

Resonance transfer of electronic excitation energy between impurity ions with the participation of virtual lattice phonons

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(Submitted 1 October 1983)

Zh. Éksp. Teor. Fiz. **86**, 2170–2178 (June 1984)

The transfer of electronic excitation energy between impurity ions via the virtual lattice phonon field is investigated for the case where the electron energy that is being transferred is much larger than the maximum lattice phonon energy ($\Delta \gg \omega_{ks}$). Using by way of example certain models of the crystal lattice we show that the probability of this transfer may decrease as a function of the spacing R between the impurity ions either exponentially or by a power law, depending on the type of crystal lattice and the mutual arrangement of the impurity ions. A general tendency is observed for a slower fall-off with R of the transfer probability for the more complex crystal lattices. In particular, for complex lattices with a basis in which the impurity ions occupy non-identical sites in the lattice, the probability of electron-phonon energy transfer falls off according to the same law as the dipole-dipole transfer ($1/R^6$).

1. INTRODUCTION

It is well known that in the quenching and sensitization of luminescence and in the process of stimulated laser emission the transfer of electronic excitation energy between impurity ions in dielectric laser crystals plays an important role. Furthermore, in disordered systems (such as the subsystem of impurity ions in crystals), under certain conditions a situation arises analogous to the Anderson localization phenomenon. It is clear that the investigation of this phenomenon, the principal of which is based on the same interaction between impurity ions as that which leads to the transfer of energy, would open up new possibilities for the spectral investigation of the degree of disorder in crystals. A review of the contemporary theory of energy transfer in all its aspects is given in Ref. 1.

The mechanism of the transfer of electron excitation energy between two paramagnetic ions coupled together by the lattice phonon field was first proposed by Sugihara.² Subsequently this idea was developed in Refs. 3 and 4, where the energy transfer probability was obtained as a function of the distance between two impurities for the case where the transferred energy is less than the maximum lattice phonon energy. However, our interest is in the effect of the energy transfer process on the optical properties of laser crystals, where the transferred electron energy is much larger than the maximum lattice phonon energy. The solution of this problem was the subject of a paper by Orbach and Tachiki,⁵ where they calculated the probability of electron-phonon energy transfer that takes place in a simple cubic lattice.¹⁾ The results of Ref. 5 reduce, in essence, to the following: 1) If the impurity ions occupy sites of a simple cubic lattice, the energy transfer probability falls off exponentially with the distance R between ions. 2) If one of the ions is in an interstitial location, a power law for electron-phonon energy transfer is obtained, $\propto 1/R^n$, with the exponent n greater than 10 ($n > 10$). Since n equals 10 for the dipole-quadrupole energy transfer mechanism, it was concluded in Ref. 5 that the electron-phonon transfer with a power law probability dependence on R is ineffective, leaving only the transfer mechanism

that depends exponentially on R , and the latter can be important only for small separations between ions.

The authors of Refs. 6 and 7 have also concluded that the electron-phonon transfer of energy is short-range (current treatments of this subject are in fact based on this idea).

These authors, by more rigorous mathematical methods (and not necessarily for a cubic lattice⁶), confirm the main conclusion of Orbach and Tachiki concerning the exponential dependence on the distance R of the probability of electron-phonon transfer. The case of a power law dependence of this probability was not considered in Refs. 6 or 7. However, the conclusion that the electron-phonon interaction can lead to an effective energy transfer only for small distances between impurity atoms is, in our opinion, not correct, because: 1) in complex crystals having a large lattice constant d even a transfer for which the probability depends exponentially on R can be effective, since the effective transfer radius in this case is $(1-2)d$; 2) in the calculation of the $1/R^n$ term in the electron-phonon transfer probability in Ref. 5, a mistake was apparently made. Rather simple calculations in the present paper show that in the case of a simple cubic lattice the exponent is $n = 10$ (and not $n > 10$ as in Ref. 5). Moreover, for complex crystal lattices, when the impurity ions can occupy in the unit cell several inequivalent sites which have the same local symmetry of the nearest neighbors (for instance, in the YAG cell there are 24 such sites with dodecahedral local symmetry), the electron-phonon transfer between impurity ions can obey the same law as the dipole-dipole energy transfer mechanism, i.e., $\propto 1/R^6$.

