh-400 stroboscopic tube ($\tau_p \cong 10\text{ }\mu\text{sec}$) was used as the excitation source. The measurements were carried out in the temperature range of 4.2 to 300 K.

The experiments showed that, as a result of increasing N , the kinetics of luminescence decay of the rare-earth impurity ions vary for all activators from almost exponential as $N \rightarrow 0$ to sharply nonexponential at $N > 10^{20}\text{ cm}^{-3}$. A photograph of the typical experimental curves for the decay, taken from the screen of the multichannel analyzer, is shown in Fig. 1. It also shows the result of a theoretical approximation of the kinetics of decay, using expression (1). The theoretical curves are in complete agreement with the experimental curves in a wide range of intensities. An analogous procedure covering a wide range of samples showed that for each activator at the given temperature there is a constant set of parameters m and C_e (Table I) independent of N , which makes it possible to describe the experimental curves for the luminescence decay by using expression (1). The parameter m is equal to 6 ± 0.1 in all the cases. On

the basis of this result, we can conclude that the investigated process of multiphonon relaxation is governed by dipole-dipole interaction of the local impurity centers. The basic difference between it and the well-known ion-ion multipole interaction is that the quantum transition in one of the dipoles—the acceptor—is purely vibrational. Nonetheless, the similarity between the mechanism of multiphonon relaxation and ion-ion resonance interactions can be traced further, if we calculate the parameters C_e using an expression analogous to that in Ferster's theory¹⁵⁾

$$C_e = 4.93 \times 10^{-25} A \frac{J}{n^4}, \quad (2)$$

where $J = \int I^H(\nu) \epsilon(\nu) \nu^4 d\nu$ is the overlapping integral of the spectra, $I^H(\nu)$ is the quantum spectral radiation density of the donor, which is normalized to unit area, $\epsilon(\nu)$ is the molar decimal excitation coefficient of the acceptor, A is the Einstein coefficient, and n is the index of refraction of the medium. As seen in Table I, these values (C_e^{calc}) are in quantitative agreement with the experimental values measured earlier.

The measurements of the temperature dependences of C_e produced a curious "anomaly." As a result of decreasing the temperature to 4.2 K, we observed a marked increase of C_e for the Nd³⁺ ions, which, from the point of view of the widely used, single-frequency model of the multiphonon relaxation,^{12,31} was not expected. This can be attributed to freezing out of the transitions from the component ${}^4F_{3/2}(2)$, which shifts the center of mass of luminescence band toward lower energies, which, in combination with the sharp change of $\epsilon(\nu)$ in the given spectral interval, is accompanied by an increase of the integral J .

In conclusion, we note that the compatibility of the physical mechanisms of ion-ion energy transfer and the multiphonon relaxation process is not limited to quenching by impurity oscillations of the OH groups, which have a uniquely high energy of the vibrational transition. The results obtained by us in the investigation of the processes of multiphonon relaxation of the rare-earth impurity ions were similar because of the interactions with the lower-frequency oscillations of the groups, which produce a structural glass network such as Si-O, P-O, B-O, Ge-O, Be-F, etc., and hence form in the usual way the nearest coordination sphere of the luminescence center. The data obtained in these studies will be published separately.

¹⁵⁾We note that in evaluating the experimental data on nonradiative degradation of the excited states of the rare-earth impurity ions in liquid solutions, Ermolaev *et al.*¹⁵⁾ used successfully a similar approach at the level of macroscopic constants.

¹⁾I.S. Andriesh, V. Ya. Gamurar', D.N. Vylegzhanin, A.A. Kaminskiĭ, S.I. Klokishner, and Yu. E. Perlin, *Fiz. Tverd. Tela* **14**, 2967 (1972) [*Sov. Phys. Solid State* **14**, 2550 (1973)].

²⁾R. Orbach, *Optical Properties of Ions in Solids*, Plenum Press, N.Y., 1975, p. 355.

³⁾C.B. Layne, W.H. Lowdermilk, and M.J. Weber, *Phys. Rev.* **B16**, 10 (1977).

⁴⁾R. Reisfeld, *Structure and Bonding* **22**, 123 (1975).

⁵⁾V.L. Ermolaev, E.N. Bodunov, E.B. Sveshnikova, and T.A. Shakhverdov, *Bezyzluchatel'nyĭ perenos energii elektronogo vzbuzhdeniya* (Radiationless Energy Transfer of Electronic Excitation), Nauka, L., 1977.

⁶⁾V.P. Gapontsev, A.K. Gromov, A.A. Izyneev, V.B. Kravchenko, N.A. Paramonova, and Yu. P. Rudnitskiĭ, *Proc. of the Fourth All-Union conf. on Crystal Spectroscopy*, Sverdlovsk, 1973; a collection of papers entitled "Crystal Spectroscopy," Nauka, M., 1975, p. 337.

⁷⁾N.E. Alekseev, V.P. Gapontsev, M.E. Zhabotinskiĭ, and Yu. E. Sverchkov, *Pis'ma Zh. Eksp. Teor. Fiz.* **27**, 118 (1978) [*JETP Lett.* **27**, 109 (1978)].