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Interaction mechanisms in the Bi^{3+} - Eu^{3+} energy transfer in germanate glass at low temperature

B. Moine, J. C. Bourcet, G. Boulon, R. Reisfeld (*)

Physico-Chimie des Matériaux Luminescents (**), Université Lyon I, 43 Bd du 11-Novembre-1918, 69622 Villeurbanne, France

and Y. Kalisky

Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel

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Résumé. — Les mécanismes du transfert d'énergie entre Bi^{3+} et Eu^{3+} dans un verre germanate ont été étudiés à basse température sous excitation par un laser à azote pulsé et en sélectionnant l'émission de quelques ions dans la bande large inhomogène ${}^3\text{P}_0 \rightarrow {}^1\text{S}_0$. Les courbes de déclin de l'émission de l'état ${}^3\text{P}_0$ de Bi^{3+} ont été obtenues pour des concentrations variées d'accepteurs Eu^{3+} . Il n'y a pas d'indication de diffusion dans le système des donneurs. Les courbes expérimentales ont été ajustées à l'équation d'Inokuti et Hirayama. Le meilleur ajustement a été obtenu pour une interaction dipole-dipole pour 0,8 % Bi^{3+} + 0,7 % Eu^{3+} et quadrupole-dipole pour 0,8 % Bi^{3+} + 5 % Eu^{3+} .

Abstract. — The mechanisms of low temperature ($T = 4$ K) energy transfer between Bi^{3+} and Eu^{3+} in germanate glass have been studied under pulsed nitrogen laser excitation by selecting the emission from a subset of ions in the ${}^3\text{P}_0 \rightarrow {}^1\text{S}_0$ band which is broadened by inhomogeneity in the glass. The decay curves of the emission from the Bi^{3+} ${}^3\text{P}_0$ state were obtained for various concentrations of acceptor ions Eu^{3+} . There is no indication of diffusion of the excitation energy within the donor system. The experimental curves were fitted to Inokuti and Hirayama's equation. The best fit was obtained with a dipole-dipole interaction for the 0.8 % Bi^{3+} + 0.7 % Eu^{3+} doped glass and with a quadrupole-dipole interaction for the 0.8 % Bi^{3+} + 5 % Eu^{3+} doped glass.

1. **Introduction.** — In a previous paper we presented spectroscopic studies of the Bi^{3+} ion in germanate glass in which we showed that both the blue emission broad band and the lifetime of the Bi^{3+} ion [1] have a strong temperature dependence. The maximum in the emission band was found at 4 650 Å at liquid helium temperature and at 4 490 Å at room temperature under N_2 laser excitation with lifetimes of respectively 650 μs and 200 ns. A three-level scheme (${}^1\text{S}_0$, ${}^3\text{P}_0$, ${}^3\text{P}_1$) was introduced to explain the radiative and non radiative mechanisms of the Bi^{3+} ion (see figure 3). Laser induced fluorescence band narrowing and time resolved spectroscopic techniques were used to establish the spectral dependence of the lifetime, the time evolution of the bandwidth and the red shift of the ${}^3\text{P}_0 \rightarrow {}^1\text{S}_0$ transition at 4 K. These experiments

show the existence of a quasi-continuum of many different sites in germanate glass [2]. Both the acceptor and the donor ions are distributed at random in the glass, which makes the study of energy transfer between Bi^{3+} and Eu^{3+} difficult. In a recent paper [3] we have shown that this energy transfer is made through both radiative and non radiative processes. The efficiency of the transfer has been measured by Reisfeld [4]. The purpose of this paper is to present a more detailed experimental study of the mechanism of energy transfer.

2. **Theory of energy transfer.** — The transfer of electronic excitations between ions in solids has been extensively studied. In addition to intrinsic decay processes, excited donor ions have been found to relax by (i) direct interaction with energy transfer to acceptor ions, or by (ii) migration of the excitation among donor ions until it comes into the vicinity of an energy acceptor where direct transfer occurs. In any case, observation of the time evolution of the donor

(*) Permanent address : Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Israel.

(**) ER N° 10 du C.N.R.S.

luminescence under pulsed laser excitation provides help in identifying the dominant relaxation mechanisms. The first process, involving resonant energy transfer between donors and acceptors has been treated by Förster [5] and Dexter [6] for a multipolar interaction and extended by Inokuti and Hirayama [7], for an exchange interaction, while the effects of diffusion on energy transfer have been treated by Yokota and Tanimoto [8].

