

*INVESTIGATION OF THE MECHANISM OF THE ELEMENTARY ACT OF EXCITATION-
ENERGY TRANSFER BETWEEN RARE-EARTH IONS IN CRYSTALS*

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We investigated the temperature dependences of the probability of the excitation-energy transfer between rare-earth ions. The chosen object of the investigation—doubly-activated fluorite—has made it possible to exclude the influence of migration of energy over the donor ions. It is shown that even in the case when there is no spectral resonance between the donor and the acceptor electron transitions, the transfer process is directly temperature dependent. Models yielding such a temperature dependence are proposed.

INTRODUCTION

RECENTLY the theoreticians and experimentors have paid much attention to various types of interactions between impurity ions in crystals. Manifestations of such interactions are such effects as the concentration quenching, energy migration, sensitization, certain spectral regularities of stimulated emission, and different cooperative effects. In spite of the large number of papers devoted to these phenomena, the "micro-mechanism" of the interaction of the impurity ions with one another and with the crystal lattice of the matrix still remains unclear to a considerable degree.

Theoretically, the greatest attention has been paid to the energy transfer when the emission spectra of the donor (D) overlap the absorption spectrum of the acceptor (A). The probability of such a transfer, without allowance for the smearing of the spectra and their incomplete overlap, was first calculated by Perrin^[1]. Subsequently, account was taken of the incompleteness of the overlap of the D emission and A absorption spectra^[2,3]. It should be noted that the aforementioned theories pertain to the elementary transfer act. Experimentally, on the other hand, one observes the emission of an ensemble of ions, the transfer probability for which may be different by virtue of the fact that the D ions in the crystals are in different surroundings of the A ions. This circumstance makes it necessary to average the expressions for the probability of the elementary transfer act. Sveshnikov and Shirkov^[4] separated the donors that have both identical and different surroundings, but have equal transfer rates. Forster^[5] combined only donors with identical surrounding of the acceptors. Both the first and the second methods of averaging lead to a non-exponential character of the damping of the D luminescence. Galanin^[6] has shown that in many cases the damping curve can be approximated by an instantaneous drop followed by an exponential.

In addition, the direct transfer of energy to the acceptor is preceded by migration of energy over the donor ions. Briskina^[7] has carried out a theoretical analysis of the transfer of energy to A with allowance for the process of migration, and has shown that the excitation is transferred to the A from the nearest D,

leading to a decrease of the non-exponential character of the damping of the luminescence of the latter. Such a situation was observed experimentally in^[8].

Many experimental results have found an explanation^[9-13] within the framework of Dexter's theory^[3]. In a number of cases the temperature dependences of the quenching of the luminescence could be explained as being due to the temperature variation of the overlap integral.^[11-13] Tolstoi, Feofilov, et al.^[14,15] observed energy transfer between Nd³⁺ and Yb³⁺ ions in glasses; this transfer could be attributed to resonant interaction of the transitions of Nd³⁺ and Yb³⁺. However, the weakening of the interaction with decreasing temperature did not fit the Dexter theory^[3], since no change in the spectra of the Nd³⁺ and Yb³⁺ were observed following cooling to 4.2°K. The authors of^[14,15] believe the reason for the observed effect to be the decrease in the efficiency of energy migration over the Nd³⁺ ions to the Yd³⁺ ions at low temperatures, by virtue of the large width and the inhomogeneous character of the broadening of the spectral lines. It is indicated that the migration over the Nd³⁺ ions can be due to resonant interaction of spectrally different centers of Nd³⁺. Finally, in a number of investigations^[16-19] they observed energy transfer between rare-earth ions without observance of spectral resonance. For such a transfer to occur it is necessary that the phonons of the crystal lattice take part. G. M. Zverev, G. Ya. Kolodnyĭ and A. M. Onishchenko (see^[18]) observed temperature dependences of the lifetime of the excited state of Er³⁺ in Y₃Al₅O₁₂ crystals, in the form

$$\tau(T) = \tau_0(1 - Ae^{-\Delta E/kT})$$

both for the case of resonant interaction (Er³⁺ → Tm³⁺) and for nonresonant interaction (Er³⁺ → Ho³⁺). The temperature dependences of the lifetimes of the excited state of Nd³⁺ in a number of other bases turned out to be similar^[18]. The authors of these papers regard migration of energy over like D ions to be responsible for such relations. It is indicated that resonant migration is less effective than nonresonant migration and that a decisive role in the temperature dependence is played by the latter.

An analysis of the published data offers evidence of the difficulty of comparing the theoretical and experi-

mental results, due to the fact that the models employed in the experiments do not make it possible to study the elementary interaction mechanism directly. As a rule, energy migration over the D ions is superimposed on this mechanism. In addition, to analyze the observed summary effects it is necessary to take into account the character of the distribution of the interacting D-A pairs: 1) with respect to distance R between them, 2) with respect to the Stark splitting in D and A centers with different structure (within the limits of inhomogeneously broadened bands or the structure of inhomogeneous splitting).

