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Energy Transfer Between Samarium and Europium in Phosphate Glasses*

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A study of energy transfer from samarium to europium in phosphate glasses was performed for a range of donor and acceptor concentrations corresponding to a donor–acceptor distance of 13–24 Å. The energy transfer probabilities were calculated. The mechanism of transfer was deduced by fitting the experimental decay curves to the theoretical curves obtained by Inokuti and Hiroyama. Theoretical transition probabilities based on Dexter's formula were calculated. It was inferred that the energy is transferred by a dipole–quadrupole mechanism which is assisted by phonons. It was possible to indicate the path by which the transfer takes place.

Introduction

The mechanism governing the energy transfer (ET) process in trivalent rare-earth ions has been the subject of several recent papers quoted in reference (*1*).

The theory of a nonradiative transfer of excitation energy from a rare earth (RE) ion acting as donor to an RE acting as acceptor was developed in a classical paper by Dexter (*2*). Numerical calculations of the efficiency of donor luminescence yield as a function of the acceptor concentration were performed by Inokuti and Hiroyama (*3*).

The purpose of this work was to obtain answers to the following questions:

1. Is the energy transfer between samarium and europium a nonradiative process?
2. What is the quantum efficiency of the ET process?
3. What are the transfer rates as a function of concentration?
4. What is the mechanism of the transfer?
5. Between which spectral levels does ET occur?

The choice was made of Sm and Eu pair because of the practical importance of europium as a phosphor and possibly a laser. The relatively large absorption of some of the samarium lines permits a good pumping to the europium levels by a light of about 400 nm.

Theories have been developed which provide formulas for the energy transfer by electric dipole–dipole interaction, electric dipole–quadrupole interaction, and exchange interaction.

While the former two interactions are electrostatic in origin, the last arises from the requirements of the antisymmetry of the electronic wave function for the system consisting of a donor molecule and an acceptor molecule. Multipolar transfer can be responsible for remote interaction (20 Å) while exchange may be important for interactions involving near neighbors.

In our experiments energy transfer could be observed at concentrations as low as 0.5 wt %, corresponding to an interionic distance of 24 Å. This fact implies that the energy transfer observed in this work is of a multipolar- rather than exchange-interaction type, and the latter will not be considered here.

Oscillator strengths and internal transfer probabilities of europium have been studied in our earlier works [*4–8*] and this information is used for the present study.

Theory

The relevant formulas for the present case will be presented now. The probability of energy transfer by dipole–dipole interaction is (*2*)

$$P_{da}(dd) = \frac{3\hbar^4 c^4 Q_a}{4\pi R^6 n^4 \tau_a}\left(\frac{\epsilon}{\kappa^{1/2}\epsilon_c}\right)^4 \int \frac{f_d(E)\,F_a(E)}{E^4}\,dE \quad (1)$$

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with the following meaning of the constants:

$\hbar$	Planck's constant,
c	velocity of light,
R	the separation of the nuclei of D and A,
ϵ_c	the electric field within the crystal,
ϵ	the electric field in vacuum,
n	index of refraction of the medium.

$f_d(E)$ is the observed shape of the emission band normalized to unity $\int f_d(E)\,dE = 1$.

$F(E)$ is the normalized function of the acceptor absorption such that $\sigma(E) = QF(E)$ and $\int F(E)\,dE = 1$.

σ is the absorption cross section.

$Q = \int \sigma(E)\,dE$ is measured as the area under the absorption band.