2.1 YOKOTA AND TANIMOTO'S THEORY. — When the rate of energy diffusion within the donor system is not negligible, Yokota and Tanimoto show that the donor excitation density $\Phi(\mathbf{r}, t)$ satisfies the diffusion equation :

$$\frac{\partial \Phi(\mathbf{r}, t)}{\partial t} = D \nabla^2 \Phi(\mathbf{r}, t) - \sum v(\mathbf{r} - \mathbf{r}_i) \Phi(\mathbf{r}, t) - \frac{1}{\tau_0} \Phi(\mathbf{r}, t)$$

where D is the diffusion constant, $v(\mathbf{r} - \mathbf{r}_i)$ the probability for energy transfer between donor and acceptor at position r_i , and τ_0 is the intrinsic decay rate of the donor. Yokota and Tanimoto's solution, for the case of dipole-dipole coupling, with

$$v(\mathbf{r} - \mathbf{r}_i) = \alpha |\mathbf{r} - \mathbf{r}_i|^{-6},$$

assuming a random distribution of acceptors and a very small diffusion constant D , is :

$$\Phi(t) = \Phi(0) e^{-t/\tau_0} \times \exp \left[-\frac{4}{3} \pi^{3/2} N_a (\alpha t)^{1/2} \left(\frac{1 + 10.87 x + 15.50 x^2}{1 + 8.74 x} \right)^{3/4} \right]$$

(1)

where $x = D\alpha^{-1/3} t^{2/3}$.

Initially when $x \ll 1$, there is a short decay-time which corresponds to the relaxation of excited donors by direct energy transfer to nearby acceptors. In such a case, diffusion is unimportant and a non exponential decay is predicted. In the long time limit, the function becomes exponential with a lifetime that can be written as,

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \frac{1}{\tau_D}$$

(2)

where $1/\tau_D$ is the decay rate due to diffusion, given by

$$\frac{1}{\tau_D} = 11.4 \cdot N_a \alpha^{1/4} D^{3/4}$$

(3)

where N_a is the number density of acceptors.

Such a time-dependent decay behaviour is characteristic of diffusion-limited transfer.

2.2 INOKUTI AND HIRAYAMA'S MODEL. — When there is no energy diffusion within the donor system, corresponding to $x = 0$ in equation (1), the general

solution for multipolar interactions as given by Inokuti and Hirayama, is as follows,

$$\Phi(t) = \Phi(0) \exp \left[-\frac{t}{\tau_0} - \frac{4}{3} \pi \Gamma(1 - 3/s) N_a R_0^3 (t/\tau_0)^{3/s} \right]$$

(4)

where $\Gamma(1 - 3/s)$ is Euler's function and R_0 is a critical transfer-distance, defined as the donor-acceptor separation at which the probability for energy transfer is equal to the intrinsic decay probability of the donor $s = 6, 8$ or 10 for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole couplings respectively. In this case, the decay is characterized by an initial non exponential portion followed by an exponential decay with a lifetime τ_0 . The analysis of decay curves thus enables the various energy transfer processes to be distinguished.

3. Experiments. — All the experiments were made at liquid helium temperature in order (a) to observe only the ${}^3P_0 \rightarrow {}^1S_0$ transition unsplit by the crystalline field and (b) to obtain lifetimes, long enough for accurate measurements ($\tau_0 \simeq 700 \mu\text{s}$). Nitrogen laser excitation of the 3P_1 levels of the Bi^{3+} ion with 1 mJ per pulse was used. A very narrow spectral range ($\sim 5 \text{ \AA}$) was selected at 4600 \AA in the wide emission band to reduce the effect of inhomogeneity in the glass. An IN 90 Intertechnique multichannel analyser and photon counting techniques were used to analyse carefully the shape of fluorescence decay modes. Each decay curve was determined using about 50 000 pulses.

Figure 1 represents the emission spectrum of glass doped with 0.8 % Bi^{3+} and 5 % Eu^{3+} . Transfer occurs by both radiative and non radiative modes. The non radiative mode can be inferred from the decrease of the integrated fluorescence of Bi^{3+} , and the radiative mode from the dip in the emission band of Bi^{3+} , corresponding to the ${}^7F_0 \rightarrow {}^5D_2$ absorption of Eu^{3+} . The

