

EXCHANGE-PHONON MECHANISM OF ENERGY MIGRATION IN SOLIDS

I. A. NAGIBAROVA and V. R. NAGIBAROV

Kazan' Physico-technical Institute, USSR Academy of Sciences

Submitted December 21, 1967

Zh. Eksp. Teor. Fiz. 55, 1277-1287 (October, 1968)

A theory is developed for the migration of energy through a phonon field between exchange pairs or an exchange pair and a single center, in cases when the multiplicities of the ground and excited levels of the single center are the same, and in the case when these multiplicities are different. Estimates of the orders of magnitude of the migration probability indicate that the proposed mechanism is effective in the optical, infrared, and radio-frequency regions.

THE first to investigate the migration of energy via exchange interaction was Dexter<sup>[1]</sup>. Energy transfer can occur in this case only when the wave functions of the interacting particles overlap and the multiplicity of the excited level of the acceptor equals the multiplicity of the excited level of the donor, and the multiplicity of the ground state of the donor is equal to the ground state of the acceptor, although the multiplicities of the ground and excited states may be different. These requirements, imposed on the interacting systems, greatly limit the physically possible number of migration processes that can be described by the theory of inductive resonance.

In addition, the theory of exchange-resonance interaction is static in that it does not take into account the influence of the lattice vibrations on these processes. Since exchange interactions are very sensitive to changes of the distance between particles, modulation of these distances by the lattice vibrations should have a very strong influence on the exchange mechanism of the migration. In the presence of an interaction between the impurities and the lattice vibrations, the phonon field is also a medium through which effective transfer of the excitation energy between the impurity centers is possible<sup>[2,3]</sup>.

Recent interesting papers by Ovsyankin and Feofilov<sup>[4,5]</sup> describe experiments on the observation of simultaneous excitation-energy transfer from two donors to one acceptor. The authors note that in phenomena of this kind an important role should be played by the migration of energy and by two-particle interactions (in particular, also exchange interactions).

Powell et al.<sup>[6]</sup> and Imbusch<sup>[7]</sup> directly observed nonresonant energy migration between the exchange pair Cr<sup>3+</sup> - Cr<sup>3+</sup> and individual Cr<sup>3+</sup> ions in ruby, and used the Forster-Dexter<sup>[1,8]</sup> theory to explain the experiments. However, from our point of view, the results of<sup>[6,7]</sup> can be interpreted as being due to the exchange-phonon mechanism, which can also be used to explain phenomena similar to the Feofilov-Ovsyankin effect<sup>[4,5]</sup>.

1. OPERATOR OF INTERACTION BETWEEN EXCHANGE PAIR AND LATTICE

The energy of the exchange interaction of two impurity centers d and a is in the general case a function of their relative distance  $|r_d - r_a|$  and the spin operators  $s_d$  and  $s_a$ <sup>[9]</sup>. Therefore the Hamiltonian of the exchange

interaction can be written in the form

$$\mathcal{H}'_{\text{exch}} = I(s_d, s_a, |r_d - r_a|), \tag{1}$$

where  $r_d(r_a)$  are the coordinates of the particle d(a);  $r_d = r_d^0 + \Delta r_d$ ;  $r_a = r_a^0 + \Delta r_a$ ;  $r_d^0$  and  $r_a^0$  are the equilibrium values of the coordinates with respect to the particles d and a;  $\Delta r_d(\Delta r_a)$  are their displacements due to the lattice vibrations.

Assuming the impurity displacements to be small, we expand (1) in powers of  $\Delta r_{da} = \Delta r_d - \Delta r_a$ , and, confining ourselves to terms linear in  $\Delta r_{da}$ , we get

$$\mathcal{H}'_{\text{exch}} = \mathcal{H}^0_{\text{exch}} + \mathcal{H}_{\text{exch}}, \quad \mathcal{H}^0_{\text{exch}} = I(s_d, s_a, |r_{da}^0|), \tag{2}$$

$$\mathcal{H}_{\text{exch}} = \left( \frac{\partial I(s_d, s_a, |r_{da}|}{\partial \Delta r_{da}} \right)_{\Delta r_{da}=0} \Delta r_{da}. \tag{2a}$$

In particular, the exchange interaction operator can be chosen in the form<sup>[10]</sup>

$$\mathcal{H}'_{\text{exch}} = I_0 s_d s_a \exp[-\xi |r_{da}|], \tag{2b}$$

$$\mathcal{H}_{\text{exch}} = I_0 s_d s_a \xi \exp[-\xi |r_{da}^0|] \frac{r_{da}^0}{|r_{da}^0|} \Delta r_{da}, \tag{2c}$$

where  $I_0$  is the exchange interval and  $\xi$  is a parameter characterizing the rate of decrease of the exchange interaction with increasing distance. Let us expand the displacement  $\Delta r_{da}$  in a series in the normal vibrations of the crystal lattice

$$\Delta r_{da} = \sum_{\mathbf{k}_s} \left( \frac{\hbar}{2M\omega_{\mathbf{k}_s}} \right)^{1/2} \Phi_{\mathbf{k}_s} [a_{\mathbf{k}_s} e^{i\mathbf{k}_s r_d^0} (e^{i\mathbf{k}_s r_{da}^0} - 1) + a_{\mathbf{k}_s}^+ e^{-i\mathbf{k}_s r_a^0} (e^{-i\mathbf{k}_s r_{da}^0} - 1)] \tag{3}$$

where  $M$  is the crystal mass,  $\Phi_{\mathbf{k}_s}$  the polarization,  $\mathbf{k}_s$  the wave vector of the s-th mode,  $\omega_{\mathbf{k}_s}$  the frequency of the phonon of the s-th mode,  $a_{\mathbf{k}_s}$  ( $a_{\mathbf{k}_s}^+$ ) the operator for annihilation (creation) of a phonon with wave vector  $\mathbf{k}_s$ , and  $\hbar$  is Planck's constant.

