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Energy Transfer between Trivalent Rare-Earth Ions in Inorganic Solids

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The purpose of the paper is to clarify the mechanism of excitation energy transfer between unlike trivalent rare-earth ions in inorganic solids. We have measured the manner in which the intensities of the luminescences of $Tb^{3+}({}^{b}D_{4} \rightarrow {}^{7}F_{5})$ and $Eu^{3+}({}^{b}D_{0} \rightarrow {}^{7}F_{2})$ are quenched and the decay rates are made faster by the coexistence of other kinds of trivalent rare-earth ions as a result of energy transfer. As the host material, calcium metaphosphate glass was used. The combination of Tb³⁺ donor and Nd³⁺ acceptor was studied most in detail. The results are discussed in terms of the resonance theory of energy transfer, and the experimental data are analyzed using the numerical calculations of the theory recently made by Inokuti and Hirayama. The overlap integrals of donor emission spectra with acceptor absorption spectra were estimated from the data of spectral measurements. Among the resonance mechanisms due to various electrostatic multipole interactions, the dipole-quadrupole interaction gave the best fit between theory and experiment. The transfer due to the exchange interaction was inferred not to be operative. It has been finally concluded that the mechanism of the energy transfer between unlike trivalent rare-earth ions in inorganic solids is predominantly governed by the dipole-quadrupole interaction.

I. INTRODUCTION

Trivalent rare-earth ions doped in inorganic solids exhibit luminescence due to the intraconfigurational transitions of the 4f electron shell. In recently developed studies on this type of luminescence it has been recognized that the luminescence intensities of various trivalent rare-earth ions are sometimes enhanced or quenched by the coexistence of other kinds of trivalent rare-earth ions.¹⁻¹⁹ These phenomena have attracted the deep interest of a number of investigators; it has

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been concluded that these phenomena take place as a result of the nonradiative transfer of excitation energy from a rare-earth ion behaving as an energy donor to another rare-earth ion behaving as an energy acceptor. Also it must be noted that these phenomena have a significant application to the research and development of laser materials. It has been demonstrated that as a result of the utilization of these phenomena it is possible to remarkably reduce the threshold energy of laser oscillation in some solid laser materials.4,20

The mechanism which governs the energy-transfer process between trivalent rare-earth ions has been the subject of several papers^{1-5,21,22} published lately. Van Uitert and his co-workers^{1,21,22} extensively studied this process, and developed very interesting and suggestive arguments on the mechanism. They stated that in many cases the energy transfer is interpreted by way of the resonance-transfer mechanism due to the electrostatic multipole interaction, although in some cases such as the self-quenching of the Eu³⁺ luminescence nonresonant exchange mechanism is active. To date, however, a firm identification of the mechanism of this energy transfer has not been possible. The present work has been undertaken to clarify this problem. Some of the preliminary results were already reported briefly.23

The Tb³⁺ and Eu³⁺ ions were chosen as the energy donors to be investigated, since these two rare-earth ions show bright visible luminescence strong enough for making precise measurements. As the energy acceptors, almost all of trivalent rare-earth ions were examined. As the host material, calcium metaphosphate glass was used. There are some advantages in using

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glasses rather than single crystals as the host material in the present investigation. Namely, it is easy to prepare samples with fairly high doping concentrations and also samples large enough for the measurement of absorption spectrum. Furthermore, the condition of the random distributions of dopants is easily realized. The resonance mechanism of energy transfer is considered, in its nature, essentially independent of the symmetry of the crystal field around rare-earth ions. Therefore, the conclusion obtained with glass samples can be very useful and pertinent in the case of crystals.

We have made measurements of the changes in the luminescence intensities and decay rates of the energy donors. In other words, we have measured the manner in which the intensities of the luminescences of the energy donors, i.e., Tb³⁺ $({}^{5}D_{4} \rightarrow {}^{7}F_{5})^{24}$ and Eu³⁺ $({}^{5}D_{0} \rightarrow {}^{7}F_{5})^{24}$ ${}^{7}F_{2}$), are quenched and the decay rates are made faster by the coexistence of the energy acceptors, i.e., other kinds of trivalent rare-earth ions. The combination of Tb³⁺ and Nd³⁺ has been studied most in detail. The experimental results have been analyzed in terms of the theory of energy transfer due to resonance mechanism.

This paper is composed of four parts. In the next section, the experimental procedures are described. In Sec. III, the theoretical background necessary for the analysis of the experimental results is given, surveying the results of the theoretical and numerical calculations of the resonance transfer theory^{25,26} recently made by Inokuti and Hirayama.^{27,28} In Sec. IV, the experimental results are described along with their theoretical analysis. Further discussions of the results are presented in Sec. V.