For the phosphate glasses used in this work formula (1) may be written in a simplified form as

$$P_{da}(dd) = \frac{1.14 \times 10^{18}}{C_d\, C_a\, l_d\, l_a} \cdot \left[\frac{\int A_d(E)\,dE \int A_a'(E)\,dE}{n^2 R^6} \times \int \frac{f_d(E)\, F_a(E)\, dE}{E^2} \right], \qquad (1a)$$

where C_d and C_a are the donor and acceptor concentrations in weight percent, l_d and l_a are the thicknesses in mm of the phosphate glass containing the rare earth, $\int A_d(E)\,d(E)$ and $\int A_a(E)\,dE$ are the areas under the donor and acceptor absorption curves on a wave number scale, R is the interionic distance in Å and n the refractive index ($n = 2.14$ in our glass). For a dipole–quadrupole mechanism the transfer probability is given by Dexter as

$$P_{da}(dq) = \frac{135 a \hbar^6 c^6 Q_d}{4\pi R^8 n^4 \tau_a} \times \frac{g_a' g_d}{g_a g_d'} \left(\frac{\epsilon}{\kappa^{1/2} \epsilon_c} \right)^4 \times \int \frac{f_d(E)\, F_a(E)}{E^6}\, dE. \qquad (2)$$

The ratio between dipole–quadrupole and dipole–dipole transition probabilities is given in Ref. (*2*) as

$$P_{dq}/P_{dd} \simeq (a/R)^2,$$

where a is the atomic radius of the rare earth and R the interionic distance. The quantum yield of energy transfer η_t is given (*9*) by

$$\eta_t = P_{da}\tau_d/(1 + P_{da}\tau_d) = 1 - (\eta/\eta_0) \qquad (3)$$

where τ_d is the radiative lifetime of pure donor, η_0 is the fluorescence yield of the pure donor, and η is the fluorescence yield of the donor in the presence of the acceptor.

By using the latter formula we can calculate the efficiency of energy transfer from experimentally measured fluorescence yield. By following the dependence of energy-transfer efficiency on the interionic distance we can derive conclusions as to the type of multipolar interaction.

Another approach to studying the type of mechanism of interaction is to compare the experimentally obtained decay curves of the donor fluorescence with those obtained theoretically by Inokuti and Hiroyama (*4*).

According to the work of Inokuti and Hiroyama, when a donor surrounded by randomly distributed acceptors is excited by a flash of light the emission intensity ϕ of the donor decays as a result of the electrostatic-multipole interactions with acceptors as:

$$\phi(\tau) = \exp\{-(t/\tau_0) - \Gamma[1 - (3/s)](C/C_0)(t/\tau_0)^{3/s}\}, \qquad (4)$$

where C is the concentration of the acceptor, C_0 is the critical transfer concentration (the concentration at which the energy-transfer rate becomes equal to the radiative rate of fluorescence from the donor), τ_0 is the decay constant of donor luminescence in the absence of an acceptor, and $s = 6$, 8 and 10 corresponds to dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions, respectively.

Experimental

For preparation of the glasses sodium dihydrogen phosphate monohydrate $NaH_2PO_4 \cdot H_2O$ Mallinckrodt 99.5 purity was used. The rare earths were Eu_2O_3 and Sm_2O_3, 99.9% Molycorp.

Glasses were prepared from the following mixtures:

I: 0.5, 1, 1.5, 2, 2.5 wt % europium,
II: 0.5, 1, 1.5, 2, 2.5 wt % samarium,
III: 0.5, 1, 1.5, 2, 2.5 wt % samarium and europium,
IV: 2 wt % samarium and varying concentrations of europium (as in I) (*6*).

The glasses were prepared by homogenizing the mixtures in an electric vibrator and melting them in platinium crucibles to 1000°C; glass discs 1 mm thick and 12 mm in diameter were obtained.

Absorption spectra of the glasses were measured with a Cary 14 spectrophotometer using undoped glasses as blanks. The excitation and emission spectra of the glasses were taken on a Model 210 Turner Spectrofluorimeter or on the spectrofluorimeter already described (*10*).