The absorption and luminescence spectra of paired rhombic Nd^{3+} centers in CaF_2 were first separated in^[20,21]. The model of such a center is shown in Fig. 1a. It turned out, further, that one of the Nd^{3+} ions in the $\text{Nd}^{3+} - \text{Nd}^{3+}$ pair can be replaced by an ion of another rare-earth element, as a result of which the pairs $\text{Nd}^{3+} - \text{Tr}^{3+}$ are produced^[22]—Fig. 1b. Rhombic pairs in CaF_2 crystals are a convenient object for the investigation of excitation-energy transfer. The data of^[23,24] show that in $\text{CaF}_2 - \text{Nd}^{3+}$ and $\text{CaF}_2 - \text{Nd}^{3+} - \text{Tr}^{3+}$ crystals, up to an Nd^{3+} concentration of 1 wt.%, there is no interaction between the ions contained in different optical centers. In this case it can be stated that if energy migration over like paired rhombic centers does exist, it cannot make a contribution to the temperature dependence of the lifetime τ of the excited state of D or to the relative quantum yield of the luminescence η .

Indeed, in the objects on which the measurements were performed, for example in^[18], the excited ions are the donors located at different distances from the acceptors. This gives rise to two subsystems of the D ions. The first system includes the D that are in the immediate vicinity of A and can transfer excitation directly to the A. The second subsystem includes the D that are remote from A and cannot transfer excitation directly to the A. The excitation in this case migrates over the D of the second subsystem until it reaches D located near A, after which direct transfer of energy from D to A takes place. It is understandable that in this case the increase in the efficiency of the migration over the D ions leads to a decrease in the lifetime of the excited state of the latter. In the model investigated by us, such an effect is excluded because in the paired centers all the donors are under absolutely identical conditions and have an identical probability of directly interacting with the A ions. In the present investigation, we have organized experiments (which will be discussed below) confirming the correctness of this conclusion. Thus, the investigation object chosen by us makes it possible to observe directly the elementary transfer process, not complicated by the factors listed above. The purpose of the present investigation was to study the elementary mechanism of excitation-energy transfer between rare-earth ions.

APPARATUS AND RESEARCH PROCEDURE

$\text{CaF}_2 - \text{NdF}_3 - \text{TRF}_3$ crystals (type I)^[25] were grown in a fluoriding atmosphere by a procedure described earlier^[26]. The concentration of the NdF_3

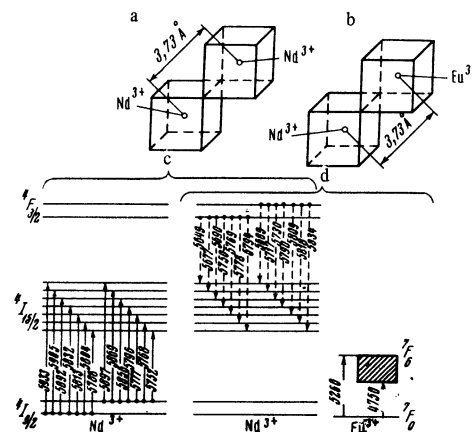


FIG. 1. a—Model of paired rhombic center $\text{Nd}^{3+} - \text{Nd}^{3+}$, b—model of paired rhombic center $\text{Nd}^{3+} - \text{Eu}^{3+}$, c—interacting transitions in the case of energy transfer in the $\text{Nd}^{3+} - \text{Nd}^{3+}$ pair, d—interacting transitions to the case of energy transfer in the $\text{Nd}^{3+} - \text{Eu}^{3+}$ pair. In Figs. c and d the numbers at the arrows indicate the frequencies in cm^{-1} .

ranged from 0.03 to 0.3 wt.%, and that of TRF_3 from 0.07 to 0.5 wt.%. The absorption and luminescence spectra at $T = 4.2^\circ\text{K}$ (the transition ${}^4\text{I}_{9/2} \rightarrow {}^4\text{F}_{3/2}$) were obtained with the aid of a DFS-12 diffraction spectrometer. The receiver was a photomultiplier (FÉU-22). In the registration of the emission spectra, the photomultiplier was cooled with liquid nitrogen. The absorption spectra at temperatures 4.2 and 77°K of the transitions Nd^{3+} (${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{15/2}$) and Eu^{3+} (${}^7\text{F}_0 \rightarrow {}^7\text{F}_6$) were also obtained with the aid of a DFS-12 diffraction spectrometer, modified to register the spectra in the infrared region.