We note also that the electron-phonon transfer of energy has been studied by Nagibarov and Nagibarova;⁸ however, the Debye approximation, which they used for the lattice vibrations, led to an incorrect dependence of the transfer probability on the distance between impurity ions.

2. PROBABILITY OF ELECTRON-PHONON ENERGY TRANSFER

A detailed calculation of the probability of the transfer of energy between two impurity ions coupled by the lattice

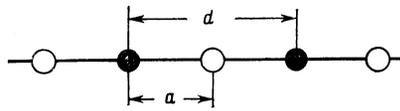


FIG. 1. One-dimensional lattice with two atoms in the unit cell. \circ and \bullet are atoms of mass m_1 and m_2 , respectively, ($m_1 \gg m_2$).

3. ENERGY TRANSFER IN A ONE-DIMENSIONAL LATTICE

Even though a one-dimensional linear lattice in its simple form is not found in nature, many of the characteristic features of energy transfer can be observed in this simple example. To this end let us calculate $H_{\text{eff}}^{\text{im}}$ for a linear chain with a basis. For the basis we choose a molecule consisting of two atoms of different kinds, with masses m_1 and m_2 (Fig. 1), spaced a distance a apart (the radius of the first coordination sphere). The lattice constant we shall designate as d and assume that $d = 2a$. The impurity ions can replace either atom, of the first or second kind, and in the process it is assumed that the electron spectra of the impurity ions (which in general are located in different crystal fields) are little changed, so that the resonance conditions for energy transfer are not destroyed.³⁾ The choice of a two-atom linear chain is further justified by the fact that its vibrational spectrum consists of acoustical and optical branches and therefore there is the possibility of comparing their contributions to the energy transfer.

The dispersion law for a two-atom linear chain has the form

$$\omega_{1,2}^2 = \frac{4\gamma}{M\mu} \left[1 \mp \left(1 - \mu \sin^2 \frac{kd}{2} \right)^{1/2} \right], \quad (4)$$

where $M = m_1 + m_2$, $\mu = 4m_1m_2/(m_1 + m_2)^2$, and γ is the elastic constant. In the special case of a simple linear chain ($m_1 = m_2$) we obtain

$$\omega_1^2 = 4\Omega_0^2 \sin^2(kd/2),$$

and where $m_1 \gg m_2$, we obtain from (4) expressions for the dispersion of both branches

$$\omega_{\text{ac}}^2(\mathbf{k}) = 2\Omega_{\text{ac}}^2 \sin^2 \frac{kd}{2}, \quad (5)$$

$$\omega_{\text{opt}}^2(\mathbf{k}) = 4\Omega_{\text{opt}}^2 \left[1 - \frac{m^2}{m_1} \sin^2 \frac{kd}{2} \right], \quad (6)$$

where $\Omega_{\text{ac}} = (\gamma/m_1)^{1/2}$ and $\Omega_{\text{opt}} = (\gamma/m_2)^{1/2}$.

For the unique symmetry coordinate of the one-dimensional lattice complex being considered, if we take into account only longitudinal vibrations [$e^x(\mathbf{k}, l) = 1$, $e^y(\mathbf{k}, t_1) = e^z(\mathbf{k}, t_2) = 0$], we can write down the following expressions (there is only one irreducible representation):

$$Q = (1/2^{1/2}) [\Delta u_x^{(2)} - \Delta u_x^{(1)}]. \quad (7)$$

Substituting (3) into (7) we obtain for the function $R_{\mathbf{k},s}(\Gamma_{ig}, m)$

$$R_{\mathbf{k},i} = 2^{1/2} \sin(k_x a). \quad (8)$$

Then substituting formulas (5), (6), and (8) into expression (1) we obtain for the effective Hamiltonian for energy transfer induced by virtual acoustical and optical phonons