Expression (3) can be simplified by assuming that the inequality  $\mathbf{k}_s r_{da}^0 \ll 1$ , which is valid up to the highest frequencies, is satisfied for all the normal vibrations. When this is taken into account, the operator (2a) can be rewritten in the form

$$\mathcal{H}'_{\text{exch}} = I^n \sum_{\mathbf{k}_s} \left( \frac{\hbar}{2M\omega_{\mathbf{k}_s}} \right)^{1/2} (r_{\mathbf{k}_s} | \mathbf{k}_s | (r_0 \Phi_{\mathbf{k}_s}) (a_{\mathbf{k}_s} e^{i\mathbf{k}_s r_n} - a_{\mathbf{k}_s}^+ e^{-i\mathbf{k}_s r_n})), \tag{4}$$

where

$$I^n = \left( \frac{\partial I(s_d, s_a, |r_{da}|)}{\partial |r_{da}|} \right)_{|r_{da}|=|r_{da}^0|} |r_{da}^0|, \quad \mathbf{k}_s^0 | \mathbf{k}_s | = \mathbf{k}_s,$$

$r_0 |r_{da}^0| = r_{da}^0$ , inasmuch as the exchange integral has an appreciable magnitude only at small distances between the interacting particles, and  $\eta$  is the index of the pair. We shall henceforth confine ourselves to acoustic branches only, assuming the propagation velocities of the longitudinal and transverse oscillations to be equal.

## 2. INTERACTION BETWEEN EXCHANGE PAIRS THROUGH THE PHONON FIELD

We consider the transfer of excitation energy from one exchange pair to another one via the phonon field. For the calculation of the excitation-energy migration probability per unit time  $W_{ij}$ , we shall use the formalism of the evolution operator<sup>[3,11]</sup>

$$W_{ij} = \lim_{t \rightarrow \infty} \frac{1}{t} |\langle \psi_m | L(t) | \psi_n \rangle|^2, \quad (5)$$

where

$$L(t) = \exp(-i\hbar^{-1}t\mathcal{H}), \quad \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{\text{exch}}^i + \mathcal{H}_{\text{exch}}^j$$

$\mathcal{H}_0$  describes the unperturbed spectrum of the system constituting the exchange pair  $i +$  exchange pair  $j +$  phonon field;  $\psi_n$  and  $\psi_m$  are respectively the initial and final wave function in the system, which are eigenfunctions of  $\mathcal{H}_0$ .

We shall assume that in the initial state the exchange pair  $i$  is excited and the exchange pair  $j$  is in the ground state, and that the opposite takes place in the final state. We shall consider here only resonant energy transfer, so that the state of the lattice remains unchanged.

The process of interest to us is described by second order perturbation theory in  $\mathcal{H}_{\text{exch}}^{i,j}$ . Substituting (4) in (5), we get after a number of evident but cumbersome calculations

$$W_{ij} = \frac{\pi}{2M^2\hbar^2} \left| \sum_{\mathbf{k}} \frac{\omega_{\mathbf{k}}}{v_{\mathbf{k}}} \left\{ \frac{\exp[i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)]}{\omega_0 + \omega_{\mathbf{k}}} - \frac{\exp[-i\mathbf{k}(\mathbf{r}_i - \mathbf{r}_j)]}{\omega_0 - \omega_{\mathbf{k}}} \right\} \right. \\ \left. \times \langle \psi_m^i | I^i | \psi_n^i \rangle \langle \psi_m^j | I^j | \psi_n^j \rangle \right|^2 g(0) \quad (6)$$

where

$$g(0) = \int_0^{\infty} g_i(\omega) g_j(\omega) d\omega,$$

and  $g_{i,j}(\omega)$  are respectively the densities of the initial and final states of the pairs  $i + j$ ,  $\hbar\omega_0$  is the excitation energy of the exchange pair. Inasmuch as we shall henceforth assume, for simplicity, that the pairs are produced by identical ions, we get  $I^i = I^j = I$ . The quantity  $I$ , which is proportional to the exchange integral, assumes different values in different cases, when:

a) both particles of the pair are excited in the initial state and both are in the ground state in the final state; b) both ions of the pair are excited in the initial state, and in the final state one ion is in the ground state and the other is excited; c) one of the pair particles is excited in the initial state and the other is in the ground state, and the situation is reversed in the final state.

For simplicity we shall assume henceforth that the exchange pairs are identical and are made up of identical particles. An analysis of expression (6) shows that the phonons interact in the migration process like virtual particles, since  $W_{ij}$  does not depend on the number of phonons  $\omega_{\mathbf{k}}$ . This indicates that formula (6) is applicable for the description of transport processes both in

the microwave and in the optical range. The role of the phonons in such processes can be visualized as follows. The lattice vibrations modulate the exchange interaction of the exchange pair  $i$ , as the result of which the pair goes over from the excited to the ground state with production (absorption) of a virtual phonon, which is then absorbed (produced) by pair  $j$  with simultaneous transition from the ground state to the excited state.