It is shown in^[24] that at $T = 77^\circ\text{K}$ the luminescence of Nd^{3+} in paired rhombic centers $\text{Nd}^{3+} - \text{TR}^{3+}$ is practically completely quenched, with the exception of the centers $\text{Nd}^{3+} - \text{La}^{3+}$, $\text{Nd}^{3+} - \text{Ce}^{3+}$, $\text{Nd}^{3+} - \text{Gd}^{3+}$ and $\text{Nd}^{3+} - \text{Lu}^{3+}$. In all the remaining cases the interaction of Nd^{3+} at $T = 77^\circ\text{K}$ with other rare-earth ions, occurring in a paired rhombic center at a distance 3.7 \AA , leads to nonradiative loss of the excitation of the Nd^{3+} ion. Cooling to helium temperature leads to flare-up of luminescence of Nd^{3+} in the paired centers $\text{Nd}^{3+} - \text{Nd}^{3+}$ and $\text{Nd}^{3+} - \text{Eu}^{3+}$. In the case of other paired centers ($\text{Nd}^{3+} - \text{Pr}^{3+}$, Sm^{3+} , Tb^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , Tm^{3+} , Yb^{3+}), no such effect is observed, i.e., the interaction of these rare-earth ions with the Nd^{3+} ions leads to complete quenching of the luminescence of the latter also at $T = 4.2^\circ\text{K}$. We have investigated in detail the interactions in the pairs $\text{Nd}^{3+} - \text{Nd}^{3+}$ and $\text{Nd}^{3+} - \text{Eu}^{3+}$. The excitation of the luminescence of the crystal $\text{CaF}_2 - \text{Nd}^{3+} - \text{Eu}^{3+}$ was carried out successively through SZS-14 filters and filter combinations SZS-14 and SZS-21, SZS-14 and ZhS-12, SZS-14 and KS-13. The levels excited thereby were in the respective spectral regions 10 000–33 000, 16 600–31 200, 10 000–22 700, and 10 000–16 200 cm^{-1} . In the latter case, not one of the Eu^{3+} levels of the multiplet ${}^5\text{D}$ was excited, nor were the higher-lying levels excited. It turned out that when the pump spectral regions are changed, no change takes place in the luminescence spectra of Nd^{3+} (transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$), thus indicat-

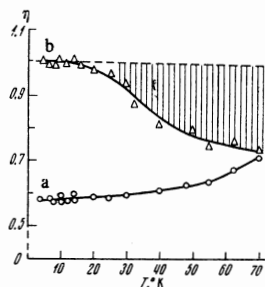


FIG. 2. Temperature dependences of the relative quantum yield of luminescence of the pair $\text{Nd}^{3+}\text{-La}^{3+}$, calculated from (1) without allowance for the function $F(T)$. The concentrations of NdF_3 and LaF_3 are respectively 0.07 and 0.14 wt. %. a—Transition to the ground component of the ground state of Nd^{3+} , b—transition to the first-excited component of the ground state of Nd^{3+} .

ing that the interaction proceeds without participation of the upper excited states of Nd^{3+} , which experience rapid relaxation to the metastable level ${}^4\text{F}_{3/2}$. In addition it can be stated that if Nd^{3+} does contribute to nonradiative relaxation of the luminescence levels of Eu^{3+} , this occurs via the levels of the ground multiplet ${}^4\text{I}$ of the Nd^{3+} ion, and these processes do not affect in any way the character of the deactivation of the metastable state ${}^4\text{F}_{3/2}$ of the Nd^{3+} ion. It follows from this that nonradiative relaxation of the level ${}^4\text{F}_{3/2}$ of the Nd^{3+} ion in the paired centers $\text{Nd}^{3+} - \text{Nd}^{3+}$ and $\text{Nd}^{3+} - \text{Eu}^{3+}$ is due to cross-relaxation processes^[12,27]. In the former case there is an interaction between the transitions ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{15/2}(\text{Nd}^{3+})$ and ${}^4\text{I}_{9/2} \rightarrow {}^4\text{I}_{15/2}(\text{Nd}^{3+})$ (Fig. 1c), and in the latter between the transitions ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{15/2}(\text{Nd}^{3+})$ and ${}^7\text{F}_0 \rightarrow {}^7\text{F}_6(\text{Eu}^{3+})$ (Fig. 1d).

We measured the temperature dependences of the relative quantum yield of luminescence of the paired centers $\text{Nd}^{3+} - \text{La}^{3+}$ (Fig. 2), $\text{Nd}^{3+} - \text{Nd}^{3+}$ (Fig. 3a) and $\text{Nd}^{3+} - \text{Eu}^{3+}$ (Fig. 3b). To this end we used the temperature dependences of the Nd^{3+} luminescence spectra (transition ${}^4\text{F}_{3/2} \rightarrow {}^4\text{I}_{9/2}$) with continuous variation of the temperature from 4.2 to 77°K. We used for the measurements a special cryostat described in^[28]. A feature of this cryostat is that the crystal is located in the helium vapor. The temperature pickup is a carbon resistor fastened directly to the crystal. Since the measurement of the temperature of the sample at continuously-fed excitation energy can in principle lead to considerable errors, we shall stop to discuss the temperature measurement in greater detail.

In the absence of excitation, a temperature of 4.2°K was established in the cryostat. The lamp was then turned on for minimum power, determined by the intensity of the excitation at which it was possible to record the luminescence spectra without noticeable apparatus distortion. The registered temperature was then raised to 7–8°K and remained constant in time. Further increase of the temperature was by heating a copper block, in which the sample was secured, by means of a coil. With the temperature varied in this manner, the luminescence spectra were recorded both while gradually raising the temperature to 70°K, and with subsequent cooling of the sample to 7–8°K. In addition, an increase of the excitation intensity by a definite amount raises the temperature of the sample, and after a definite time there is established a new stationary thermal regime. This circumstance has made it possible to obtain the temperature dependence in the entire investigated temperature interval by heating the sample with absorbed radiation.

