# Energy transfer between $Er^{3+}$ ions in $LaF_3$

E. Okamoto, M. Sekita, and H. Masui

*Central Research Laboratory, Mitsubishi Electric Corporation, Amagasaki, Hyogo, Japan*

(Received 16 December 1974)

The decay of the excited $^4S_{3/2}$ state of $Er^{3+}$ ions in $LaF_3$ at 295 °K has been investigated in detail. The energy is transferred from the thermally populated multiplet $^2H_{11/2}$. The decay curve of the luminescence from $^4S_{3/2}$ after a flash lamp excitation is explained well by taking into account diffusion and cross relaxation simultaneously. The obtained diffusion coefficient $D$ is inversely proportional to the fourth power of the average separation between $Er^{3+}$ ions, indicating that the coupling between the ions responsible for the diffusion is the electric dipole-dipole interaction. The energy-transfer constant $C_{dd}$ of the diffusions $^2H_{11/2} \leftrightarrow \, ^4I_{15/2}$ and $^4S_{3/2} \leftrightarrow \, ^4I_{15/2}$ and the energy-transfer constant $C$ of the cross relaxations $^2H_{11/2} \rightarrow \, ^4I_{9/2}$, $^4I_{15/2} \rightarrow \, ^4I_{13/2}$ and $^2H_{11/2} \rightarrow \, ^4I_{13/2}$, $^4I_{15/2} \rightarrow \, ^4I_{9/2}$ are $7.0 \times 10^{-40}$ $cm^6/sec$ and $4.5 \times 10^{-41}$ $cm^6/sec$, respectively. The fact that $C_{dd}$ is larger than $C$ by more than one order of magnitude indicates that the energy transfer is essentially the diffusion-limited relaxation. The other cross relaxations, $^4F_{7/2} \rightarrow \, ^4I_{11/2}$, $^4I_{15/2} \rightarrow \, ^4I_{11/2}$, and $^4F_{5/2} \rightarrow \, ^4F_{9/2}$, $^4I_{15/2} \rightarrow \, ^4I_{13/2}$ and $^4F_{5/2} \rightarrow \, ^4I_{13/2}$, $^4I_{15/2} \rightarrow \, ^4F_{9/2}$, have been observed in $LaF_3{:}Er^{3+}$. The ensemble-averaged energy-transfer constants of these cross relaxations calculated by the theory of Dexter for the electric dipole-dipole interaction are in good agreement with the energy-transfer constants obtained by the phenomenological rate-equation model.

## I. INTRODUCTION

A considerable effort has been made to elucidate the mechanism of the concentration quenching of the radiative yield and the transient decay curve of luminescence. It was shown that the quenching of the luminescence takes place by cross relaxation from an excited ion behaving as an energy donor (a donor ion) to another ion behaving as an energy acceptor (an acceptor ion) with or without diffusion of the excitation energy among donor ions,[1] which allows the excitation to migrate to the vicinity of an acceptor ion, resulting in the quenching through donor-acceptor interaction.[2]

Weber[3] has classified the energy transfer into three limiting cases according to the diffusion length of the excitation: direct cross relaxation, diffusion-limited relaxation, and rapid diffusion. He has found that the diffusion-limited relaxation takes place in europium-phosphate glass containing a small amount of chromium. Watts and Richter[4] have studied the energy transfer from $Yb^{3+}$ to $Ho^{3+}$ ions in $YF_3$, and found all the three cases. The former two cases have been found by Krasutsky and Moos[5] in $LaCl_3{:}Pr^{3+}$, $Nd^{3+}$.

As is well known, there are several kinds of interactions between two ions responsible for the energy transfer: electric dipole-dipole (d-d), electric dipole-quadrupole (d-q), electric quadrupole-quadrupole interaction (q-q), and exchange interaction. The theory of the energy transfer due to these interactions has been developed by many investigators, and the formula of the energy-transfer rate has been given in Refs. 6 and 7. The energy-transfer rates in these cases do not have

the same dependence on the donor-acceptor separation, but in all cases it is proportional to the overlap integral between the emission spectrum of a donor ion and the absorption spectrum of an acceptor ion. This information can be obtained experimentally by measuring the transient decay curve of the donor luminescence if the donor level associated with energy transfer is a luminescent one. The emission of a donor level from which the energy transfer takes place cannot always be detected because of the small quantum efficiency of the radiative yield. This situation sometimes makes it difficult to obtain the energy-transfer constant.

The overlap integral is expressed by the product of the oscillator strengths of the optical transitions of donor and acceptor ions and the overlap of the normalized emission and absorption spectra, as mentioned later. If the oscillator strengths and the spectral shapes of the emission of a donor and of the absorption of an acceptor are known, the energy-transfer constant can be calculated by the theory of Dexter.[6] Some of the optical-transition probabilities between $J$ multiplets of an $Er^{3+}$ ion in $LaF_3$ have been computed by Weber[8] using the theory of Judd[9] and Ofelt.[10] He has shown that the optical transitions in this system are mainly due to the electric dipole mechanism, and has obtained the three phenomenological parameters $T_2$, $T_4$, and $T_6$, which contain the crystal-field strengths, the energy separation between the $4f^N$ and $4f^{N-1}5d$ configurations, the refractive index of the medium, and the interconfigurational radial integrals.

In the present study the parameters governing the energy transfer in the $LaF_3{:}Er^{3+}$ system have been obtained experimentally and compared with

the theoretical values.

## II. THEORETICAL BACKGROUND

The energy transfers due to electric multipolar interactions have been discussed in detail by Dexter.[6] The energy transfer probability $P(R)$ between a pair of ions can be written using oscillator strengths ($f$'s) as follows[11]:

$$P(R) = CR^{-s}$$

$$= \frac{3e^4}{8\pi^2 m^2 c^3 n^4 R^6} \sum_{i,f} \sum_{i',f'} \frac{1}{\nu_{if}^2} f_d(\alpha_i J_i \Gamma_i; \alpha_f J_f \Gamma_f)$$

$$\times f_a(\alpha_{i'} J_{i'} \Gamma_{i'}; \alpha_{f'} J_{f'} \Gamma_{f'}) \int d\nu F_{if}^d(\nu) F_{i'f'}^a(\nu),$$

(1)

where $C$ is the energy-transfer constant; $\nu_{if}$ means the energy to be transferred in cm$^{-1}$; $\Gamma$'s denote the irreducible representations of the Stark levels of a $J$ multiplet; $F_{if}^d(\nu)$ and $F_{i'f'}^a(\nu)$ are the lineshape function of the emission of a donor ion and that of the absorption of an acceptor ion, respectively, and the integral of each function over $\nu$ is normalized to unity. For perfet overlap and identical linewidths of the two spectra, the overlap integral is the inverse of the linewidth. The exponent $s$ in Eq. (1) is 6, 8, or 10 according to d-d, d-q, or q-q interaction, respectively.