II. EXPERIMENTAL PROCEDURES

A. Samples

All the measurements were made with block samples of calcium metaphosphate $[Ca(PO_3)_2]$ glass doped with trivalent rare-earth ions. Reagent-grade calcium dihydrogen phosphate was mixed with trivalent rare-earth oxides and phosphoric acid. The mixture was dehydrated and melted in a semi-sintered alumina crucible by heating it at 1200°C for 30-40 min. Then the crucible was taken out of the furnace, and the molten contents were dropped onto a gypsum plate. Thus a glass sample 10-15 mm in diameter and 5-7 mm thick was obtained.

The following series of samples were prepared and

used in the measurements. The contents of dopants are shown in cationic mole ratio.

(a) Tb-RE series— $Ca(PO_3)_2$: Tb_{0.03}(RE)_{0.03}, RE = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, or Yb. (b) Tb-Nd series— $Cs(PO_3)_2$: Tb_{0.03}Nd_xGd_{0.03-x}, x=

0.001, 0.003, 0.006, 0.01, 0.012, 0.015, 0.021, 0.024, or 0.03.

(c) Eu-RE series— $Ca(PO_3)_2$: Eu_{0.03}(RE)_{0.03}, RE = La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Tm, or Yb.

(d) RE series— $Ca(PO_3)_2$: (RE)_{0.03}, RE=Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, or Yb.

In the case of (b) series, Gd³⁺ ion was added simultaneously in order that the total content of rare-earth ions was 0.06 mole/mole throughout the series. It was confirmed that Gd^{3+} ion gives no effect on the Tb^{3+} luminescence intensity with the excitation method used here. Further it was ascertained from spectroscopic properties that all the rare-earth ions doped are in the trivalent state.

B. Spectral Measurements

All the experimental measurements were performed at room temperature. The emission spectra of Tb³⁺ and Eu³⁺ used as the energy donors were measured in the visible region with the combination of a Kipp and Zonen double-prism monochromator (slitwidth: 0.07 mm) and a photomultiplier, RCA 1P21 or cooled RCA 7102. The effective spectral width of the monochromator was about 5 A in 5000-6000-Å region. The calibration for the spectral sensitivity of the measuring system was made by using a standard tungsten lamp made by the U.S. National Bureau of Standards.

In order to observe the spectrum of the emission starting from the lowest excited state of interest, excitation was made by monochromatic light that excites directly the lowest excited state, i.e., for Tb³⁺ 4800-Å light due to ${}^{7}F_{6} \rightarrow {}^{5}D_{4}$ transition and for Eu³⁺ 5800-Å light due to ${}^7F_0 \rightarrow {}^5D_0$ transition. These monochromatic lights were obtained from a 500-W xenon discharge lamp by using suitable interference filters. Since the intensities of these monochromatic lights were fairly weak, the observed spectra were not very accurate. Then the measurement was also made under the excitation of a strong 3650-A light from a 100-W mercury lamp. By comparing these two kinds of the emission spectra, it was possible to obtain an accurate spectrum of the emission from the lowest excited state.

Absorption spectra in the near-infrared and visible region were taken for all the rare-earth ions used with a Cary Model 14 spectrometer with a resolving power of about 2 Å.

C. Emission Intensity

The measurements of the change of emission intensity were made with respect to the strongest line in the emission spectra; i.e., for Tb³⁺ the 5400-Å (${}^{5}D_{4} \rightarrow {}^{7}F_{5}$)

²⁴ See the diagram by G. H. Dieke, in American Institute of Physics Handbook, D. E. Gray et al., Eds. (McGraw-Hill Book Co., New York, 1963), 2nd ed., pp. 7-39.
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line and for Eu³⁺ the 6100-Å (${}^{5}D_{0} \rightarrow {}^{7}F_{2}$) line. The emission line to be observed was picked up by the combination of color filters and an interference filter (half-width: 7 m μ). For excitation, the monochromatic light that excites directly the emitting state was used in order to eliminate complexities which might appear if higher excited states are involved. This monochromatic light, having an effective spectral width of 10 A, was obtained by the combination of the 500-W xenon lamp and the Kipp and Zonen double monochromator.

In case of Tb^{3+} , the emission and absorption lines to be measured were considerably separated, so that there was no anxiety that the emission light being observed might contain excitation light. However, in case of Eu^{3+} , the emission and absorption lines are close, so that precise measurement of the emission intensity was rather difficult.