As a control, we used also the following procedure. By increasing the intensity of the exciting light, we

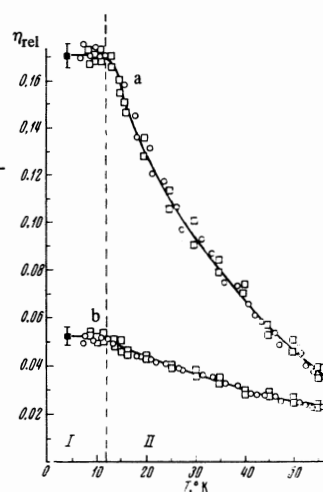


FIG. 3. Temperature dependences of the relative quantum yield of luminescence of Nd^{3+} : a—in the pair $\text{Nd}^{3+}\text{-Nd}^{3+}$; b—in the pair $\text{Nd}^{3+}\text{-Eu}^{3+}$. □—experimental points obtained by heating the sample from the surface with subsequent lowering and raising of the temperature; ○—experimental points obtained by heating the sample over the volume, ■—measurements made on a sample in liquid helium.

established a temperature corresponding to a large value of $d\eta/dT$ (Fig. 3) (for example, 20°K), and recorded the luminescence spectrum. The minimum excitation intensity was then set. This caused the registered temperature to drop to 7–8°K. Further, a temperature of 20°K was established by heating the copper block and the luminescence spectrum was again recorded. The maximum relative error in the temperature dependence, calculated from the temperature dependences of the luminescence spectra obtained by the indicated method, did not exceed 12%.

The described experiments indicate that the radial temperature gradient in the crystal is small in the stationary regime, since reversal of its sign (heating from the surface by the first method and heating in the volume by the second method) does not alter the final result significantly. The longitudinal temperature gradient is likewise small, since the absorption coefficients of the excitation bands do not exceed several tenths of a reciprocal centimeter at the maximum investigated concentrations of the Nd^{3+} , and the length of the sample does not exceed 20 mm. The same circumstance also explains the slight heating of the sample by the exciting radiation at its minimum intensity. Also contributing to this is the relatively narrow spectral region of the excitation and the small width of the luminescence line. The described experiments show that the measured temperature corresponded to the real temperature of the sample. The measurements were performed on crystals having different concentrations of both Nd^{3+} and TR^{3+} .

According to the data obtained in preceding investigations at the laboratory^[20,24,29], the relative quantum yield of the luminescence of the pairs $\text{Nd}^{3+} - \text{Nd}^{3+}$ and $\text{Nd}^{3+} - \text{Eu}^{3+}$ was determined by us from the formula

$$\eta(T) = \frac{I_M}{k_M} \frac{k_L}{I_L} \frac{b_L B_M(T)}{b_M B_L(T)} CF(T), \quad (1)$$

where I_M and k_M are the luminescence intensity and the absorption coefficient corresponding to transitions between fixed components of the metastable (${}^4\text{F}_{3/2}$) and ground (${}^4\text{I}_{9/2}$) states of the Nd^{3+} in the paired rhombic centers; I_L and k_L are the analogous quantities for a single tetragonal center L. The factor k_L/I_L takes into account the different conditions of the luminescence excitations and makes it possible to compare the

measurement results obtained with different crystals.

The coefficients b_M and b_L take into account the populations of the first excited Stark components of the ground state ${}^4I_{9/2}$ for Nd^{3+} in the paired and the single centers. Introduction of these coefficients makes it possible to verify the values of the relative quantum yield against transitions to the ground and first excited Stark components of the ground state ${}^4I_{9/2}$. The functions $B_M(T)$ and $B_L(T)$ take into account the populations of the excited Stark components of the level ${}^4F_{3/2}$ in the paired and single centers.

The meaning of the coefficient C and of the function $F(T)$ becomes clear from the following. The temperature dependences of the relative quantum yield in the "unquenched" centers $Nd^{3+} - La^{3+}$, $Nd^{3+} - Ce^{3+}$, $Nd^{3+} - Gd^{3+}$, and $Nd^{3+} - Lu^{3+}$ for transitions to the ground and first excited Stark components of the ground state ${}^4I_{9/2}$, calculated from formula (1) without allowance for the function $F(T)$, behave as shown in Fig. 2 (a—calculation based on transition to the ground Stark component of the ground state, b—to the first excited component). A simple calculation and measurements performed on crystals of different length and with different Nd^{3+} concentrations show that the difference in the values of η at $T = 4.2^\circ K$, calculated for different transitions, and the temperature dependence of η in the form shown in Fig. 2 are due to the reabsorption effect. Thus, the intensity of the luminescent transition to the ground component of the ground state ${}^4I_{9/2}$ is decreased by resonant absorption, and in the transition to the first excited component, which is not populated at $T = 4.2^\circ K$, there is no such effect. The temperature dependences of η in the "unquenched" paired centers are due to the same effect, namely, the decrease of the population of the ground Stark component and the population of the first excited component with increasing temperature. Thus, the relative quantum yield of the luminescence of the "unquenched" paired centers turns out to be, as expected, independent of the temperature in the investigated temperature interval. The coefficient C in formula (1) normalizes the value of the relative quantum yield in the "unquenched" paired centers to unity, and the function $F(T)$ takes into account effects connected with reabsorption.

