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Phonon-Assisted Energy Transfer between Trivalent Rare Earth Ions

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Nonresonant phonon-assisted energy transfer between trivalent rare earth ions is studied using Y_2O_3 as the host crystal. The transfer probabilities are obtained from the analysis of the decay rates of donor luminescence for various combinations of donor and acceptor ions in which energy gap, *i.e.* mismatch of energy, is varied in a wide range up to 4000 cm^{-1}. The probabilities are decreased exponentially with the increase of energy gap in agreement with the theory of Miyakawa and Dexter. The observed value of the parameter expressing the exponential dependence agrees with the theoretically estimated value. The temperature dependence of the probabilities presents the direct evidence that the mismatch of energy is compensated by the emission of phonons. It is revealed that the phonon of about 400 cm^{-1} which produces the highest intensity in vibronic sidebands contributes dominantly to the phonon-assisted process.

§ 1. Introduction

It has been pointed out recently that phonon-assisted energy transfer plays an important role in the infrared-to-visible conversion process in some phosphors activated with trivalent rare earth ions.[1-3] By the word of the phonon-assisted energy transfer is meant a nonresonant energy transfer process in which the mismatch of energy between the levels of energy donor and acceptor ions is compensated by the simultaneous emission or absorption of one or more phonons. This energy transfer process is governed by electron-phonon interaction as other vibronic processes are.

Recently, Miyakawa and Dexter[4] have made a unified theoretical treatment for various multiphonon processes involving vibronic transition, multiphonon relaxation transition and phonon-assisted energy transfer, on the basis of the adiabatic approximation and by the use of the generating function method. They have shown that the probabilities of these processes are expressed by very simplified forms, if suitable empirical parameters common to all the processes are used. As a result it was indicated that the probabilities of phonon-assisted energy transfer as well as multiphonon relaxation transition are decreased approximately obeying exponential functions with the increase of energy gap, and that parameters expressing the exponential dependence in these two processes are related with each other. Before the presentation of this theory Moos and his coworkers[5-8] and also Weber[9,10] have revealed experimentally that the multiphonon relaxation rates between $4f^n$ states of trivalent rate earth ions in some crystals show exponential dependences on energy gap. The Miyakawa and Dexter's theory is regarded as giving the theoretical interpretation for these experimental results.

The purpose of the present paper is to investigate in detail the nature of phonon-assisted energy transfer between trivalent rare earth ions in solids. Some of the preliminary results has been already published.[11] We have selected Y_2O_3 as the host crystal for the following reasons. Rare earth ions are easily doped to this crystal and bright luminescence is observed. Further the study on multiphonon relaxation transition has been made with this crystal by Moos and his coworkers and by Weber, and we can use their results. Various combinations of donor and acceptor rare earth ions which have no energy matching between their levels were selected, and the dependence of nonresonant phonon-assisted energy transfer rate on energy gap, *i.e.* mismatch of energy, was measured. The energy transfer rates were obtained by making comparison between the luminescence decay rates of donor ion in the presence and abscence of acceptor ion. The analysis of observed decay curves was made according to the equation given by Inokuti and Hirayama.[12]

It has been revealed that the energy transfer probability decreases obeying an exponential function of energy gap, in agreement with the Miyakawa-Dexter theory. In addition, it has been

indicated that the obtained value of the parameter which governs the exponential dependence on energy gap nearly agrees with the theoretically estimated value. For some combinations of donor and acceptor ions, the temperature dependence of energy transfer rate was measured. The results clearly assure that the observed nonreasonant energy transfer processes are really associated with the simultaneous emisson of phonons. Conclusively saying, the Miyakawa-Dexter theory on phonon-assisted energy transfer is applicable for the system investigated, in other words, the mechanism of the nonresonant energy transfer between trivalent rare earth ions can be interpreted by the phonon-assisted process in the case where the concentrations of donor and acceptor ions are low and the energy gap is less than at least 4000 cm^{-1}.

§ 2. Experimental Procedures

Yttrium oxide of powder crystal was used as the host. The concentration of donor and acceptor rare earth ions were 1 and 4 mol%, respectively. The samples were prepared by heating coprecipitated mixtures of the oxalates of yttrium and rare earths to be doped at 1,000°C for two hours. Purity of yttrium oxide and rare earth oxides used were of four nine besides europium oxide whose purity was of three nine.

As the excitation source for the measurement of luminescence decay, we used a tunable pulsed dye laser Model 1000 made by Avco-Everett Research Laboratory. This laser is operated by the excitation of a nitrogen laser and is tunable in the wavelength range of 355–655 nm. The characteristics of this pulsed dye laser light are that peak power is 4 to 8 kW, pulse duration is 2 to 8 nsec and spectral width is about 0.3 nm. This laser is very useful, since this makes it possible to give strong and direct excitation to any emitting level selected from various excited levels. In the analysis of observed decay curves, we used a theoretical equation, given by Inokuti and Hirayama,[12] for the case of excitation by a flash of light. This equation is based on the assumption that the duration of exciting flash is much shorter than the lifetime of excited level. The characteristics of this dye laser satisfy well this assumption. Emitted light from the sample was selected by a Spex Model-1702 3/4 m grating monochromator with the reciprocal dispersion of 1.1 nm/mm, and was detected by an EMI 9558A photomultiplier. The output was put into a Tektronix Model 545A oscilloscope, and the decay curve was photographed. The measurements were made in the temperature range of 77 to 800 K.