For subsequent calculations it is necessary to sum over  $\mathbf{k}$  in (6), for which purpose we use the Debye model of a crystal lattice, replacing the summation over  $\mathbf{k}$  by integration over  $\omega$  from zero to the limiting Debye frequency  $\omega_D$ ,  $z$  axis parallel to  $\mathbf{r}$ :

$$W_{ij} = \frac{1}{16\pi^5\hbar^2\rho^2} |\langle \psi_m | I | \psi_n \rangle|^4 \left| \int_0^{\omega_D} d\omega \int_0^{\pi} (\cos^2\theta + 2\sin^2\theta \cos^2\theta) d\theta \int_0^{2\pi} \frac{\omega^3}{v^5} \right. \\ \left. \times \left\{ \frac{\exp[i\omega r v^{-1} \cos\theta]}{\omega_0 + \omega} - \frac{\exp[-i\omega r v^{-1} \cos\theta]}{\omega_0 - \omega} \right\} d\varphi \right|^2 g(0), \quad (7)$$

where  $\rho$  is the density of the crystal,  $\theta$  and  $\varphi$  are spherical coordinates, and  $r = |\mathbf{r}_i - \mathbf{r}_j|$ .

In integrating (7) over  $\omega$ , two cases are possible,  $\omega_0 > \omega_D$  and  $\omega_0 < \omega_D$ . When  $\omega_0 > \omega_D$ , the integrand contains no singularities. On the other hand, when  $\omega_0 < \omega_D$ , singular points appear in (7), making it possible to extend the integration to infinity and evaluating the resultant integral

$$\int_0^{\infty} \omega^3 \sin\left(\frac{\omega r}{v}\right) (\omega_0^2 - \omega^2)^{-1} d\omega$$

by residues. It is clear from this that the results of the integration are essentially different for  $\omega_0 > \omega_D$  and  $\omega_0 < \omega_D$ , and correspond to different physical conditions. We shall therefore consider both these cases separately.

1. For  $\omega_0 > \omega_D$ , the migration probability is equal to

$$W_{ij} = \frac{|f_1(\omega_D, r)|^2}{8\pi^5\hbar^2v^2\omega_0^4} |\langle \psi_m | I | \psi_n \rangle|^4 g(0), \quad (7a)$$

where

$$f_1(\omega_D, r) = \frac{\omega_D^3}{r^2v^3} \cos\varphi_D - 3 \frac{\omega_D^2}{r^2v^2} \sin\varphi_D \\ - 14 \frac{\omega_D}{r^2v} \cos\varphi_D - \frac{1}{r^5} (10 \sin\varphi_D - 12\pi), \quad \frac{\omega_D r}{v} = \varphi_D.$$

In the optical range,  $\omega_0 > \omega_D$ , a characteristic feature is the different dependence of  $W_{ij}$  on the distance between the exchange pairs  $i$  and  $j$ ; the average distance between the exchange pairs can be obtained by starting from the fact that the pair concentration is proportional to the square of the impurity concentration  $c'$  ( $c' = N/N_0$ ,  $N$ —number of impurities,  $N_0$ —number of lattice points that can be occupied by these impurities). For the concentrations  $c' \sim 10^{-2}$  employed in practice, the distance between exchange pairs is  $r \sim 10^{-6} - 10^{-5}$  cm. At such a value of  $r$  and at the following values of the parameters which enter in formula (7a) (all the data, except the values of the exchange integral, pertain to ruby):

$$v = 6 \cdot 10^5 \text{ cm} \cdot \text{sec}^{-1}, \quad \omega_0 = 3 \cdot 10^{15} \text{ sec}^{-1}, \quad \rho = 3 \text{ g} \cdot \text{cm}^{-3} \\ \omega_D = 6 \cdot 10^{13} \text{ sec}^{-1}, \quad I = 10^{-12} \text{ erg}, \quad r = 10^{-5} - 10^{-6} \text{ cm},$$

$g(0) = 10^{-7} \text{ sec}$ ; the largest contribution to  $f_1(\omega_D, r)$  is made by the first term. Omitting all the other terms of

$f_1(\omega_D, r)$ , we obtain for the probability of energy transfer from one exchange period to the other the expression

$$W_{ij} = \frac{\omega_D^6}{(2\pi)^3 \hbar^2 \rho^2 \omega_0^4 v^6} |\langle \psi_m | I | \psi_n \rangle|^4 g(0),$$

$$W_{ij} \sim 10^{-4} \text{ sec}^{-1}.$$

2. When  $\omega_0 < \omega_D$ , the transfer probability takes the form

$$W_{ij} = \frac{|f_2(\omega_0, r)|^2}{2^5 \pi^3 \rho^2 \hbar^2} |\langle \psi_m | I | \psi_n \rangle|^4 g(0),$$

$$f_2(\omega_0, r) = e^{i\varphi_0} \left[ -\frac{\omega_0^2}{rv^4} - \frac{8}{r^2 v^2} + \frac{24(i-1)}{\omega_0 r^2 v} \right] + \frac{48}{\omega_0^2 r^5}, \quad \varphi_0 = \frac{\omega_0 r}{v}. \quad (7b)$$

For the same values of the parameters as for (7a), but with  $g(0) = 10^{-9} \text{ sec}$ , we get  $\omega_0 = 10^{11} \text{ sec}^{-1}$  and  $W_{ik} = 10^2 - 10^4 \text{ sec}^{-1}$ .

