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Energy Transfer Between Gd^{3+} and Sm^{3+}

The Effect of Gd^{3+} on Quenching of Sm^{3+} and Intensity Parameters of Sm^{3+} in Borate Glasses*

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Intensity parameters of Sm^{3+} in borate glasses were obtained by fitting the oscillator strengths to the Judd–Ofelt formula and a study of energy transfer from gadolinium to samarium was performed. An increase of samarium fluorescence originating from the ${}^4G_{5/2}$ level was observed in the presence of gadolinium, in the concentration range of 0.1–3 wt% samarium with gadolinium constant at 3 wt%. The intensity of samarium fluorescence on excitation at 273 nm increased by one order of magnitude in the presence of gadolinium. From the excitation spectrum of the double-doped glasses (Gd + Sm), it was deduced that energy absorbed by gadolinium is transferred from ${}^6P_{7/2}$ gadolinium levels to the ${}^4P_{3/2}$ and ${}^4P_{5/2}$ samarium levels.

The mechanism of this energy transfer was obtained by plotting the energy transfer probabilities as a function of samarium concentration. A linear dependence of η_0/η (η intensity of gadolinium in the presence of samarium) versus square of concentration of Sm + Gd is obtained. From this it is concluded that the transfer is of electric-multipolar type, mainly dipole–dipole. A small increase (about 10%) of fluorescence of samarium in the presence of gadolinium excited at levels where no energy transfer can take place is attributed to the fact that the quenching of samarium occurring by the cross relaxation $({}^4G_{5/2} \rightarrow {}^6F_{9/2}) \rightsquigarrow ({}^6H_{5/2} \rightarrow {}^6F_{9/2})$ is suppressed by the presence of gadolinium as seen from concentration dependence of samarium doped glasses compared to double-doped glasses.

Introduction

In our recent papers we have reported the mechanisms and probabilities of energy transfer between gadolinium and terbium (*1*), samarium and europium (*2*) and thulium and erbium (*3*). Energy transfer between terbium and samarium in phosphate crystals was studied by Hirano and Shionoya (*4*) and in other crystals by Van Uitert, Dearborn and Rubin (*5*) and Blasse and Bril (*6*) but to our knowledge no information is found in the literature on energy transfer between gadolinium and samarium in any medium. In this work we are presenting evidence of such a transfer and use the experimental methods and formulae developed previously (*1*, *2*, *3*, *7*) in order to measure the transfer probabilities and the mechanism of transfer of energy between gadolinium and samarium.

Gadolinium has already been studied extensively because of its simple scheme of absorption and emission resulting from the electronic configuration $4f^7$. The spectrum of samarium is much more complicated and a short summary of the data present in literature is given below.

Trivalent samarium emits fluorescence in the visible and near infrared region in various host materials. This luminescence which is due to transitions between the energy levels in the $4f^5$ electron configuration was studied in $BaTiO_3$ (*8*), in $TbPO_4$ and YPO_4 crystals (*4*) and in many other crystals by Van Uitert and Johnson (*9*).

We shall describe below the optical spectra of borate glasses doped by the samarium ion, calculate the intensity parameters by use of Judd–Ofelt theory and show how the emission intensities of samarium can be increased by the presence of gadolinium; we shall also demonstrate the presence of energy transfer between gadolinium and samarium and measure the

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transfer probability as a function of donor-acceptor distance.

Intensity Parameters

The spectra of the tripositive rare earths arise from interconfigurational transitions within the $4f$ shell. Those transitions, which are responsible for the crystal spectra, are forbidden in the free ion by the parity rule for electric dipole transitions. In a crystal or glass they become allowed by vibronic interaction or by admixture of odd electronic wavefunctions due to the odd parity terms in the crystal field. In the calculations of Ofelt (*10*) and Judd (*11*) the contribution of the odd parity part of the crystal field was considered in mixing states of different parity.

Carnall et al. (*12*) have correlated the experimentally determined band intensities in the solution absorption spectra of the trivalent lanthanides with a theoretical expression derived by Judd (*11*):

$$P = \sum_{\lambda} T_\lambda \sigma (f^N \psi J \| U^{(\lambda)} \| f^N \psi' J')^2, \quad \lambda = 2, 4, 6 \qquad (1)$$

where P is the oscillator strength corresponding to the induced electric-dipole transition, between the levels $\psi J \rightarrow \psi' J'$ at energy σ (cm^{-1}), and $U^{(\lambda)}$ is a tensor operator of rank λ. The symbol ψ stands for additional quantum numbers that may be necessary to define the level uniquely. The three quantities T_λ are related to the radial parts of the $4f^N$ wavefunctions, the wavefunctions of perturbing configurations of which the nearest is the $5d$ or charge transfer, the refractive index of the medium, and the ligand field terms which characterize the environment of the ion. From our experimentally obtained oscillator strengths and theoretically calculated reduced matrix elements of Carnall (*12*), we have obtained T_λ coefficients by the RMS method (*13*) calculating the minimum deviation between the observed oscillator strengths and those calculated by means of Eq. (1). The matrix elements do not depend on the environment as shown in Ref. 13.