phonon field has been given in Ref. 9, where it is shown that this probability is comprised of two terms: the "short range" term, where the transfer takes place as a result of the exchange of electrons between two impurity ions, and the "long range" term, where electronic transitions occur in two different ions, and the excitation energy is transmitted from one ion to the other by the absorption and emission of virtual phonons. Since the probability of the short range energy transfer contains the overlap integral of the wave functions of the two interacting ions, this probability can become appreciable only for small distances,²⁾ whereas the probability for the long range energy transfer does not contain such integrals, and such a transfer can in principle be effective at large distances.

If, in formula (13) of Ref. 9, the electron-phonon interaction coefficients $B_{\alpha}^{(1)}(\nu', \nu)$ are decomposed along the symmetry coordinates of the molecule formed by the impurity ion and its nearest neighbors, then it is easy to show that the formula of Orbach and Tachika (formula (5) of Ref. 5) is obtained. If we consider only a dependence on the distance R , then this dependence can be written in the following form:

$$W_{\text{eff}} = \sum_{i,m} |H_{\text{eff}}^{i,m}|^2, \quad (1)$$

$$H_{\text{eff}}^{i,m} = \frac{C\hbar}{d^2} \sum_{\mathbf{k},s} \frac{|R_{\mathbf{k},s}(\Gamma_{ig}, m)|^2 \cos(\mathbf{kR})}{\Delta^2 - \omega^2(\mathbf{k}, s)},$$

where C is a quantity independent of R , $\hbar\Delta$ is the energy difference between the excited and ground states of the donor and acceptor ions, $\hbar\omega(\mathbf{k}, s)$ is the energy of phonon of wave vector \mathbf{k} and polarization index s , and $R_{\mathbf{k},s}(\Gamma_{ig}, m)_j$ are functions that enter into the decomposition of the symmetry coordinates $Q(\Gamma_{ig}, m)$ of the complex (the impurity ion plus the nearest neighbors) along the normal coordinates of the lattice

$$Q(\Gamma_{ig}, m)_j = \sum_{\mathbf{k},s} (i/d) [\hbar/2M\omega(\mathbf{k}, s)]^{1/2} \quad (2)$$

$$\times [b_{\mathbf{k},s} \exp(i\mathbf{k}\mathbf{r}_j) - b_{\mathbf{k},s}^+ \exp(-i\mathbf{k}\mathbf{r}_j)] R_{\mathbf{k},s}(\Gamma_{ig}, m),$$

where M is the mass of the crystal, d is the lattice constant, and $b_{\mathbf{k},s}^+$ and $b_{\mathbf{k},s}$ are, respectively, the creation and annihilation operators of lattice phonons.

It is not hard to show that an explicit expression for the functions $R_{\mathbf{k},s}(\Gamma_{ig}, m)$ can be obtained by group-theory methods (e.g., with the use of projection operators) if first the symmetry coordinates $Q(\Gamma_{ig}, m)$ (which are formed by the m th row of the irreducible representation Γ_{ig} of the point group of the symmetry of the complex considered) are decomposed along cartesian coordinates of the relative displacements $\Delta u_{\alpha}^{(\nu)}$ ($\alpha = x, y, z$; and ν is the number of the ions in the complex), and then in the decomposition obtained, the following substitution is made:

$$\Delta u_{\alpha}^{(\nu)} = e^{\alpha}(\mathbf{k}, s) \sin(\mathbf{k}\mathbf{r}_{\nu}). \quad (3)$$

In (3), $e^{\alpha}(\mathbf{k}, s)$ is the α th component of the unit vector of the polarization of the phonons, and \mathbf{r}_{ν} is the position vector of the ν th ion of the complex.