For  $\omega_0 < \omega_D$ , the interaction between the exchange pairs remains greatly long-range. If we take into account the fact that, for the total probability of migration from  $i$  to all the  $j$  which can absorb the excitation energy, it is necessary to sum the obtained formulas over all the  $j$ , then we can obtain in principle large values for  $W_{ij}$ . In this case, however, the summation over  $j$  is limited by the phonon mean free path.

It is necessary to note also that the formulas (7a) and (7b) are essentially different. Whereas for  $\omega_0 > \omega_D$  we have  $W_{ij} \sim \omega_0^4$ , then for  $\omega_0 < \omega_D$  we get  $W_{ij} \sim \omega_0^4$ , and consequently here  $W_{ij}$  has a maximum value for frequencies on the order of the Debye frequency (at  $\omega_0 \sim \omega_D$  we have  $W_{ij} \sim 10^5 - 10^7 \text{ sec}^{-1}$ ). As already noted above, in the processes under consideration the phonons take part as virtual particles, and therefore formulas (7a) and (7b) (as well as those given below) contain parameters characterizing the dynamic properties of the crystal lattices (density, speed of sound, Debye frequency). And although in (7a) and (7b) there is no explicit dependence on the temperature, there is an implicit dependence of  $W_{ij}$  on the temperature as a result of the presence in the  $W_{ij}$  of the aforementioned lattice characteristics.

### 3. INTERACTION OF EXCHANGE PAIR AND SINGLE ION

A. Let the multiplicities of the ground state and excited states of the single ion be the same. The Hamiltonian of the perturbation ensuring energy transfer from the exchange pair  $i$  to the ion  $j$  can be written in the form

$$\mathcal{H}^{ij} = \mathcal{H}_{\text{exch}}^i + \mathcal{H}_{\text{iph}}^j; \quad (8)$$

The expression for  $\mathcal{H}_{\text{exch}}^i$  is given above (see formula (4)),  $\mathcal{H}_{\text{iph}}^j$  is the Hamiltonian of the ion-phonon interaction of the particle  $j$  and is given by<sup>[3]</sup>

$$\mathcal{H}_{\text{iph}}^j = \frac{i}{2} \sum_{g\mathbf{h}\mathbf{k}_s} \left( \frac{\hbar \omega_{\mathbf{k}_s}}{2Mv_s^2} \right)^{1/2} (a_{\mathbf{k}_s} e^{i\mathbf{k}_s \cdot \mathbf{r}_j} + a_{\mathbf{k}_s}^+ e^{-i\mathbf{k}_s \cdot \mathbf{r}_j}) d_{s7h} \left( \frac{\partial \mathcal{H}^j}{\partial u_{qh}} \right)_{u_{qh}=0}. \quad (8a)$$

Here  $d_{sqh} = \Phi_{sq} k_{sh}^0 + k_{sq}^0 \Phi_{sh}$ ,  $\mathbf{k}^0 = \mathbf{k}/|\mathbf{k}|$ ,  $\Phi_{sq}$  is the  $q$ -th component of the unit vector of polarization of the  $s$ -th mode of lattice vibration,  $u_{qh}$  is the component of the deformation tensor;  $q, h = x, y, z$ ;  $\mathcal{H}^j$  is the potential energy of the  $j$ -th ion in the crystal field; in the case of iron-group impurities in a cubic field of symme-

try  $O_h$ , the expressions for  $(\partial \mathcal{H}^j / \partial u_{qh})_{u_{qh}=0} = \mathcal{H}_{qh}^j$  are given in<sup>[3,12]</sup>.

Substituting (8) in (5), using the Debye model of the crystal lattice, in analogy with the analysis given in<sup>[3,11]</sup> and in Sec. 2 of the present article, and replacing the summation with respect to  $\mathbf{k}_s$  by integration with respect to  $\omega$ , we obtain

$$W_{ij} = \frac{9}{2^5 \rho^2 \hbar^2 v^5} \left| \sum_{qh} \int_0^{\omega_D} \frac{\omega^3}{v^5} d\omega \int_0^\pi \cos^4 \theta \sin \theta d\theta \int_0^{2\pi} \left[ \frac{\exp(i\omega r v^{-1} \cos \theta)}{\omega_0 + \omega} - \frac{\exp(-i\omega r v^{-1} \cos \theta)}{\omega_0 - \omega} \right] d\varphi \langle \psi_m | I^i | \psi_n \rangle \langle \psi_j' | \mathcal{H}_{qh}^j | \psi_j \rangle \right|^2 g(0), \quad (9)$$

where  $\psi_j'(\psi_j)$  is the wave function of the excited (ground) state of the ion.

Just as in Sec. 2, the exchange interaction will be different, depending on the realization of the different possibilities of exciting the particles in the initial and final states.

In formula (9) and below we assume for simplicity that the pair is made up of identical particles.

1. For  $\omega_0 > \omega_D$ , the probability of energy transfer from the exchange period to the ion is

$$W_{ij} = \frac{|f_3(\omega_D, r)|^2}{\pi^5 \hbar^2 \rho^2 \omega_0^4} \left| \sum_{qh} \langle \psi_m | I^i | \psi_n \rangle \langle \psi_j' | \mathcal{H}_{qh}^j | \psi_j \rangle \right|^2 g(0),$$

$$f_3(\omega_D, r) = \frac{\omega_D^3}{v^3 r^2} \cos \varphi_D - 7 \frac{\omega_D^2}{v^2 r^3} \sin \varphi_D - \frac{26 \omega_D}{v r^4} \cos \varphi_D + \frac{50}{r^5} \sin \varphi_D - \frac{12 \pi}{r^5}, \quad (9a)$$

where  $\varphi_D = \omega_D r / v$ .