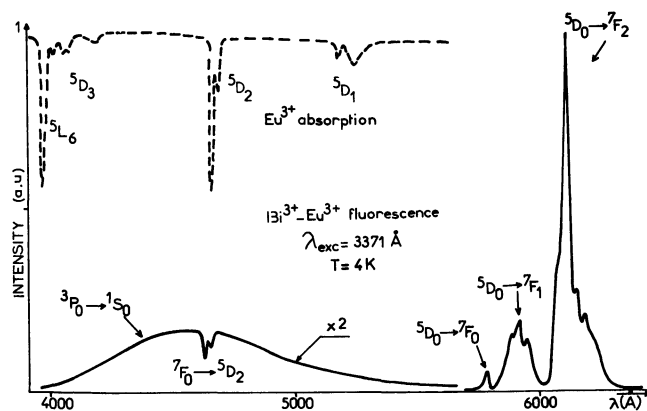


Fig. 1. — a) Fluorescence spectrum of 0.8 % Bi^{3+} + 5 % Eu^{3+} doped germanate glass at 4 K under N_2 pulsed laser excitation (full line). The intensity of the ${}^3P_0 \rightarrow {}^1S_0$ emission has been multiplied by a factor of two. b) Absorption spectrum of Eu^{3+} in germanate glass (dashed curve). Absorption and fluorescence intensities are given in arbitrary units.

radiative transfer efficiency η_R can be approximately calculated by comparing the area of the dip to the area of the emission band included in the spectral range of the ⁵D₂ absorption (see table I). The Bi³⁺ fluorescence

Table I.

0.8 % Bi ³⁺ + x % Eu ³⁺ (weight %)	0.5	1	2	3	5
η_R	0.05	0.07	0.12	0.18	0.3

from glass doped only with Bi³⁺ decays exponentially following pulsed excitation. When Eu³⁺ ions are added, the decay initially deviates from a simple exponential dependence, as can be seen in figure 2, where the Bi³⁺ decay for different Eu³⁺ concentrations are plotted on a semi-logarithmic scale. As the number of Eu³⁺ ions decreases to zero, the time dependence of the Bi³⁺ fluorescence approaches a single exponential with a lifetime equal to the intrinsic decay time. Moreover, the final portion of all the decay curves tends to the same slope. This means that in equation (2) $1/\tau_D$ is very small and that therefore we can neglect diffusion within the donor system.

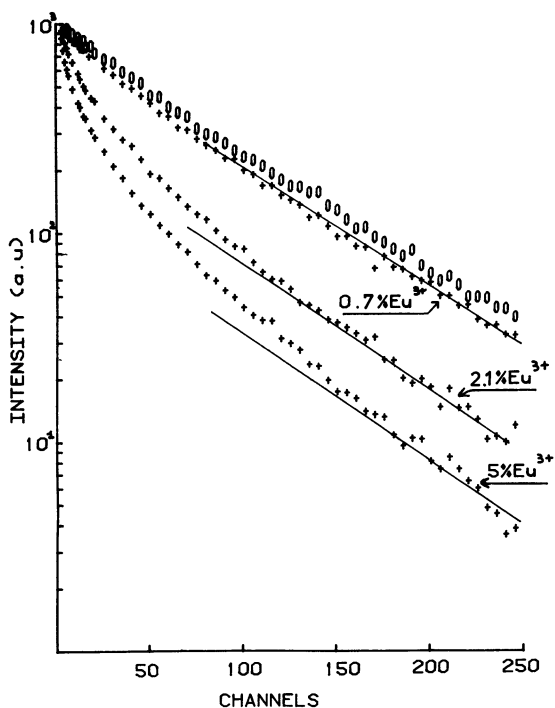


Fig. 2. — Semi-logarithmic plots of the fluorescence decay of the Bi³⁺ ion in singly doped glass (0) and in samples doped with both Bi³⁺ and Eu³⁺ (+) for three different acceptor concentrations. The channel-width is equal to 8 μ s.

4. Discussion. — Before discussing the mechanism of energy transfer between Bi³⁺ and Eu³⁺ in germanate glass, it is important to consider the nature of the transitions of the Bi³⁺ and Eu³⁺ ions.

As shown in figure 3, at 4 K the ³P₀ → ¹S₀ transition of Bi³⁺ and the ⁷F₀ → ⁵D₂ transition of Eu³⁺ are in

resonance. It is reasonable to assume that energy transfer is primarily due to interaction between the ³P₀ Bi³⁺ level and the ⁵D₂ Eu³⁺ level. The spin forbidden transitions become partially allowed as a result of strong spin-orbit coupling in Bi³⁺ and Eu³⁺.