Judd[9] and Ofelt[10] have calculated the oscillator strength of an optical transition due to the electric dipole between $J$ multiplets of $4f^N$ configuration of a rare-earth ion in a crystal, assuming all levels of the $4f^{N-1}5d$ configuration to be located at an average energy. This excited configuration is mixed into the $4f^N$ configuration due to the odd-parity terms of the crystalline field. They have given the formula for the oscillator strength which can be simplified into a sum of products of the phenomenological parameter $T_\lambda$ and a matrix element of unit tensor operator $U^{(\lambda)}$:

$$f_{ed}(\alpha_i J_i; \alpha_f J_f) = \frac{c\nu}{2J_i + 1}$$

$$\times \sum_\lambda T_\lambda \langle 4f^N(\alpha SL)_i J_i \| U^{(\lambda)} \| 4f^N(\alpha SL)_f J_f \rangle^2 ,$$

$$\lambda = 2, 4, 6 , \qquad (2)$$

where $c$ and $\nu$ denote the light velocity and a mean energy in cm$^{-1}$ of the transition between $J$ multiplets, respectively. A $J$ multiplet of $4f^N$ configuration of a rare-earth ion in a crystal is generally split into Stark levels. In Eq. (2), the condition that the transition probability between any pair of Stark levels of the two $J$ multiplets is equal or the condition that all the Stark levels of the initial $J$ multiplet are equally populated is implicitly included. The latter condition is only approximately fulfilled at ambient temperatures. In LaF$_3$:Er$^{3+}$, however, because of the low crystal-field symmetry, each Stark component is composed of a linear combination of many substates of $J_z$ quantum numbers. This fact tends to average out the generally unequal transition probabilities between the two Stark levels of the initial and the final $J$ multiplets.

In fact, Weber[8] has determined the parameters $T_\lambda$ in Eq. (2) by observing the absorption spectra for Er$^{3+}$ ions in LaF$_3$ at (6–10) °K. Though only a few of the lower Stark levels have appreciable population at such low temperatures, the fact that the absorption intensity has been explained well by these parameters shows that the former condition seems to be fulfilled fairly well in LaF$_3$. He has also measured the absorption from the $^4I_{15/2}$ state to upper multiplets at liquid-nitrogen temperature, and found that the oscillator strengths differ a little from the values obtained at (6–10) °K, but that the differences are always less than a factor of 2. The transition probability at low temperatures due to the electric dipole between any pair of $J$ multiplets can be calculated using these parameters. Those probabilities for some pairs of $J$ multiplets have already been calculated by Weber.[8]

If we postulate that the oscillator strength is the same for any transition between Stark levels of different $J$ multiplets which is actually allowed in LaF$_3$:Er$^{3+}$,[12] Eq. (1) can be rewritten using Eq. (2) as follows (see Appendix):

$$P(R) = \frac{3e^4}{8\pi^2 m^2 c^3 n^4 R^6} \sum_{J_f} \frac{1}{\nu_{J_f J_{f'}}^2} \frac{1}{n(J_f)n(J_{f'})} f_d(\alpha_i J_i; \alpha_f J_f) f_a(\alpha_{i'} J_{i'}; \alpha_{f'} J_{f'}) \sum_{i,f} \sum_{i',f'} \int d\nu F_{if}^d(\nu) F_{i'f'}^a(\nu) , \qquad (3)$$

where $n(J)$ denotes the number of Stark levels of a $J_f$ multiplet. In the present case, $n(J_f) = (2J_f + 1)/2$, since all the Stark levels of an Er$^{3+}$ ion in LaF$_3$ are only Kramers doublets.[12]

The observed energy-transfer rate in an actual system, however, is not the pairwise form of $P(R)$, but the ensemble average of $P(R)$. The ensemble-averaged energy-transfer rate per ion ($W$) has been obtained by Fong and Diestler[13] for the system of randomly mixed donor and acceptor

ions in a host lattice, in the form of

$$W = N \int_\sigma^\infty P(R) 4\pi R^2 dR , \qquad (4)$$

where $N$ is the concentration of acceptor ions in a host lattice; $\sigma$ is the nearest-neighbor separation between a donor ion and an acceptor ion.

Inokuti and Hirayama[7] have discussed the transient decay of a donor luminescence in the presence of a direct-cross-relaxation process only. When

diffusion is present in addition to the direct cross relaxation, and when the interaction between ions is assumed to be the d-d interaction, the donor luminescence intensity as a function of time after a flash excitation has been given by Yokota and Tanimoto[14] as follows:

$$\phi(t) = \phi(0) \exp\left[\frac{t}{\tau_0} - \frac{4}{3}\pi^{3/2}N(Ct)^{1/2}\right.$$
$$\left. \times \left(\frac{1+10.87z+15.50z^2}{1+8.743z}\right)^{3/4}\right], \quad (5)$$

where $t$, $\tau_0$, and $C$ are time, the intrinsic decay time of a donor ion, and the donor-acceptor energy-transfer constant, respectively, and

$$z = DC^{-1/3}t^{2/3},$$

in which $D$ is the diffusion coefficient, which is expressed by the donor-donor energy transfer constant $C_{dd}$ as follows:[5]

$$D = \frac{8}{3\pi}C_{dd}R_m^{-4}, \quad (6)$$

where $R_m$ is the mean separation between donor ions. Equation (5) is identical to the theory of Inokuti and Hirayama for negligibly small $D$ and small time $t \ll D^{-3/2}C^{1/2}$. For large $D$, Eq. (5) becomes a simple exponential function with the decay rate,

$$1/\tau = 1/\tau_0 + 4\pi DN\rho, \quad (7)$$

where $\rho = 0.68(C/D)^{1/4}$.

### III. EXPERIMENTAL AND RESULTS

Polycrystalline-powder samples of lanthanum fluoride activated with Er$^{3+}$ were synthesized by coprecipitating the oxalate from a nitric-acid solution of the oxides, by decomposition of the oxalate to the oxide at 800 °C in air, and finally by reaction of the oxide with anhydrous HF gas at a temperature of 1100 °C. The reactions were carried out in a platinum container in a platinum furnace. This procedure led to well-crystallized single-phase powder as determined by standard powder x-ray diffraction technique. The samples synthesized contain Er$^{3+}$ of 0.03, 0.1, 0.3, 1.0, and 2.0 mole% nominally.