As seen from formula (9a),  $W_{ij}$  has a complicated dependence on the distance between the interacting systems. At  $r \sim 10^{-7} \text{ cm}$  all the terms of  $f_3(\omega_D, r)$  make equal contributions to the value of  $W_{ij}$ . However, when  $r \gtrsim 10^{-7} \text{ cm}$  all the terms in  $f_3(\omega_D, r)$ , except the first, can be neglected, and we get for  $W_{ij}$

$$W_{ij} = \frac{9 \omega_D^6}{2^5 \pi^5 \rho^2 \hbar^2 \omega_0^4 v^6 r^4} \left| \sum_{qh} \langle \psi_m | I^i | \psi_n \rangle \langle \psi_j' | \mathcal{H}_{qh}^j | \psi_j \rangle \right|^2 g(0). \quad (9b)$$

We see thus that when  $r \gtrsim 10^{-7} \text{ cm}$  the interaction of the exchange pair with the single ion decreases much more slowly with distance than in the case of dipole-dipole, dipole-quadrupole, etc. interactions. This indicates that the pair effectively interacts simultaneously with a large number of single impurity centers via the exchange-phonon mechanism. An estimate of the order of magnitude of  $W_{ij}$  using the data of Sec. 2, and for  $r = 10^{-7} \text{ cm}$ ,  $\langle \psi_j' | \mathcal{H}_{qh}^j | \psi_j \rangle = 10^{-14} \text{ erg}$  yields  $W_{ij} = 10^8 \text{ sec}^{-1}$ .

2. For  $\omega_0 < \omega_D$ , the energy migration probability is given by

$$W_{ij} = \frac{9 |f_4(\omega_0, r)|^2}{(2\pi)^3 \rho^2 \hbar^2} \left| \sum_{qh} \langle \psi_m | I^i | \psi_n \rangle \langle \psi_j' | \mathcal{H}_{qh}^j | \psi_j \rangle \right|^2 g(0),$$

$$f_4(\omega_0, r) = \frac{\pi}{2} \left\{ e^{i\varphi_0} \left[ \frac{\omega_0^2}{rv^4} - \frac{6i\omega_0}{r^2 v^3} - \frac{12}{r^2 v^2} - \frac{24(i-1)}{r^4 v \omega_0} \right] - \frac{48}{\omega_0 r^5} \right\}$$

Using the characteristic values of the parameters entering in (9c) for  $\omega_0 = 10^{11} \text{ sec}^{-1}$  it turns out that the largest contribution to  $W_{ij}$  is made by the term proportional to  $r^{-6} v^{-4}$  ( $W_{ij} = 10^9 \text{ sec}^{-1}$ ). For  $\omega_0 \sim \omega_D = 6$

$\times 10^{13} \text{ sec}^{-1}$ , we get  $W_{ij} \sim \omega_0^4 r^{-2} v^{-8}$ ; unlike formula (9b), the splitting frequency enters in the numerator. Consequently, the migration occurs with maximum efficiency at frequencies on the order of the Debye frequency, as is confirmed by our estimates (for  $\omega_0 \sim \omega_D$ ,  $W_{ij} = 10^{16} \text{ sec}^{-1}$ ).

B. From the point of view of laser technology, and possibly from the point of view of a number of problems in biology, of greatest interest is the case when the multiplicity of the ground and excited levels of the single ion are different. For the calculation of  $W_{ij}$  it is then necessary that the Hamiltonian of the ion-phonon interaction contain, besides the orbital operators, also the spin operators (s) and the operators acting on the lattice states. Such a Hamiltonian was obtained in<sup>[11]</sup> and is given by

$$\mathcal{H}_{\text{iph}}^j = \frac{\hbar}{2m^2c^2} \sum_{\beta} s_{\beta}^j \left\{ u_{qh}^j [\text{grad } \mathcal{H}_{qh}^{\beta j}, Q_j^{\beta}] + \mathcal{H}_{qh}^{\beta j} [\text{grad } u_{qh}^j, Q_j^{\beta}] \right\}, \quad (10)$$

where  $m$  is the electron mass,  $c$  the velocity of light,  $Q_j^{\beta}$  the momentum operator of the  $\beta$ -th electron of the  $j$ -th particle:  $Q_j^{\beta} = m \dot{\mathbf{r}}_j^{\beta}$ ;  $\mathbf{r}_j^{\beta}$  is the radius vector of the  $\beta$ -th electron of the  $j$ -th particle; the dot denotes differentiation with respect to time;

$$\sum_{\beta} \dot{\mathbf{r}}_j^{\beta} = \frac{i}{\hbar} \left[ \mathcal{H}_0 + \sum_{\beta} \bar{\mathbf{r}}_j^{\beta} \right];$$

$\mathcal{H}_0$  is the Hamiltonian which gives the spectrum of the aggregate system made up of the exchange pair plus the ion  $j$ ;  $s_{\beta}^j$  is the spin operator of the  $\beta$ -th electron of the  $j$ -th particle;

$$\text{grad } u_{qh}^j = -\frac{1}{2} \sum_{\mathbf{k}_s} \left( \frac{\hbar \omega_{\mathbf{k}_s}}{2Mv_s^2} \right)^{1/2} (a_{\mathbf{k}_s} e^{i\mathbf{k}_s \cdot \mathbf{r}_j} + a_{\mathbf{k}_s}^{\dagger} e^{-i\mathbf{k}_s \cdot \mathbf{r}_j}) \mathbf{k}_s d_{s q h}, \quad (10a)$$

Expressions for  $\text{grad } \sum_{\beta} \mathcal{H}_{qh}^{\beta j}$  are given in<sup>[11]</sup>,

$$\mathcal{H}_{qh}^{\beta j} = \sum_{q'} (\partial \mathcal{H}^{\beta j} / \partial u_{q h}) u_{q h} = 0;$$

$u_{qh}$  is the tensor component of the deformations due to the acoustic vibrations. The subsequent calculations are perfectly similar to those described above. Omitting all the calculations, we confine ourselves only to the final results (as before, we use the Debye model of a crystal).