The anxiety that the observed donor emission intensity might contain the emission of the acceptor could be eliminated by performing the blank test of using the (d) series samples singly doped with rare-earth ions. In case of the Eu-Pr system, this anxiety was justified, and reliable data could not be obtained.

D. Luminescence Decay

The decay rate of the donor luminescence was measured by using pulse light excitation. The source was an Edgerton FX-3 xenon flash lamp which has the duration of 2 μ sec and the energy of 1 J/flash when operated at 10 kV. Also in this case monochromatic excitation to the emitting state was made by means of color filters and an interference filter. Only the strongest line in the emission was observed as in the case of the emission intensity measurements. The emission was detected by an RCA 931A photomultiplier connected to Tektronix 531 syncroscope, and the decay curve appearing on the screen was photographed.

Blank tests were performed by using the (d) series samples. It was confirmed that the Pr^{3+} red emission which interfered with the intensity measurement of the Eu-Pr sample as mentioned has by far faster decay time than the Eu³⁺ red emission and so it does not hinder the measurement of the decay time of Eu³⁺.

III. THEORETICAL BACKGROUND

As is well known, Förster,²⁵ and further Dexter,²⁶ developed the theory for the transfer of excitation energy due to resonance mechanism. Recently, Inokuti and Hirayama²⁷ investigated in detail the resonance energy transfer due to the electrostatic multipole and exchange interactions in systems in which many acceptors are randomly distributed around a donor. They made precise numerical calculations on the yield and decay time of the luminescence of the energy donor as functions of the concentration of the energy acceptor, and presented the relationships among these quantities which enable one to analyze experimental data in a

quantitative manner and thereby to decide the type of interaction responsible for resonance transfer. Some parts of their results which are necessary for the analysis of our present experimental data are briefly described below.

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 according to the following equation:

$$\phi(t) = \exp\left[-\frac{t}{\tau_0} - \Gamma\left(1 - \frac{3}{s}\right) \frac{C}{C_0} \left(\frac{t}{\tau_0}\right)^{3/s}\right], \quad (1)$$

where C is the concentration of acceptor, C_0 is the "critical transfer concentration" of acceptor as defined below, τ_0 is the decay constant of donor luminescence in the absence of acceptor, and s=6, 8, and 10 corresponding to the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole²⁹ interactions, respectively. The critical transfer concentration C_0 is defined from the critical transfer distance R_0 as $C_0=3/4\pi R_0^3$. R_0 is the distance of a donor-acceptor pair at which the probability of energy transfer from the donor to acceptor becomes equal to the probability given as $1/\tau_0$, in other words to the probability of the internal (radiative and nonradiative) transitions of the donor.

The emission intensity of the donor under continuous excitation can be calculated with Eq. (1) as

$$\frac{I}{I_0} = \tau_0^{-1} \int_0^\infty \phi(t) \, dt, \tag{2}$$

where I_0 is the intensity in the absence of the acceptor. Inokuti and Hirayama^{27,28} made numerical calculations of I/I_0 as the function of C/C_0 for various interactions. The results for the case of the dipole-quadrupole interaction (s=8) are shown in Fig. 7 in Sec. IV.

The decay curve of donor luminescence given by Eq. (1) is not simple exponential except in the absence of acceptors. As the decay constant of donor luminescence, therefore, Inokuti and Hirayama²⁷ used the "mean duration" and "1/e decay time," and made the calculations of the dependence of these decay constants on the acceptor concentration. In the present investigation, however, we have newly defined another decay constant τ_h given by the following equation because of the experimental convenience:

$$\phi(\frac{1}{4}\tau_0 + \tau_h) = \frac{1}{2}\phi(\frac{1}{4}\tau_0). \tag{3}$$

Although this definition is rather complicated and has no simple physical meaning, it was possible by its use to estimate the values of the decay constant more accurately than using the mean duration or 1/e decay time. We have performed the numerical calculation of the dependence of τ_h on the acceptor concentration by using Eq. (1). The result for the case of the dipole-

²⁰ D. L. Dexter and J. H. Schulman, J. Chem. Phys. 22, 1063 (1954).



FIG. 1. Emission spectrum of Tb^{3+} (0.03 mole/mole) in Ca(PO₃)₂ glass at room temperature. Only the emission from the lowest excited state ${}^{5}D_{4}$ of Tb^{3+} is shown. Emission intensity is represented by emitted photon number in an arbitrary unit. The terminating level is shown on each line.

quadrupole interaction is shown in Fig. 7 in Sec. IV.