$$H_{\text{eff}}^{(\text{ac})} = \frac{Cd}{2\pi(\hbar\Omega_{\text{ac}})^2} \text{Re} \int_{-\pi/d}^{\pi/d} \frac{\sin^2(ka) e^{ikR}}{A_1 + \cos(kd)} dk, \quad (9)$$

$$H_{\text{eff}}^{(\text{opt})} = \frac{Cd(m_1/m_2)}{2\pi(\hbar\Omega_{\text{opt}})^2} \text{Re} \int_{-\pi/d}^{\pi/d} \frac{\sin^2(ka) e^{ikR}}{A_2 - \cos(kd)} dk, \quad (10)$$

where

$$A_1 = \left(\frac{\Delta}{\Omega_{\text{ac}}}\right)^2 - 1, \quad A_2 = \frac{m_1}{m_2} \left(\frac{\Delta}{\Omega_{\text{opt}}}\right)^2 - \frac{2m_1}{m_2} + 1.$$

Since, in the case we are considering, $\Delta \gg \Omega_{\text{ac}}, \Omega_{\text{opt}}$, we have

$$A_1 \approx (\Delta/\Omega_{\text{ac}})^2, \quad A_2 \approx (m_1/m_2) (\Delta/\Omega_{\text{opt}})^2.$$

Going over to the complex plane by making the substitution of variables $z = e^{ikd}$, the integrals appearing in (9) and (10) can easily be represented in the form

$$I = \text{Re} \oint \frac{(z^\beta - z^{-\beta})^2 z^\alpha dz}{z^2 - (-1)^\mu A_\mu z + 1}, \quad (11)$$

where $\alpha = R/d, \beta = a/d$, and $\mu = 1, 2$.

Let us consider two particular cases.

1) We assume that both impurity ions replace atoms of the same kind ($\alpha = n$ is an integer). Then the contour of integration is a unit circle within which lies one of the poles of the integrand ($1/2A_\mu$). Calculating the integral (11) using the residue theorem, we obtain for the acoustic and optical branches

$$H_{\text{eff}}^{(\text{ac})} = \frac{(-1)^{n+1}}{2(\hbar\Omega_{\text{ac}})^2} \left(\frac{\Omega_{\text{ac}}^2}{2\Delta^2}\right)^{n-2\beta+1}, \quad (12)$$

$$H_{\text{eff}}^{(\text{opt})} = \frac{m_1/m_2}{2(\hbar\Omega_{\text{opt}})^2} \left(\frac{m_2 \Omega_{\text{opt}}^2}{m_1 2\Delta^2}\right)^{n-2\beta+1} \quad (13)$$

Thus, in this particular case the probability of energy transfer falls off exponentially with distance, and because in the argument (13) of the exponential there appears the factor m_2/m_1 , which is much less than unity, energy transfer involving the optical phonons is less effective than transfer via the acoustic phonons. From formulas (12) and (13) it follows also that the probability of transfer depends on the ratio $\beta = a/d$.

2) When the impurity ions replace both kinds of atom ($\alpha = R/d$ is noninteger), the calculation of the integral is complicated by the fact that the point $z = 0$ is a branch point of the integrand. Now the contour of integration is a unit circle with a cut along the negative real axis (Fig. 2). From the calculation of the integral (11) with the use of the residue

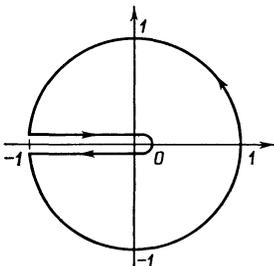


FIG. 2.

theorem, we obtain, in addition an exponential term like (12), a term

$$I = \frac{2 \sin \pi \alpha}{\alpha} \frac{\sin \pi (\alpha + 2\beta)}{\alpha + 2\beta} \frac{\sin \pi (\alpha - 2\beta)}{\alpha - 2\beta} \quad (14)$$

which, for integer values of α (if $\beta = 1$ or $1/2$), obviously vanishes.

