PHYSICAL REVIEW B VOLUME 29, NUMBER 12 15 JUNE 1984

# Concentration dependence of the phonon-assisted energy transfer between rare-earth ions

W. Strek
*Institute for Low Temperature and Structure Research, Polish Academy of Sciences,*
*P.O. Box 937, PL-50-950 Wroclaw 2, Poland*

(Received 2 March 1983; revised manuscript received 27 December 1983)

In this paper we derive an expression for the rate constant of phonon-assisted energy transfer in which the donor ion interacts with $N$ acceptors. This expression is compared with the appropriate expression for the rate constant of resonant energy transfer. It is postulated that in the system with nonresonant energy transfer the rate constant is proportional to the number of acceptors. The results are discussed in connection with the linear concentration dependence of cross relaxation in the $Nd^{3+}$ stoichiometric crystals.

## I. INTRODUCTION

The theoretical interpretation of electronic energy-transfer phenomena is based on the classical Förster-Dexter[1,2] model describing the resonant interaction between a pair of spatially localized ions via electrostatic multipolar or exchange interactions. The extension of the Förster-Dexter model to systems with nonresonant energy transfer involving phonon absorption or emission to match the energy difference in an overlap factor has been made by Orbach,[3] and Miyakawa and Dexter.[4] The problem of concentration dependence of the energy transfer between impurity ions in crystals has been studied by many authors.

This interest was due to an attempt to interpret the mechanism of energy transfer from the distance dependence. According to the electrostatic multipolar interaction model the concentration dependence of the dipole-dipole energy transfer is believed to be ruled by the distance dependence $R^{-6}$. Owing to this model it is assumed that the concentration dependence in these systems should change with the square of concentration $k_{da} \sim c^2$.

According to Förster's theory,[1] developed on a basis of kinetic treatment, the quantum yield of the acceptor at a low concentration of acceptors should be a linear function of acceptor concentration. This problem was later reexamined by Fong and Diestler,[5] who have postulated many-body interactions to explain a nonlinear concentration dependence. A discovery of a class of neodymium stoichiometric crystals exhibiting a linear concentration quenching of fluorescence at high concentrations of acceptors introduces a question of the importance of Förster's model. A phenomenon of linear concentration quenching of neodymium fluorescence at a high-concentration limit was for the first time reported by Singh *et al.*[6] in 1973. Since then this phenomenon was extensively investigated theoretically and experimentally.[6–15] A linear concentration dependence of energy transfer between different lanthanide ions was reported by Okamoto *et al.*[18,19] and Fay *et al.*[11]

The experimental results on concentration quenching of lanthanide-ion fluorescence in stoichiometric materials indicate that the linear dependence appears in the nonresonant cross relaxation. This fact is known; however, it has been believed only to indicate a small magnitude of cross relaxation in such materials.

In Sec. II we shall outline a simple semiclassical model of the phonon-assisted energy transfer for a donor ion interacting with $N$ acceptor ions. Our findings will be discussed with respect to experimental results in Sec. III.

## II. THEORETICAL APPROACH

The system under consideration consists of the donor ion surrounded by the $N$ unexcited acceptors. The electrostatic interaction between donor and acceptors is assumed to be of the dipole-dipole nature and may be generally written[15] in a point-dipole approximation as

$$H_{da}=\sum_{k=1}^{N}\sum_{q,q'}T^{(2)}_{-q-q'}(R_k,\Theta_k,\Phi_k)D^1_qD^1_{q'}(k)=\sum_{k=1}^{N}H^k_{da}\ , \tag{1}$$

where $T^{(2)}_{-q-q'}(k)$ is the orientation tensor of rank 2 describing the geometrical dependence of the donor-acceptor interaction

$$T^{(2)}_{-q-q'}(k)=R_k^{-3}(-1)^{q+q'}\times\left[\frac{(2+q+q')!(2-q-q')!}{(1+q)!(1-q)!(1+q')!(1-q')!}\right]^{1/2}\times C^{(2)}_{-q-q'}(\Theta_k,\Phi_k)\ . \tag{2}$$

The position of donor $k$ with respect to the acceptor is described by the set of coordinates $(R_k,\Theta_k,\Phi_k)$.