§ 3. Experimental Results and Their Analysis

In the following, we describe first in 3.1 the method used to determine the probability of energy transfer from a donor ion to an acceptor ion. Next in 3.2, we present the results of the measurements on the probabilities of phonon-assisted energy transfer in various combinations of donor and acceptor rate earth ions, and discuss the dependence of the transfer probability on energy gap, *i.e.* mismatch of energy, between the levels of donor and acceptor ions. Finally in 3.3, we show the results of the measurements on the temperature dependence of energy transfer probability.

3.1 Method of the determination of energy transfer probability

In the case of trivalent rare earth ions in solids, dominant ion-ion interaction which governs the energy transfer is considered to be electric multipole interaction such as dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions. One may ignore the possibility of exchange or superexchange interaction, since the $4f$ wavefunction is very much localized so that the overlap of the wavefunctions of ions is very small even between the nearest neighbor sites. Previously, Nakazawa and one of the present authors[13] have indicated experimentally that the resonance energy transfer between trivalent rare earth ions in a glass host is governed by the dipole-quadrupole interaction. Further, there have been found no reliable experimental results which show that exchange or superexchange interaction is operative in the energy transfer between trivalent rare earth ions.

In the case of electric multipole interaction, the dependence of energy transfer probability $n(R)$ on the separation between donor and acceptor ions can be written by

$$n(R)=(R_0/R)^s/\tau_0 , \qquad (1)$$

where R_0 is the critical distance, *i.e.* the distance at which the probability of energy transfer becomes equal to the reciprocal of the lifetime τ_0 of donor level in the absence of acceptor ions, and s is 6, 8 and 10, respectively, for dipole-dipole, dipole-quadrupole and quadrupole-quadrupole interactions. The decay curve of donor luminescence deviates from simple exponential curve in the presence of acceptor ions because of the statistic distribution of acceptor ions in the crystal. In this case, the decay curve $\phi(t)$ under excitation by a flash of light is expressed, according to Inokuti and Hirayama,[12] by

$$\phi(t)=\exp\{-t/\tau_0-\Gamma(1-3/s)(C/C_0)(t/\tau_0)^{3/s}\}\ , \qquad (2)$$

where C is the concentration of acceptor ions and C_0 is the critical concentration related to R_0 by $C_0=3/4\pi R_0^3$. By using lifetime τ_e defined by $\phi(\tau_e)=(1/e)\phi(0)$, one obtains the following expression as energy transfer probability,

$$n(R)=\Gamma(1-3/s)^{-s/3}\tau_e^{-1}(1-\tau_e/\tau_0)^{s/3}\ , \qquad (3)$$

and

$$R=(4\pi C/3)^{-1/3}\ . \qquad (4)$$

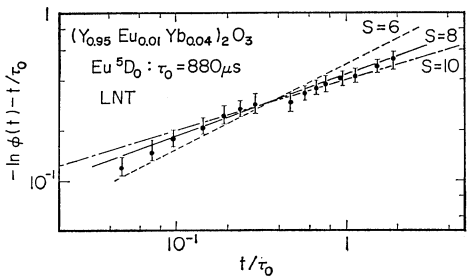

Fig. 1. Decay of luminescence from $^5D_0$ state of Eu^{3+} ion in $(Y_{0.95}Eu_{0.01}Yb_{0.04})_2O_3$ at 77 K expressed by plotting $-\ln\phi(t)-t/\tau_0$ against t/τ_0. As to three straight lines with $s=6$, 8 and 10, see the text.

In order to evaluate energy transfer probability according to eq. (3), one must determine s value suitably. This is made by plotting $-\ln\phi(t)-t/\tau_0$ against t/τ_0 and by measuring the slope. In Fig. 1 is shown, as an example, the result of this plotting in the case where the luminescence decay from $^5D_0$ state of Eu^{3+} ion as a donor is observed in the presence of Yb^{3+} ion as an acceptor. From the comparison with theoretical slopes for $s=6$, 8 and 10 shown in the figure, the value of s is determined to be 8, indicating that the dipole-quadrupole interaction is responsible for the energy transfer. This result it consistent with the conclusion previously given by Nakazawa and Shionoya.[13] The slope of decay curve, however, does not change very drastically with the nature of interaction as shown in the figure. Therefore, the s value determined by this method is not very accurate. Fortunately, however, the energy transfer probability expressed by eq. (3) is rather insensitive to s value, especially if τ_e is much smaller than τ_0. Therefore, in this study, we have assumed the dipole-quadrupole interaction in the calculation of the probabilities of energy transfer for all the combinations of donor and acceptor rare earth ions investigated. This assumption would not cause any serious influence to the results. Thus the transfer probabilities were estimated from the observed values of τ_0 and τ_e by the use of eq. (3) with the assumption of $s=8$.