A mass-spectrograph analysis of LaF$_3$:Er$^{3+}$ showed that the Er$^{3+}$ concentration coincides with the nominal mole% within the experimental error of 20%, and that the following impurities are present in mole%: 0.01% Eu, 0.005% Ho, and less than 0.001% other impurities.

The light sources used for observing steady-state absorption and luminescence spectra were a tungsten lamp and a high-pressure xenon arc lamp. The absorption and the emission spectra were measured in the visible and near-infrared region with a grating monochrometer ($f$/6.2, 11 Å/mm) equipped with a S-11 photomultiplier tube or a cooled S-20

photomultiplier tube. Transient luminescence intensities were observed by exciting samples with a pulsed light of 2-μsec duration from a xenon flash lamp, and the output of a photomultiplier tube was introduced to a boxcar integrator. A pulsed excitation light was led to a monochrometer ($f$/4.5, 60 Å/mm) to excite samples only into the first and/or the second upper multiplet above a luminescence state under consideration.

The absorption and the emission spectra of our samples coincided with those of Krupke and Gruber,[12] and the lifetimes of the luminescence states of the sample containing the lowest concentration of Er$^{3+}$ ions were equal to those of Weber[15] within experimental error. We have observed luminescence at low temperatures from the $^4I_{11/2}$, $^4F_{9/2}$, $^4S_{3/2}$, $^2H_{9/2}$, and $^4G_{11/2}$ states and at high temperatures from a thermally populated $^2H_{11/2}$ state in the region between 10 000 and 30 000 cm$^{-1}$. The energy levels of an Er$^{3+}$ ion and the three strong emissions are shown in Fig. 1. Concentration quenching of the radiative yield was observed distinctly in the emission from the thermally populated $^2H_{11/2}$ state and from the $^4S_{3/2}$ state at room temperature.[16] This suggests that an Er$^{3+}$ ion excited into the $^2H_{11/2}$ state relaxes to lower multiplets exciting another Er$^{3+}$ ion by means of the ion-ion interaction such as the d-d interaction. Energy transfer from an Er$^{3+}$ ion to other impurity ions may be neglected because the concentration of other impurities is much lower than that of the Er$^{3+}$ ions.

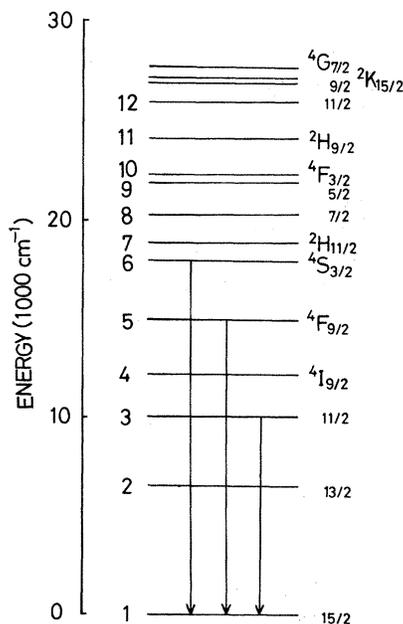The decay curves of the $^4S_{3/2} \rightarrow ^4I_{15/2}$ transition at



FIG. 1. Energy levels of an Er$^{3+}$ ion and the luminescence transitions studied in the present paper.

295 °K are shown in Fig. 2. The decay at 77 °K
was observed, being the same from sample to sam-
ple. Since the optical transitions in $LaF_3$:$Er^{3+}$ are
mainly due to the electric dipole,[8] it is natural to
consider that the energy transfer is due to the d-d
interaction in the first approximation. The solid
lines in Fig. 2 are plots of $\phi(t)$ in Eq. (5) which
give the theoretical decay curve for the d-d inter-
action. The parameters $C$ and $D$ in Eq. (5) were
determined to obtain the best fit to the experimental
decay curves using the nominal concentration $N$ of
$Er^{3+}$ ions and the decay time $\tau_0 = 0.923$ msec of the
sample containing 0.03-mole %$Er^{3+}$ ions, which is
considered to be the intrinsic decay time of the
$^4S_{3/2}$ state at 295 °K since the ion-ion interaction
may be neglected in such a low-concentration sys-
tem. The parameters so determined are shown
in Fig. 3.

The broken lines in Fig. 2 are the fits to the
theory of Inokuti and Hirayama obtained for the
d-d interaction. Since there is some departure in
$Er^{3+}$ concentration from the nominal value in the
samples studied, the value $N$ in addition to the
parameter $C$ was allowed to vary around its nomi-
nal value by about 20% in applying the theory of
Inokuti and Hirayama. As can be seen in Fig. 2,
the fits to the theory are quite poor in the samples
of higher concentration of $Er^{3+}$ ions, while in the
samples of lower concentration the fits are fairly
good, especially in the sample containing 0.1-mole %
$Er^{3+}$ ions, in which the decay curve can be explained
well by either theory, suggesting that the diffusion
coefficient $D$ is too small to be determined from
the experimental decay curve for the 0.1-mole %
$Er^{3+}$ sample.

Figure 4 shows the luminescence intensity of a 2-
mole %$Er^{3+}$ sample corresponding to the



FIG. 3. The cross-relaxation constant $C$ and the dif-
fusion coefficient $D$ which govern the relaxation of the
$^4S_{3/2}$ state at 295 °K. The horizontal axis is expanded by
four times with respect to the vertical axis. $C$ is almost
independent of the mean separation of the $Er^{3+}$ ions,
while $D$ is inversely proportional to the fourth power of
the mean separation of the $Er^{3+}$ ions.