The dipole-moment operators $D^1_q$ and $D^1_q$ may be expressed as

$$D^1_q=\sum_i er_iC^{(1)}_q(\phi_i,\psi_i) \tag{3}$$

and

$$D^1_{q'}=\sum_j er_jC^{(1)}_{q'}(\phi_j,\psi_j)\ , \tag{4}$$

where the electrons of the acceptor are denoted by $j$ with coordinates $(r_j,\phi_j,\psi_j)$ and the electrons of the donor are denoted by $i$ with coordinates $(r_i,\phi_i,\psi_i)$.

The general form of $C_q^{(1)}(\psi,\phi)$ is

$$C_q^{(1)}(\psi,\phi)=(4\pi/3)^{1/2}Y_{1,q}(\psi,\phi)\ , \tag{5}$$

where $Y_{1,q}$ is a spherical harmonic function of rank 1.

The zeroth-order basis states of the system may be expressed as product functions of the following type: (i) the initial state

$$|i)=|d',a)=|d')|a_1)|a_2)\cdots|a_k)\cdots|a_N)\ , \tag{6}$$

and (ii) the final state

$$|f)=|d,a')=|d)|a_1)|a_2)\cdots|a_k')\cdots|a_N)\ . \tag{7}$$

$N$ is a number of acceptors. The vibronic wave functions $|d)$ and $|a)$ are products of electronic and vibrational wave functions $|d)=|d\rangle|dn\rangle$, where $|dn\rangle=\pi_v|dn_v\rangle$ and $|a)=|a\rangle|an\rangle$, where $|an\rangle=\pi_\gamma|an_\gamma\rangle$. The primes denote the excited states.

To provide a description of the phonon-assisted energy transfer, the perturbation operator is assumed to be

$$H'=H_{da}+V_I\ , \tag{8}$$

where the vibronic potential $V_I$ is separated into the donor and acceptor parts

$$V_I=V_I^d+V_I^a=\sum_v\left[\frac{\partial V}{\partial Q_v}\right]_0 Q_v+\sum_\gamma\left[\frac{\partial V}{\partial Q_\gamma^k}\right]_0 Q_\gamma^k\ . \tag{9}$$

Here, $Q_v$ and $Q_\gamma^k$ represent the normal modes of the donor and $k$th acceptor, respectively. $V$ represents electrostatic interaction between all pairs of particles.

The rate constant for the energy transfer is given by the "golden-rule" formula,[16]

$$k_{da}=\left[\frac{2\pi}{\hbar}\right]\sum_i\sum_f p(E_i)(i|\tau|f)^2\delta(E_i-E_f)\ , \tag{10}$$

where $\tau$ is given to the second order in the perturbation by

$$\tau=H'+\sum_{q\,(\neq i)}H'|q)(q|H'(E_i-E_q)^{-1}\ . \tag{11}$$

$p(E_i)$ is the probability that the system is in the initial state, given as follows:

$$\begin{aligned}E_i&=E_{d'n}+\sum_k E_{a_kn}+\Delta E^d\ ,\\ E_f&=E_{dn}+E_{a_k'n}+\sum_{l\,(\neq k)}E_{a_ln}+\Delta E^{a_k}\ ,\end{aligned} \tag{12}$$

where

$$E_{d'n}=\sum_v(n_v^{d'}+\tfrac{1}{2})\hbar\omega_v\ ,\quad E_{a_kn}=\sum_\gamma(n_\gamma^k+\tfrac{1}{2})\hbar\omega_\gamma\ ,$$

and

$$E_{a_k'n}=\sum_\gamma(n_\gamma^{k'}+\tfrac{1}{2})\hbar\omega_\gamma\ .$$

$\Delta E^a$ and $\Delta E^d$ are the electronic energy gaps between the $a'$ and $a$ states of the acceptor and the $d'$ and $d$ states of the donor, respectively.