The τ_λ parameters $[\tau_\lambda = T_\lambda(2J+1)]$ of Sm^{3+} in borate glass are compared to previously obtained parameters of Sm^{3+} in phosphate glass and presented in Table I. The results are compared with those of Carnall in aqueous solutions (*12*).

The oscillator strengths of Sm^{3+} may be arranged in two groups, one referring to transitions up to 10 700 cm^{-1} labelled in the table as "low" and the second to transitions in the energy range 17 600–32 800 cm^{-1} labelled as "high." The τ_λ parameters were calculated separately in the "low" and "high" energy regions.

Since Judd's equation (1) applied to the case where the f^n splitting are small compared to the f–d energy gap, it is not correct to use the high lying levels for calculations of τ_λ: especially in Sm^{3+} where the high lying levels are close to the charge transfer band it is not appropriate to take these levels into calculation. Indeed it is seen in Table I that τ_2 "low" is lower than τ_2 "high," illustrating the different behavior of the "low" and "high" levels as expected. It is interesting to note that this result is also consistent with the sensitivity of τ to environment, in the sense that interaction between R.E. and ligand is stronger in the upper levels of the R.E. ion than in the lower.

TABLE I

τ_λ PARAMETERS FOR Sm^{3+} IN VARIOUS MATRICES

Matrix	Energy range (cm^{-1})	Number of data points	τ_2 (cm)	τ_4 (cm)	τ_6 (cm)
Phosphate low	4525–10600	7	6.66×10^{-9}	4.17×10^{-9}	8.04×10^{-9}
Phosphate high	17800–32800	15	106.8×10^{-9}	6.24×10^{-9}	4.76×10^{-9}
Borate low	4520–10700	8	3.14×10^{-9}	6.00×10^{-9}	0.54×10^{-9}
Borate high	17600–32700	14	99.6×10^{-9}	7.20×10^{-9}	4.79×10^{-9}
* Ref. (12) Dilute $HClO_4$	—	—	1.17×10^{-9}	5.32×10^{-9}	3.47×10^{-9}

Energy Transfer

1. Theory

The classical formula of Dexter (*14*) relates the probability of transfer of energy by electric dipole–dipole interaction.

For the borate glass used in this work formula 17 of Ref. 14 may be written in a simplified form as (*1, 15*)

$$P_{da}(dd) = \frac{1.47 \times 10^{18}}{C_d C_a 1_d 1_a}\left[\frac{\int A_d(E)\,dE \int A_a(E)\,dE}{n^2 R^6}\right. \times \left.\int \frac{f_d(E)\,F_a(E)\,dE}{E^2}\right] \tag{2}$$

where C_d and C_a are the donor and acceptor concentrations in weight percent, 1_d and 1_a are the thickness in mm of the borate glass containing the rare earth, $\int A_d(E)dE$ 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 ($n = 1.44$ in our glass).

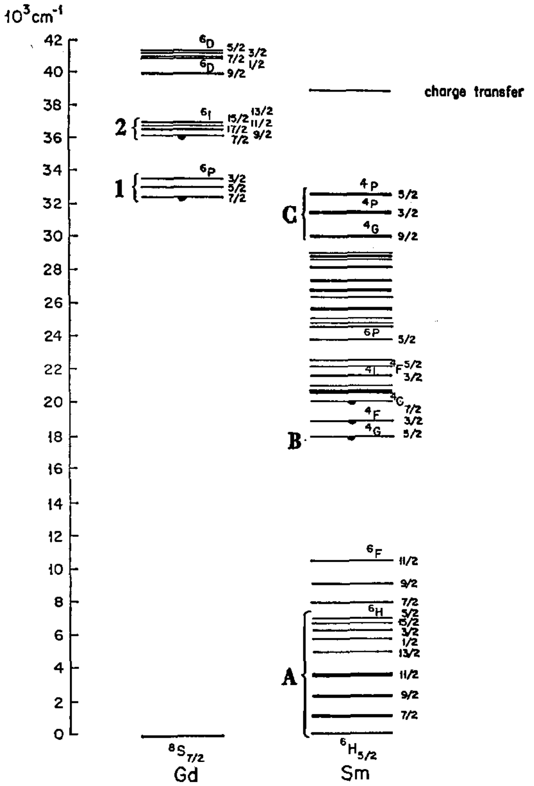

FIG. 1. Schematic energy level diagram for the Gd–Sm System.