$^4F_{9/2} \rightarrow {}^4I_{15/2}$ transition for the excitation into some
higher multiplets indicated in the figure. The in-
tensity was normalized with the amount of optical
absorption to the multiplet into which $Er^{3+}$ ions
were excited. The luminescence intensity for the
excitation into the $^2H_{11/2}$ state coincided with that
for the excitation into the $^4S_{3/2}$ state within experi-
mental error. At lower temperatures, the lumines-
cence intensity for the excitation into the $^4F_{5/2}$
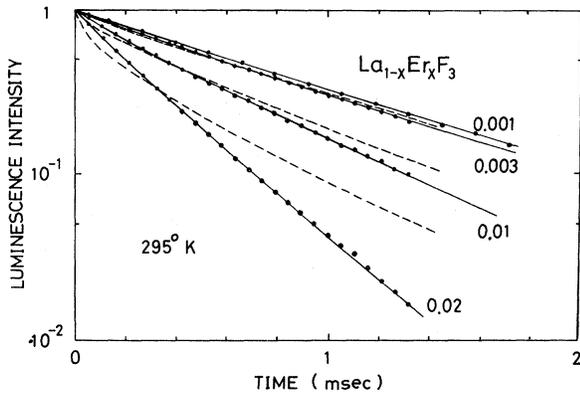


FIG. 2. Decay curves of the $^4S_{3/2}$ luminescence at
295 °K. The dots show the experimental results. The
solid and the broken lines are the best fits obtained by
the theory of Yokota and Tanimoto and that of Inokuti and
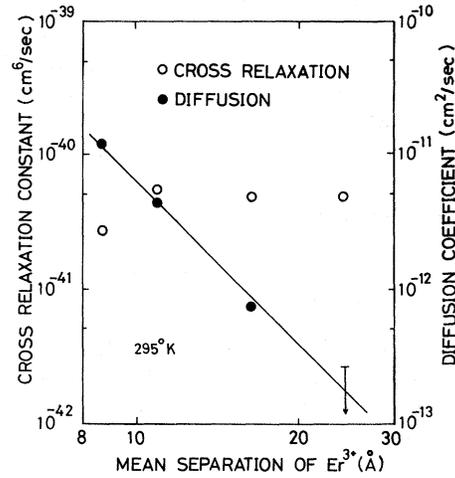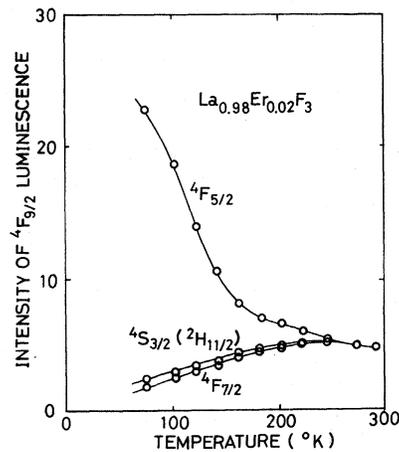Hirayama for the d-d interaction, respectively.



FIG. 4. The luminescence intensities from the $^4F_{9/2}$
to the $^4I_{15/2}$ state for the excitations into the multiplets
indicated in the figure. The intensity is normalized with
the amount of absorption to the multiplet into which $Er^{3+}$
ions were excited.

state is much larger than those for the excitation into the other multiplets, and the intensity for the excitation into the $^4F_{7/2}$ state is smaller than that for the excitation into the $^4S_{3/2}$ and $^2H_{11/2}$ states. The intensity for the excitation into any multiplet, however, is the same at room temperature. In the samples of lower concentration of Er$^{3+}$ ions, the normalized $^4F_{9/2}$ luminescence intensities for the excitation into those multiplets coincided at any temperature within experimental error. If the excited $^4F_{5/2}$, $^4F_{7/2}$, and $^2H_{11/2}$ states relaxed only through multiphonon relaxation even in a sample of high concentration, the excitation into those multiplets would give the same normalized $^4F_{9/2}$ luminescence intensity as that into the $^4S_{3/2}$ state. The fact that the $^4F_{9/2}$ luminescence intensity for the excitation into the $^4F_{5/2}$ state is much larger at lower temperatures suggests that the excited energy of the $^4F_{5/2}$ state partially relaxes to the $^4F_{9/2}$ bypassing the $^4S_{3/2}$ state. The same consideration applies to the case of the excitation into the $^4F_{7/2}$ state at lower temperatures: the fact that the $^4F_{9/2}$ luminescence intensity for the excitation into the $^4F_{7/2}$ state is smaller than that for the excitation into the $^2H_{11/2}$ or $^4S_{3/2}$ states at lower temperatures suggests that the excited $^4F_{7/2}$ state partially relaxes to some lower multiplet, probably $^4I_{11/2}$, bypassing both the $^4S_{3/2}$ and $^4F_{9/2}$ states. It is due to the large quantum efficiency of the $^4S_{3/2}$ emission[8] that these two energy transfers are observed distinctly at lower temperatures in spite of the small energy-transfer rates as compared with the total relaxation rates of the $^4F_{5/2}$ and $^4F_{7/2}$ states, as mentioned later.

Generally, the multiphonon relaxation rate of a rare-earth ion in solids at room temperature is much larger than that at 77 °K,[17] while the radiative transition rate and the energy-transfer rate at room temperature are nearly equal to those at 77 °K. When the total relaxation rate is much larger than the energy-transfer rate, the energy transfer cannot generally be observed experimentally. It is presumably due to the multiphonon relaxation rates of the $^4F_{5/2}$ state at room temperature being much larger than those at 77 °K that the normalized $^4F_{9/2}$ luminescence intensity for the excitation into any multiplet indicated in Fig. 4 is the same at room temperature.

Figure 5 shows the luminescence intensities of the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions at 77 °K. The black and the white circles correspond to the luminescence intensities from the $^4I_{11/2}$ and the $^4F_{9/2}$ state, respectively. The multiplets into which Er$^{3+}$ ions were excited are indicated in the figure, and the emission intensity for the sample of 0.03-mole % Er$^{3+}$ ions was made equal in the figure. This procedure means that the luminescence intensity was normalized with the amount of absorption of the multiplet into which Er$^{3+}$ ions were ex-
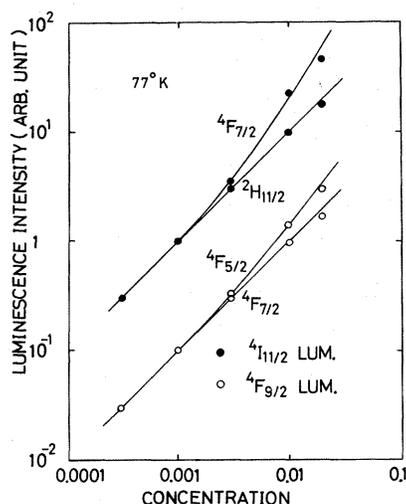


FIG. 5. The luminescence intensities corresponding to the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ (filled circles) and the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions (open circles) at 77 °K for the excitation into the multiplets indicated in the figure. The lines are the best fits to the rate-equation model.

cited, on the assumption that the oscillator strength of the optical transition is independent of Er$^{3+}$ concentration. The solid lines in this figure are the theoretical curves discussed in the following section.