If energy transfer processes between donor ions themselves, such as so-called excitation migration and cross relaxation processes, take place, it causes the deviation of the decay curve of donor luminescence from eq. (2), and makes the analysis of decay curve difficult. In order to minimize these effects, it is necessary that the concentration of donor ion is as low as possible and the concentration of acceptor ion is much higher than that of donor ion. For the donor concentration used here, *i.e.* 1 mol%, the excitation migration effect may be neglected in the case where the lifetime of donor level is less than millisecond.[14]

3.2 *Energy gap dependence of transfer probability*

According to the Miyakawa-Dexter theory, the probability of phonon-assisted energy transfer is expressed by

$$W_{PAT}(\Delta E)=W_{PAT}(0)e^{-\beta\Delta E}\ , \qquad (5)$$

where ΔE is the energy gap between the levels of donor and acceptor ions and β is a parameter determined by the strength of electron-lattice coupling as well as by the nature of the phonon involved. The above equation has the same form as that for the energy gap dependence of the multiphonon relaxation rate, which is also given by the Miyakawa-Dexter theory as

$$W_{MPR}(\Delta E)=W_{MPR}(0)e^{-\alpha\Delta E}\ . \qquad (6)$$

It is further indicated that the parameter α is given by

$$\alpha=\frac{1}{\hbar\omega}[\ln\{N/g(n+1)\}-1]\ , \qquad (7)$$

and α and β are connected with each other as

$$\beta=\alpha-\gamma\ , \qquad (8)$$

and

$$\gamma=\frac{1}{\hbar\omega}\ln(1+g_b/g_a)\ . \qquad (9)$$

Here, g is electron-lattice coupling constant, suffixes a and b mean donor and acceptor ions, respectively, n is the number of phonons excited at the temperature of the system, $\hbar\omega$ is the energy of phonon which contributes dominantly to these multiphonon processes and N is the number of phonons emitted in the processes, namely,

$$N=\Delta E/\hbar\omega\ .$$

Although the exponential dependence given by eq. (6) is of approximation, its validity has been already verified for the multiphonon relaxation process between $4f^n$ states of trivalent rare earth

Table I. Observed values of τ_0 and τ_e, the decay times of donor luminescence in the absence and presence of acceptor, and calculated rates of phonon-assisted energy transfer for various combinations of donor and acceptor rare earth ions in Y_2O_3 at 77 K.

Donor ion	Donor level excited	Acceptor ion	Transition of energy transfer		Energy gap (cm^{-1})	Decay time		Energy transfer rate (sec^{-1})
			Donor	Acceptor		τ_0(μsec)	τ_e(μsec)	
Sm	$^4G_{5/2}$	Eu	$^4G_{5/2}\rightarrow{}^6H_{5/2}$	$^7F_0\rightarrow{}^5D_0$	600	290±10	87±5	1.7×10^3
Eu	$^5D_0$	Yb	$^5D_0\rightarrow{}^7F_6$	$^2F_{7/2}\rightarrow{}^2F_{5/2}$	1670	880±20	650±20	1.7×10
〃	$^5D_1$	〃	$^5D_1\rightarrow{}^5D_0$	$^2F_{7/2}\rightarrow{}^2F_{7/2}$	1225	77±5	69±5	4.0×10
〃	$^5D_2$	〃	$^5D_2\rightarrow{}^5D_1$	$^2F_{7/2}\rightarrow{}^2F_{7/2}$	1935	29±2	20±2	1.1×10^3
Tb	$^5D_4$	〃	$^5D_4\rightarrow{}^7F_0$	$^2F_{7/2}\rightarrow{}^2F_{5/2}$	4200	990±20	850±20	2.3
Ho	$^5S_2$	Sm	$^5S_2\rightarrow{}^5I_4$	$^6H_{5/2}\rightarrow{}^6H_{13/2}$	190	91±2	5.5±0.5	5.9×10^4
〃	〃	Tm	$^5S_2\rightarrow{}^5I_7$	$^3H_6\rightarrow{}^3F_4$	480	〃	13.6±0.5	1.8×10^4
〃	$^5I_4$	Yb	$^5I_4\rightarrow{}^5I_8$	$^2F_{7/2}\rightarrow{}^2F_{5/2}$	2610	47±5	32±5	4.6×10^2
Er	$^4S_{3/2}$	〃	$^4S_{3/2}\rightarrow{}^4I_{13/2}$	$^2F_{7/2}\rightarrow{}^2F_{5/2}$	1070	88±5	33±2	8.4×10^3
Tm	$^1G_4$	〃	$^1G_4\rightarrow{}^3H_5$	$^2F_{7/2}\rightarrow{}^2F_{5/2}$	1840	42±5	30±2	5.3×10^2