The ratio between dipole–quadrupole and dipole–dipole transition probabilities is given by Dexter (*14*) as

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

where a is the atomic radius of the rare earth and R the interionic distance.

A method for calculating from the experimental fluorescence data the probability and efficiency of energy transfer between inorganic ions with well-defined electronic levels is described in Ref. 7. The formulae, which were derived from rate equations applicable to a system consisting of a pair of unlike rare earth ions in a glass medium, are as follows for the Gd + Sm system which is shown schematically in Fig. 1. Here the numbers specify the levels of the donor Gd^{3+} ion and the letters, the levels of the acceptor Sm^{3+} ions. For the sake of simplicity in the donor scheme one label corresponds to all close-lying levels between which rapid relaxation occurs (*2*). For the acceptor only two levels are labelled, level C to which the energy transfer takes place and level B from which fluorescence is observed. The superscripts "r" and "nr" refer to radiative and nonradiative transitions respectively. The P's are the transition probabilities between various levels designated in the figures. The η are the quantum efficiencies defined as

$$\eta_1 = \frac{P_{10}^r}{P_{10}^{nr} + P_{10}^r} \tag{3}$$

$$\eta_2 = \frac{P_{21}}{P_{21} + P_{20}} \tag{4}$$

when the probability of radiative transition P_{20} is lower than the probability of internal relaxation P_{21} between the levels 2 and 1, $P_{20} \ll P_{21}$ and $\eta_2 \to 1$ (which was shown to be true in work between Gd^{3+} and Tb^{3+} (*1*)). In such a case the energy transfer occurs between level 1 and C and its probability P_{1C} is related to the donor emission quantum efficiency with no acceptor present $\eta^0{}_d$ and the donor emission efficiency in the presence of acceptor η_d by

$$P_{1C} = \frac{1}{\tau_d}\left(\frac{\eta_d{}^0}{\eta_d} - 1\right) \tag{5}$$

in which τ_d is the measured decay time of the fluorescence of level 1 of the pure donor.

The efficiency of energy transfer is given by

$$\eta_t = \frac{P_{1C}\,\tau_d}{1 + P_{1C}\,\tau_d} = 1 - \frac{\eta_d}{\eta^0{}_d}. \tag{6}$$

Alternatively energy transfer probability between the donor and the acceptor can be derived from the increase of the acceptor fluorescence as the result of energy transfer. Such an expression for P_{1C} was derived in detail in Ref. 7 and explicitly it is

$$P_{1C} = \frac{\eta_1}{\eta_B^{(c)}} \frac{1}{\tau_d} \frac{\Delta\eta_a}{\eta_d} \tag{7}$$

where η_1 and τ_d are related to the pure donor quantum efficiency and lifetime as in formula 5, $\Delta\eta_a$ is the increase of the acceptor fluorescence from level B and $\eta_B^{(c)}$ is the quantum efficiency of this fluorescence excited at level c where the energy transfer takes place. Equations (5) and (7) give the energy transfer probability in terms of experimentally measurable quantities.

It was shown by us that when the calculation of energy transfer for Gd–Tb, (*1*) Sm–Eu (*2*) and Tm–Er (*3*) was made by use of the Dexter formula (*14*) using the overlap between donor and acceptor, it was about four to five orders of magnitude less than the transfer obtained by using Eqs. 5 and 7. From those results it was therefore concluded that the transfer of energy between rare earths in glasses is assisted by the phonons of the glass.

Miyakawa and Dexter (*16*), Riseberg, Gandrud and Moos (*17*) and Fong and Miller (*18*) point out that for narrow separated levels (as in our case) the resonance transfer, which is governed by $\int f_d(E)F_a(E)dE$, is almost negligible. On the other hand an analysis of the expression for phonon-assisted transfer (*19*) 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 on the interionic distance R still obeys the equation for the multipolar transfer. 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.

It should be noted that energy transfer can be expected not only between different ions but also between the same ions if the interionic distances are small.

In Sm^{3+} the transition $^4G_{5/2} \rightarrow {}^6F_{9/2}$ will result in cross-relaxation, because of a coincidence of energy gaps: the energy released in this transition

TABLE II

OSCILLATOR STRENGTH OF GADOLINIUM IN BORATE GLASS

Assignments[a, b]	Wavenumber (cm^{-1}) b	Wavenumber (cm^{-1}) This work	Wavelength (nm)	Oscillator strength × 10^6 This work	Oscillator strength × 10^6 Exptl[b]	Oscillator strength × 10^6 Calc[b]	Quantum yield of the $^6P_{7/2}$ level
$^8S_{7/2} \rightarrow {}^6P_{7/2}$	32 100–32 300	31 949	313.0	0.176	0.073	0.055 0.013	1.00
$^6P_{5/2}$	32 700–32 900	32 573	307.0	0.074	0.041	0.031 0.005	
$^6I_{7/2}$	35 800–36 100	35 682	280.25	0.117	0.121	0.112	
$^6I_{9/2}$ $^6I_{17/2}$	36 100–36 450	36 101	277.0	0.781	0.845	0.877	
$^6I_{11/2}$ $^6I_{13/2}$ $^6I_{15/2}$	36 450–37 400	36 456	274.3	1.679	1.914	1.918	0.765
$^6D_{9/2}$	39 400–40 400	39 432	253.6	0.406	0.078	0.093	
$^6D_{7/2}$ $^6D_{3/2}$ $^6D_{5/2}$	40 500–41 200	40 388 40 733	247.6 245.5	0.385 0.099	0.082	0.008 0.130	0.590