The form of the function $F(T)$ was determined separately for each crystal. To this end, the temperature dependences of the luminescence spectra were obtained for $CaF_2 - Nd^{3+} - La^{3+} (Ce^{3+})$ crystals having the same geometrical dimensions and having the same pair concentrations as the crystals $CaF_2 - Nd^{3+}$ and $CaF_2 - Nd^{3+} - Eu^{3+}$. The distance to the first excited Stark component of the ground state of Nd^{3+} amounts to 38 cm^{-1} in the center $Nd^{3+} - La^{3+} (Ce^{3+})$, 36 cm^{-1} in the center $Nd^{3+} - Nd^{3+}$, and 35 cm^{-1} in $Nd^{3+} - Eu^{3+}$ [29]. Under these conditions, the function $F(T)$ for the "quenched" ($Nd^{3+} - Nd^{3+}$ and $Nd^{3+} - Eu^{3+}$) and "unquenched" ($Nd^{3+} - La^{3+}$, $Nd^{3+} - Ce^{3+}$) pairs is practically the same when their concentrations are equal.

EXPERIMENTAL RESULTS AND THEIR DISCUSSIONS

To investigate the interaction mechanism it is necessary to know the schemes of the crystal splittings of the levels between which the interacting transitions

take place. Figs. 1c and 1d show the scheme of the crystal splitting of the level ${}^4I_{15/2}$ of Nd^{3+} in paired centers and the region of absorption of Eu^{3+} corresponding to the transition ${}^7F_0 \rightarrow {}^7F_6$. We see that at $T = 4.2^\circ K$ there is no exact resonance of the cross relaxation transitions for the center $Nd^{3+} - Nd^{3+}$. The detuning of the resonance towards the Stokes side takes place only for the shortest-wavelength transition ${}^4F_{3/2} \rightarrow {}^4I_{15/2} (5794\text{ cm}^{-1})$ and for the longest-wavelength transition ${}^4I_{9/2} \rightarrow {}^4I_{15/2} (5788\text{ cm}^{-1})$ and amounts to 6 cm^{-1} . (The accuracy of the position of the Stark components is $\pm 2\text{ cm}^{-1}$.) With increasing temperature, there appears the possibility of resonant interaction of several transitions, owing to the population of the excited Stark components of the levels ${}^4I_{9/2}$ and ${}^4F_{3/2}$. In addition, there appear several nonresonating transitions with Stokes detunings, the magnitudes of which lie in the region from 0 to 82 cm^{-1} . An entirely different picture is observed for the $Nd^{3+} - Eu^{3+}$ pair. The region of the Stokes detunings for $T = 4.2^\circ K$ lies in the region $390\text{--}1044\text{ cm}^{-1}$, and at increased temperature in the region $390\text{--}1084\text{ cm}^{-1}$. We see that the minimum detuning (390 cm^{-1}) does not depend on the temperature. The slight relative increase of the upper limit is connected with the population of the excited component of the level ${}^4F_{3/2}$ of the ion Nd^{3+} (Fig. 1d).

Figure 3 shows experimental temperature dependences of the relative quantum yield of the luminescence of Nd^{3+} in the paired centers $Nd^{3+} - Nd^{3+}$ (a) and $Nd^{3+} - Eu^{3+}$ (b). These dependences were obtained with crystals having different contents of Nd^{3+} and TR^{3+} . A change in the pair concentration by more than one order does not lead to a change in the form of the $\eta(T)$ dependence. This is a confirmation of the conclusion that the migration of the energy over the D of the paired centers, if it does occur at all, does not influence the character of the deactivation of the excited state of Nd^{3+} . Let us examine the $\eta(T)$ curves (Fig. 3). We see that in the region of low temperatures (up to $12^\circ K$, Sec. I), the value of the relative quantum yield does not depend on the temperature. It is typical, however, that already in Sec. I the luminescence of Nd^{3+} is quenched to a considerable degree. Thus, for the pair $Nd^{3+} - Nd^{3+}$ the value of η amounts to 0.17 of η in the "unquenched" paired centers, and for the pair $Nd^{3+} - Eu^{3+}$ the corresponding value is 0.055. The first case of weaker quenching of the luminescence corresponds to a resonant detuning of 6 cm^{-1} in the Stokes direction, while in the second case of strong quenching the minimum detuning is 390 cm^{-1} . Since in both cases the interaction is effected with participation of the lattice phonons, the stronger quenching in the second case is naturally explained as being due to the larger density of the phonon states at the frequency 390 cm^{-1} than at 6 cm^{-1} .

The same circumstance also explains the fact that the relative quantum yield of the luminescence of the centers $Nd^{3+} - TR^{3+}$, where $TR^{3+} = Pr^{3+}, Sm^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, Er^{3+}, Tm^{3+}, Yb^{3+}$, is so low that we cannot observe luminescence of these centers even at $T = 4.2^\circ K$. An analysis of the luminescence spectra of Nd^{3+} and of the absorption spectra of the indicated ions shows that the regions of resonance detuning of the transitions of Nd^{3+} from the level ${}^4F_{3/2}$ to the levels

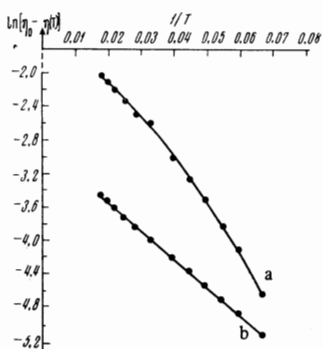


FIG. 4. Plot of $\ln[\eta_0 - \eta(T)] = f(1/T)$ in the case of the Nd^{3+} - Nd^{3+} pair (a) and the Nd^{3+} - Eu^{3+} pair (b). Here η_0 is the relative luminescence quantum yield on section I (Fig. 3) and $\eta(T)$ is the temperature-dependent part of the relative luminescence quantum yield on section II.