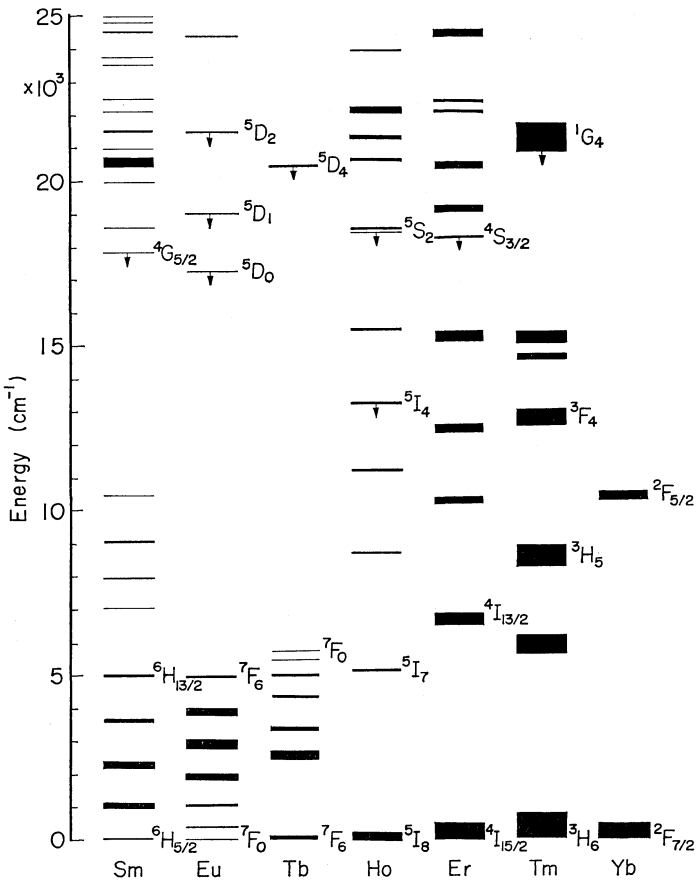

Fig. 2. Energy level diagrams of trivalent rare earth ions used in the present investigation. The observed emitting levels are indicated by arrows.

ions, as mentioned already, by Moos and his coworkers[5-8] and also by Weber.[9,10] They have found that the multiphonon relaxation rates in various rare earth ions in a given host are determined only by the energy gaps. Saying in other words, $W_{MPR}(0)$ and α are independent of the character of $4f^n$ states involved and are dependent only on the nature of the host crystal. These facts

imply that, in the multiphonon processes such as multiphonon relaxation transition, the individual character of $4f^n$ state is smoothed out and only the gross nature is concerned. One can expect a similar situation also for phonon-assisted energy transfer process.

In order to measure the dependence of phonon-assisted energy transfer probability on energy gap, we have selected various combinations of donor and acceptor rare earth ions, as shown in Table I. These combinations were selected so that the spectrum of the luminescence from a certain excited level of the donor ion is not overlapped at all with the absorption spectrum of the acceptor ion. In Fig. 2 is shown the energy level diagram of trivalent rare earth ions used in this study. Here, the energy levels of Eu^{3+},[15] Er^{3+}[16] and Tm^{3+}[16] ions are those determined for Y_2O_3 host by other investigators, but the levels of other ions are quoted from the Dieke's diagram[17] determined for $LaCl_3$ host.

In Table I are shown the observed values of τ_0 and τ_e which are, as mentioned already, the decay times of the luminescence emitted from a certain excited level of a donor ion in the absence and presence of an acceptor ion, respectively. These decay times were measured, as mentioned already, by directly exciting the donor excited level to be observed. Energy transfer probabilities were estimated, on the basis of the assumption of dipole-quadrupole interaction, for the donor-acceptor separation given by eq. (4), which is 10A for the acceptor concentration of 4 mol%. In the table are also listed the manners of the transition in the donor and acceptor ions responsible for the energy transfers and the values of the energy gap. It is assumed there that the transitions take place between energy levels that give the minimum energy