[a] H. H. CASPERS, S. A. MILLER, AND H. E. RAST, *Phys. Rev.* **180**, 329 (1969).

[b] Reference 12.

TABLE III

Oscillator Strength of Sm^{3+} in Phosphate and Borate Glasses. Absorption from $^6H_{5/2}$ Level

		$f \times 10^6$		Phosphate glass		Borate glass		Quantum yield of the $^4G_{5/2}$ level
Transition (12) assignment	Spectral region(12) or energy level cm^{-1}	Expl (12)	Calc (12)	Wavenumber cm^{-1}	$f \times 10^6$	Wavenumber cm^{-1}	$f \times 10^6$	
$^6H_{13/2}$				4525	0.44	4515	1.01	
$^6F_{1/2}$	5600–6500	0.26	0.26			6154	0.86	
$^6F_{3/2}$	6500–6800	0.97	0.99	6301 6468	1.49	6329 6559	1.19	
$^6H_{15/2}$	6800–7600	1.70	1.84	6693	1.79	6826	2.85	
$^6F_{5/2}$				7256	2.30	7326	2.30	
$^6F_{7/2}$	7600–8600	2.74	3.00	8130	4.36	8163	4.36	
$^6F_{9/2}$	8800–9800	1.97	1.98	9259	5.63	8889 9050 9302	2.74	
$^6F_{11/2}$	10200–11000	0.31	0.32	10615	0.88	10638	0.51	
$^4G_{5/2}$	17600–18200	0.03	0.023 0.012	17730	0.05	17606	0.09	0.95
$^4F_{3/2}$	18700–19300	0.009	0.001	18939	0.01	18692	0.02	
$^4G_{7/2}$	19800–20300	0.52	0.62	19880	0.18	19920	0.16	
$^4I_{9/2}$, $^4M_{15/2}$, $^4I_{11/2}$	20300–21300	1.53	0.54	20982	1.54	20513 20964 21277	1.50	0.59
$^4I_{13/2}$	21300–22000	0.68	0.34	21651	0.14	21645	0.40	
$^4F_{5/2}$	22000–22200	0.03	0.006 0.010	22222	0.03	22099	0.05	
$^4M_{17/2}$, $^4G_{9/2}$, $^4I_{15/2}$, $^4M_{19/2}$	22200–23400	0.39	0.13	22805	0.22	22727	0.45	
$(^6P, {}^4P)_{5/2}$	23776			23809	1.01	23679 23952 24213	0.93	
$^4F_{7/2}$, $^6P_{3/2}$, $^4K_{11/2}$, $^4M_{21/2}$	24700–25500	3.84	3.80	24875	4.07	24630 24814	5.05	
$^4L_{15/2}$, $^4G_{11/2}$	25500–26200	0.42	0.11	25710	0.23	25641	0.13	
$^4D_{1/2}$, $^6P_{7/2}$, $^4L_{17/2}$, $^4K_{13/2}$, $^4F_{9/2}$	26400–27200	1.06	1.26	26666	1.82	26631	1.98	
$^4D_{3/2}(^4D, {}^6P)_{5/2}$	27200–28110	1.23	1.03	27410	1.97	27360 27662	1.75	
$^4K_{15/2}$, $^4H_{9/2}$, $^4D_{7/2}$, $(^4K, {}^4L)_{17/2}$, $^4L_{19/2}$, $^4H_{11/2}$	28600–29800	0.80	0.67	28985	1.37	28985	1.40	
$^4G_{9/2}$	30099			30165	0.12	30030	0.16	
$^4P_{3/2}$	31508			31620	1.53	31546	0.83	0.24
$^4P_{5/2}$	32706			32786	0.83	32680	0.65	

will cause an excitation in the neighbouring ion. Symbolically (*9*):

$$({}^4G_{5/2} \rightarrow {}^6F_{9/2}) \rightsquigarrow ({}^6H_{5/2} \rightarrow {}^6F_{9/2})$$

or

$$(Sm^{3+}\,{}^4G_{5/2})^* + (Sm^{3+}\,{}^6H_{5/2}) \rightarrow 2(Sm^{3+}\,{}^6F_{9/2})^*$$

But ${}^6F_{9/2}$ is not a metastable level, being connected to the ground state via a sequence of ${}^6F$ and ${}^6H$ states, and the energy transferred to ${}^6F_{9/2}$ is thus lost and appears as lattice vibrations. The transfer begins to be important when the mean distance Sm^{3+}–Sm^{3+} approaches 12–15 Å, (*1*) i.e., at this distance the transfer rate $P(dd)$ begins to be comparable with the total transition rate $P_r + P_{nr}$ for an isolated ion.