The former instruments corrects automatically for the wavelength dependence of intensity of the

TABLE I

OSCILLATOR STRENGTHS AND QUANTUM YIELDS OF $^5D_0$-LEVEL OF Eu^{3+} IN PHOSPHATE GLASS

Transition assignment	Wave number	Oscillator strength × 10^7	Quantum yield
$^7F_2 \rightarrow {}^5D_0$	17256	0.013	
$^7F_1 \rightarrow {}^5D_0$	16771	0.089	
$^7F_0 \rightarrow {}^5D_0$	16319	0.015	0.953
$^7F_1 \rightarrow {}^5D_1$	18700	0.505	
$^7F_0 \rightarrow {}^5D_1$	18993	0.146	0.822
$^7F_0 \rightarrow {}^5D_2$	21493	1.248	0.693
$^7F_1 \rightarrow {}^5D_3$	24009	0.547	0.612
$^7F_0 \rightarrow {}^5L_6$	25380	8.981	0.581
$^7F_1 \rightarrow {}^5G_5, {}^5G_6$	26041	6.019	
$^7F_0 \rightarrow {}^5G_3$	26507	2.726	
$^7F_1 \rightarrow {}^5L_8$	27285	0.391	
$^7F_0 \rightarrow {}^5D_4$	27567	1.926	
$^7F_1 \rightarrow {}^5H_3$	30464	1.242	
$^7F_1 \rightarrow {}^5H_5$	31152	3.001	
$^7F_0 \rightarrow {}^5H_6$	31397	6.776	

source and the sensitivity of the detectors; when the latter instrument was used, the same corrections were made from the data obtained. The decay times were measured using monochromatic excitation by an apparatus already described. All measurements were made at room temperature.

Results

Oscillator Strength and Quantum Yield of Europium and Samarium

Oscillator strength of various levels of europium are presented in Table I. They were calculated from the areas under the absorption spectrum (*4*). The quantum yields of the fluorescence of the $^5D_0$ level upon excitation to the $^5D_0$ level and to higher levels are also presented in Table I (*5*). The decay constant of europium, 2.8 msec ± 0.03, are independent of concentration.

Oscillator strengths for samarium and the quantum yields of the $^4G_{5/2}$ fluorescence of samarium are presented in Table II. The quantum yields of samarium were calculated by the comparative method using europium glasses as standards. The quantum yield Q_f of the $^4G_{5/2}$ level under $^4G_{5/2}$ excitation was determined independently from the natural lifetime using the formula:

$$Q_f = \tau_{\text{meas}}/\sum \tau_{\text{nat}}, \tag{5a}$$

where τ_{meas} is the measured lifetime and $1/\sum \tau_{\text{nat}} = \sum A.$ is the sum of the radiative transition probabilities from the $^4G_{5/2}$ level.

The transition probability $A\,{}^6H_{5/2} \rightarrow {}^4G_{5/2}$ was calculated using the formula (*11*)

$$A = 2.880 \times 10^{-9} (g_l/g_u) n^2 \nu^2 \int \epsilon(\nu)\, d\nu. \tag{5b}$$

The other transition probabilities from the $^4G_{5/2}$ level were obtained using the corrected emission spectrum for the transitions

$$^4G_{5/2} \rightarrow {}^6H_{5/2}, {}^6H_{7/2}, {}^6H_{9/2}, {}^6H_{11/2}.$$

The value so obtained was 0.89 ± 0.05. We can assume that the additional fluorescence to the higher ground multiplet lying in the IR region amounts to an addition of about 5%. Thus the quantum efficiency of the $^4G_{5/2}$ level of samarium