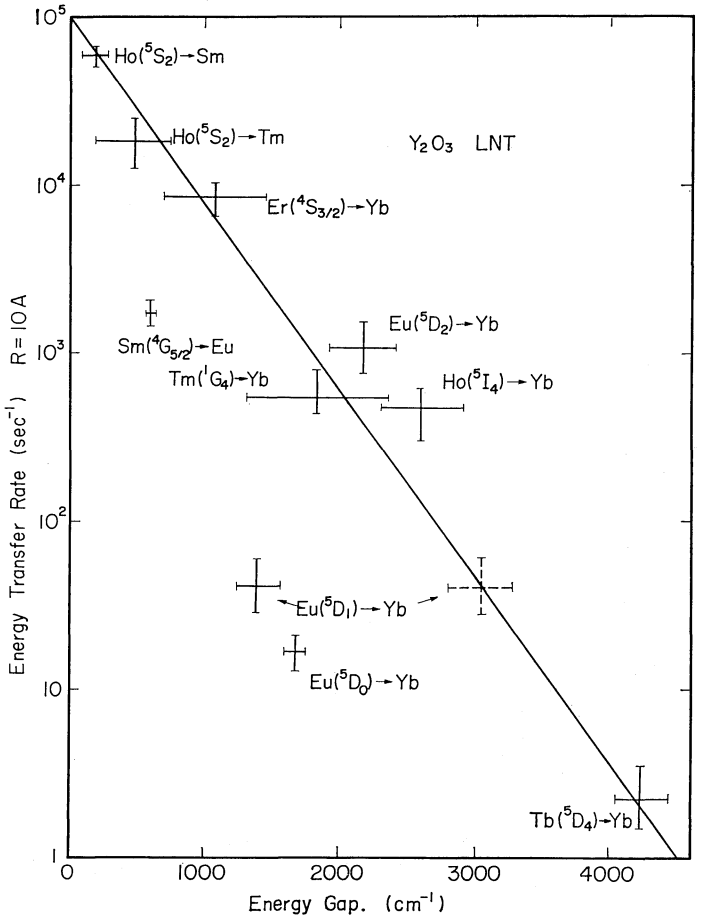

Fig. 3. Energy gap dependence of the rates of phonon-assisted energy transfer between rare earth ions in Y_2O_3 at 77 K. The energy transfer rates are evaluated for the separation of 10A between donor and acceptor ions. The solid line is the best fit for the Miyakawa-Dexter theory with the slope of $\beta=2.5\times10^{-3}$ cm. As to the solid and dashed points for Eu($^5D_1$)→Yb, see the text.

gaps. In the calculation of the minimum energy gaps, the lowest energy state in the crystal field splitting levels of the J multiplet is used for the initial state, but the medium energy state is used for the final state. The transition of $Yb\,^2F_{7/2} \rightarrow Yb\,^2F_{7/2}$, which appears in some donor-acceptor combinations, means the transition within the crystal field splitting levels of $^2F_{7/2}$ multiplet of Yb^{3+} ion.

In Fig. 3 are plotted the observed energy transfer rates against energy gaps ΔE. Here, the error bar in the direction of horizontal axis expresses the sum of the width of the crystal field splitting levels of the final J multiplets. As shown in the figure, most of all the points falls on a straight line fairly well, indicating the exponential dependence of the energy transfer rate on energy gap. This fact agrees with the Miyakawa-Dexter theory on phonon-assisted energy transfer mentioned above.

From the slope of the straight line in Fig. 3, one obtains 2.5×10^{-3} cm as β of eq. (5). According to eqs. (8) and (9) the value of β is calculated by using the known value of α and $\hbar\omega$ of Y_2O_3. The values of α and $\hbar\omega$ obtained by Moos and coworkers and by Weber are different. Namely, Moos and coworkers[8] suggested that $\alpha=3.8\times10^{-8}\,\mathrm{cm}$[18] and $\hbar\omega = 550\,\mathrm{cm}^{-1}$, while Weber[10] obtained that $\alpha=5.1\times10^{-8}\,\mathrm{cm}$[18] and $\hbar\omega=430\,\mathrm{cm}^{-1}$. We have used $\alpha=3.8\times10^{-8}$ cm and $\hbar\omega=430\,\mathrm{cm}^{-1}$ for the calculation of β from the reasons discussed later. Assuming that the electron-lattice coupling constant is the same between donor and acceptor ions, namely that $g_a=g_b$, one obtains $\beta=2.2\times10^{-3}$ cm. This is close to the observed value of 2.5×10^{-3} cm. This fact confirms the validity of the Miyakawa-Dexter theory.

For the estimation of multiphonon relaxation rates, Moos and coworkers used only experimental values. However, Weber used partly theoretical calculations, and there is the possibility that in his calculation he missed some important factors to take into consideration, as he said. Therefore, one can say that Moos' value of α is more reliable than Weber's value. This is the reason that we used Moos' value.

Weber obtained $\hbar\omega=430\,\mathrm{cm}^{-1}$ from the measurement of the temperature dependence of multiphonon relaxation rate. On the other hand, Moos and coworkers suggested $\hbar\omega=550\,\mathrm{cm}^{-1}$ which was obtained as the cutoff phonon energy from vibronic spectrum, on the basis of the fact that the phonon which contributes to the multiphonon relaxation is generally the one with a near cutoff energy. To judge which is better, the vibronic sideband appearing in excitation spectrum was precisely measured at 4.2 K for the emission of $^5D_0\rightarrow{}^7F_2$ of Eu^{3+} ion in Y_2O_3. Figure 4 shows the observed spectrum of vibronic sideband associated with the

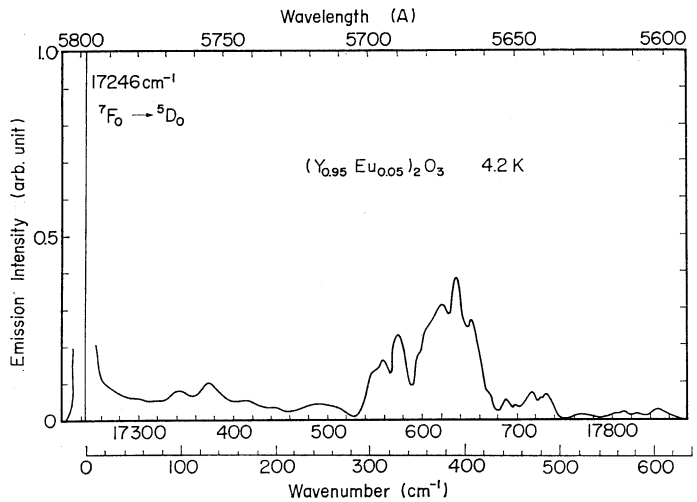

Fig. 4. Vibronic sidebands associated with the $^7F_0\rightarrow{}^5D_0$ transition of Eu^{3+} ion appearing in the excitation spectrum for the emission of the $^5D_0\rightarrow{}^7F_2$ transition in $(Y_{0.95}Eu_{0.05})_2O_3$ at 4.2 K.