The critical transfer concentration of acceptor C_0 reflects the property of overlap integral S according to the following relation in the case of the multipole interactions:

$$C_0 = k S^{-3/s},\tag{4}$$

where k is a constant independent of the species of acceptor. The overlap integral S to be used in this case is defined as,

$$S = \int_0^\infty \frac{I(E)\sigma(E)}{E^{s-2}} dE,$$
 (5)

where I(E) is the emission spectrum of the donor normalized as

$$\int I(E) dE = 1,$$

and $\sigma(E)$ is the absorption spectrum of the acceptor expressed by absorption cross section. On the basis of Eq. (4), one can express the emission intensity and decay time of donor as a function of the overlap integral.

Inokuti and Hirayama²⁷ further pointed out that in order to decide the type of the interaction responsible for resonance transfer, it is very useful and reliable to make a comparison between theory and experiment with respect to the relationship between the intensity and



decay constant of donor luminescence in a series of samples with different acceptor concentrations. The calculation of the relationship between I/I_0 and τ_h/τ_{h0} was performed for the cases of the various multipole interactions; the results are shown in Fig. 6 of Sec. IV.

IV. EXPERIMENTAL RESULTS AND THEIR ANALYSIS

The emission spectra of Tb^{3+} and Eu^{3+} are shown in Figs. 1 and 2, respectively. These emission spectra involve only the lines starting from the lowest excited



FIG. 3. Solid lines are absorption spectra $\sigma(E)$ of Er^{3+} , Nd^{3+} , and Ho^{3+} (0.03 mole/mole) in $Ca(PO_3)_2$ glass at room temperature. The terminating level is shown on each line. Dotted lines are the overlap of the absorption spectra with the Tb^{3+} emission spectrum shown in Fig. 1, i.e., $I(E)\sigma(E)$.

state, i.e., ${}^{5}D_{4}$ for Tb³⁺ and ${}^{5}D_{0}$ for Eu³⁺. In Figs. 3-5 are shown the absorption spectra of rare-earth ions behaving as acceptors.

Both the absorption and emission spectral lines in these glass samples are by far broader than in the case of ordinary crystalline matrices. However, since these linewidths are larger than the effective slitwidths of the spectrometers used in the measurements, it is obvious that these widths represent the actual ones. These large widths are caused by the inhomogeneous broadening due to the fact that the site occupied by each rare-earth ion in glass is slightly different in its nature of crystal field. The positions of the absorptions and emission lines agree well with the energy-level diagrams given for trivalent rare-earth ions in crystalline matrices.²⁴ This fact gives the confirmation that all kinds of these rare-earth ions are in the trivalent state. The characters of the transitions responsible for these absorption and emission lines are not well understood. However, it is considered that electric dipole transition induced by a noncentrosymmetric crystal field or by the coupling with phonons is mostly responsible, although magnetic dipole transition is also sometimes involved.

From these emission I(E) and absorption spectra $\sigma(E)$, the overlap integral S defined by Eq. (5) can be estimated. In Figs. 3-5, quantity of $I(E)\sigma(E)$ are



FIG. 4. Solid lines are absorption spectra of Yb³⁺, Pr³⁺, and Sm^{3+} (0.03) mole/mole) in Ca(PO₃)₂ glass at room temperature. Dotted lines are the overlap of the absorption spectra with the Tb³⁺ emission spectrum.

shown by dotted lines for the case of the Tb-RE series [(a) series]. It is noted that $I(E)\sigma(E)$ changes by three orders of magnitude in this series. The overlap integral estimated from these figures is used later in the analysis of the experimental results.

As already mentioned, the combination of Tb³⁺ donor and Nd³⁺ acceptor was studied most in detail. The results for this combination are described first. In Fig. 6 the experimentally obtained relationship between the normalized emission intensity I/I_0 and decay constant τ_h/τ_{h0} of Tb³⁺ in the Tb-Nd (b) series is shown by circles. The normalization is made with respect to the values for the case of no Nd³⁺ acceptor. The decay curve



F1G. 5. Solid lines are absorption spectra of Eu^{3+} , Tm^{3+} , and Dy^{3+} (0.03 mole/mole) in $\mathrm{Ca}(\mathrm{PO}_3)_2$ glass at room temperature. Dotted lines are the overlap of the absorption spectra with the Tb^{3+} emission spectrum.