TABLE II

OSCILLATOR STRENGTH AND QUANTUM YIELDS OF $^4G_{5/2}$ OF Sm^{3+} EXCITED TO SELECTED LEVELS IN PHOSPHATE GLASS

Transition assignment	Wave number	Oscillator strength × 10^6	Quantum yields
$^4G_{5/2}$	17467–18348	0.0476	0.930
$^4F_{3/2}$	18779–19047	0.0115	
$^4G_{7/2}$	19800–20100	0.0183	
$^4I_{9/2}, {}^4M_{15/2}, {}^4I_{11/2}$	20181–21621	1.5370	0.647
$^4I_{13/2}$	21267–21978	0.1388	
$^4F_{5/2}$	21978–22346	0.0273	0.457
$^4M_{17/2}, {}^4G_{9/2}, {}^4I_{15/2}$	22321–23255	0.2169	
$({}^6P, {}^4P)_{5/2}$	23255–24630	1.0039	0.182
$^4L_{13/2}, {}^4F_{7/2}, {}^6P_{3/2}, {}^4K_{11/2}, {}^4M_{21/2}, {}^4L_{15/2}$	24242–25316	4.0749	0.220
$^4G_{11/2}, {}^4D_{1/2}, {}^6P_{7/2}$	25252–26109	0.2298	0.199
$^4L_{17/2}, {}^4K_{13/2}, {}^4F_{9/2}$	26109–27173	1.2246	0.174
$^4D_{3/2}, ({}^4D, {}^6P)_{5/2}$	27173–28089	1.2230	0.168
$^4H_{7/2}$	27972–28368	0.0264	
$^4K_{15/2}, {}^4H_{9/2}, {}^4D_{7/2}, ({}^4K, {}^4L)_{17/2}, {}^4L_{19/2}, {}^4H_{11/2}$	28490–29450	0.7457	0.111

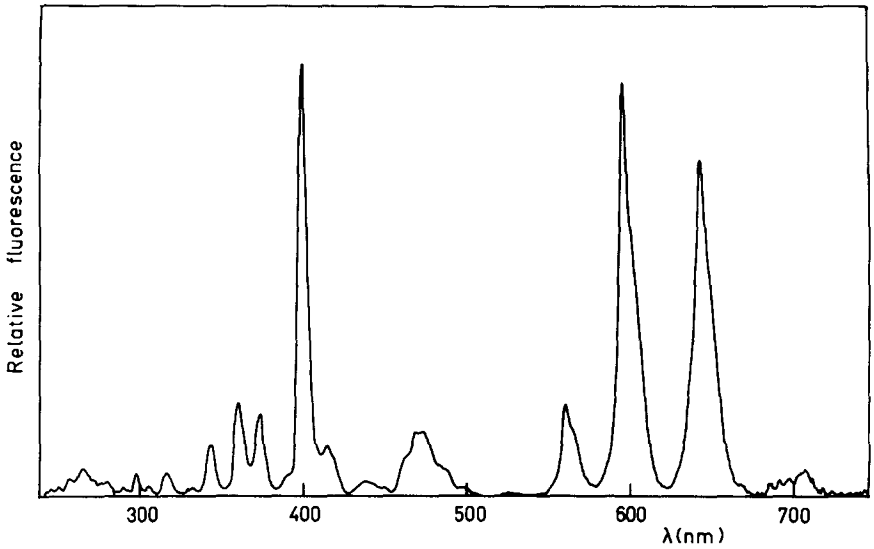

FIG. 1. Excitation and emission spectrum of samarium in phosphate glass.

will be 0.93 ± 0.05. The excitation and emission spectrum of samarium is presented in Fig. 1. The fluorescence measured here consists of the fluorescence from the $^4G_{5/2}$ level to the ground ^6H multiplet. The transitions are tabulated in Table III.

Samarium shows concentration quenching of fluorescence as seen from Table IV. However, in the range of our measurements there was no concentration quenching of europium (*6*).

Energy Transfer

The evidence of energy transfer from samarium to europium can be found in Fig. 2, where additional peaks of samarium are observed in the excitation spectrum of europium in a glass which contains samarium and europium. These peaks occur at 356–368 (27173–28089 cm^{-1}), 395.0–412.0 (24242–25316 cm^{-1}) and 462–495 nm (20181–21621 cm^{-1}). These additional peaks occur at those levels where the oscillator strength of samarium is the highest (Table II). The increase of the fluorescence as indicated from the relative areas in the excitation spectrum is 0.183:1 and 0.97, respectively.

TABLE III

MAIN FLUORESCENT TRANSITIONS FROM THE $^4G_{5/2}$ LEVEL OF Sm^{3+}

Transition assignment	Wave length	Relative area
$^4G_{5/2} \to {}^6H_{5/2}$	562	0.195
$^4G_{5/2} \to {}^6H_{7/2}$	597	1.000
$^4G_{5/2} \to {}^6H_{9/2}$	645	0.947
$^4G_{5/2} \to {}^6H_{11/2}$	707	0.112

The results described henceforth were obtained for excitation of samarium(III) at 402 nm, which corresponds to the transition having the high oscillator strength.