transition of $^7F_0\rightarrow{}^5D_0$. This transition is suitable for the present purpose, since it has only one pure electronic line. As seen in the figure, the most intense band exists at about 400 cm^{-1} and is stronger by one order of magnitude than the cutoff phonon band located at about 600 cm^{-1}. The phonon of 400 cm^{-1} is disadvantageous compared with the cutoff phonon of 600 cm^{-1} from the point

of view on the number of phonons involved in multiphonon processes. However, the observed value of β of 2.5×10^{-3} cm indicates that when the number of involved phonons is increased by one the energy transfer probability is decreased to only about one third. Therefore, these facts lead to the conclusion that the phonon of about 400 cm^{-1}, but not the one with a near cutoff energy, contributes dominantly to the energy transfer process. This conclusion is further supported, as will be mentioned in 3.3, by the results on the temperature dependence of transfer probability.

The above-mentioned experimental facts show that the probability of the phonon-assisted energy transfer is mainly governed by the magnitude of energy gap. However, it is noticed in Fig. 3 that the observed rates for the transfers involving $^5D_0$ and $^5D_1$ states of Eu^{3+} ion as the donor level are located below the straight line in excess of experimental errors. This fact suggests that the above-mentioned general rule is not always valid. Similar phenomena have been also observed in the multiphonon relaxation processes.[10] Namely, it was found that the probability of the multiphonon relaxation from $^5D_1$ to $^5D_0$ state of Eu^{3+} ion is extremely small. This facts was explained by the selection rule of electron-lattice coupling concerning J value.

The radiative transition of $J=1 \rightarrow J=0$ is forbidden by electric dipole in the limit of the theory by Judd[19] and Ofelt,[20] and is also forbidden by electric quadrupole. Therefore, if the mixing of other J-states into $^5D_1$ or $^5D_0$ through electron-lattice interaction or crystal field potential is not very remarkable, the phonon-assisted energy transfer due to the transition of (Eu, $^5D_1 \rightarrow ^5D_0$): (Yb, $^2F_{7/2} \rightarrow ^2F_{7/2}$) would be very weak. The possibility is considered that the probability of the energy transfer from $^5D_1$ state of Eu^{3+} ion to Yb^{3+} ion is determined not by (Eu, $^5D_1 \rightarrow ^5D_0$): (Yb, $^2F_{7/2} \rightarrow ^2F_{7/2}$) $+1225\ cm^{-1}$, but by (Eu, $^5D_1 \rightarrow ^7F_6$): (Yb, $^2F_{7/2} \rightarrow ^2F_{5/2}$) $+3400\ cm^{-1}$ which involves the next minimum energy gap. In Fig. 3, the dashed point shows the plotting with the assumption of the latter transition. As is seen, it fits the straight line well. Therefore, one may conclude that the energy transfer of (Eu, $^5D_1 \rightarrow ^5D_0$): (Yb, $^2F_{7/2} \rightarrow ^2F_{7/2}$) involving a forbidden transition is weaker at least by two orders of magnitude than other transfers involving only allowed transitions. This corresponds to the fact, observed by two of the present authors,[21] that the calculated strength of one-phonon vibronic sidebands associated with the forbidden transition of $^7F_0 \rightarrow ^5D_1$ of Eu^{3+} ion is much smaller than that of $^7F_0 \rightarrow ^5D_2$ which is allowed by electric dipole in the limit of the Judd and Ofelt's theory.

In the case of the transfer of (Eu, $^5D_0 \rightarrow ^7F_6$): (Yb, $^2F_{7/2} \rightarrow ^2F_{5/2}$), the $^5D_0 \rightarrow ^7F_6$ transition is allowed by electric dipole transition in the limit of the Judd and Ofelt's theory, but is known to be weaker by one or two orders of magnitude than other allowed transitions between $4f^n$ states.[22] Therefore, it is not unreasonable that the observed probability of this energy transfer is smaller, as is seen in Fig. 3, by about two orders of magnitude than the value expected from the simple exponential dependence.

3.3 *Temperature dependence of transfer probability*

At low temperatures such as 77 K, only spontaneous emission of phonons can occur. As temperature is raised, phonon-assisted energy transfer rate grows, since stimulated emission of phonons becomes operative. As easily seen from eqs. (5) to (9), the temperature dependence of phonon-assisted energy transfer rate is expressed by

$$W(T) = W(0)(n+1)^N , \qquad (10)$$

if it is assumed that the phonons involved in the energy transfer are of equal energy.