The phonon-assisted energy transfer (PAET) is the induced second-order term in (11). In this treatment, we assume that among all frequency modes of the acceptor, only one phonon with frequency $\hbar\omega$ is necessary to match the energy difference $\Delta E$ (equal to $\Delta E^d-\Delta E^{a_k}$). Combining (10) with (9), (11), and (12), we may rewrite the rate constant as follows:

$$\begin{aligned}k_{da}=(Z_d'Z_a)^{-1}\sum_{d'n}\sum_{dn}\sum_{a_kn}\sum_{a_k'n}&\exp[-\beta(E_{d'n}+E_{a_kn}+E_{dn}+E_{a_k'n})]\\ &\times\left|\sum_k\left[\frac{\langle d'a_k|H_{da}^k|da_k'\rangle\langle d'n|dn\rangle\langle a_kn|a_k'n'\rangle\langle a_k'n'|V_I^a|a_k'n\rangle}{\hbar\omega}\right.\right.\\ &\qquad\left.\left.+\frac{\langle a_kn|V_I^a|a_kn\rangle\langle a_kn'|a_k'n\rangle\langle d'a_k|H_{da}^k|da_k'\rangle\langle d'n|dn\rangle}{\Delta E}\right]\right|^2\\ &\times\delta\left[E_{d'n}+\sum_k E_{a_kn}+\Delta E^d-E_{dn}-\sum_k E'_{a_k'nn}-\Delta E^a\right]\ .\end{aligned} \tag{13}$$

Here, $\Delta E\simeq\hbar\omega$ and $Z_d$ and $Z_a$ are the partition functions for donor and acceptors in their initial states.

In the model of harmonic-oscillator wave functions,

$$\begin{aligned}\langle a_k'n'|V_I^a|a_k'n\rangle&=\left\langle a_k'\left|\frac{\partial V}{\partial Q}\right|a_k'\right\rangle\langle a_k'n'|Q|a_k'n\rangle\\ &=V_{a_k'a_k'}^k(\hbar/2M\omega)^{1/2}[(n^k+1)^{1/2}\delta(n'^k,n^k+1)+(n^k)^{1/2}\delta(n'^k,n^k-1)]\ .\end{aligned} \tag{14}$$

Invoking the Faltung theorem we can perform Eq. (13) in terms of the convolution integrals,

$$k_{da}=\frac{2\pi}{\hbar}\sum_k \begin{bmatrix} n^k+1 \\ n^k \end{bmatrix} (D^k_{a'a}/\Delta E)^2 \times \langle d'a_k \,|\, H^k_{da} \,|\, da'_k \rangle^2 F^k_{\pm}(0) , \qquad (15)$$

where

$$D^k_{aa'}=V^k_{a'a'}-V^k_{aa} , \qquad (16)$$

$$F^k_{\pm}(0)=\int_{-\infty}^{\infty} f_d(E) f^k_a(E \pm \hbar\omega) dE . \qquad (17)$$

The generating function for donor emission is

$$f_d(E)=(Z_{d'})^{-1}\sum_{d'n}\sum_{dn}\exp(-\beta E_{dn})\langle d'n \,|\, dn\rangle^2 \times \delta(E_{d'n}-E_{dn}-E) , \qquad (18)$$

and the generating function for acceptor absorption is

$$f^k_a(E\pm\hbar\omega)=(Z_{a_k})^{-1} \times \sum_{a_k n}\sum_{a'_k n}\exp(-\beta E_{a_k n})\langle a_k n \,|\, a'_k n\rangle^2 \times \delta(E_{a'_k n}-E_{a_k n}\pm\hbar\omega-E) . \qquad (19)$$

Here, we are not interested in the precise calculation of the vibrational factor; its solution is well known.[4] Our discussion will focus on a discussion of the functional dependence of Eqs. (12) on the number of acceptor ions.