of the Tb³⁺ emission in the case of no Nd³⁺ acceptor is, as predicted by Eq. (1), exactly simple exponential with τ_0 of 2.3 msec. This gives 1.6 msec for $\tau_{h0} (= \tau_0/\log 2)$. The data of the decay curves are presented later. Three solid curves in Fig. 6 represent the results of the theoretical calculations of the $I/I_0 - \tau_h/\tau_{h0}$ relationship for the various electrostatic multipole interactions. It is observed that the theoretical curve for s=8 gives the best fit with the experimental results, indicating that



FIG. 6. Three solid curves show the theoretically calculated relationship between the emission intensity I/I_0 and decay constant τ_h/τ_{h0} of donor luminescence for the multipole interactions. The curves marked with s = 6, 8, and 10 correspond, respectively, to the dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. Circles show experimental data for the Tb-Nd donor-acceptor series (b) in Ca (PO₈)₂ glass.



FIG. 7. Solid curves show the theoretically calculated dependence of the emission intensity I/I_0 and decay constant τ_h/τ_{h0} of donor luminescence on acceptor concentration C/C_0 for the case of the dipole-quadrupole interaction (s=8). Circles show experimental data for the Tb-Nd donor-acceptor series (b).

the dipole-quadrupole interaction is most probably operative.

In Fig. 7 the same I/I_0 and τ_h/τ_{h0} data for Tb³⁺ as in Fig. 6 are plotted as circles arainst the Nd³⁺ concentration C. The two solid curves represent the results of the theoretical calculations for the case of s=8. The scale of the abscissa for the theoretical curves was suitably adjusted so as to be able to obtain the best fit of the theoretical I/I_0 curve with the experimental I/I_0 values. It is noticed that both I/I_0 and τ_h/τ_{h0} data are satisfactorily represented by the theoretical curves. From this figure the critical transfer concentration C_0 of the Tb-Nd system is found to be 0.017 mole/mole. It was further found to be rather impossible to fit the data with theoretical curves for the cases of s=6 and s=10.

Figure 8 presents the experimental $I/I_0 - \tau_h/\tau_{h0}$ relationship in the Tb-RE (a) series where Tb³⁺ behaves



FIG. 8. Relationship between I/I_0 and τ_h/τ_{h0} for the Tb-RE donor-acceptor series (a). Solid curves show the theoretically calculated relationship. Open circles show experimental data, and closed circles for Pr^{3+} and Ho^{3+} show the results with the ground samples used to ascertain the feedback effect of excitation energy (see the text, Sec. V).

as an energy donor while other various rare-earth ions play the roll of acceptors. The normalization of the values of I and τ_h was made by using samples containing La³⁺ or Gd³⁺ of 0.03 mole/mole as an acceptor rareearth ion. It was ascertained that both La³⁺ and Gd³⁺ are ineffective for the luminescence of Tb³⁺. From the figure it appears that as a whole the theoretical curve for the case of s=8 gives the best fit with the experimental data, although in the case of the Pr³⁺, Er³⁺, and Ho⁸⁺ acceptors the deviation from the curve for s=8is considerable. The reason for this deviation is discussed later.

The same data as in this figure are plotted against the overlap integral S with the acceptor in Fig. 9 by circles. The overlap integrals were estimated from the data of $I(E)\sigma(E)$ shown in Figs. 3-5 by using Eq. (5).



FIG. 9. Dependence of I/I_0 and τ_h/τ_{h0} on overlap integral S (arbitrary unit) for the Tb-RE donor-acceptor series(a). Open and dotted circles show experimental data, and closed circles for the decay time of Pr^{3+} and Ho^{3+} show the results with the ground samples used to ascertain the feedback effect of excitation energy (see the text, Sec. V). Solid curves are theoretically calculated ones for the case of the dipole-quadrupole interaction (s=8).

The unit of S is arbitrary. The overlap integral and critical transfer concentration are related by Eq. (4). Therefore, one can transfer the observed relationship of I/I_0 and τ_h/τ_{h0} versus S to the diagram of I/I_0 and τ_h/τ_{h0} versus C_0 as shown in Fig. 9. We know the theoretical relations of I/I_0 and τ_h/τ_{h0} versus C/C_0 . These relations can be used also in the case, such as the present Tb-RE series, where C is fixed but C_0 is changed. In this way one can make a theoretical analysis of the experimental data shown in Fig. 9.

The theoretical curves for the case of s=8 are shown in the figure by solid lines. The agreement between theory and experiment is fairly good, although there are some deviations in the decay times of Pr^{3+} and Ho^{3+} acceptors. As seen from Fig. 8, there is a deviation also in case of Er^{3+} .