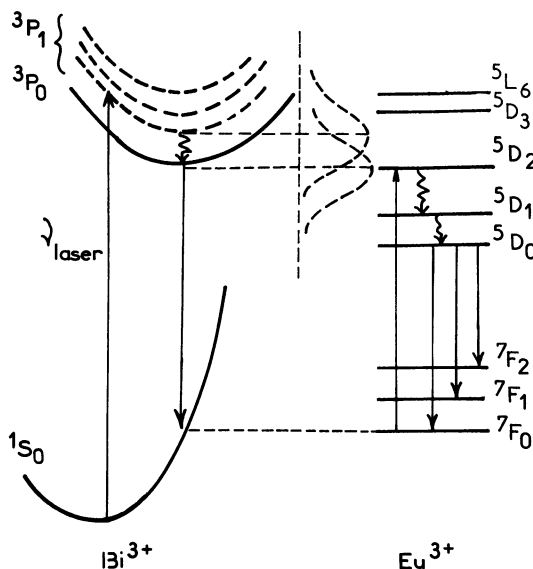


Fig. 3. — The configurational coordinate model used to interpret the absorption and emission processes for the Bi³⁺ centre. The horizontal lines represent the energy levels of the Eu³⁺ ion. The vertical lines represent radiative transitions. Note that the N₂ laser does not excite the Eu³⁺ ion.

The exchange interaction is, in general, effective only at very small distances between donor and acceptor. Optical properties of Eu³⁺ in germanate glass have been studied by Reisfeld and Lieblich [9]. Transitions within the 4f⁶ Eu³⁺ shell are responsible for the spectra observed. These transitions are forbidden in a free ion, but in a crystal or a glass, electric dipole transitions become allowed as a consequence of coupling of odd electronic wave functions by the odd parity terms in the crystal field expansion. For the Bi³⁺ ion, the ³P₀ → ¹S₀ transition is also forbidden in the free ion, but becomes allowed in a solid. Static perturbations may induce electric quadrupole or magnetic dipole transitions, and dynamic perturbations (that is to say a coupling between an electronic state and a vibrational mode) may induce electric dipole transitions. In the glass, the ³P₀ → ¹S₀ transition becomes allowed within the electric dipole and quadrupole approximations due to site-to-site variations in the degree of mixing between ³P₁ and ³P₀ levels.

Since there is no diffusion, we can use equation (4) to fit the experimental decay curves of the 4 600 Å emission associated with the ³P₀ → ¹S₀ transition which corresponds to absorption of the ⁵D₂ Eu³⁺ energy level. Figure 2 clearly shows that for two different acceptor concentrations, $N_a = 0.7\%$ and $N'_a = 5\%$, the corresponding values of the function

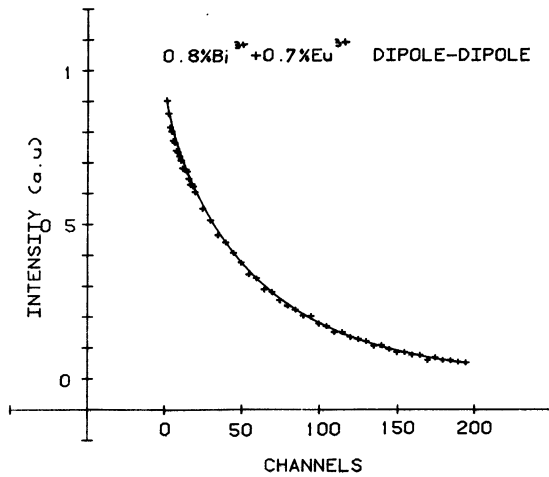


Fig. 4. — Fluorescence decay of Bi^{3+} ion in the presence of 0.7% Eu^{3+} ions. Experimental points (+) and a theoretical curve fitted to Inokuti and Hirayama's equation in the case of a dipole-dipole interaction. The channel-width is equal to $8 \mu\text{s}$.

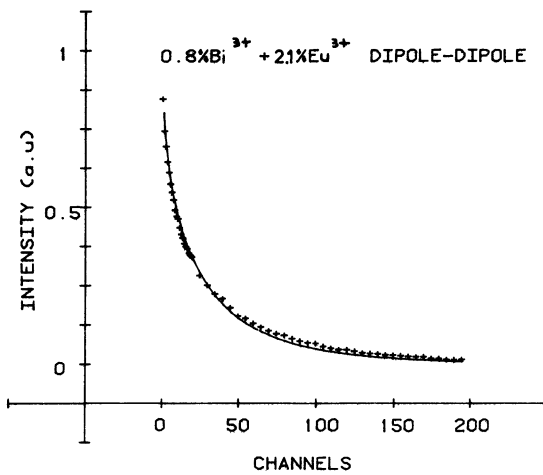


Fig. 5. — Fluorescence decay of Bi^{3+} ion in the presence of 2.1% Eu^{3+} ions. Experimental points (+) and a theoretical fit to Inokuti and Hirayama's equation in the case of a dipole-dipole interaction. The channel-width is equal to $8 \mu\text{s}$.