In the study of energy transfer between Gd^{3+} and Sm^{3+} this Sm^{3+} self-quenching has to be taken into account and deduced from the results obtained.

2. *Experimental*

Borax (analytical grade) was supplied by the Riedel de Haen Company and boric acid by Frutarom. Spectroscopic analysis of these reagents did not reveal the presence of any rare earths. Gadolinium and samarium oxides (99.9% purity) were supplied by Molycorp.

The technique of preparation of the glasses was described earlier (*20*, *21*).

Three series of glasses were prepared with the following rare earth contents:

(1) Gd	1, 2, 3, 4 wt%
(2) Sm	0.1, 0.2, 0.5, 1, 2, 3 wt%
(3) Gd 3% and Sm	0.1, 0.2, 0.5, 1, 2, 3 wt%

Absorption spectra. These were taken on a Cary 14 Spectrophotometer using undoped borate glass disks as blanks. The spectrum of gadolinium has already been studied (*1*). The spectrum of samarium was measured throughout the entire range uv, visible and IR, from 200 nm to 2500 nm using an 0.5%, 1 mm thick sample for less than 250 nm, a 3%, 2 mm thick sample for uv and a 2%, 1 mm thick sample for the visible and infrared range.

Excitation and emission spectra. These were obtained by using a Xenon light source and a spectrofluorimeter which was previously described (*22*). The spectra were corrected with respect to the spectral distribution of the light source and spectral response of the detection unit. Both the absorption and fluorescence spectra which were obtained on a wavelength scale were transformed to the energy scale by use of a computer program.

The decay times were measured by monochromatic excitation as described in Ref. 1.

3. *Results and Discussion*

The oscillator strengths obtained from the absorption spectra by use of the formula

$$P = 4.318 \times 10^{-9} \int \varepsilon(\sigma)\, d\sigma \qquad (8)$$

are presented in Tables II and III together with the spectral assignments of the relevant transitions as taken from the work of Carnall, Fields and Rajnak (*12*).

Our experimental results are compared to those taken from aqueous solutions (*12*) and phosphate glasses (*23*). In this work the oscillator strengths are slightly larger for most levels as the symmetry in glass is lower (*15*) and the forced electric dipole higher. The τ_λ parameters were calculated from these values of oscillator strengths as described in the introduction.

Figure 2 shows a portion of the excitation spectrum of Sm^{3+} alone and Sm^{3+} with addition of Gd^{3+} in borate glass at room temperature. In the presence of Gd^{3+} an additional band is observed at 273 nm due to Gd^{3+} providing evidence of energy transfer. The emission spec-

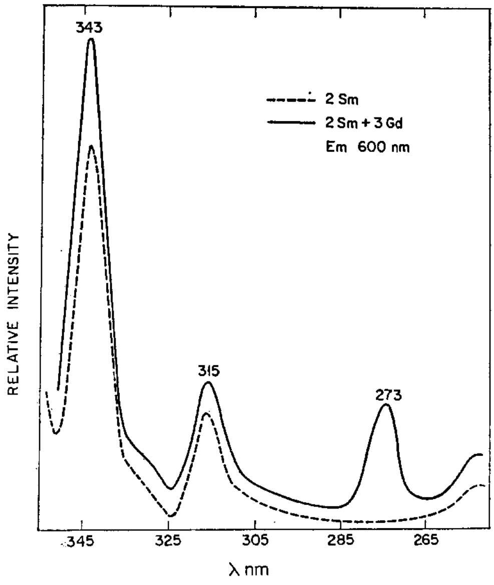

FIG. 2. Part of the excitation spectrum of 2 wt% Sm^{3+} (broken line) and in the presence of 3 wt% Gd^{3+} (full line). Emission at 600 nm.