The absorption spectra corresponding to the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and the $^4I_{15/2} \rightarrow {}^4F_{9/2}$ transitions at 77 °K are shown in Fig. 6. The average linewidths were about 10 cm$^{-1}$ for the samples studied. These rather broad linewidths may be caused by the inhomogeneous broadening: the crystal fields seen by individual rare-earth ions are slightly different from one another due to lattice defects. The intensity of the components of the absorption spectra varies within a factor of 5, so that Eq. (3) may be valid within a factor of 5. The emissions corresponding to the transitions indicated in the upper sides of the absorption spectra were not detected due to the small radiative yields of these transitions. The vertical bars shown in the figure are the positions of the expected luminescence lines of these transitions. We assume that the luminescence lines are as broad as the absorption lines and that the intensity of the luminescence line also varies within a factor of 5 as in the case of the absorption line.

In Fig. 7 are shown the absorption spectra of the $^4I_{15/2} \rightarrow {}^4F_{7/2}$ and the $^4I_{15/2} \rightarrow {}^4F_{5/2}$ transitions and the expected emission lines corresponding to the $^4F_{7/2} \rightarrow {}^4I_{15/2}$ and the $^4F_{5/2} \rightarrow {}^4I_{15/2}$ transitions at 77 °K.

## IV. DISCUSSION

Generally, the energy migration cannot be neglected in discussing the relaxation of the excited energy. In Fig. 3 the cross-relaxation constant $C$
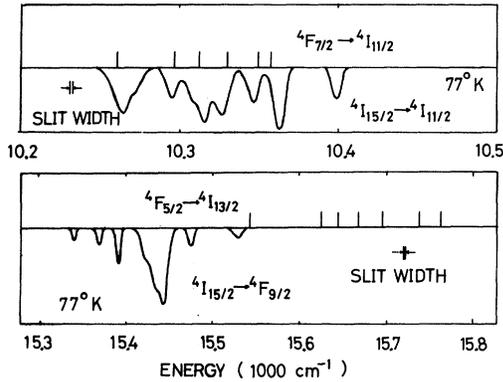
FIG. 6. The absorption spectra of the $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and the $^4I_{15/2} \rightarrow {}^4F_{9/2}$ transitions at 77 °K. The vertical lines are the positions of the luminescence lines expected for the transitions indicated in the figure at low temperatures.

and the diffusion coefficient $D$ are shown, which were obtained in the analysis of the decay of the $^4S_{3/2}$ emission at 295 °K using Eq. (5). The cross relaxation can occur only through the thermally populated $^2H_{11/2}$ state as mentioned in the last section. The constant $C$ is the sum of the two cross-relaxation constants for the energy transfers $^2H_{11/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$ and $^2H_{11/2} \rightarrow {}^4I_{13/2}$, $^2H_{11/2} \rightarrow {}^4I_{9/2}$. The cross-relaxation probability can be evaluated by Eq. (3) using the calculated oscillator strengths of the transitions associated with the cross relaxation. The product of the calculated oscillator strengths in Eq. (3) for the former cross relaxation is larger by two orders of magnitude than that for the latter cross relaxation, and the overlaps of the emission and the absorption spectra associated with the two cross relaxations can be estimated to be in the same order, so that the main process is considered to be the former cross relaxation: $^2H_{11/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$.

The cross-relaxation constant $C$ is independent of the donor-acceptor separation $R$. Watts and Richter[4] have studied the energy transfer from $Yb^{3+}$ to $Ho^{3+}$ in $YF_3$, and found that the cross-relaxation constant $C$ varied from sample to sample by a factor of 3. The $C$ value of our samples, as can be seen in Fig. 3, varies by only a factor of 2; this may be partially because we used the nominal value of the $Er^{3+}$ concentration $N$ in the analysis of the decay curves instead of the actual value. The averaged value of $C$ is $4.5 \times 10^{-41}$ cm$^6$/sec.

In Fig. 3 are also shown the diffusion coefficients which are inversely proportional to the fourth power of the mean separation $R_m$ in Eq. (6), indicating that the interaction causing the diffusions $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^2H_{11/2} \rightarrow {}^4I_{15/2}$ is the d-d interaction. The donor-donor energy transfer constant $C_{dd}$ in

Eq. (6) is determined to be $7.0 \times 10^{-40}$ cm$^6$/sec, which is about sixteen times as large as the cross relaxation constant $C$. As can be seen in Fig. 2, the decay curve is not a simple exponential function with the decay rate defined by Eq. (7). These facts indicate that the decay of the $^4S_{3/2}$ state at high temperatures is essentially the diffusion-limited relaxation.

The diffusion coefficient $D$ for the sample containing 0.1-mole % $Er^{3+}$ ions could not be determined from the decay curve of the $^4S_{3/2}$ emission at 295 °K. The decay curve of this sample could be explained as well by the theory of Inokuti and Hirayama as by the theory of Yokota and Tanimoto. This fact suggests that the diffusion process does not contribute effectively to the relaxation of the $^4S_{3/2}$ state. The cross-relaxation rate for this sample can be calculated to be 43 sec$^{-1}$ by Eq. (4) using the value of $C = 4.5 \times 10^{-41}$ cm$^6$/sec. The energy-transfer rate can be also expressed as the difference between the total decay rate $1/\tau_m$ and the intrinsic decay rate $1/\tau_0$, $(1/\tau_m - 1/\tau_0)$, where $\tau_m$ is the mean decay time defined as $\tau_m = \int t\phi(t)dt / \int \phi(t)dt$.[7] The $\tau_m$ of the $^4S_{3/2}$ state of the sample of 0.1-mole % $Er^{3+}$ ions is 0.897 msec, so that the value of $1/\tau_m - 1/\tau_0$ is about 30 sec$^{-1}$, which is favorably compared with the cross relaxation rate of 43 sec$^{-1}$ calculated by Eq. (4).

In Table I, the total decay rate $(1/\tau_m)$, the diffusion rate between donor ions $[1/\tau_d ( = N\int(C_{dd}/R^6) \times 4\pi R^2 dR$, where $C_{dd} = 7.0 \times 10^{-40}$ cm$^6$/sec)], and the energy transfer rate $(1/\tau_m - 1/\tau_0)$ are shown for each sample. The $1/\tau_d$ is smaller than the $1/\tau_m$ for the sample of 0.1-mole % $Er^{3+}$ ions: the excited energy relaxes to lower states more probably than the donor-donor energy transfer takes place. For the samples of higher concentration of $Er^{3+}$ ions, the $1/\tau_d$ is larger than the $1/\tau_m$. This means that
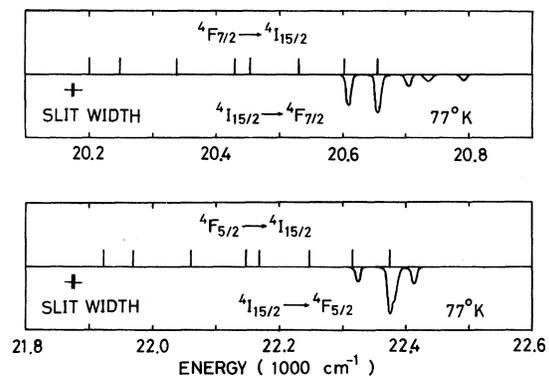


FIG. 7. The absorption spectra of the $^4I_{15/2} \rightarrow {}^4F_{7/2}$ and the $^4I_{15/2} \rightarrow {}^4F_{5/2}$ transitions at 77 °K. The vertical lines are the positions of the luminescence lines expected for the transitions indicated in the figure at low temperatures.