of the ground multiplet 4I with the transitions of these TR^{3+} include also the frequency of the main TO resonance of the CaF_2 crystals (260 cm^{-1})^[30]. Such a situation is ensured by the following transitions:

Nd^{3+} transition	TR^{3+} transition
$^4F_{3/2} \rightarrow ^4I_{11/2}$	$^7F_6 \rightarrow ^7F_0 \text{ Tb}^{3+}$, $^6H_{11/2} \rightarrow ^6H_{11/2} \text{ Dy}^{3+}$,
$^4F_{3/2} \rightarrow ^4I_{11/2}$	$^3H_4 \rightarrow ^3F_4 \text{ Pr}^{3+}$, $^6H_{11/2} \rightarrow ^6F_{11/2} \text{ Sm}^{3+}$,
$^4F_{3/2} \rightarrow ^4I_{11/2}$	$^4I_{11/2} \rightarrow ^4I_{11/2} \text{ Er}^{3+}$, $^3H_6 \rightarrow ^3H_4 \text{ Tm}^{3+}$,
$^4F_{3/2} \rightarrow ^4I_{11/2}$	$^6H_{11/2} \rightarrow ^6F_{11/2}$, $^6H_{11/2} \text{ Dy}^{3+}$
$^4F_{3/2} \rightarrow ^4I_{11/2}$	$^6H_{11/2} \rightarrow ^6F_{11/2} \text{ Dy}^{3+}$, $^5I_8 \rightarrow ^5I_8 \text{ Ho}^{3+}$, $^2F_{7/2} \rightarrow ^2F_{7/2} \text{ Yb}^{3+}$

The detuning values corresponding to the larger density of the phonon states of the lattice cause practically complete quenching of the luminescence of these centers. The succeeding $\eta(T)$ dependence in the Nd^{3+} - Eu^{3+} pair (Fig. 3b) turns out to be exponential (Fig. 4b) and the curve is well described by the formula

$$\eta_{\text{rel}}(T) = \eta_0(1 - e^{-\Delta E/kT}), \quad (2)$$

where η_0 is the relative quantum yield in the temperature region I. The value of ΔE is 22 cm^{-1} .

As shown by the experimental results, the transfer probability consists of two terms: one of them does not depend on the temperature, and the other does. The temperature-independent component is determined by the density of the phonon states at the detuning frequency. Obviously, with increasing temperature the energy $\Delta E = 22 \text{ cm}^{-1}$ plays the role of a kind of "activation" energy in the transfer.

It is known that in the far infrared, crystals have considerable absorption also at frequencies much lower than the main TO resonance^[31,32]. There exist detailed theoretical explanations of this fact^[33,34]. The physical model of such a process of absorption becomes clear when the dispersion diagram of the crystal is examined. Since it is impossible to excite low-frequency acoustic phonons in crystals having a symmetry center, owing to their optical inactivity, a considerable contribution to the absorption is made by transitions in which one phonon of the lower branch is annihilated and another "difference" phonon is produced with the same momentum but with higher energy. The energy difference is made up by absorption of an infrared quantum.

As a result of an experimental investigation of the absorption spectra of the crystal lattice of alkali-halide crystals in the far infrared, Stolen and Dransfeld^[31] obtained "selection rules" that forbid transitions between branches with different polarizations. Burstein et al.^[35] developed selection rules for two-phonon transitions in crystals of the rock-salt type on the

basis of a group-theoretical analysis. Perlin et al.^[36] have shown that in a number of cases a greater probability is possessed by relaxation with participation of a set of optical and acoustic phonons. Dispersion curves of the CaF_2 crystal were obtained in a number of studies^[30,37]. Elcombe and Pryor^[30] also give the frequency dependence of the density of the phonon states. On the basis of these published data we can propose two models determining the temperature dependence of the elementary process of nonresonant excitation-energy transfer.

As follows from^[30], the condensation sections in the phonon spectrum of CaF_2 extend to $\sim 480 \text{ cm}^{-1}$, and to effect the energy transfer from the Nd^{3+} ion to the Eu^{3+} ion it is necessary to cover an energy deficit exceeding 390 cm^{-1} . Phonons of such energy are absorbed on the temperature Section I. With increasing temperature, population of the phonon state corresponding to the acoustic branch takes place. A transition then becomes possible between the state corresponding to the acoustic branch and the state determined by the short-wave condensation section in the phonon spectrum of the crystal. Since the population of the acoustic branch increases with increasing temperature, a corresponding increase takes place also in the probability of such a process, and consequently in the probability of excitation-energy transfer. A similar mechanism is responsible for the temperature dependence of the absorption of the crystals at frequencies below the main TO resonance. The only difference is that in the latter case the absorption corresponds to transitions to the boundary of the band. Transitions with participation of acoustic phonons with small wave vectors do not occur, since transitions between acoustic branches are forbidden. In the model proposed by us, the process is effected with participation of phonons of the acoustic and optical branches with small values of the wave vector.