From Eq. (15) it follows immediately that the rate constant of PAET is a sum of all the acceptor terms,

$$k^{\mathrm{PAET}}_{da}=\sum_k (\cdots)^2 . \qquad (20)$$

This result is a direct consequence of using our calculation in the relation (14) and resembles the propensity rule in the theory of radiationless transitions.[17] Owing to that rule the rate constant of the radiationless transition is summed over all of the terms associated with promoting modes. It must be noted, however, that the relation (14) as opposed to the propensity rule operates only between the same electronic states.

In a case of the resonant energy transfer (RET) it may be easily anticipated that the rate constant is proportional to the square of acceptor terms,

$$k^{\mathrm{RET}}_{da}=\left|\sum_k (\cdots)\right|^2 . \qquad (21)$$

## III. DISCUSSION

In the preceding section we have developed a single model of the PAET. We have shown that due to the boson algebra properties of the phonon system, the rate constant is a sum of squares of all partial acceptor contributions arising from donor-acceptor interactions, so the PAET is an incoherent process.

In a resonant system the rate constant is given by a square of a sum of all partial contributions. In view of these results it is seen that the functional dependence of energy transfer on the number of acceptors is substantially different in resonant and nonresonant systems. As we have mentioned in the Introduction the concentration dependence of energy transfer is usually related to the distance dependence of the donor-acceptor interaction. In experiments on the concentration dependence of dipole-dipole energy transfer, the approximate formula $k(d\text{-}d)\propto R^{-6}\propto C^2$ is usually applied. Such a simple picture is very approximate and incorrect. Usually in a sphere of the strongest donor-acceptor interactions associated with the smallest donor-acceptor distance there is more than one acceptor. Let us assume that in that sphere the donor ion interacts with $N$ identical acceptors. It is evident that the probability for energy transfer in nonresonant systems, where the process is combined with emission or absorption of phonons, is proportional to $N$. In a case of RET the probability is proportional to $N^2$.

The fact that PAET is an incoherent process is well known;[21] however, the problem of linear concentration quenching has not been directly linked with this property. A microscopic model for the time development of the donor fluorescence in the presence of traps when the cross relaxation is completely incoherent has been formulated by Huber (see Ref. 21). The author has shown that the decay of the donor population, being in general nonexponential, is in two limits of fast donor-donor transfer and no donor-donor transfer at small times, approximated by an exponential function which shows linear dependence on concentration.

Following the observation that the linear concentration quenching in $\mathrm{La}_{1-x}\mathrm{Nd}_x\mathrm{P}_5\mathrm{O}_{14}$ has occured at a high concentration of $\mathrm{Nd}^{3+}$ ions, whereas at low concentration the fluorescence yield exhibited a nonlinear dependence, Lenth, Huber, and Fay[22] have developed a statistical model of fluorescence quenching stressing the importance

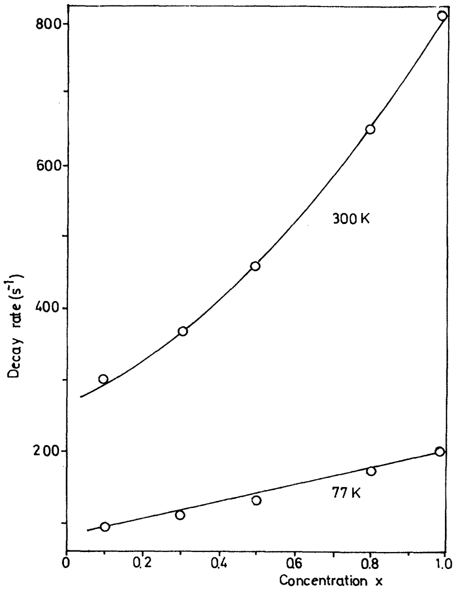

FIG. 1. Decay rate of Nd fluorescence vs concentration in $\mathrm{Cs_2NaNd}_x\mathrm{La}_{1-x}\mathrm{Cl}_6$ crystal at room and liquid-nitrogen temperatures.