1. For the optical range ( $\omega_0 > \omega_D$ ), the probability of migration from the exchange period to the ion can be written in the form

$$W_{ij} = \frac{1}{2^8 \pi^3 \rho^2 m^4 c^4} \left| \sum_{qh} \left\{ \frac{1}{\omega_0^2} A_{qh} \langle \Psi_j' | G_{qh}^j | \Psi_j \rangle + \frac{i}{\omega_0} \langle \Psi_j' | R_{qh}^j | \Psi_j \rangle \right\} \langle \Psi_m^i | I^i | \Psi_n^i \rangle \right|^2 g(0), \quad (11)$$

$$R_{qh}^j = \sum_{\beta} \mathcal{H}_{qh}^{\beta j} \bar{s}_{\beta}^j [\mathbf{B}_{qh}, \mathbf{Q}_j^{\beta}], \quad G_{qh}^j = \sum_{\beta} s_{\beta}^j [\text{grad } \mathcal{H}_{qh}^{\beta j}, \mathbf{Q}_j^{\beta}].$$

For the case when  $\sum_{\beta} \mathcal{H}_{qh}^{\beta j}$  has the symmetry of group  $O_{\eta}$ , we get

$$A_{uE} = 8 \left[ \frac{\omega_D^3}{r^2 v^3} \cos \varphi_D - 5 \frac{\omega_D^2}{r^3 v^2} \sin \varphi_D - \frac{12 \omega_D}{v r^4} \cos \varphi_D + \frac{12}{r^5} \sin \varphi_D \right],$$

$$A_{iA} = 16 \left[ \frac{3 \omega_D^3}{r^2 v^3} \cos \varphi_D - 14 \frac{\omega_D^2}{r^3 v^2} \sin \varphi_D - \frac{36 \omega_D}{r^4 v} \cos \varphi_D + \frac{54}{r^5} \sin \varphi_D - \frac{9\pi}{r^5} \right],$$

$$B_{iA}(x) = 8 \left[ \frac{\omega_D^3}{r^2 v^4} \sin \varphi_D + 6 \frac{\omega_D^2}{r^3 v^3} \cos \varphi_D - \frac{18 \omega_D}{r^4 v^2} \sin \varphi_D - \frac{24}{r^5 v} \cos \varphi_D \right],$$

$$B_{\eta F_2}(x) = B_{\xi F_2}(y) = 16 \left[ \frac{\omega_D^3}{r^3 v^3} \cos \varphi_D + 9 \frac{\omega_D^2}{r^4 v^2} \sin \varphi_D - 45 \frac{\omega_D}{r^5 v} \cos \varphi_D - \frac{132}{r^5 v} \cos \varphi_D \right],$$

$$B_{uE}(z) = 16 \left[ \frac{\omega_D^3}{r^2 v^4} \sin \varphi_D - 9 \frac{\omega_D^2}{r^3 v^3} \cos \varphi_D - \frac{45 \omega_D}{r^4 v^2} \sin \varphi_D + \frac{132}{r^5 v} \cos \varphi_D \right];$$

The remaining coefficients vanish.

Although formula (11) is quite cumbersome in form, in concrete calculations it always turns out that the majority of the terms can be neglected. Thus, if we assume that  $|\langle \Psi_j' | \mathbf{Q}_j^{\beta} | \Psi_j \rangle| = 10^{-19} \text{ g-cm-sec}^{-1}$ ,

$$|\langle \Psi_j' | \text{grad } \mathcal{H}_{qh}^{\beta j} | \Psi_j \rangle| = 10^{-6} \text{ erg}, \quad \langle \Psi_j' | \mathcal{H}_{qh}^{\beta j} | \Psi_j \rangle = 10^{-14} \text{ erg-cm}^{-1},$$

and if we use the values of the remaining parameters as given above, then

$$W_{ij} = \frac{\omega_D^2}{2^8 \pi^3 \rho^2 r^8 v^4 m^4 c^4 \omega_0^2} \left| \sum_{qh} \langle \Psi_j' | R_{qh}^j | \Psi_j \rangle \langle \Psi_m^i | I^i | \Psi_n^i \rangle \right|^2 g(0), \quad (12)$$

$W_{ij} = 10^{10} \text{ sec}^{-1}$  at  $r = 10^{-7} \text{ cm}$ .

It is interesting to note that the dependence of  $W_{ij}$  on the distance for (12) ( $W_{ij} \sim r^{-8}$ ) approaches the dependences for quadrupole-quadrupole interactions, and is much stronger than in the case of (9b).