This considerable deviation can be explained in the

following way. As seen from the energy-level diagram²⁴ of trivalent rare-earth ions, these three acceptor ions have excited states with almost the same energy as the ${}^{5}D_{4}$ emitting level of Tb³⁺. The absorptions for these excited states are found to be rather strong. Suppose that a Tb³⁺ ion is excited into the ${}^{5}D_{4}$ excited state and shows the emission, then some part of the emitted light will be absorbed by these acceptor ions. The excitation energy stored in these ions will be returned to the Tb³⁺ ion by radiative or nonradiative energy transfer. This feedback of excitation energy should cause the apparent prolongation of the decay time of Tb³⁺. In order to ascertain this explanation, the glass block sample was ground, and the decay time was measured. In the ground sample, since the reabsorption effect of the Tb³⁺ emission, and therefore the feedback effect, will be less effective than in the block sample, one expects that the apparent prolongation effect is not as remarkable as in the block sample. The results of the measurements with the ground samples are shown by closed circles in Figs. 8 and 9. As is expected, the ground samples show shorter decay time, giving the evidence that the abovementioned explanation is correct.

Figure 10 presents the results of I/I_0 and τ_h/τ_{h0} of Eu³⁺ donor in the Eu-RE (c) series. The values of τ_0 and τ_{h0} are 2.2 and 1.5 msec, respectively. The solid lines are theoretical curves for s=8. Although the agreement between theory and experiment is not as good as in the case of the Tb³⁺ donor, it appears that the results of the Eu³⁺ case may also be interpreted by the dipole-quadrupole transfer mechanism.

Figure 11 presents the decay curves of the Tb^{3+} donor in the Tb-Nd (b) series. The experimental curves are shown by dotted circles. It is observed that in the absence of the Nd³⁺ acceptor the Tb³⁺ decay is exactly simple exponential with a time constant of 2.3 msec,



FIG. 10. Dependence of I/I_0 and τ_h/τ_{h0} on overlap integral S (arbitrary unit) for the Eu-RE donor-acceptor series(c). Open and dotted circles show experimental data, and solid curves are theoretically calculated ones for the case of the dipole-quadrupole interaction (s=8).



FIG. 11. Decay curves of the Tb^{3+} emission at room temperature in the Tb-Nd donor-acceptor series(b). Dotted circles show experimental curves, and solid lines are theoretically calculated ones for the case of the dipole-quadrupole interaction (s=8). The concentration of the Nd³⁺ acceptor is shown besides the curves in units of mole/mole.

while it deviates substantially from the simple exponential function with increasing the Nd^{3+} concentration.

One can calculate the theoretical decay curve with Eq. (1). As mentioned above, the dipole-quadrupole interaction is the most probable mechanism in the $Tb^{3+}-Nd^{3+}$ system. The theoretical curves calculated by using s=8, $C_0=0.017$ mole/mole (as obtained from Fig. 7) and $\tau_0=2.3$ msec are shown in the figure by solid lines. We would like to emphasize that the agreement between theory and experiment is really satisfactory.

V. DISCUSSION

So far we have discussed and analyzed the experimental results assuming that the electrostatic multipole interactions are responsible for the energy transfer. However, according to the resonance-transfer theory, not only the multipole interactions but also the exchange interaction can be responsible. Then we have to examine whether the transfer mechanism due to the exchange interaction contributes to the present case.

As Dexter²⁶ stated, and also as the results of the calculations made by Inokuti and Hirayama^{27,28} indicate, it is very difficult to distinguish the dipole-quadrupole and quadrupole-quadrupole interactions from the exchange interaction with the analysis on the dependence of the intensity and decay time of donor emission on acceptor concentration. However, there are two ways to do this. The first is to take the theoretically derived correlation of the energy-transfer probability with the absorption oscillator strength of the acceptor into consideration. As discussed by Dexter,26 the transfer probability is proportional to the overlap integral of the donor emission spectrum and acceptor absorption spectrum. There is, however, a difference with respect to the definition of the overlap integral between the cases of the multipole and exchange interactions. Namely, in the case of the multipole interactions the absorption spectrum of acceptor involved in the integral is that expressed by the absorption oscillator strength, while in the case of exchange interaction the absorption spectrum normalized as

 $\int \sigma(E) dE = 1$

is used.