The second model consists in the following: the energy deficit of more than 390 cm^{-1} that must be absorbed by the lattice in order to realize the act of energy transfer from Nd^{3+} to Eu^{3+} is made up in the entire temperature interval by a set consisting of an optical phonon, corresponding to the maximum density of the phonon state, and an acoustical phonon^[36]. Within the framework of these concepts one can explain also the temperature dependence of the elementary act of transfer of excitation energy. Indeed, even after a slight temperature rise there occurs population of the vibrational state corresponding to the acoustic branch, and the process of absorption of the acoustic phonon becomes stimulated. With further increase of the temperature, the population of this vibrational level increases, the probability of releasing an acoustic phonon to the lattice increases, and consequently the probability of energy transfer increases. Optical phonons remain spontaneous in the investigated temperature region.

In both proposed models, phonons with small values of the wave vector take part in the transfer. If we take into account the low density of states of the acoustic phonons with small values of the wave vector, then at first glance this seems strange. However, according to Stolen and Dransfeld^[31], acoustic phonons can make

an appreciable contribution to the absorption in the far infrared region, and consequently to the transfer probability considered by us. The low density of states of the acoustic phonons is compensated by the low frequency of these phonons, which stands in the denominator of the expression for the absorption coefficient. It is also clear why the $\eta(T)$ dependence on section II is exponential for the $\text{Nd}^{3+} - \text{Eu}^{3+}$ pair. Indeed, since the detuning in this case is practically independent of the temperature, the energy deficit is made up by a temperature-independent combination of optical and acoustic phonons. In the case of energy transfer from an Nd^{3+} to an Nd^{3+} ion, the detuning changes with temperature and ΔE in (2) turns out to be a function of the temperature (Fig. 4a).

The quantum yield of excitation-energy transfer is determined by the well-known expression

$$\eta_t = \frac{W_{DA} \tau_{ec}}{1 + W_{DA} \tau_{ec}}, \quad (3)$$

where W_{DA} is the probability of transfer from D to A, and τ_{ec} is the lifetime of the excited state in the "unquenched" center and is determined by its symmetry¹⁾. The quantity η_t is connected with the measured relative luminescence quantum yield by the expression

$$\eta = 1 - \eta_t.$$

Using these relations, we determine the probabilities of excitation-energy transfer and the corresponding lifetimes of the excited state ($1/\tau_{\text{obs}} = 1/\tau_{ec} + W_{DA}$). The results of the calculations are presented in Tables I and II.

CONCLUSION

Thus, the results of the present paper offer evidence that the probability of excitation-energy transfer in the absence of overlap of the spectra of the donor and acceptor is determined by the density of the phonon states in the region of frequencies corresponding to the Stokes detuning of the resonance. The temperature activation leading to the increase of the transfer probability is inherent in the very elementary act of donor-acceptor transfer to the same degree as it is to the process of energy migration over the donor ions. The mechanism of temperature activation is connected with the population of the phonon state corresponding to the acoustic branch of the dispersion diagram. These effects are manifest also in the temperature dependence of the infrared absorption spectra both of crystals of the fluoride type and of alkali-halide crystals and other compounds. In some cases the population of the first excited Stark component of the donor ions can play a role, in accord with the results of Zverev, Kolodnyĭ, and Onishchenko (see^[18]). Such a situation, however, can be realized only if the new detuning resulting from the population of the excited level corresponds to a region of the phonon spectrum with a larger density of phonon states than the initial detuning, i.e., $\rho_{\nu_i} - \rho_{\nu_0} > 0$, where ρ_{ν_i} and ρ_{ν_0} are the densities of the phonon states corresponding to the "new" and initial detunings.

Table I. Interaction in the $\text{Nd}^{3+} - \text{Nd}^{3+}$ pair

$T, ^\circ\text{K}$	$10^4 W_{DA}, \text{sec}^{-1}$	$\tau_{\text{obs}}, \mu\text{sec}$
4,2-12	0,98	85
17	1,14	75
23	1,34	65
27	1,62	55
33	2,02	45
40	2,66	35
49	3,8	25
54	4,8	20

Table II. Interaction in the $\text{Nd}^{3+} - \text{Eu}^{3+}$ pair

$T, ^\circ\text{K}$	$10^4 W_{DA}, \text{sec}^{-1}$	$\tau_{\text{obs}}, \mu\text{sec}$
4,2-12	3,5	27
20	4,3	22
25	4,8	20
30	5,2	19
40	6,47	15
50	8,5	12
54	9,8	10

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¹F. Perrin, *Ann. der Phys.*, **17**, 283 (1932).

²Th. Forster, *Ann. der Phys.*, **2**, 55 (1948).

³D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).

⁴B. Ya. Sveshnikov, *Dokl. Akad. Nauk SSSR* **115**, 274 (1957) [*Sov. Phys.-Doklady* **2**, 336 (1958)]; B. Ya. Sveshnikov and V. I. Shirkov, *Opt. Spektrosk.* **12**, 576 (1962).

⁵Th. Forster, *Zs. Naturforsch.*, **4a**, 321 (1949).

⁶M. D. Galanin, *Trudy FIAN* **12**, 3 (1960).

⁷Ch. M. Briskina, Candidate's dissertation, Moscow, 1968.

⁸Yu. K. Voroniko, M. V. Dmitruk, V. V. Osiko, and V. T. Udovenchik, *Zh. Eksp. Teor. Fiz.* **54**, 367 (1968) [*Sov. Phys.-JETP* **27**, 197 (1968)].