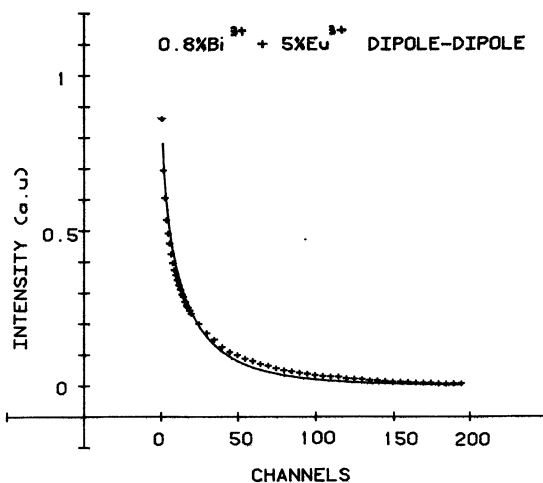


Fig. 6. — Fluorescence decay of Bi^{3+} ion in the presence of 5% Eu^{3+} ions. Experimental points (+) and theoretical fit to Inokuti and Hirayama's equation in the case of a dipole-dipole interaction. The channel-width is equal to $8 \mu\text{s}$.

$\text{Log} \left[\frac{\Phi(t)}{\Phi(0)} + \frac{t}{\tau_0} \right]$ in equation (4) are proportional. The proportionality coefficient is roughly equal to 7 in good agreement with the value given by $\frac{N'_a}{N_a}$. We considered first a dipole-dipole coupling (Figs. 4, 5 and 6). and subsequently a quadrupole-dipole coupling (Figs. 7, 8, 9). The fits were obtained by the standard least squares method. Watts [10] has shown in the case of the $\text{Yb}^{3+}-\text{Er}^{3+}$ energy transfer that the two mechanisms (dipole-dipole and quadrupole-dipole) may both contribute to the energy transfer, depending on the donor-acceptor distance : for large distances transfer is due to the dipole-dipole coupling and the contribution from quadrupole-dipole coupling is negligible but for short distances both are effective, the quadrupole-dipole contribution becoming more important than the dipole-dipole contribution. In the

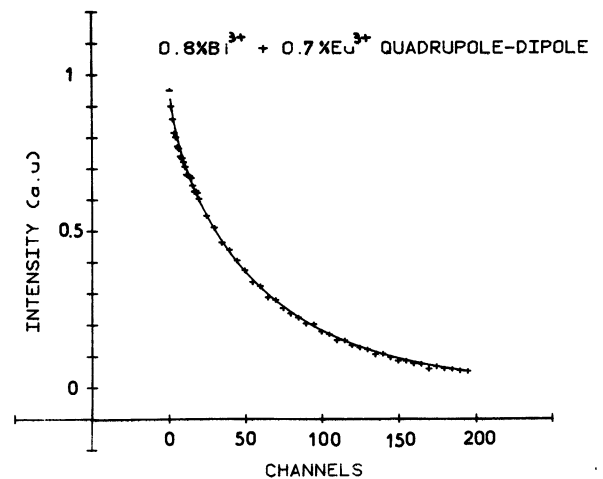


Fig. 7. — Fluorescence decay of Bi^{3+} ion in the presence of 0.7% Eu^{3+} ions. Experimental points (+) and theoretical fit to Inokuti and Hirayama's equation in the case of a quadrupole-dipole interaction. The channel-width is equal to $8 \mu\text{s}$.