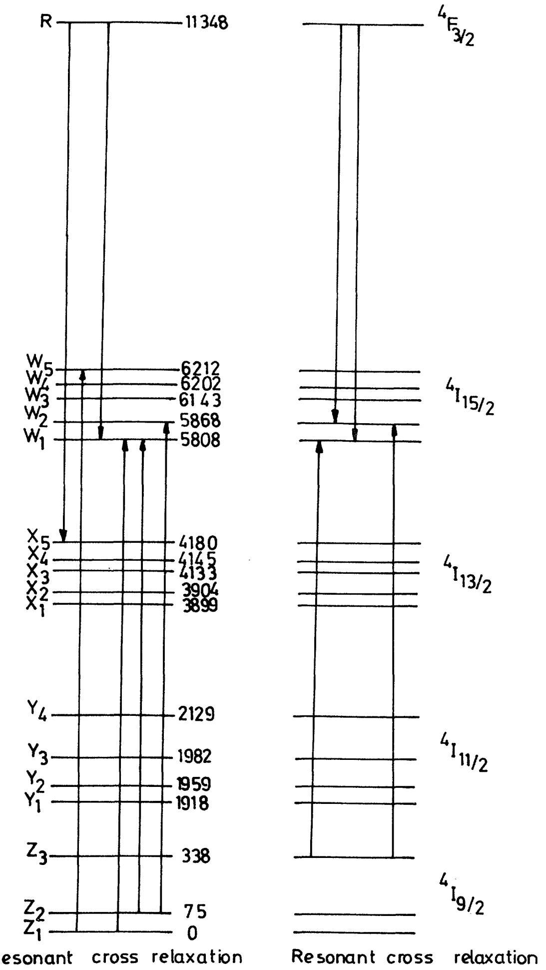

FIG. 2. Energy-level diagram and cross relaxation for $Cs_2NaNdCl_6$.

of fast energy migration.

The fast energy migration has been observed for the $NdP_5O_{14}$ crystal at room temperature by Lawson, Dowell, and Zwicker[23] by the use of a degenerate four-wave-mixing technique.

Recently Broer, Huber, Yen, and Zwicker[24] have shown using a resonant fluorescence line-narrowing measurement the absence of fast diffusion in $NdP_5O_{14}$ below 20 K in spite of the linear concentration dependence observed in this temperature. Their results have proved that the fast-diffusion mechanism[22] is not responsible for the linear dependence in the low-temperature limit. Based on the theory[21] of Huber the authors in Ref. 24 have attempted to explain the linear concentration dependence in $NdP_5O_{14}$. With Huber's model the observed decay of donor population in the limit of no donor-donor transfer is given for short times by an identical functional dependence as in the limit of fast donor-donor transfer in the model of Lenth, Huber, and Fay[22] describing the linear concentration quenching of donor fluorescence in the rapid donor-donor transfer limit.

Following Broer's argument a linear concentration dependence of fluorescence quenching in the low-concentration limit in room temperature is predicted for