2. For  $\omega_0 < \omega_D$ , the transfer probability is

$$W_{ij} = \frac{1}{2^8 \pi^3 \rho^2 m^4 c^4} \left| \sum_{qh} \left\{ A_{qh} \langle \Psi_j' | G_{qh}^j | \Psi_j \rangle + \frac{i}{\omega_0} \langle \Psi_j' | R_{qh}^j | \Psi_j \rangle \right\} \cdot \langle \Psi_m^i | I^i | \Psi_n^i \rangle \right|^2 g(0),$$

$R_{qh}^j$  and  $G_{qh}^j$  are obtained from  $R_{qh}^j$  and  $G_{qh}^j$  by making the substitutions  $\mathbf{B}_{qh} \rightarrow \mathbf{B}'_{qh}$  and  $\mathbf{A}_{qh} \rightarrow \mathbf{A}'_{qh}$ , where

$$A_{uE}' = 8\pi e^{i\varphi_0} \left[ \frac{\omega_0^2}{r v^4} + \frac{5i\omega_0}{r^2 v^3} - \frac{8}{r^3 v^2} - \frac{18(i-1)}{\omega_0 r^4 v} \right] - \frac{288\pi}{\omega_0^2 r^5},$$

$$A'_{iA} = 4\pi e^{i\varphi_0} \left[ \frac{\omega_0^2}{r v^4} + \frac{2i\omega_0}{r^2 v^3} - \frac{2}{r^3 v^2} \right],$$

$$B_{uE}'(z) = 2\pi e^{i\varphi_0} \left[ \frac{\omega_0^3}{r v^5} - 24i \frac{\omega_0^2}{r^2 v^4} + 18 \frac{\omega_0}{r^3 v^3} - \frac{720+372i}{r^4 v^2} \right] - (2+i) \frac{1440\pi}{r^5 \omega_0 v},$$

$$B_{iA}'(z) = 4\pi e^{i\varphi_0} \left[ \frac{3\omega_0^3}{r v^5} - \frac{3i\omega_0^2}{r^2 v^4} - \frac{6\omega_0}{r^3 v^3} - \frac{6i}{r^4 v^2} \right],$$

$$B'_{\eta F_2}(x) = B'_{\xi F_2}(y) = 8\pi e^{i\varphi_0} \left[ \frac{19i\omega_0^2}{r^2 v^4} + \frac{88\omega_0}{r^3 v^3} - \frac{3\omega_0^3}{r v^5} + \frac{312i+600}{r^4 v^2} \right].$$

The remaining coefficients vanish.

Using the presented values of the parameters that enter in formula (13), and discarding all the terms that make a negligible contribution to  $W_{ij}$ , we obtain for the case  $\omega_0 \ll \omega_D$  and  $r = 10^{-7} \text{ cm}$

$$W_{ij} = \frac{1}{2^8 \pi^3 \rho^2 m^4 c^4 r^8 v^4} \left| \sum_{qh} \langle \Psi_j' | R_{qh}^j | \Psi_j \rangle \langle \Psi_m^i | I^i | \Psi_n^i \rangle \right|^2 g(0), \quad (14)$$

$$W_{ij} = 10^6 \text{ sec}^{-1}$$

On the other hand, for the case  $\omega_0 \sim \omega_D$  and  $r = 10^{-7} \text{ cm}$  we get

$$W_{ij} = \frac{\omega_0^6}{2^8 \pi^3 \rho^2 m^4 c^4 r^8 v^4} \left| \sum_{qh} \langle \Psi_j' | R_{qh}^j | \Psi_j \rangle \langle \Psi_m^i | I^i | \Psi_n^i \rangle \right|^2 g(0),$$

$$W_{ij} = 10^{14} \text{ sec}^{-1} \quad (14a)$$

From a comparison of formulas (12), (14), (14a) and the corresponding estimates we see that the mechanism of the exchange-phonon energy migration from an exchange pair to an impurity center having levels with different multiplicity for the ground and excited states, has the longest range of action and the largest efficiency for frequencies on the order of the Debye frequency.

## DISCUSSION

Although the obtained expressions for the probabilities of the excitation energy migration via the virtual phonon field do not contain the temperature explicitly, they do depend on a number of parameters whose temperature dependence determines the temperature dependence of  $W_{ij}$ . This includes, primarily, the factor  $g(0)$  formula (6) which, as usual<sup>[1,8,9]</sup>, occurs as a result of the summation over the final states of the system of impurities  $i$  and  $j$  and averaging over the initial states; the factor  $g(0)$  takes into account the finite nature of the lifetime of the states of the impurity particles, which depends on the temperature of the host lattice, two-particle interactions, etc. If the widths of the excited states of particles  $i$  and  $j$  are much larger than the width of the levels of the ground states, but much smaller than the energy interval between the ground and excited states, then  $g_i(\omega)$  and  $g_j(\omega)$  describe respectively the normalized density of the excited states  $i$  and  $j$ . If at the same time  $(W_{ij})^{-1}$  is much larger than the time necessary to establish thermal equilibrium in the system of sublevels of the excited state  $i$ , then  $g(0)$  can be reduced to an expression analogous to the overlap integral of the emission spectra ( $i$ ) and absorption spectra ( $j$ ) in the well known Forster-Dexter formulas<sup>[1,8]</sup> for the probability of energy migration due to dipole-dipole interactions.

Other parameters which determine the implicit temperature dependence of  $W_{ij}$  are the crystal density  $\rho$  and the velocity of sound  $v$ , which enters in the expressions for  $W_{ij}$  raised to rather high powers.