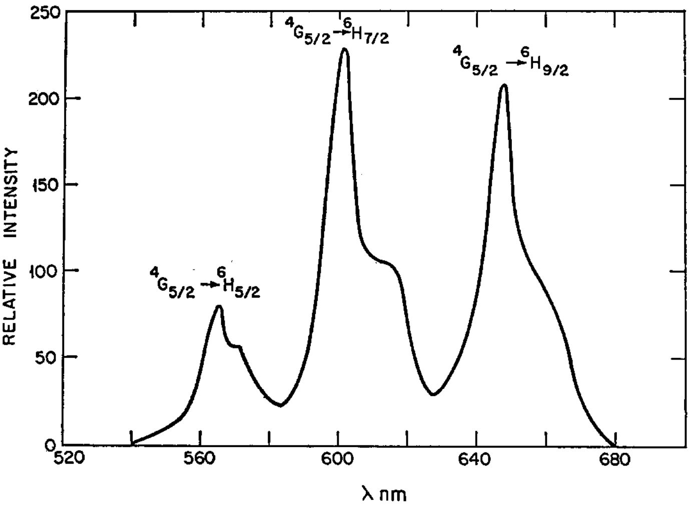

FIG. 3. Corrected emission spectrum of Sm^{3+} excited at 403 nm.

trum is presented in Fig. 3. All the emission lines detectable are due to the transitions from the lowest excited state $^4G_{5/2}$ manifold to the ^6H ground multiplet. In our experimental setup we were able to detect the transitions $^4G_{5/2} \to {}^6H_{5/2}$ peaking at 563 nm, $^4G_{5/2} \to {}^6H_{7/2}$ peaking at 600 nm and $^4G_{5/2} \to {}^6H_{9/2}$ peaking at 647 nm. The relative areas of the transitions are presented in Table IV.

The remaining transitions which could not be measured were estimated to give an additional 6% to the total intensity in a similar way as for phosphate glasses (*2*).

All the peaks show splitting which is probably due to the removal of the degeneracy by the crystal field of the glass.

TABLE IV

EMISSION WAVELENGTH AND RELATIVE AREAS OF $^4G_{5/2}$ LEVEL OF Sm^{3+} IN BORATE GLASS

Transition assignment	Wavelength nm	$\frac{1}{2}$ *B.W.* cm^{-1}	Relative areas
$^4G_{5/2} \to {}^6H_{5/2}$	563	312	1.00
$^4G_{5/2} \to {}^6H_{7/2}$	600	450	4.87
$^4G_{5/2} \to {}^6H_{9/2}$	647	250	4.47
$^4G_{5/2} \to {}^6H_{11/2}$[a]	707		0.6
$^4G_{5/2} \to {}^6H_{13/2}$	830		
$^4G_{5/2} \to {}^6H_{15/2}$	900		

[a] These three transitions were obtained by calculation assuming quantum yield of level $^4G_{5/2}$ to be 0.95.

The concentration dependence of fluorescence of Sm^{3+} alone and of Sm^{3+} in presence of Gd^{3+} is presented in Fig. 4. The excitation of this fluorescence was made at 403 nm. A linear dependence on concentration is obtained only at very small concentrations. At above 0.2 wt% a decrease from linearity is observed because of the cross-relaxation

$$(Sm^{3+}\,{}^4G_{5/2})^* + (Sm^{3+}\,{}^6H_{5/2}) \to 2(Sm^{3+}\,{}^6F_{9/2})^*$$

The quenching is slightly repressed by addition of Gd^{3+} whose presence hinders the aggregation, increasing the distance and decreasing cross-relaxation.

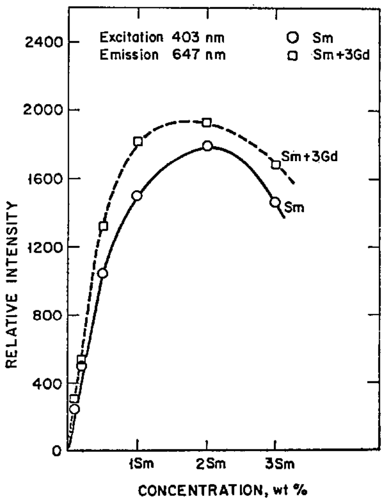

FIG. 4. Concentration dependence of Sm^{3+} alone and Sm + 3 wt% Gd.

The decrease from linearity of Sm^{3+} fluorescence in the presence of Gd^{3+} is at 0.5%. The excitation and emission spectra of Gd^{3+} in borate glass were described in our previous paper (*1*). The emission of Gd^{3+} resulting from the ${}^6P_{7/2}$ and ${}^6P_{5/2}$ levels to the ground ${}^8S_{7/2}$ multiplet is at 312 and 307 nm. The excitation spectrum of the 312 nm fluorescence from the ${}^6I$ multiplet peaks at around 275 nm and the ${}^6D$ multiplet around 250 nm.

Quantum Yields. The quantum yields of the ${}^6P$ multiplets of gadolinium excited to the ${}^6D$, ${}^6I$ and ${}^6P$ levels in borate glasses were calculated. The quantum yield of the ${}^6P_{7/2}$ level was determined by natural lifetime measurements. The quantum yields of the ${}^6P$ multiplet on excitation to ${}^6D$ and ${}^6I$ were then determined relative to the ${}^6P_{7/2}$ level. The results are presented in Table II.