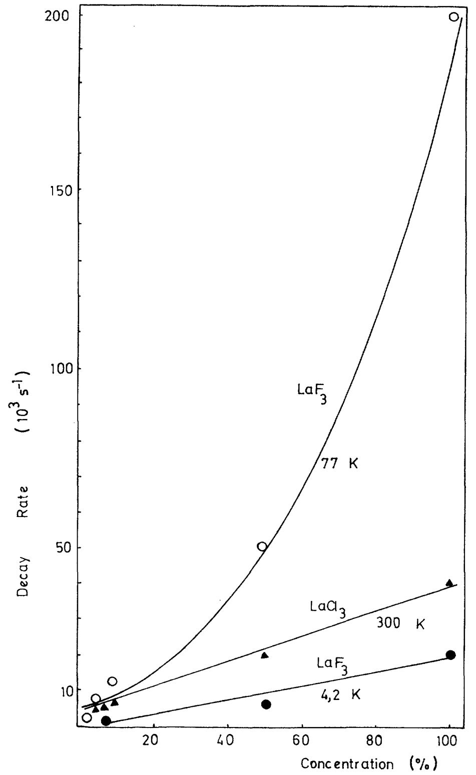

FIG. 3. Decay rate of Nd fluorescence vs concentration in $LaF_3$ crystal at 4.2 and 77 K and in $LaCl_3$ at 300 K. The experimental data were taken from Ref. 26.

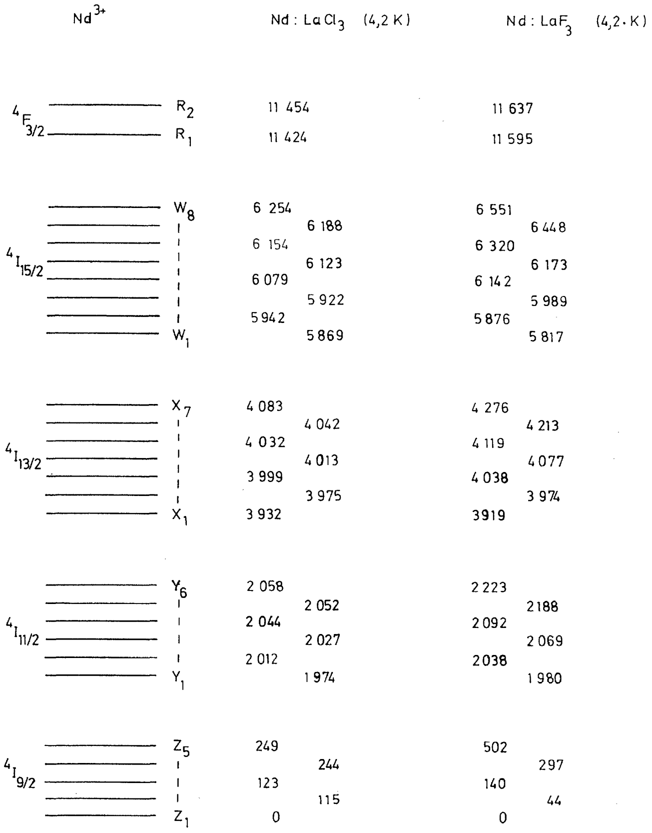

FIG. 4. Partial energy-level diagrams of $Nd^{3+}$ in $LaF_3$ and $LaCl_3$ crystal.

TABLE I. Cross-relaxation scheme and minimal energy mismatch for several crystals. The fluorescent level measured is denoted by an asterisk.