In the Tb-RE and Eu-RE series, the emission intensities and decay times of the Tb³⁺ and Eu³⁺ donors may be satisfactorily interpreted, as shown in Figs. 9 and 10, by assuming the dipole-quadrupole interaction and using the overlap integrals involving the oscillator strengths. As is seen from Figs. 3–5, the variation of absorption oscillator strength among the various rareearth ions is considerable. Thus, it is said that the energy-transfer probability between unlike rare-earth ions strength of the acceptor. This implies that the multipole interaction is operative.

The second way to distinguish between the multipole and exchange interactions is to estimate the "effective average Bohr radii" L, as defined by Dexter,26 of donor and acceptor by assuming the exchange interaction and to examine whether they have appropriate values. It should be pointed out that the experimental results for the Tb-Nd series as shown in Fig. 7 can be interpreted, in terms of the theoretical calculations of Inokuti and Hirayama,^{27,28} not only by the dipole-quadrupole interaction but also by the exchange interaction. In the case of the latter interaction, the transfer probability is proportional to an exponential function of the distance of a donor-acceptor pair; the dependence of the emission intensity and decay time of donor on acceptor concentration is expressed^{27,28} by a parameter γ . This is defined by $\gamma = 2R_0/L$, where R_0 is the critical transfer distance as described already. Fitting the Tb-Nd data shown in Fig. 7 with the exchange interaction theory leads to $\gamma = 8$. This value of γ gives L = 3 Å, if one uses the experimentally obtained value 12.1 Å of R_0 (see below). This estimation of L seems too large for the 4f electrons of rare-earth ions, if one takes it into account that the ionic radii of trivalent rare-earth ions are about 1 Å and further that the 4f orbit is mechanically shielded by the outer 5s and 5p orbits.

On the basis of these arguments, one may rule out the possibility that the exchange interaction is operative, or one can at least conclude that even if there is some contribution of the exchange interaction, it is very small. The results of the analysis of the experimental data presented in Figs. 6–11, especially in Fig. 6, unambiguously indicate that among the various multipole interactions the dipole-quadrupole interaction is most probable. Then, as the conclusion, one can evidently say that the energy transfer between unlike trivalent rare-earth ions observed here is caused by the resonance due to the dipole-quadrupole interaction.

One might consider that the above-mentioned conclusion is rather strange, if one notices the results of order estimation made by Dexter²⁶ that the transfer probability decreases according to the order of the dipole-dipole, dipole-quadrupole, and quadrupolequadrupole interactions. Axe and Weller⁵ pointed out that this order of transfer probability may be inverted in some special cases such as those of rare-earth ions. In the case of the intraconfigurational transitions of 4felectrons in rare-earth ions, dipole transitions are nominally forbidden; the forbiddenness is removed by the perturbation of noncentrosymmetric crystal field and/or by the coupling with phonons. The oscillator strength of the dipole transition thus allowed is by far smaller than that of the usual allowed ones. This fact may cause, as Axe and Weller inferred, the inversion of the order of the transfer probability.

From the results of the analysis of the experimental data for the Tb-RE and Eu-RE series, it is possible to estimate the critical transfer concentration C_0 for the combination of the Tb³⁺ or Eu³⁺ donor with various other rare-earth ions as the acceptors. This estimation can be made by using any of three kinds of the experimental data, i.e., donor emission intensity, donor decay time, and overlap integral. From the values of C_0 one can calculate the critical transfer distance R_0 by using the value 2.7 of the specific gravity of the glass samples. The results are shown in Table I. In the cases of the Tb-Nd and Tb-Pr systems, R_0 was also estimated from the experimental data of the dependence of the emission intensity of the donor on the concentrations of the acceptors. All the values seem to be reasonable for electrostatic multipole interaction.

In the process of estimating the overlap integral, the energy levels of resonant transition can be found for all the donor-acceptor pairs. For instance, in case of the Tb-Nd series, an excited Tb³⁺ ion is relaxed from the ⁵D₄ level mainly to the ⁷F₄ level interacting with an Nd³⁺ ion, and the Nd³⁺ ion is excited from the ground level ⁴I_{9/2} to ⁴G_{7/2,5/2} level. Such resonant transitions are listed in the last column of Table I for all the donor-acceptor pairs.