TABLE I. The total decay rate $(1/\tau_m)$ of the $^4S_{3/2}$ state, the ensemble-averaged transfer rate of the diffusion $(1/\tau_d)$, and the energy-transfer rate $(1/\tau_m - 1/\tau_0)$ at 295 °K.

| $Er^{3+}$ concentration (mole %) | 0.1 | 0.3 | 1.0 | 2.0 |
|---|---|---|---|---|
| $1/\tau_m$ (sec$^{-1}$) | $1.12 \times 10^3$ | $1.17 \times 10^3$ | $1.73 \times 10^3$ | $3.15 \times 10^3$ |
| $1/\tau_d$ (sec$^{-1}$) | $7.50 \times 10^2$ | $2.25 \times 10^3$ | $7.50 \times 10^3$ | $1.50 \times 10^4$ |
| $1/\tau_m - 1/\tau_0$ (sec$^{-1}$) | 30 | 90 | 650 | 2070 |

the donor-donor energy transfer takes place more often than the excited energy relaxes to lower states and that the donor-donor energy transfer contributes to the relaxation of the excited energy because of the local density fluctuation of $Er^{3+}$ ions; if all $Er^{3+}$ ions were separated from each other by an equal distance, the diffusion process would not contribute to the relaxation of the excited energy because it would not change the state of the total system.

The energy-transfer rate $(1/\tau_m - 1/\tau_0)$ increases with the concentration more rapidly than in proportion to it. This indicates the actual contribution of the diffusion process to the energy transfer, since if there were no diffusion effect the cross relaxation rate would increase in proportion to the $Er^{3+}$ concentration according to Eq. (4).[7,13]

In Fig. 5 are shown the luminescence intensities of the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions at 77 °K for the excitation into the multiplets indicated in the figure. The solid lines are the curves calculated by the following rate-equation model. The experimental result shown in this figure suggests that the cross relaxations $^4F_{7/2} \rightarrow {}^4I_{11/2}$, $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4F_{5/2} \rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$ and $^4F_{5/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$ take place in the $LaF_3$: $Er^{3+}$ system. As mentioned later, the energy-transfer constants ($C$'s) of these cross relaxations are larger than the $C_{dd}$'s of the diffusions of the $^4F_{7/2}$ and the $^4F_{5/2}$ excited-state energies. Then the direct cross relaxations are dominant for the energy transfers from the multiplets $^4F_{7/2}$ and $^4F_{5/2}$.

Generally, the relaxation of the excited state in rare-earth ions in a solid can be explained well by the rate-equation model.[18] Assuming the cross relaxation $^4F_{7/2} \rightarrow {}^4I_{11/2}$, $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and neglecting the higher-order interactions such as phonon-assisted energy transfer,[19] one gets the following rate equations for the excitation into the $^4F_{7/2}$ state at low temperatures:

$$\frac{dN_8}{dt} = \phi_0 \sigma_8 N_1 - U_{83} N_1 N_8 - R_{87} N_8 ,$$

$$\frac{dN_7}{dt} = R_{87} N_8 - R_{76} N_7 ,$$

$$\frac{dN_6}{dt} = R_{76} N_7 - R_6 N_6 ,$$

$$\frac{dN_5}{dt} = R_{65} N_6 - R_5 N_5 ,$$

$$\frac{dN_4}{dt} = R_{54} N_5 - R_{43} N_4 ,$$

$$\frac{dN_3}{dt} = R_{43} N_4 + 2 U_{83} N_1 N_8 - R_3 N_3 ,$$

(8)

where $N_i$, $\phi_0$, and $\sigma_8$ are the population of the state $i$ in Fig. 1, the excitation photon flux, and the absorption cross section corresponding to the $^4I_{15/2} \rightarrow {}^4F_{7/2}$ transition, respectively; $R_i$, $R_{ij}$, and $U_{83}$ denote the total relaxation rate of the state $i$, the multiphonon relaxation rate from the multiplet $i$ to the lower multiplet $j$, and the cross-relaxation rate mentioned above, respectively. We also assume that the excited energies of the multiplets 7 and 4 mainly decay through the multiphonon relaxation.[8] Actually the luminescences from these two multiplets were not observed at 77 °K, indicating that the relaxations are mainly due to the multiphonon relaxation. The values of the $R_{87}$, $R_6$, $R_{65}$, $R_5$, and $R_{54}$ have been estimated to be $\sim 5 \times 10^5$ sec$^{-1}$,[20] $1.0 \times 10^3$ sec$^{-1}$, $0.022 \times 10^3$ sec$^{-1}$, $1.3 \times 10^3$ sec$^{-1}$, and $0.79 \times 10^3$ sec$^{-1}$, respectively.[8,15] Using these values, the $N_3$ is written in the steady state as follows:

$$N_3 \propto \frac{6 \times 10^3 N_1}{U_{83} N_1 + 5 \times 10^5} + \frac{2 U_{83} N_1^2}{U_{83} N_1 + 5 \times 10^5} .$$

The $U_{83}$ was obtained by the best fit to the concentration dependence of the $^4I_{11/2}$ luminescence, and determined to be $2 \times 10^{-17}$ cm$^3$/sec. The same procedure can be applied to the $^4F_{9/2}$ luminescence for the excitation into the $^4F_{5/2}$ state. In this case, we assume another energy transfer constant $U_{95}$ which corresponds to the cross relaxations $^4F_{5/2} \rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$ and $^4F_{5/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$. Using the values $R_{98} \sim 2 \times 10^5$ sec$^{-1}$,[15] and $U_{83} \sim 2 \times 10^{-17}$ cm$^3$ sec in addition to the values used in the analysis of Eq. (8), we have obtained the $U_{95} \sim 8 \times 10^{-18}$ cm$^3$/sec. These phenomenological values of the cross relaxations are in good agreement with that of $2 \times 10^{-17}$ cm$^3$/sec obtained by Mita[21] for $YF_3$:Er, Yb powders. As can be

seen in Fig. 5, the theoretical curves obtained by the rate equations explain well the experimental results, though the experimental results observed for the sample of 2.0-mole % $Er^{3+}$ concentration deviate a little from the theoretical curves. This is presumably due to the neglection of higher order interactions like the phonon-assisted energy transfer and the dependence of the energy-transfer rate on the higher order of the concentration of the ions.[7,11]

$U_{83}N_1$ and $U_{95}N_1$ are equal to $W$ in Eq. (4), since these energy transfers are in the first approximation the direct cross relaxations with negligibly small diffusion as mentioned later. We can therefore compare these values determined by the rate equations with the values calculated by the equations (3) and (4).