| Crystal | Cross-relaxation scheme | Minimal energy mismatch $\Delta E_{\min}$ (cm$^{-1}$) | Reference |
|---|---|---|---|
| $La_{1-x}Nd_xP_5O_{14}$ | ${}^4F^*_{3/2}\rightarrow{}^4I_{15/2}\Longleftrightarrow{}^4I_{9/2}\rightarrow{}^4I_{15/2}$ | 270 | 6 |
| $K_5La_{1-x}Nd_xMoO_4$ | ${}^4F^*_{3/2}\rightarrow{}^4I_{15/2}\Longleftrightarrow{}^4I_{9/2}\rightarrow{}^4I_{15/2}$ | 177 | 20 |
| $Nd_xLa_{1-x}Cl_3$ | ${}^4F^*_{3/2}\rightarrow{}^4I_{15/2}\Longleftrightarrow{}^4I_{9/2}\rightarrow{}^4I_{15/2}$ | 314 | 25 |
| $Er_xLa_{1-x}F_3$ | ${}^4I^*_{11/2}\rightarrow{}^4I_{13/2}\Longleftrightarrow{}^4I_{15/2}\rightarrow{}^4I_{13/2}$ | 1008 | 19 |
|  | ${}^4F^*_{9/2}\rightarrow{}^4I_{11/2}\Longleftrightarrow{}^4I_{15/2}{}^{4}{}^{13/2}$ | 1514 |  |
| $Er_xYb_yLa_{1-x-y}F_3$ | $({}^4F^*_{3/2}\rightarrow{}^4I_{13/2})_{Er}\Longleftrightarrow({}^2F_{7/2}\rightarrow{}^2F_{5/2})_{Yb}$ | 1050 | 18 |
| $Eu_{1-x}Yb_xP_5O_{14}$ | $({}^5D^*_0\rightarrow{}^7F_6)_{Eu}\Longleftrightarrow({}^2F_{7/2}\rightarrow{}^2F_{5/2})_{Yb}$ | 1090 | 11 |

$La_{1-x}Nd_xP_5O_{14}$ crystal, whereas in the observation of Lenth, Huber, and Fay,[22] the quadratic dependence was found. According to Broer, Huber, Yen, and Zwicker,[24] the temperature plays a crucial role in enhancing the donor-donor transfer with a $T^3$ or higher-power dependence. A strong onset of spectral diffusion was observed by them at 20 K on the $x=0.75$ sample. However, it is interesting to note that no strong-temperature effect on fluorescence lifetimes of $Nd^{3+}$ in pentaphosphate crystal was observed.[25]

A strong temperature dependence of fluorescence quenching was reported by Asawa and Robinson[26] for $Nd^{3+}$ in $LaF_3$. Recently, we have found[27] that the concentration dependence of $Nd^{3+}$ fluorescence in the $Cs_2NaLa_{1-x}Nd_xCl_6$ crystal was strongly affected by temperature. The dependence of fluorescence decay time was linear at 77 K whereas at room temperature it was nonlinear (see Fig. 1).

An analysis of energy levels for $Nd^{3+}$ in the $Cs_2NaNdCl_6$ crystal (see Fig. 2) indicates that at low temperature the cross relaxation is nonresonant and may proceed via PAET involving emission of four phonons with energy of 245 cm$^{-1}$.

At room temperature the enhanced Boltzmann population of the $Z_3$ level allows the occurrence of the resonant cross relaxations $RW_1\Longleftrightarrow Z_3W_2$ and $RW_2\Longleftrightarrow Z_3W_1$. These processes which are first order prevail at room temperature.

Following the experimental results of Asawa and Robinson,[26] a similar dependence is found by us for $Nd^{3+}$ in $LaF_3$ (see Fig. 3). The cross relaxation in this crystal is nonresonant at 4.2 K, with the minimum energy mismatch $\Delta E=38$ cm$^{-1}$. At this temperature the concentration dependence of the fluorescence decay rate is linear. With a slight temperature increase the anti-Stokes resonant cross relaxation takes a place and nonlinear concentration dependence is manifested.

Quite the opposite situation occurs for $Nd^{3+}$ in $LaCl_3$,[26] where a linear concentration dependence is observed at room temperature (see Fig. 3). The minimum energy mismatch for the nonresonant cross relaxation $\Delta E(R_1W_1-Z_1W_1)=314$ cm$^{-1}$ that exceeds the energy splitting of the ground electronic term $\Delta E({}^4I_{9/2})=249$ cm$^{-1}$ (see Fig. 4) excludes a possibility of anti-Stokes resonant cross relaxation.