The quantum yield of the ${}^4G_{5/2}$ levels of samarium under ${}^5G_{5/2}$ excitation was determined from the natural lifetime using the formula

$$\eta = \tau_{\text{meas}}/\sum \tau_{\text{nat}}$$

where τ_{meas} is the measured lifetime and $1/\sum \tau_{\text{nat}} = \sum A$ is the sum of the radiation transition probabilities from the ${}^4G_{5/2}$ levels. The radiative probability from ${}^6H_{5/2}$ to ${}^4G_{5/2}$ was calculated using formula (9) (*24*)

$$A = 2.88 \times 10^{-9}(g_l/g_u)\, n^2 \nu^2 \int \varepsilon(\nu)\, d\nu \qquad (9)$$

where g_l and g_u are the degeneracies of the lower and upper states respectively, n is the index of refraction, ν^2 is the squared wavenumber of absorption and $\varepsilon(\nu)$ the extinction coefficient as a function of wavenumber. The value obtained for A in borate glass is 37.7 sec^{-1}.

The total radiative transition probabilities from the ${}^4G_{5/2}$ level $K^4G_{5/2} = \sum_{i=5/2}^{15/2} {}^4G_{5/2} \rightarrow {}^6H_i$ were obtained using the corrected emission spectrum for the transitions

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

By assuming the quantum efficiency of fluoresence from this level to be 0.95 (*24*) we can calculate the transition rates ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$, ${}^6H_{13/2}$, ${}^6H_{15/2}$ which are out of the range of measurement, by the formula

$$Q.Y. = \tau_{\text{exp}} A({}^6H_{5/2} \rightarrow {}^4G_{5/2})\,[1 + \frac{A({}^4G_{5/2} \rightarrow {}^6H_{7/2})}{A({}^6H_{5/2} \rightarrow {}^4G_{5/2})} + \frac{A({}^4G_{5/2} \rightarrow {}^6H_{9/2})}{A({}^6H_{5/2} \rightarrow {}^4G_{5/2})} + x^*.] \qquad (10)$$

The measured lifetime of the fluorescence from the ${}^4G_{5/2}$ level is 2.3 msec. The numbers for borate glass were

$$0.95 = 0.0023[37.7(1.00 + 4.87 + 4.47 + x^*)]$$

The numbers in parentheses are the relative fluorescence intensities of the transitions ${}^4G_{5/2} \rightarrow {}^6H_i$ as given in Table IV. The relative areas of ${}^4G_{5/2} \rightarrow {}^6H_{11/2}$, ${}^6H_{13/2}$, ${}^6H_{15/2}$ thus calculated amount to 6% of the total emission of the ${}^4G_{5/2}$ level.

The quantum efficiencies of the ${}^4G_{5/2}$ level of Sm^{3+} excited at higher levels was calculated by the comparative method using samarium-doped phosphate glasses as a standard the quantum yield of which was calculated previously.

The quantum efficiencies of the ${}^4G_{5/2}$ level of samarium excited to different levels for a concentration (where no quenching was observed),

TABLE V

ENERGY TRANSFER PROBABILITIES BETWEEN Gd^{3+} AND Sm^{3+a}

Sm conc. wt%	$\frac{\eta^\circ d}{\eta d}$	$P\frac{nr}{1C} = \frac{1}{\tau d}\left(\frac{\eta^\circ d}{\eta d} - 1\right)$ (sec^{-1})	$\frac{\Delta\eta a}{\eta d}$	$\eta_B^{(c)}$	$P\frac{nr}{1C} = \frac{\eta_1}{\eta_B^{(c)}} \cdot \frac{1}{\tau d}\frac{\Delta\eta a}{\eta d}$ (sec^{-1})
0.1	1.04	11	51.13×10^{-4}	0.24	5
0.2	1.08	20	116.37×10^{-4}	0.24	12
0.5	1.24	60	260.29×10^{-4}	0.24	26
1.0	1.51	125	385.78×10^{-4}	0.15	63
2.0	2.15	281	512.92×10^{-4}	0.07	179
3.0	2.60	391	519.33×10^{-4}	0.04	317

[a] Gd conc. 3 wt% $\eta = 1$ $\tau d = 4.1$ msec; excitation 273 nm; Gd emission ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$; Sm emission ${}^4G_{5/2} \rightarrow \sum {}^6H_i$.