It is easy to see that this same result can be obtained directly from formula (1) if one neglects in the integrand the quantity $\omega^2(\mathbf{k}, s)$ in comparison with Δ^2 . This latter approximation means that expression (14) is independent of the specific form of the dispersion law, and therefore it is valid, in particular, for a lattice whose basis is a three-atom linear molecule having a center of inversion. A three-dimensional generalization of this model is carried out in the next section.

From formula (14) it follows that for a simple lattice ($\beta = 1$)

$$I = \frac{\sin(\pi R/d)}{(R/d) [1 - (R/d)^2]};$$

where I falls off as $1/R^3$ as $R \rightarrow \infty$. In the case of a two-atom lattice ($\beta = 1/2$) we obtain

$$I = \frac{\sin(\pi R/2a)}{R/2a}.$$

Here, if the impurity ions replace atoms of just one kind ($R = 2an$) then $I = 0$, and in the opposite case I falls off as $1/R$ as $R \rightarrow \infty$.

From (14) it can be seen also that for values of β different from 1 or $1/2$ energy transfer for which the probability falls off with distance according to a power law ($I \propto 1/R^2$) is possible even if the impurity ions are located at lattice sites (i.e., if $R/d = n$ is an integer). Actually, in this case (14) can easily be converted into the form

$$I = \frac{(-1)^{n+4\beta}}{n^2 - \beta^2} \sin 2\pi\beta.$$

Thus, already in the model of a one-dimensional linear lattice it can be seen that the law according to which the probability of energy transfer falls off is different for different lattices. The transfer probability falls off faster for a simple lattice than for a complex one.

4. ENERGY TRANSFER IN A THREE-DIMENSIONAL LATTICE

For a three-dimensional lattice we shall consider only the case of energy transfer between ions which occupy nonidentical sites in the unit cells. Here, as in the case of the linear lattice, a nonvanishing contribution is obtained from the first term of the expansion of the function (1) in the small parameter $\omega^2(\mathbf{k}, s)/\Delta^2$, with this expansion being given in the form

$$H_{\text{eff}}^{i,m} = \frac{C\hbar}{\tilde{d}^2 \Delta^2} \sum_{\mathbf{k}} \int |R_{\mathbf{k},s}(\Gamma_{ig}, m)|^2 \cos(\mathbf{kR}) d^3k, \quad (15)$$

where the integration is carried out over the first Brillouin zone. As a model we shall choose a cubic lattice with a basis which consists of a three-atom linearly symmetric molecule whose axis points in the Z direction. Clearly, this model is a particular case of a lattice with an octahedral basis where

there are six ions in the first coordination sphere around the impurity ion (two in each of the directions X , Y , and Z). In the particular case where the radius a of the first coordinate sphere is equal to the lattice constant d , both lattices mentioned above go over into a simple cubic lattice.

It is clear that a three-atom linear molecule has three symmetry coordinates

$$Q^{(\alpha)} = (1/\sqrt{2}) [\Delta u_{\alpha}^{(2)} - \Delta u_{\alpha}^{(4)}], \quad (16)$$

where $\alpha = x, y$, and z . Performing the substitution (3) for the function $R_{k,s}(\Gamma_{ig}, m)$ we obtain in this particular case

$$R_{k,s}^{\alpha} = 2^{1/2} e^{\alpha}(\mathbf{k}, s) \sin(k_z a). \quad (17)$$

If we choose the projections of the polarization unit vector as in Ref. 5 (Fig. 3), then for these projections it is not difficult to obtain the expressions

$$\begin{aligned} e^x(\mathbf{k}, t_1) &= \frac{k_x k_z}{|\mathbf{k}| (k_x^2 + k_y^2)^{1/2}}, & e^y(\mathbf{k}, t_1) &= \frac{k_y k_z}{|\mathbf{k}| (k_x^2 + k_y^2)^{1/2}}, \\ e^z(\mathbf{k}, t_1) &= -\frac{(k_x^2 + k_y^2)^{1/2}}{|\mathbf{k}|}, & e^x(\mathbf{k}, t_2) &= \frac{k_y}{(k_x^2 + k_y^2)^{1/2}}, \\ e^y(\mathbf{k}, t_2) &= -\frac{k_x}{(k_x^2 + k_y^2)^{1/2}}, \\ e^z(\mathbf{k}, t_2) &= 0, & e^{\alpha}(\mathbf{k}, l) &= \frac{k_{\alpha}}{|\mathbf{k}|}, \quad \alpha = x, y, z. \end{aligned} \quad (18)$$