As can be seen in Fig. 6, the overlap between the absorption spectrum of the transition $^4I_{15/2}$ $\rightarrow {}^4I_{11/2}$ and the expected emission spectrum of the transition $^4F_{7/2} \rightarrow {}^4I_{11/2}$ is fairly good. Assuming that the six emission lines overlap well with the absorption lines, we can calculate the cross-relaxation constant $C$ by Eq. (3) to be $5 \times 10^{-40}$ $cm^6/$sec. The overlap for the cross relaxation $^4F_{5/2}$ $\rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$ is poor: one absorption line and one expected line partially overlap each other. The overlap of the cross relaxation $^4F_{5/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$ is also poor,[22] and may be in the same order of that of the cross relaxation $^4F_{5/2}$ $\rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$. Assuming that the magnitude of the overlap for each case is one-tenth of the perfect overlap of one line, we can calculate the cross-relaxation constant $C$, which is the sum of the two cross-relaxation constants, by Eq. (3) to be $1 \times 10^{-40}$ $cm^6/$sec. Using these two values, $U_{83}$ and $U_{95}$ can be calculated by Eq. (4) to be $3 \times 10^{-17}$ and $6 \times 10^{-18}$ $cm^3/$sec, respectively. These values are in good agreement with the values obtained by the rate equation model: $U_{83} \sim 2 \times 10^{-17}$ $cm^3/$sec and $U_{95} \sim 8 \times 10^{-18}$ $cm^3/$sec. The critical energy-transfer distances $R_0 = (C\tau_0)^{1/6}$ of the two cross relaxations are both 3 Å, which is less than the nearest-neighbor separation.

Next we estimate the energy transfer constants of the diffusions $^4F_{7/2} \leftrightarrow {}^4I_{15/2}$ and $^4F_{5/2} \leftrightarrow {}^4I_{15/2}$. As can be seen in Fig. 7, only two lines are expected to overlap for each case. The calculated energy-transfer constant $C_{dd}$ is $8 \times 10^{-41}$ $cm^6/$sec for the former diffusion and $2 \times 10^{-41}$ $cm^6/$sec for the latter diffusion. These values are several times as small as those of the cross-relaxation constants associated with those diffusions. Therefore, the energy transfers from the $^4F_{7/2}$ and $^4F_{5/2}$ states are classified into the direct cross relaxations.

In Eq. (3), it is assumed that the oscillator strengths of the optical transitions between Stark levels of different multiplets are equal to one an-

other, although the intensity of the absorption lines in the actual system vary within a factor of 5. The energy-transfer constants calculated by Eqs. (3) and (4), however, are in good agreement with the values estimated by the rate equation model. This is presumably due to the fact that the unequal oscillator strengths may be averaged out because the absorption and the expected emission lines overlap very well for the cross relaxation $^4F_{7/2}$ $\rightarrow {}^4I_{11/2}$, $^4I_{15/2} \rightarrow {}^4I_{11/2}$.

The energy-transfer constants governing the energy transfer in $LaF_3: Er^{3+}$ have been obtained experimentally. These values are in $10^{-41}$–$10^{-40}$ $cm^6/$sec, which are smaller by two or three orders of magnitude than the energy-transfer constant $(2-6)$ $\times 10^{-38}$ $cm^6/$sec found in $LaCl_3: Pr^{3+}$ and $LaCl_3: Nd^{3+}$ by Krasutsky and Moos,[5] who have concluded that the energy transfer is due to the d-d interaction. This difference may be attributed to the different oscillator strengths of the optical transitions of the rare-earth ions and the different overlaps between the absorption and emission spectra in the two systems.

## V. SUMMARY AND CONCLUSION

The decay curve of the $^4S_{3/2}$ emission at room temperature can be explained well by the theory of Yokota and Tanimoto, in which the ion-ion interaction is assumed to be the d – d interaction. The $^4S_{3/2}$ excited state relaxes through cross relaxation from the thermally populated $^2H_{11/2}$ state in addition to the intrinsic relaxation. The energy transfer is essentially the diffusion-limited relaxation because the energy transfer constant $C_{dd}$ of the diffusions $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^2H_{11/2} \rightarrow {}^4I_{15/2}$ is larger by more than one order of magnitude than the energy transfer constant $C$ of the cross relaxations $^2H_{11/2} \rightarrow {}^4I_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$ and $^2H_{11/2} \rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4I_{9/2}$. The diffusion, however, is not effective for the relaxation in the sample containing 0.1-mole % $Er^{3+}$ ions in which the total decay rate of the $^4S_{3/2}$ state is larger than the ensemble-averaged diffusion rate.

The luminescences of a sample of high concentration of $Er^{3+}$ ions corresponding to the $^4I_{11/2} \rightarrow {}^4I_{15/2}$ and the $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions at lower temperatures are enhanced for the excitation into the $^4F_{7/2}$ and $^4F_{5/2}$ states, respectively, due to the cross relaxations $^4F_{7/2} \rightarrow {}^4I_{11/2}$, $^4I_{15/2} \rightarrow {}^4I_{11/2}$ and $^4F_{5/2} \rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$ and $^4F_{5/2} \rightarrow {}^4F_{9/2}$, $^4I_{15/2} \rightarrow {}^4I_{13/2}$. The ensemble-averaged energy-transfer rates calculated by the theory of Dexter for the d – d interaction is in good agreement with the phenomenological energy-transfer rates obtained by the rate-equation model. These energy transfers are the direct cross relaxations because the cross-relaxation constants are several times as large as the energy-transfer constants of the diffusions.