In summary, the results obtained indicate that the linear concentration dependence of fluorescence quenching is related to the incoherent PAETS as opposed to the resonant coherent energy transfer, where a nonlinear dependence is predicted. The theoretical model developed herein is very simplified. In real systems the migration of excitation energy must be taken into account. To exclude the presence of fast migration the experiments with nonresonant systems should be made in the low-concentration limit. Such a condition was fulfilled in the experiments of Okamoto *et al.*[18,19] An additional problem appearing in investigations of energy transfer in lanthanide crystals is a possibility of anti-Stokes resonant coherent transfer at enhanced temperature, and therefore the experiments should be made in the low-temperature limit.

## ACKNOWLEDGMENTS

The author would like to thank Professor J. Heber for a critical reading of the manuscript.

---

[1] T. Förster, Z. Naturforsch. 4a, 321 (1949).

[2] D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

[3] R. Orbach, *Optical Properties of Ions in Crystals*, edited by Crosswhite and Moss (Interscience, New York, 1967), p. 445.

[4] T. Miyakawa and D. L. Dexter, Phys. Rev. B 1, 70 (1970).

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

[6] S. Singh, D. C. Miller, J. R. Potopowicz, and L. K. Shick, J. Appl. Phys. 46, 1191 (1975).

[7] I. A. Bondar, D. C. Deker, A. I. Domański, T. G. Mamedov, L. P. Metentseva, and I. A. Shcherbakov, Kvant. Elektron. (Moscow) 4, 302 (1977).

[8] W. Strek, C. Szafrański, and B. Jeżowska-Trzebiatowska, J. Mol. Struct. 46, 345 (1977).

[9] W. Strek, C. Szafrański, E. Łukowiak, Z. Mazurak, and B. Jeżowska-Trzebiatowska, Phys. Status Solidi A 41, 547 (1977).

[10] A. Lempicki, Opt. Commun. 23, 376 (1977).

[11] D. Fay, G. Huber, and W. Lenth, Opt. Commun. 28, 117 (1979).

[12] J. M. Flaherty and R. C. Powell, Phys. Rev. B 19, 32 (1979).

[13] H. C. Chow and R. C. Powell, Phys. Rev. B 21, 3785 (1980).

[14] E. Auzel, Mater. Res. Bull. 14, 223 (1979).

[15] S. R. Chinn, Y. P. Hong, and J. W. Pierce, Laser Focus 12, 64 (1976).

[16] B. G. Carlson and G. S. Rushbrooke, Proc. Cambridge Philos. Soc. 46, 626 (1950).

[17] K. Freed and J. Jortner, J. Chem. Phys. 52, 6272 (1970).

[18] E. Okamoto, H. Masui, K. Muto, and K. Awazu, J. Appl. Phys. 43, 2122 (1972).

[19] E. Okamoto, M. Sekita, and H. Masui, Phys. Rev. B 11, 5103 (1975).

[20] A. A. Kaminskii, *Laser Crystals,* Vol. 14 of *Springer Series in Optical Sciences* (Springer, Berlin, 1981).

[21] D. L. Weber, Phys. Rev. B 20, 2307 (1979).

[22] W. Lenth, G. Huber, and D. Fay, Phys. Rev. B 23, 3877 (1981).

[23] C. M. Lawson, R. C. Dowell, and W. K. Zwicker, Phys. Rev. B 26, 4836 (1982).

[24] M. M. Broer, D. L. Huber, W. M. Yen, and W. K. Zwicker, Phys. Rev. Lett. 49, 394 (1982).

[25] W. Strek, C. Szafrański, E. Łukowiak, Z. Mazurak, and B. Jeżowska-Trzebiatowska, Phys. Status Solidi A 41, 547 (1977).

[26] C. K. Asawa and M. Robinson, Phys. Rev. 141, 251 (1966).

[27] W. Strek, C. Szafrański, and B. Jeżowska-Trzebiatowska, in *Laser and Applications* (Institute for Atomic Physics, Bucharest, 1982), p. 376, and unpublished.