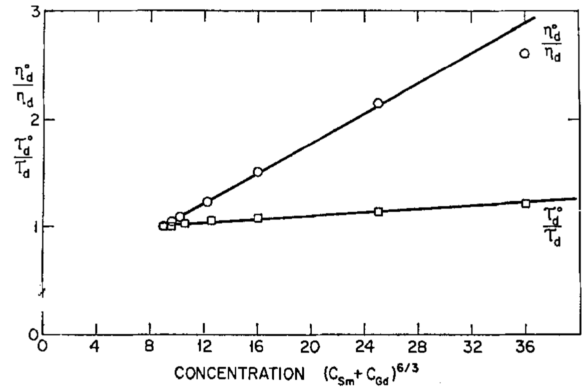

FIG. 5. η°/η and τ°/τ of gadolinium versus $(C_{Sm}+C_{Gd})^{6/3}$.

is given in Table III. The concentration dependence of the quantum efficiency of the level $^4P_{3/2}$ to which the energy transfer occurs $\eta_B^{(c)}$, is presented in Table V.

The decay time of Gd^{3+} fluorescence is a simple exponential with a value of 4.1 msec, which decreases in presence of Sm^{3+} remaining a simple exponential: the ratios of the intensities of pure Gd^{3+} to Gd^{3+} in presence of various concentrations of Sm^{3+}, η°/η is compared to τ°/τ where τ° is the decay constant of pure Gd^{3+} and τ the decay constant in presence of Sm^{3+}, and are presented in Fig. 5 versus square of sum of concentration.

The τ°/τ ratio does not decrease in the same way as η°/η similarly to what was observed previously (*1*) for Gd^{3+} and Tb^{3+}.

Energy transfer. The behaviour of the decay time of Gd^{3+} on concentration of samarium indicates that the decrease is a result of nonradiative energy transfer between gadolinium and samarium.

An additional evidence for energy transfer is the appearance of a Gd^{3+} excitation band at 273 nm in the excitation spectrum of Sm^{3+} in the presence of Gd^{3+}; this is presented in Fig. 2.

The probability of energy transfer obtained by means of formulae (5) and (7) are presented in Table V.

For P_{1C} (obtained by 5) the decrease of the 312 nm fluorescence of Gd^{3+} excited at 273 nm was used and for P_{1C} (calculated by formula 7) the increase of Sm^{3+} fluorescence excited at 273 nm.

The plot of P, the energy transfer probability (obtained by both methods) versus square of sum of the concentrations of samarium and gadolinium is presented in Fig. 6. This graph shows a

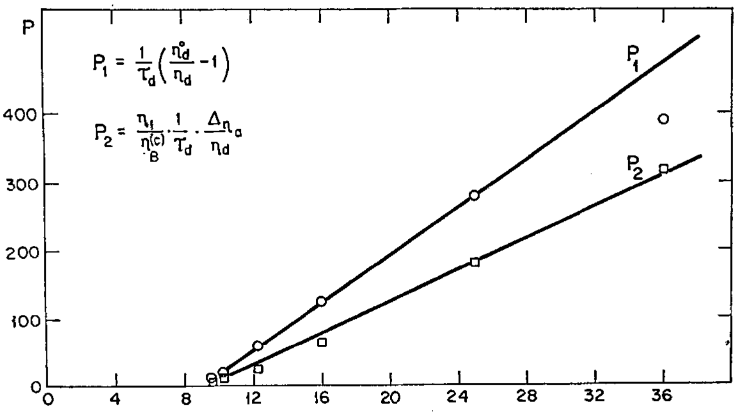

FIG. 6. Probability of energy transfer versus $(C_{Sm}+C_{Gd})^{6/3}$. P_1 calculated from decrease of Gd^{3+} fluorescence. P_2 calculated from increase of Sm^{3+} fluorescence.

linear dependence. In a similar plot $P \propto (C_{Gd} + C_{Sm})^{8/3}$ deviation from linearity was observed.

We conclude therefore that the energy transfer between samarium and gadolinium which occurs between the ^6P multiplets of Gd^{3+} and the ^4P multiplets of Sm^{3+} arises from dipole–dipole interaction as predicted by formula (2) (Dexter). The experimental values are higher by about four orders of magnitude than those obtained by using formula (2) and the experimentally obtained overlap: here again we come to the conclusion that the energy transfer is assisted by the phonons of the glass in a similar way as the transfers obtained by Gd–Tb, Sm–Eu and Tm–Er.

In conclusion: (a) nonradiative energy transfer between Gd^{3+} and Sm^{3+} occurs in borate glass; (b) the transfer takes place between the ^6P multiplet of Gd^{3+} and the ^4P multiplet of Sm^{3+}; (c) the transfer is dipole–dipole in character; (d) the transfer is assisted by the phonons of the glass; (e) the absolute values of the transfer are of the same order of magnitude as those obtained for Gd–Tb, Sm–Eu and Tm–Er; (f) The cross-relaxation in Sm^{3+} is decreased by the presence of gadolinium. The mechanism of energy transfer between Gd^{3+} and Sm^{3+} does not seem, however, to depend on the concentration of Sm^{3+}.

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