⁹L. G. Van Uitert, E. F. Dearborn, and H. M. Marcos, *Appl. Phys. Lett.*, **9**, 255 (1966).

¹⁰L. G. Van Uitert, E. F. Dearborn, and I. I. Rubin, *J. Chem. Phys.*, **45**, 1578 (1966); **47**, 547 (1967).

¹¹L. G. Van Uitert, E. F. Dearborn, and I. I. Rubin, *J. Chem. Phys.*, **46**, 3551 (1967).

¹²L. G. Van Uitert and L. F. Johnson, *J. Chem. Phys.*, **44**, 3514 (1966).

¹³C. K. Asawa and M. Robinson, *Phys. Rev.*, **141**, 251 (1966).

¹⁴M. N. Tolstoĭ, P. P. Feofilov, and V. N. Shapovalov, *Izv. AN SSSR, Seriya Fiz.* **31**, 2064 (1967).

¹⁵G. O. Karapetyan, M. N. Tolstoĭ, P. P. Feofilov, and V. N. Shapovalov, *Zh. Prikl. Spektrosk.* **7**, 174 (1967).

¹⁶L. F. Johnson, L. G. Van Uitert, I. I. Rubin, and R. A. Thomas, *Phys. Rev.*, **133**, A494 (1964).

¹⁷Yu. K. Voroniko, B. I. Denker and V. V. Osiko, *Trudy FIAN* **59** (1971) (in press).

¹⁸G. Ya. Kolodnyĭ, Candidate's dissertation, Moscow, 1970.

¹⁹M. R. Brown, I. S. S. Whiting, and W. A. Shand,

¹⁾The time τ_{ec} was measured in ^[24] for Nd^{3+} rhombic centers.

J. Chem. Phys., 43, 1 (1965).

²⁰Yu. K. Voron'ko, A. A. Kaminskiĭ, and V. V. Osiko, Zh. Eksp. Teor. Fiz. 49, 420 (1965) [Sov. Phys.-JETP 22, 295 (1966)].

²¹N. E. Kask, L. S. Kornienko, and M. Fakir, Fiz. Tverd. Tela 6, 549 (1964) [Sov. Phys.-Solid State 6, 430 (1964)].

²²Yu. K. Voron'ko, R. G. Mikaélyan and V. V. Osiko, Zh. Eksp. Teor. Fiz. 53, 484 (1967) [Sov. Phys.-JETP 26, 318 (1968)].

²³Yu. K. Voron'ko and V. V. Osiko, ZhETF Pis. Red. 5, 357 (1967) [JETP Lett. 5, 295 (1967)].

²⁴S. Kh. Batygov, Yu. K. Voron'ko, M. V. Dmitruk, V. V. Osiko, A. M. Prokhorov, and I. A. Shcherbakov, Trudy FIAN 59, (1971) (in press).

²⁵V. V. Osiko, in Rost kristallov (Crystal Growing) 5, 373 (1965).

²⁶Yu. K. Voron'ko, V. V. Osiko, V. T. Udovenchik, and M. M. Fursikov, Fiz. Tverd. Tela 7, 267 (1965) [Sov. Phys.-Solid State 7, 204 (1965)].

²⁷J. F. Porter and H. W. Moos, Phys. Rev., 152, 300 (1966).

²⁸N. D. Kozlova, L. F. Myzenkova, and V. V. Baron, in Fiziko-khimiya, metallovedenie i metallofizika sverkhprovodnikov, Trudy IV Vsesoyuznogo soveshchaniya (Physical Chemistry, Physical Metallurgy, and Metal Physics of Superconductors. Transactions of Fourth All-union Conference), Nauka, 1969, p. 120.

²⁹Yu. K. Voron'ko, É. K. Murav'ev, and I. A. Shcherbakov, Kratkie soobshcheniya po fizike (Short Communications in Physics) (FIAN SSSR) 9, 64 (1970).

³⁰M. M. Elcombe and Q. W. Pryor, J. of Phys. C. (Solid State Physics, 3, 492 (1970).

³¹R. Stolen and K. Dransfeld, Phys. Rev., 139, A1295 (1965).

³²D. R. Bosomworth, Phys. Rev., 157, 157 (1967).

³³H. Bilz and L. Genzel, Zs. Phys., 169, 53 (1962).

³⁴V. V. Mitskevich, Fiz. Tverd. Tela 3, 3036 (1961); 4, 3035 (1962) [Sov. Phys.-Solid State 3, 2211 (1962); 4, 2224 (1963)].

³⁵E. Burstein, F. Q. Johnson, and R. London, Phys. Rev., 139, A1239 (1965).

³⁶Yu. E. Perlin, V. Ya. Gamurar and B. S. Tsukerblat, Vtoroi seminar po spektroskopii i svoistvam lyuminoforov, aktivirovannykh redkimi zemlyami (Second Seminar on the Spectroscopy and Properties of Rare-Earth-Activated Luminors (collected papers)). Institute of Radio Engineering and Electronics of the Academy of Sciences of the USSR, 1969, p. 171.

³⁷S. Ganesan and E. J. Burstein, J. Phys., 26, 645 (1965). S. Ganesan and R. Srinivason, Can. J. Phys., 40, 74 (1962).

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100