Substituting the values of the polarization vector projections (17) into (18) and summing over s , we obtain

$$\sum_s |R_{k,s}(\Gamma_{ig}, m)|^2 = 2 \sin^2(k_z a), \quad (19)$$

after which the integral in (15) can be easily represented in the form of the product of single integrals:

$$I = \text{Re} \left[\int_{-\pi}^{\pi} dx e^{i\alpha_1 x} \int_{-\pi}^{\pi} dy e^{i\alpha_2 y} \int_{-\pi}^{\pi} dz \sin^2 \beta z e^{i\alpha_3 z} \right], \quad (20)$$

where $\beta = a/d$, $\alpha_1 = R_x/d$, $\alpha_2 = R_y/d$, and $\alpha_3 = R_z/d$.

It is easy to see that the calculation of the probability of energy transfer in a lattice with an octahedral basis also reduced to the calculation of the integral (20). This follows from the fact that sums of the form (19), which are constructed for different types of oscillations of the octahedral envi-

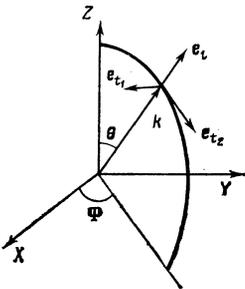


FIG. 3. Definition of the projections of the unit vectors of lattice phonon polarization. e_l , e_{t1} and e_{t2} are, respectively, the unit vectors of the polarization of the longitudinal and the two transverse lattice phonons.

ronments, (the functions $R_{k,s}(\Gamma_{ig}, m)$ for octahedral environments are given in Ref. 5), have the form

$$\sum_{\alpha} \sin^2(k_{\alpha} a)$$

(where α assumes either all three values x, y , and z , or else two of them).

The integral (20) can be written in the form

$$I = \frac{\sin \pi \alpha_2 \sin \pi \alpha_3}{\alpha_2 \alpha_3} \left\{ \frac{2 \sin \pi \alpha_1}{\alpha_1} - \frac{\sin \pi (\alpha_1 + 2\beta)}{\alpha_1 + 2\beta} - \frac{\sin \pi (\alpha_1 - 2\beta)}{\alpha_1 - 2\beta} \right\} \quad (21)$$

On the basis of the asymptotic properties, investigated in section 3, of the expression in the curly brackets as $R \rightarrow \infty$ it is easy to draw the following conclusions: 1) in a simple cubic lattice in which the impurity ions occupy nonidentical positions ($\alpha_1 \neq n_1$, $\alpha_2 \neq n_2$, and $\alpha_3 \neq n_3$, where n_1 , n_2 , and n_3 are integers), the effective Hamiltonian for the transfer of energy between the ions decreases with R as $1/R^5$. This contradicts the results obtained in Ref. 5 for the analogous case. Our method of calculating the integral (15) differs from that used in Ref. 5 only in that, in order to simplify the calculations, we changed the order of the operations, and this, of course, should not be reflected in the final result.⁴⁾ 2) For more complex lattices longer-range terms are obtained for the probability of electron-phonon transfer. Thus, for example, if the acceptors lie on the face of the unit cube (it is assumed that the donor occupies the cubic lattice sites), then it is easy to see that $H_{\text{eff}} \propto 1/R^4$, while if the acceptor is located inside the unit cell, then $H_{\text{eff}} \propto 1/R^3$.