Another evidence of energy transfer between samarium and europium can be found in Fig. 3, which shows concentration dependence of pure europium excited at 402 nm and of europium in the presence of samarium excited at the same wavelength. Here we see the increase for europium fluorescence due to the energy transfer from samarium.

Figure 4 presents the increase in europium fluorescence and decrease in samarium fluorescence as a result of energy transfer.

TABLE IV

DEPENDENCE OF SAMARIUM FLUORESCENCE ON CONCENTRATION

Concentration wt %	Relative fluorescence $\lambda_{ex} = 402$ nm $\lambda_{em} = 562$ nm	Relative fluorescence $\lambda_{ex} = 402$ nm $\lambda_{em} = 645$ nm
0.5	110	190
1.0	140	270
1.5	150	290
2.0	160	300
2.5	190	390
3.0	120	260
3.5	70	220

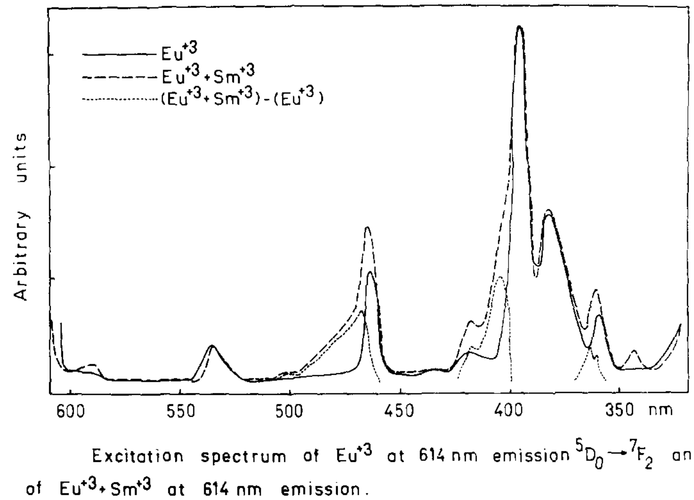

FIG. 2. Excitation spectrum of europium fluorescence ${}^5D_0 \rightarrow {}^7F_2$ (612 nm) with and without samarium in phosphate glass.

Discussion

Using Eq. (3) we have calculated the efficiency of energy transfer from the ratio of fluorescence of samarium in the presence of europium in glasses to the fluorescence of samarium alone. The energy transfer efficiencies η_t so obtained, $\eta_t = (1 - \eta/\eta_0)$ are presented in Table V for varying concentrations of europium. Applying the second part of Eq. (3) we obtain $\eta_t = P_{da}/(P_{da} + P_{d0})$ where P_{da} is the probability of energy transfer and P_{d0} is the sum of the probabilities of excitation of the excited levels of samarium when no europium is present. P_{d0} was measured experimentally as the inverse of decay constant of fluorescence of glasses containing samarium only (where no quenching occurs) and it equals 1.87×10^{-3} sec. The values of P_{da} are also presented in Table V together with the average donor–acceptor distance calculated from the concentration.

Another way to obtain the probability of energy transfer experimentally is by using the value of increase of fluorescence of acceptor (*12*), by using the formula

$$P_{da} = (1/\tau_d)(\Delta I_a/\eta), \qquad (6)$$

where ΔI_a is the increase of acceptor fluorescence when excited via the donor.

The values obtained are presented in Table V.

The agreement between the transfer probabilities calculated in the two different ways is very satisfactory.