VI. CONCLUDING SUMMARY

The mechanism of the energy transfer between unlike trivalent rare-earth ions has been investigated. The change of the emission intensities and decay times of Tb^{3+} and Eu^{3+} ions behaving as donors caused by the coexistence of other rare-earth ions behaving as acceptors was measured. In the case of Tb^{3+} donor and Nd^{3+} acceptor the dependence of these quantities of the donor on the concentration of the acceptor was investigated in detail. Further the dependence of these quantities on the overlap integral of donor emission spectrum with acceptor absorption spectrum was examined. On

Ion	R_0 (Å)				Transition of	
	From emission intensity	From decay time	From overlap integral	From concentration dependence	Donor	Acceptor
From: Tb $({}^{5}D_{4})$	<u> </u>	0				
10: La, Gd, Yb	0	0	0	•••		
Dy	4.6	5.5	4.5	•••	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$	${}^{6}H_{15/2} \rightarrow (F)$
(Tb)	•••	•••	5.3	•••	${}^{5}D_{4} \rightarrow {}^{7}F_{6}$	$^{7}F_{6} \rightarrow ^{5}D_{4}$
Eu	6.9	6.9	6.4	•••	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	${}^{7}F_{0} \rightarrow {}^{5}D_{1}$
Sm	7.0	6.9	6.7	* * *	$^{5}D_{4} \rightarrow ^{7}F_{6}$	${}^{6}H_{5/2} \rightarrow (C)(D)$
Tm	7.5	7.5	7.3	• • •	$^{5}D_{4} \rightarrow ^{7}F_{0,1}$	${}^{3}H_{6} \rightarrow {}^{3}F_{3}$
Pr	9.4	8.4*	9.5	9.0	${}^{5}D_{4} \rightarrow {}^{7}F_{4}$	${}^{3}H_{4} \rightarrow {}^{1}D_{2}$
Er	10.8	10.1ª	10.3	•••	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	⁵ <i>I</i> ₈ → ⁵ <i>S</i> ₂ , ⁵ <i>F</i> ₄
Ho	11.3	10.2ª	11.6	• • •	${}^{5}D_{4} \rightarrow {}^{7}F_{5}$	⁵ <i>I</i> ₈ → ⁵ <i>S</i> ₂ , ⁵ <i>F</i> ₄
Nd	12.3	12.3	12.4	12.1	${}^{5}D_{4} \rightarrow {}^{7}F_{4}$	⁴ <i>I</i> _{9/2} → ⁴ <i>G</i> _{5/2}
From: Eu (⁵ D ₀)						
To: Gd, La	0	0	0	•••		
Sm	3.7	•••	•••	• • •		
Yb	4.8	5.1	3.3	• • •	${}^{5}D_{0} \rightarrow {}^{7}F_{6}$	${}^{6}H_{15/2} \rightarrow {}^{6}F_{7/2}$
Dy	6.4	7.1	7.2	•••	${}^{5}D_{0} \rightarrow {}^{7}F_{5}$	${}^{6}H_{15/2} \rightarrow {}^{6}F_{5/2}$
Ho	8.3	8.1	7.6	• • •	${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	${}^{5}I_{8} \rightarrow {}^{5}F_{5}$
Er	8.5	8.1	7.9	• • •	${}^{5}D_{0} \rightarrow {}^{7}F_{3}$	${}^{4}I_{15/2} \rightarrow {}^{4}F_{9/2}$
Pr	• • •	8.0	9.0	• • •	${}^{5}D_{0} \rightarrow {}^{7}F_{1,2}$	${}^{3}H_{4} \rightarrow {}^{1}D_{2}$
Tm	9.1	8.8	9.4	•••	${}^{5}D_{0} \rightarrow {}^{7}F_{4}$	${}^{3}H_{6} \rightarrow {}^{3}F_{3}$
Nd	12.8	10.5ª	11.5	• * •	${}^{5}D_{0} \rightarrow {}^{7}F_{1}$	${}^{4}I_{9/2} \rightarrow {}^{4}G_{5/2}$

TABLE I. Critical transfer distances R_0 calculated from various experimental data and energy levels of resonant transition for the Tb-RE and Eu-RE series.

^a There is the feedback effect.

the basis of the analysis of the experimental results, it has been concluded that the mechanism of the energy transfer taking place in the optical region between unlike trivalent rare-earth ions in glasses is predominantly governed by the resonance due to the electrostatic dipole-quadrupole interaction, and that the energy transfer due to the exchange interaction is not operative. The resonance mechanism due to the electrostatic multipole interaction is, in its nature, essentially independent of the symmetry of crystal field. Therefore, the conclusion obtained here in the case of glass host may be generally correct for the case of host materials of inorganic solids including crystals, provided that there exists some overlap of the emission spectrum of donor with the absorption spectrum of acceptor and that the characters of the transitions of absorption and emission are the same as in the case investigated here.

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