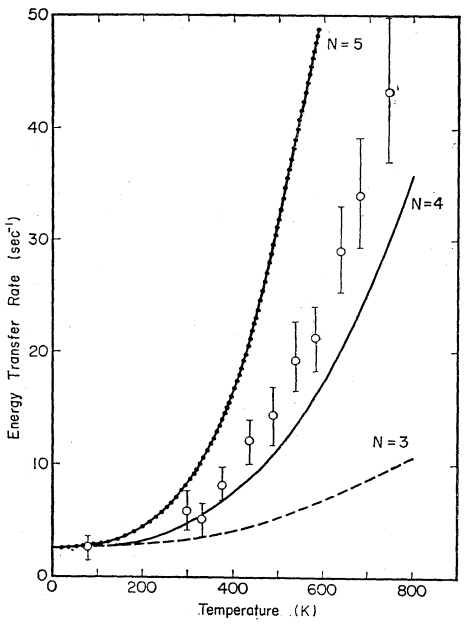

Fig. 5. Temperature dependence of the rate of the phonon-assisted energy transfer of (Eu, $^5D_0 \rightarrow ^7F_6$): (Yb, $^2F_{7/2} \rightarrow ^2F_{5/2}$) $+1670\ cm^{-1}$ in Y_2O_3. The three curves with $N=3$, 4 and 5 are theoretical curves corresponding to the emission of three, four and five phonons with energies of 335, 420 and 560 cm^{-1}, respectively.

Figure 5 shows the observed temperature dependence of the rate of the energy transfer of (Eu, $^5D_0 \rightarrow {}^7F_6$) : (Yb, $^2F_{7/2} \rightarrow {}^2F_{5/2}$) + 1670 cm^{-1}. The energy gap of 1670 cm^{-1} corresponds to four phonons of about 420 cm^{-1}. Therefore, the expression for the temperature dependence of this $N=4$ transfer process is given by

$$W(T)=W(0)\{1-\exp(-420\,\mathrm{cm}^{-1}/kT)\}^{-4}\,. \tag{11}$$

In the figure, not only this theoretical curve but also those for $N=3$ and 5 are shown. These curves are drawn so as to fit the experimental value at 77 K. It is seen that the theoretical curve for $N=4$ is closest to the experimental data. This indicates that the phonon of about 420 cm^{-1} dominantly contributes to the energy transfer process, consistently with the conclusion obtained in 3.2.

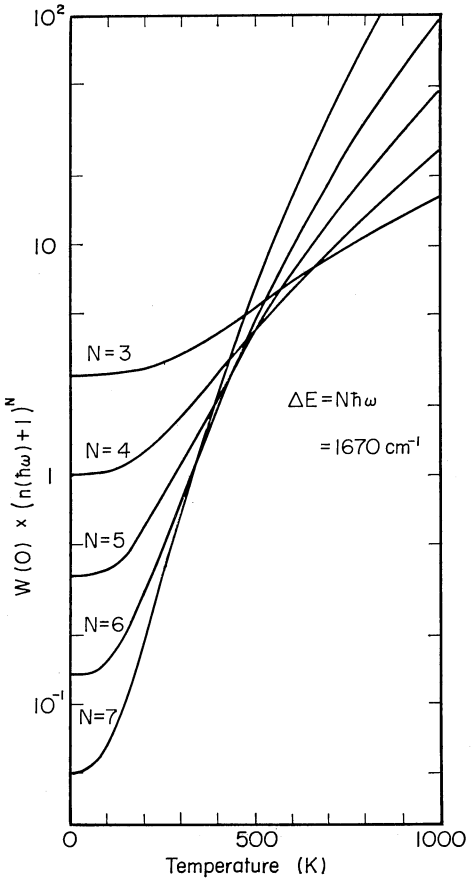

Fig. 6. Theoretical curves for the temperature dependence of the rate of phonon-assisted energy transfer for various processes which are different in the number of phonons to compensate the energy gap of 1670 cm^{-1}. Here, the fact that the rate decreases to one third as the phonon number increases by one is used (see the text).

However, a deviation from the theoretical curve becomes prominent as temperature is raised. This is interpreted by the fact that the stimulated emission of phonons takes place more strongly associated with lower energy phonons at higher temperatures. We have calculated the temperature dependences of various processes which are different in the number of phonons to compensate the energy gap of 1670 cm^{-1}, taking account of the fact that in the present case the energy transfer rate decreases to about one third as the phonon number increases by one as mentioned already. The results are shown in Fig. 6. In the case of $N=6$ and 7 processes, the energies of contributing phonons are less than 300 cm^{-1}. The intensities of such low energy phonons in the vibronic spectrum shown in Fig. 4 are much weaker than the intensity of the phonon of about 420 cm^{-1}. Therefore, one can say that the magnitudes of the theoretical curves for $N=6$ and 7 in Fig. 6 are over-estimated. In any case, the temperature dependence of the phonon-assisted energy transfer probability should be expressed by the combination of all the possible processes different in the phonon number. Therefore, it is not unreasonable that the observed temperature dependence does not