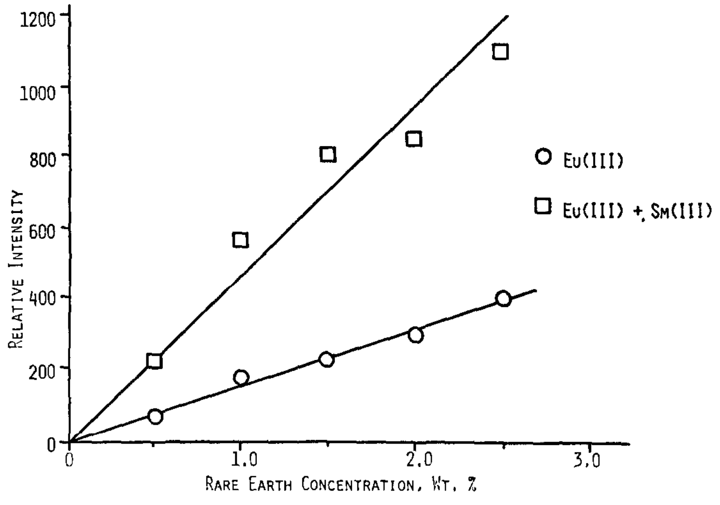

FIG. 3. Concentration dependence of europium fluorescence alone and with samarium.

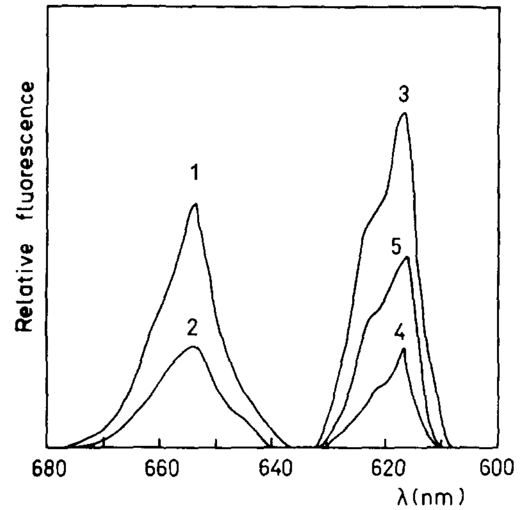

FIG. 4. Increase of Eu fluorescence and decrease of Sm fluorescence as a result of energy transfer.

In order to decide whether the energy transfer is by a dipole–dipole or a dipole–quadrupole mechanism, we have plotted η_0/η vs $C^{6/3} \sim 1/R^6$ (Fig. 5) and η_0/η vs $C^{8/3} \sim 1/R^8$ (Fig. 6). The straight-line dependence of the transition probability on the eighth power of the distance is clearly indicative of the dipole–quadrupole mechanism.

Additional evidence for the latter mechanism was obtained by fitting the experimental points of the decay time to the theoretical curves obtained using Eq. (4). In this equation the critical concentration C_0 was taken as the concentration at which $I = I_0/2$ (the fluorescence intensity equals half of the intensity of samarium in the absence of europium). The distance corresponding to this concentration was found to be 14.4 Å.

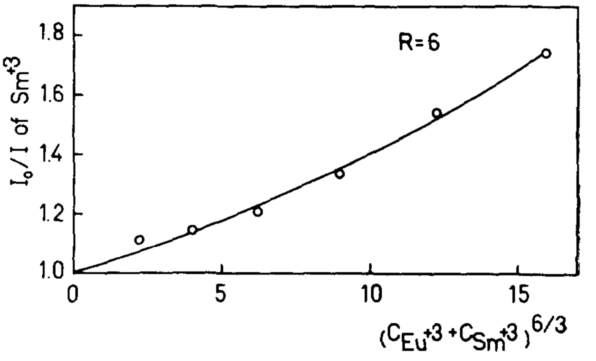

FIG. 5. Dependence of η_0/η of Sm on $C^{6/3}$.

From Fig. 7 it is clearly seen that Eq. (4) ($s = 8$) is operative in the case of the Sm → Eu transfer.

The transition probabilities were also calculated using Dexter's formula (*2*) for dipole–quadrupole interactions for a resonant transfer. The concentration of Sm was 1.5 wt %, and that of Eu was 2 wt % in this calculation. The overlap between various levels $\int f(\nu)F(\nu)d\nu$ used for this calculation are presented in Table VI.