## APPENDIX

The polarization spectra of an $Er^{3+}$ ion in $LaF_3$ have been explained well by $D_{3h}$ site symmetry.[12] A $J$ multiplet is split into Stark levels of the representations $\Gamma_7$, $\Gamma_8$, and $\Gamma_9$, which are all Kramers doublets. The electric dipole components parallel to and perpendicular to the $c$ axis belong to the represenatations $\Gamma_4$ and $\Gamma_5$, respectively. The representation $\Gamma_k \times \Gamma_f$ ($k=4$ and 5, $f=7$, 8, and 9.) does not contain two or more times the same representation $\Gamma_f$. Therefore the matrix element of the electric dipole $\vec{P}$, $(\Gamma_i | \vec{P} | \Gamma_f)$ for $i=7$, 8, and 9, is proportional to $(\gamma_i \pm | \gamma_k | \gamma_f \pm)$ according to the Wigner-Eckart theorm,[23] where $\gamma_i \pm (\gamma_f \pm)$ and $\gamma_k$ are the bases of the $\Gamma_i$ ($\Gamma_f$) and $\Gamma_k$ representations, respectively. The nonzero matrix elements are
$(\gamma_7 \pm | \gamma_4 | \gamma_8 \pm)$, $(\gamma_9 \pm | \gamma_4 | \gamma_9 \mp)$, $(\gamma_7 \pm | \gamma_5 | \gamma_7 \mp)$, $(\gamma_7 \pm | \gamma_5 | \gamma_9 \pm)$, $(\gamma_8 \pm | \gamma_5 | \gamma_8 \pm)$, and $(\gamma_8 \pm | \gamma_5 | \gamma_9 \mp)$, where $(\gamma_i \pm | \gamma_k | \gamma_f \pm)$ means $(\gamma_i + | \gamma_k | \gamma_f +)$ and $(\gamma_i - | \gamma_k | \gamma_f -)$, and the square of the absolute value

of the former is equal to that of the latter.[24] This means that the transition from one state of a Kramers doublet $\Gamma_i$ to that of a Kramers doublet $\Gamma_f$ is allowed and that the transition probabilities are equal to each other. Then the transition probability due to the electric dipole $\vec{P}$ between two Stark levels from the initial and the final $J$ multiplets can be written $2(\alpha_i J_i \Gamma_i \gamma_i + \text{or} -) | \vec{P} | \alpha_f J_f \Gamma_f (\gamma_f + \text{or} -))^2$, which will be rewritten simply as $(\alpha_i J_i \Gamma_i | \vec{P} | \alpha_f J_f \Gamma_f)^2$ hereafter.

Assuming the transition probabilities of the electric dipole $\vec{P}$ between Kramers doublets of different multiplets to be equal to one another, we may give the following equation,

$$(\alpha_i J_i \Gamma_i | \vec{P} | \alpha_f J_f \Gamma_f)^2 = \frac{1}{n(J_i)n(J_f)} \times \sum_{\Gamma_i, \Gamma_f} (\alpha_i J_i \Gamma_i | \vec{P} | \alpha_f J_f \Gamma_f)^2,$$

where $n(J)$ denotes the number of Kramers doublets of a $J$ multiplet and is equal to $(2J+1)/2$. The above equation can, then, be written using the corresponding oscillator strengths between $J$ multiplets as follows:

$$f(\alpha_i J_i \Gamma_i; \ \alpha_f J_f \Gamma_f) = \frac{1}{n(J_f)} f(\alpha_i J_i; \ \alpha_f J_f).$$

Using this result, Eq. (1) can be written as Eq. (3).

---

[1] When the diffusion of the excited-state energy takes place, it is said that the energy is transfered from a donor ion to another donor ion.

[2] E. Nakazawa and S. Shionoya, J. Chem. Phys. 47, 3211 (1967); W. B. Gandrud and H. W. Moos, ibid. 49, 2170 (1968); J. P. van der Ziel, L. Kopf. and L. G. Van Uitert, Phys. Rev. B 6, 615 (1972).

[3] M. J. Weber, Phys. Rev. B 4, 2932 (1971).

[4] R. K. Watts and H. J. Richter, Phys. Rev. B 6, 1584 (1972).

[5] N. Krasutsky and H. W. Moos, Phys. Rev. B 8, 1010 (1973).

[6] T. Förster, Ann. Phys. (Leipz.) 2, 55 (1948); Z. Naturforsch. 4a, 321 (1949); D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

[7] M. Inokuti and F. Hirayama, J. Chem. Phys. 43, 1978 (1965).

[8] M. J. Weber, Phys. Rev. 157, 262 (1967).

[9] B. R. Judd, Phys. Rev. 127, 750 (1962).

[10] G. S. Ofelt, J. Chem. Phys. 37, 511 (1962).

[11] J. F. Porter and H. W. Moos, Phys. Rev. 152, 300 (1966).

[12] W. K. Krupke and J. B. Gruber, J. Chem. Phys. 39, 1024 (1963); 41, 1225 (1964); 42, 1134 (1965).

[13] F. K. Fong and D. J. Diestler, J. Chem. Phys. 56, 2875 (1972).

[14] M. Yokota and O. Tanimoto, J. Phys. Soc. Jpn. 22,

779 (1967).

[15] M. J. Weber, Phys. Rev. 156, 231 (1967).

[16] L. G. Van Uitert and L. F. Johnston, J. Chem. Phys. 44, 3514 (1966).

[17] L. A. Riseberg and H. W. Moos, Phys. Rev. Lett. 19, 1423 (1967); Phys. Rev. 174, 429 (1968).

[18] For example, J. D. Kingsley, G. E. Fenner, and S. V. Galginaitis, Appl. Phys. Lett. 15, 115 (1969); J. D. Kingsley, J. Appl. Phys. 41, 175 (1970); Y. Mita and E. Nagasawa, Jpn. J. Appl. Phys. 12, 540 (1973).

[19] T. Miyakawa and D. L. Dexter, Phys. Rev. B 1, 2961 (1970).

[20] The decay time of the $^4F_{7/2}$ state was $\sim 2 \times 10^{-6}$ sec, which was determined from the rise time of the luminescence from the lower multiplet $^4S_{3/2}$ after pulsed excitation into the multiplet $^4F_{7/2}$.

[21] Y. Mita, J. Appl. Phys. 43, 1772 (1972).

[22] The overlap integral of this cross relaxation can be expected to be poor from the energy levels of the Stark components of $Er^{3+}$ in $LaF_3$ (see Ref. 12), and be estimated to be in the same order of the cross relaxation $^4F_{5/2} \rightarrow {}^4I_{13/2}$, $^4I_{15/2} \rightarrow {}^4F_{9/2}$.

[23] For example, B. R. Judd, Operator Techniques in Atomic Spectroscopy (McGraw-Hill, New York, 1963).

[24] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups (MIT Press, Cambridge, Mass., 1963).