It should be noted that the exchange pair can be produced also by two ions which are in an excited state. If the crystal contains besides such pairs (we shall call them dynamic) also other impurities that have energy levels equal to the energy of the pair with the two excited ions, then the pair can give up all of its excitation energy to the ion, and both its particles turn out to be in the ground state. It is possible here that the exchange interaction of the particles in the ground state is much weaker than the exchange interaction of the dynamic pair, i.e., the interaction of the dynamic pair with the lattice is strong. Therefore the transition of both ions of such a pair to the ground state is equivalent to vanishing of the pair. The inverse situation is also quite probable. It seems to us that the described mechanism is one of the possible ones capable of explaining the Feofilov-Ovsyankin effect<sup>[4,5]</sup>. The migration probability is calculated in this case by means of the formulas of Sec. 3, in which we substitute  $2\omega_0$  for  $\omega_0$ , corresponding to excitation of both ions forming the exchange pair.

We have confined ourselves to consideration of only resonant migration of energy. However, the mechanism described by us can be extended also to include the non-

resonant case, when the process of energy exchange via virtual phonons is accompanied simultaneously by the creation or annihilation of real phonons<sup>[13]</sup>. Here the formulas contain an explicit dependence on the temperature. The form of this dependence is determined by the processes (single-phonon or multi-phonon) that accompany the energy transfer. When phonon production accompanies migration we have  $W_{ij} \sim (n\Delta\omega + 1)$ ; in absorption we have  $W_{ij} \sim n\Delta\omega$ , where

$$n_{\Delta\omega} = \left[ \exp\left(\frac{\hbar\Delta\omega}{k_B T}\right) - 1 \right]^{-1},$$

$\hbar\Delta\omega$  is the energy difference between the excited levels of the interacting systems,  $k_B$  is the Boltzmann constant, and  $T$  is the temperature.

The probability of this process can be obtained from formula (5) in the third perturbation-theory order in the ion-phonon and exchange interactions. In view of the unusual complexity of the resultant formulas for  $W_{ij}$ , we do not present them in this paper.

Nonresonant energy migration between the  $\text{Cr}^{3+} - \text{Cr}^{3+}$  exchange pair and a single  $\text{Cr}^{3+}$  ion in  $\text{Al}_2\text{O}_3$  was observed in<sup>[6,7]</sup>. To interpret the obtained results, Imbusch<sup>[7]</sup> used the theory of inductive resonance and reached the conclusion that the migration has a quadrupole-quadrupole mechanism. However, the formulas used by him are valid only in the case of rigorous resonance between the interacting systems, and inasmuch as the observed process is essentially a nonresonant one, it follows, in our opinion, that the question of the mechanism of energy migration between the exchange pair and the single ion in ruby remains open and calls for further study. In addition, the operator of the quadrupole-quadrupole interaction does not contain an operator responsible for the change of the multiplicity of the states of the single ion, whereas the ground and excited levels of  $\text{Cr}^{3+}$  in ruby have different multiplicities.

In particular, using formula (12) of the present paper and the characteristic values of the parameters of the interaction of single  $\text{Cr}^{3+}$  ions with the  $\text{Al}_2\text{O}_3$  lattice and  $I^1 = 10^{-15}$  erg (value of the exchange-interaction energy of the  $\text{Cr}^{3+} - \text{Cr}^{3+}$  pair), we get  $W_{ij} \sim 10^4 \text{ sec}^{-1}$ . This exceeds the experimentally observed value. But the process considered by Imbusch is nonresonant and should be described by the next order of perturbation theory in the ion-phonon interaction<sup>[13]</sup>, which should naturally lead to a decrease of  $W_{ij}$ .

In conclusion, we consider it our pleasant duty to thank U. Kh. Kopvillem for his interest in the work and valuable remarks.

<sup>1</sup>D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

<sup>2</sup>V. R. Nagibarov, Zh. Eksp. Teor. Fiz. 49, 1836 (1965) [Sov. Phys.-JETP 22, 1255 (1966)].

<sup>3</sup>V. R. Nagibarov and I. A. Nagibarova, Opt. Spektrosk. 20, 814 (1966).

<sup>4</sup>V. V. Ovsyankin and P. P. Feofilov, Opt. Spektrosk. 20, 526 (1966).

<sup>5</sup>V. V. Ovsyankin and P. P. Feofilov, ZhETF Pis. Red. 3, 494 (1966) [JETP Lett. 3, 322 (1966)].

<sup>6</sup>R. C. Powell, B. Di Bartolo, B. Burang, and C. S. Naiman, Phys. Rev. 155, 154 (1967).

<sup>7</sup>G. F. Imbusch, Phys. Rev. **153**, 326 (1967).

<sup>8</sup>Th. Forster, Ann. of Phys. **2**, 55 (1948).

<sup>9</sup>L. D. Landau and E. M. Lifshitz, Kvantovaya mekhanika, Fizmatgiz, 1963 [Quantum Mechanics, Addison-Wesley, 1965].

<sup>10</sup>M. Born and K. Huang, Dynamical Theory of Crystal Lattices, Oxford, 1954.

<sup>11</sup>I. A. Nagibarova, Migratsiya energii mezhdu urovnyami s razlichnoĭ mul'tipletnost'yu (Energy

Migration Between Levels with Different Multipolarity), VINITI, Kazan', 1967.

<sup>12</sup>A. L. Schawlow, A. H. Piksis, and S. Sugano, Phys. Rev. **122**, 1469 (1969).

<sup>13</sup>V. R. Nagibarov, Fiz. Tverd. Tela **8**, 484 (1966) [Sov. Phys.-Solid State **8**, 384 (1966)].

Translated by J. G. Adashko

143