The values for the transition probability for a dipole–quadrupole transfer between the ($^4L_{13/2}$, $^4F_{7/5}$ and $^6P_{3/2}$) of Sm^{3+} and $^5L_6$ of Eu^{3+} (for which the expression in the brackets of formula 2 is the highest) calculated using Eq. (2) (see Table VI) was 4×10^{-3} sec^{-1}. When the same calculation was made for levels between which the actual transfer takes place, this expression was smaller by five orders of magnitude. As we have seen from Table V the measured transition probability is 286 sec^{-1}.

This implies that we have here a nonresonant interaction which is assisted by the phonons of the glass. Such type of interaction in crystals was

TABLE V

EFFICIENCY AND PROBABILITY OF ENERGY TRANSFER FROM SAMARIUM TO EUROPIUM[a]

Concentration of acceptor Eu^{3+} wt %	R Donor–acceptor distance in Å	Quantum efficiency of transfer $\eta_t = [1 - (\eta/\eta_0)]$	Probability of transfer calculated by formula $P_{da} = (1/\tau_d)[(\eta_0/\eta) - 1]$ sec^{-1}	Probability of transfer calculated by formula $P_{da} = (1/\tau_d)(\Delta I_a/\eta)$ sec^{-1}
0.5	24.0	0.10	59.5	—
1.0	19.2	0.15	73.0	67.6
1.5	16.8	0.17	109.9	—
2.0	15.2	0.25	178.6	175.6
2.5	14.4	0.35	285.7	266.7
3.0	13.0	0.43	400.0	373.3

[a] Donor concentration constant 1 wt %.

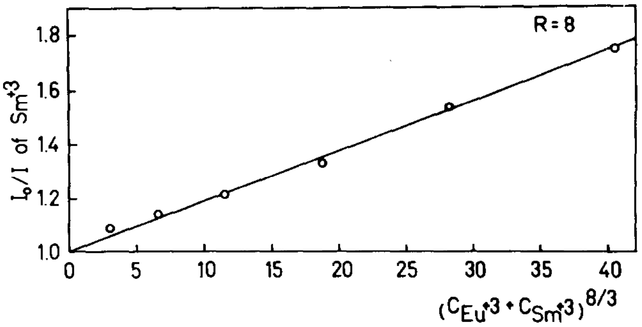

FIG. 6. Dependence of η_0/η of Sm on $C^{8/3}$.

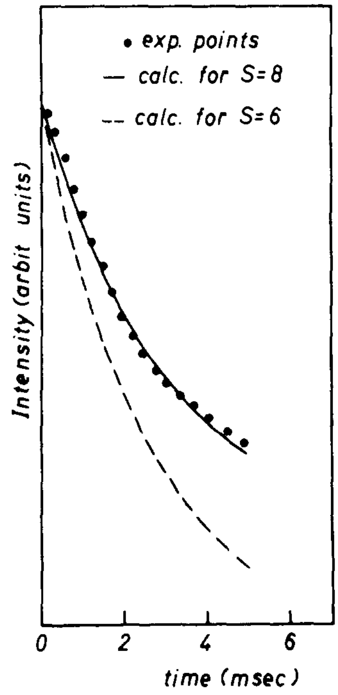

FIG. 7. Decay time of samarium, experimental and calculated from Inokuti for $S = 6$ and $S = 8$.

considered by Orbach (*13*), Moos (*14*) and Miyakawa and Dexter (*15*) who point out that for narrow-separated lines (as in our case) the probability of resonance transfer which is governed by the $\int f_d(E) F_a(E) dE$ is almost negligible. An analysis of the expression for phonon-assisted transfer (*13*) shows that the transfer probability depends on the matrix elements of the multipole interaction as defined by Eq. (2). Hence the dependence of the transfer probability of the interionic distance R still obeys the equation for the dipole–quadrupole transfer (Fig. 3). In addition, P_{da} depends on the difference between the matrix elements of the dynamic part of the lattice–orbit interaction between the excited and ground states of the acceptor ion and between the ground and excited states of the donor ion. It is therefore possible that such an interaction will increase the transfer probability by many orders of magnitude.