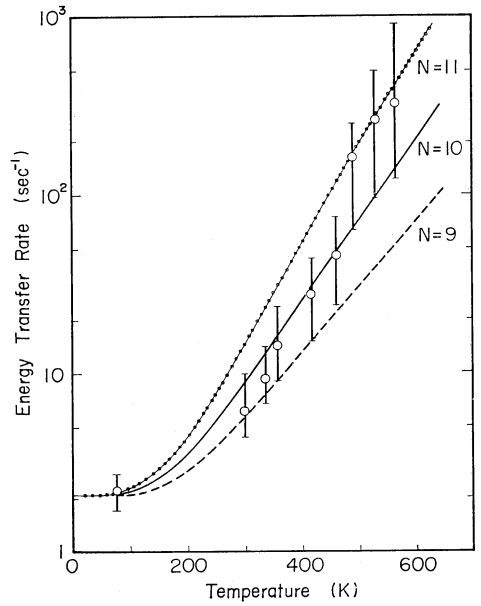

Fig. 7. Temperature dependence of the rate of the phonon-assisted energy transfer of (Tb, $^5D_4 \rightarrow {}^7F_0$): (Yb, $^2F_{7/2} \rightarrow {}^2F_{5/2}$) + 4200 cm^{-1} in Y_2O_3. The three curves with $N=9$, 10 and 11 are theoretical curves corresponding to the emission of nine, ten and eleven phonons with energies of 465, 420 and 380 cm^{-1}, respectively.

exactly fit a theoretical curve corresponding to a fixed number of phonon over a wide temperature range.

In Fig. 7 is shown the observed temperature dependence of the probability of the energy transfer of $(\mathrm{Tb}, {}^5D_4 \rightarrow {}^7F_0) : (\mathrm{Yb}, {}^2F_{7/2} \rightarrow {}^2F_{5/2}) + 4200\ \mathrm{cm}^{-1}$. As is seen, the experimental points roughly fit the theoretical curve

$$W(T) = W(0)\{1 - \exp(-420\ \mathrm{cm}^{-1}/kT)\}^{-10} . \quad (12)$$

At higher temperatures, they approach to the theoretical curve for the emission of eleven phonons of about $380\ \mathrm{cm}^{-1}$. This fact is also explained by the same reason as mentioned above.

The results obtained by the above two cases suggest that the phonon which contributes most dominantly to the phonon-assisted energy transfer in Y_2O_3 is the one of about $400\ \mathrm{cm}^{-1}$. This is consistant with the conclusion mentioned in 3.2.

In the case of the energy transfer from ${}^5D_4$ state of Tb^{3+} ion to Yb^{3+} ion, the energy separation between ${}^5D_4$ and ${}^7F_6$ states of Tb^{3+} ion is roughly two times of the separation between ${}^2F_{7/2}$ and ${}^2F_{5/2}$ states of Yb^{3+} ion. Then there is the possibility that the cooperative energy transfer, *i.e.* the simultaneous energy transfer from an excited Tb^{3+} ion to two unexcited Yb^{3+} ions, takes place. The inverse of this energy transfer process has been observed in $CaF_2(SrF_2):Tb,Yb$[23] and $YF_3:Tb$.[24] However, the fact that the observed temperature dependence is well interpreted by the phonon-assisted process indicates that this possibility can be neglected. Further this is supported by the fact that, in the energy gap dependence shown in Fig. 3, the experimental point for this energy transfer fits the straight line.

§ 5. Concluding Summary

The nature of nonresonant phonon-assisted energy transfer between trivalent rare earth ions has been investigated in detail using Y_2O_3 as the host crystal. The probabilities of energy transfer have been obtained from the analysis of the decay rates of donor luminescence. The measurements have been made for various combinations of donor and acceptor rare earth ions in which the energy gap, *i.e.* the mismatch of energy between the levels of donor and acceptor ions, is varied in a wide range up to $4000\ \mathrm{cm}^{-1}$.

The observed probabilities of energy transfer have been found to depend exponentially on the energy gaps. This indicates that the theory of Miyakawa and Dexter on phonon-assisted energy transfer is applicable for the present case. The temperature dependence of the probabilities observed in the range of 77 to 800 K provides the direct evidence that the mismatch of energy is compensated by the emission of phonons.

The parameter β which expresses the exponential dependence of the rate of phonon-assisted energy transfer has been obtained to be 2.5×10^{-8} cm. The estimation of β has been made, according to the Miyakawa-Dexter theory, by using the corresponding parameter α in the case of multiphonon relaxation transition, and a value close to the experimental one has been given. On the basis of the observation on the vibronic sidebands appearing in excitation spectrum as well as of the consideration on the manner of the energy gap dependence of transfer rate, it is concluded that the phonon contributing dominantly to the energy transfer process is the one of about $400\ \mathrm{cm}^{-1}$ which produces the highest intensity in the vibronic sidebands, but not the one of the cutoff energy of about $600\ \mathrm{cm}^{-1}$. This conclusion is further supported by the analysis of the observed temperature dependence of the energy transfer rate, although there is indication that at higher temperatures phonons with lower energies also contribute.

In higher-order processes such as phonon-assisted energy transfer, the individual characters of involved *J*-states of rare earth ions are smoothed out through the mixing of other *J*-states. However, the probabilities of the phonon-assisted energy transfer including ${}^5D_0$ and ${}^5D_1$ states of Eu^{3+} ion are much smaller than expected from the values of energy gap. This fact may be interpreted by the *J*-selection rule for multipole interaction between ions.

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