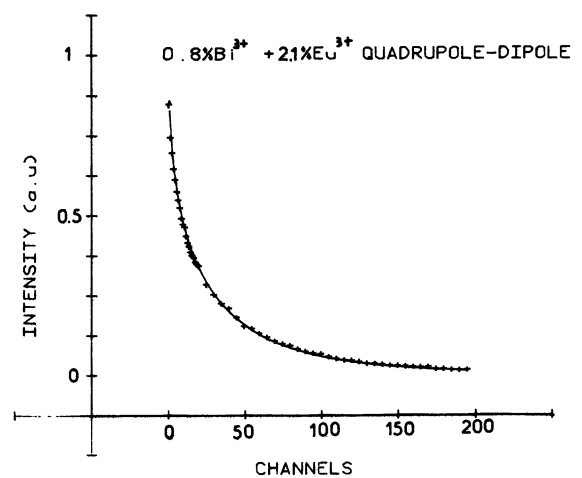


Fig. 8. — Fluorescence decay of Bi^{3+} ion in the presence of 2.1% Eu^{3+} ions. Experimental points (+) and theoretical fit to Inokuti and Hirayama's equation in the case of a quadrupole-dipole interaction. The channel-width is equal to $8 \mu\text{s}$.

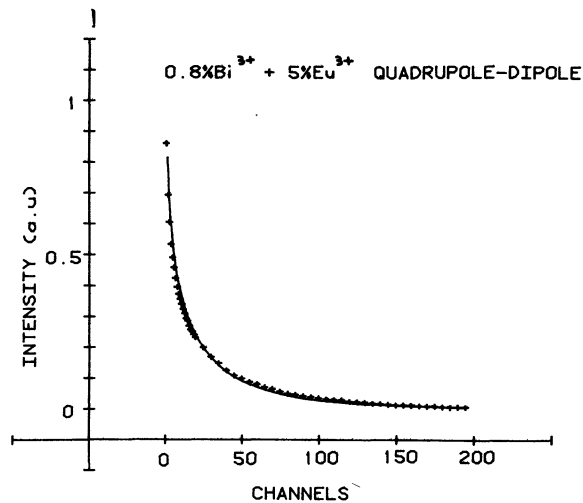


Fig. 9. — Fluorescence decay of Bi³⁺ ion in the presence of 5% Eu³⁺ ions. Experimental points (+) and theoretical fit to Inokuti and Hirayama's equation in the case of a quadrupole-dipole interaction. The channel-width is equal to 8 μ s.

case of the Bi³⁺-Eu³⁺ energy transfer we think that both mechanisms are important for all concentrations of acceptors. For low concentrations of Eu³⁺ the decay curve is practically exponential (as in Bi³⁺ doped germanate glass) and can be fitted with a dipole-dipole or quadrupole-dipole coupling. However when the Eu³⁺ concentration is increased, the distance between donors and acceptors decreases and the quadrupole-dipole interaction plays a more important part in the decay of the donors. This explains the high quality of the fits shown in figures 8 and 9. This result seems to be in good agreement with the nature of the transitions of the Bi³⁺ ion and the Eu³⁺ ion discussed above. We find a mean critical distance, $R_0 \approx 9 \text{ \AA}$ (where R_0 is the distance between donors and acceptors for the which the transfer efficiency is equal to 0.5).

The mean distance between ions is given by the formula :

$$R = 2 \times \left(\frac{4 \pi C_i}{3} \right)^{-1/3}$$

where C_i is the combined number density of the Bi³⁺ and Eu³⁺ ions. Thus $R_0 = 9 \text{ \AA}$ corresponds to a sample with approximately 0.8 wt % of Bi³⁺ ions, and 11 wt % of Eu³⁺ ions. (Extrapolate concentration.) This result is in good agreement with Reisfeld who finds for the Pb²⁺-Eu³⁺ energy transfer in germanate glass a critical distance approximately equal to 11 \AA [11]. Note that the Pb²⁺ ion is isoelectronic with the Bi³⁺ ion.

In order to justify the approximation we have made in neglecting the diffusion process, we have evaluated the diffusion constant D from equation (3). This gives $D < 10^{-13} \text{ cm}^2/\text{s}$ which is much smaller than typical values [12] ($10^{-10} \leq D \leq 10^{-5} \text{ cm}^2/\text{s}$). The absence of diffusion within the donor system may be a result of the Stokes shift in the Bi³⁺ system which means there is no resonance matching between the various donor ions. Phonon assistance which might be important at higher temperatures is, of course, absent at liquid helium temperature.

In conclusion, by selecting a narrow spectral range in donor emission under N₂ pulsed laser excitation, in order to reduce the effect of glass inhomogeneity, we have shown that (i) the diffusion process is inefficient, (ii) the transfer occurs by both radiative and non radiative mechanisms and (iii) the non radiative process is due to dipole-dipole and quadrupole-dipole interactions, the influence of quadrupole-dipole coupling being clearly seen at higher Eu³⁺ acceptor concentrations.

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