Finally, the levels at which the energy transfer takes place can be estimated from the excitation spectrum of europium in the presence of samarium (Fig. 2). It is seen that europium can be excited at 465 nm with the highest efficiency. This means that excitation at 402 nm causes a nonradiative deactiva-

TABLE VI

OVERLAPS BETWEEN DIFFERENT LEVELS OF SAMARIUM AND EUROPIUM

Transition assignment of donor samarium	Wave number Sm^{3+}	Transition assignment of acceptor europium	Wave number Eu^{3+}	S-Overlap $S = \int f_d(E) F_a(E) dE$	Absorption probability of donor $A_d = f_d/4 \times 10^{-9}$	Absorption probability of acceptor $A_a = f_a/4 \times 10^{-9}$	$S \cdot As \cdot Aa$
$^4F_{3/2}$	18797–19300	$^7F_1 \rightarrow {}^5D_1$	18676	8.516×10^{-4}	2.660	11.683	0.026
$^4I_{13.2}$	21300–22000	$^7F_0 \rightarrow {}^5D_2$	21499	2.444×10^{-3}	89,894	28.909	6.351
$(^6P, {}^4P)_{5/2}$	23400–24400	$^7F_1 \rightarrow {}^5D_3$	24040	1.304×10^{-3}	232.507	54.709	16.598
$^4L_{13/2}, {}^4F_{7/2}, {}^6P_{3/2}$	24400–24700	$^7F_0 \rightarrow {}^5L_6$	25375	1.304×10^{-3}	943.700	898.071	1105.500
$^4G_{11/2}, {}^4D_{1/2}, {}^6P_{7/2}$	25500–26200	$^7F_1 \rightarrow {}^5G_5, {}^5G_6$	26390	3.018×10^{-4}	53.215	601.930	9.667
$^4L_{17/2}, {}^4K_{13/2}, {}^4F_{9/2}$	26400–27200	$^7F_0 \rightarrow {}^5G_3$	26535	1.450×10^{-3}	283.608	272.636	112.108
$^4D_{3/2}, (^4D, {}^6P)_{5/2}$	27200–28100	$^7F_1 \rightarrow {}^5L_8$	27086	8.450×10^{-4}	283.235	39.135	9.369

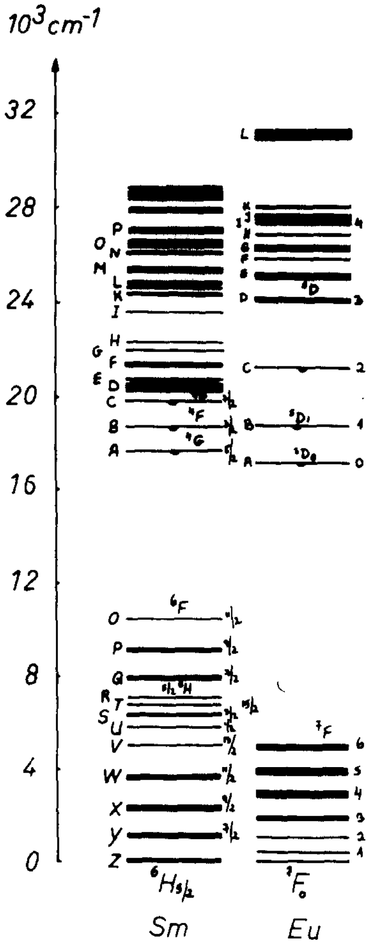

FIG. 8. Electronic levels of samarium and europium in glasses.

tion within the samarium ion and energy transfer at the $^4F_{3/2}$ of samarium to $^5D_1$ of europium or $^4G_{5/2}$ of samarium to $^5D_0$ of europium. In the latter case there is no overlap between the two levels (Fig. 8). However, the difference of energy is 200 cm^{-1} and can therefore be easily surmounted by assistance of phonons.

Acknowledgments

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