5. CONCLUSIONS

Although we have carried out calculations only for cubic lattices having comparatively simple bases, there is a trend (even for a one-dimensional lattice) to a more gradual fall-off of the probability of electron-phonon transfer with the distance R between the impurity ions as the crystal lattice becomes more complex. This suggests that in many crystals having a unit cell with a complex structure, as is the case for many laser crystals, energy transfer may possibly occur via the electron-phonon interaction, and not by the dipole-dipole mechanism, as is ordinarily thought. The electron-phonon mechanism most probably can occur in crystals that are activated with transition metals (the iron group, the rare earths, etc.), since, as is well known, dipole transitions between states of the same parity in these ions are forbidden by the LaPorte rule. This suggestion is also indirectly supported by the well-known "anomalous" (from the standpoint of the dipole-dipole transition) behavior of the so-called "concentration" crystals,¹¹ in which no appreciable energy transfer between rare earth impurity ions is observed even at the maximum impurity ion concentration in the crystal. On the other hand, in other crystals, (e.g., YAG) energy transfer proceeds so effectively that even at very low impurity ion concentrations it causes quenching of luminescence. It is obvious that this cannot be dipole-dipole transfer, since the dipole-dipole interaction of the ions cannot depend so

strongly on the structure of the medium, in as much as the indices of refraction of these media differ very little. However, if we take the point of view that in the above-mentioned crystals the transfer takes place via the electron-phonon mechanism, then the difference in behavior of the two kinds of systems becomes clear. Actually the ratio $\beta = a/d$ is usually close to unity for the concentration crystals (and in respect to this ratio they have a more "simple" structure than the garnets, for which $a/d \approx 1/4$), and therefore in these crystals electron-phonon transfer is less effective than in the garnets.

We note also that when there is a short-range interaction between the ions of the impurity subsystem (e.g., exchange), where this interaction falls off with inter-ion distance R faster than $1/R^3$, then, as Anderson has shown,¹² for relatively low concentrations $C < C_{cr}$, where C_{cr} is a critical concentration for a given system, any impurity excitation is, with overwhelming probability, localized. Subsequently Mott showed¹³ that for large concentrations, $C \gg C_{cr}$ there is a mobility edge E_c in the spectra of extrinsic crystals: excitations of energy E less than E_c are localized and those of $E > E_c$ are delocalized. Experimental investigations of Anderson localization carried out, for example, for the system CaWO_4 containing samarium ions¹⁴ and for ruby,¹⁵ have demonstrated that the basic propositions of the theory of Refs. 12 and 13 are correct. However, in the transition of the system from the localized to the delocalized state, a more or less smooth transition is observed instead of the expected discontinuity. This is explained by the fact that in addition to the exchange interaction between impurity ions, a long-range dipole-dipole interaction is also possible, and as a result of the latter, the falloff in the probability for energy transfer observed at the mobility threshold is not so abrupt.¹ However, since dipole-dipole transitions between transition metal ions are forbidden, we believe that the resonance electron-phonon energy transfer that we have studied here may appear in the role of the above-mentioned long-ranged transitions.

The authors thank L. P. Pitaevskii and V. M. Agronovich for valuable discussions and M. L. Ter-Mikaelyan for constant attention to this work.

¹The authors of Ref. 5 also examined the case where the transferred energy is less than the maximum lattice phonon energy. However, in this particular case the results of Ref. 5 were the same as those of Refs. 3 and 4.

²Short-range transfer has been studied e.g., in Ref. 10.

³If this condition is violated, then instead of resonance transfer we can consider nonresonance transfer with the absorption (emission) of real lattice phonons. This process differs in no way from resonance energy transfer.

⁴In Ref. 5 triple integrals with respect to $k_x, k_y,$ and k_z are first calculated separately for the longitudinal and the two transverse oscillations. In these calculations rather complicated integrals are obtained, and to solve them additional assumptions are made: the Z axis points along the direction of R , it is assumed that $R \gg d$, etc. Then the contributions obtained are summed over s , and as a result the terms that are proportional to $1/R^5$ in some obscure way cancel out, with the higher-order terms remaining.

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Translated by J. R. Anderson