Interaction of impurity centers in anisotropic elastic media

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The method for solution of the equation of elasticity of an anisotropic infinite body developed by I. M. Lifshitz and L. N. Rozentsveĭg [Zh. Eksp. Teor. Fiz. **17**, 783 (1947)] is used to obtain an expression for the energy of the interaction of impurity centers in cubic crystals in the case of arbitrary relationships between the elastic moduli. This expression is used to explain qualitatively the appearance of long-range correlations of Jahn-Teller centers on increase in the concentration of these centers in a regular diamagnetic crystal. It is shown that an analysis made within the framework of the theory of elasticity corresponds exactly to the quantum theory of the interaction of impurity centers via acoustic phonons with a wave vector $q \neq 0$ if the retardation effects are ignored. Moreover, in the case of isotropic media this approach provides a compact general expression for the operator of the interaction when the retardation effects and the exchange between real acoustic phonons are taken into account.

1. INTRODUCTION

The problem of the interaction of impurity centers via the deformation field in a crystal lattice is of very general interest. Several solutions of this problem have been proposed on the assumption that the medium is isotropic. The interaction of point defects in the case of some special positions in a diamagnetic crystal is considered in Ref. 1 and the elastic interaction of spins in a paramagnet is discussed in Ref. 2; the diagonal part of the interaction of two-level centers in glasses is studied in Ref. 3. A detailed derivation of the expression for the interaction energy of point defects in an isotropic medium is given by Kosevich[4] in the case when an allowance for local rotations of defects relative to one another is unimportant.

We shall obtain an expression for the energy of the interaction of impurity centers of general type in cubic crystals in the case of arbitrary relationships between elastic moduli and we shall allow for local rotation of impurity centers relative to one another. We shall then use the expressions obtained in this way to analyze the effects of self-localization of cooperative distortions of Jahn-Teller (JT) centers and to estimate quantitatively the probabilities of transfer of an excitation energy smaller than the limiting energy of phonons between different ions in a crystal lattice.

We shall also carry out another task. Two different approaches have been used in the published literature to study the interaction between localized centers via the lattice: within the framework of the theory of elasticity and via the phonon field. The interaction of spins via the phonon field was estimated for the first time in Ref. 5. A solution of this problem was given in Ref. 6 on the assumption that the longitudinal and transverse velocities of sound are identical. A generalization of this result was made in Ref. 7 and the retardation effects were considered in greater detail than in Ref. 6. We shall show that the results of a calculation of the interaction energy carried out within the framework of the theory of elasticity are exactly the same as those obtained from the theory of the indirect interaction of acoustic phonons in Refs. 6 and 7 if we ignore the retardation effects.[1)] In this sense the result obtained from the theory of elasticity is valid also at short distances between impurities.

2. IMPURITY-CENTERS INTERACTION ENERGY OPERATOR DERIVED ALLOWING FOR THEIR LOCAL ROTATIONS

The energy of an impurity center i in the deformation field of a crystal lattice will be described by

$$H^i = \sigma_{\alpha\beta}{}^i \nabla_\beta{}^i u_\alpha, \qquad (1)$$

where u_α are components of the displacement vector. The actual form of the operators depends on the nature of the centers. In the case of ions with partly filled $3d$ or $4f$ shells this is a combination of irreducible tensors found by expanding the crystal field operator as a series in relative displacements. In the case of two-level centers in glasses the quantities $\sigma_{\alpha\beta}$ are linear combinations of the Pauli matrices.[3] In the case of JT centers with tunneling or in the case of paraelectric centers these quantities can be expressed in terms of the effective operators allowing for the vibronic reduction factors. The quantities $\sigma_{\alpha\beta}$ are related to the force density vector by[4]

$$f_\alpha{}^i = \sigma_{\alpha\beta}{}^i \nabla_\beta \delta(\mathbf{r} - \mathbf{r}_i). \qquad (2)$$

To avoid misunderstanding, we must point out that a formula analogous to Eq. (2) is obtained in Ref. 4 in the quasistatic limit after averaging over all the microscopic states of an impurity center (when $\sigma_{\alpha\beta} = \sigma_{\beta\alpha}$). In our treatment the orientation of impurity centers relative to the lattice appears as an additional dynamic variable, so that we have $\sigma_{\alpha\beta} \neq \sigma_{\beta\alpha}$. Although the total angular momentum of a sample vanishes, the system of impurity centers may exhibit local rotation in different directions, so that the state of the system becomes more stable.

The components of the displacement vector u_α will be written in the form

$$u_\alpha = \int G_{\alpha\gamma}(\mathbf{r} - \mathbf{r}') f_\gamma{}^i(\mathbf{r}' - \mathbf{r}_i)\, dV' = \sum_i \sigma_{\delta\gamma}{}^i \nabla_\gamma G_{\alpha\delta}(\mathbf{r} - \mathbf{r}_i). \qquad (3)$$

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Then, neglecting the local change in the elastic moduli and assuming that the medium is unbounded, we find that the energy of the interaction of impurity centers with one another, obtained from Eq. (1), is given by

$$H={}^1/_2\sum_{ij}\sigma_{\alpha\beta}{}^i\sigma_{\gamma\delta}{}^j\nabla_\beta\nabla_\delta G(\mathbf{r}_i-\mathbf{r}_j), \tag{4}$$

where $G_{\alpha\gamma}$ is the static Green tensor satisfying the familiar equation[4]

$$\lambda_{\alpha\beta\gamma\delta}\nabla_\beta\nabla_\gamma G_{\delta\mu}(\mathbf{r})+\delta_{\alpha\mu}(\mathbf{r})=0, \tag{5}$$

where as $\lambda_{\alpha\beta\gamma\delta}$ are the components of the tensor of the elastic moduli.

The antisymmetric components of $\sigma_{\alpha\beta}$ can generally be expressed in terms of the angular momentum operators[8]

$${}^1/_2(\sigma_{\beta\alpha}-\sigma_{\alpha\beta})=-{}^1/_2 ie_{\mu\beta\alpha}[L_\mu,V_{\mathrm{cr}}], \tag{6}$$

where $e_{\mu\beta\alpha}$ is a totally antisymmetric tensor and $[L_\mu, V_{\mathrm{cr}}]$ is a commutator of the component of the total orbital momentum of an impurity center with the crystal field operator. The relationship (6) is satisfied by arbitrary media. Substituting this relationship in Eq. (4), we find that some of the interaction operators associated with local rotations of impurity centers relative to one another are given by

$$H_2={}^1/_2\sum_{ij}K_{\mu\nu}^{ij}[L_\mu{}^i,V_{\mathrm{cr}}{}^i][L_\nu{}^j,V_{\mathrm{cr}}{}^j], \tag{7}$$

$$K_{\mu\nu}^{ij}=-{}^1/_4\sum_{\alpha\beta\gamma\delta}e_{\mu\beta\alpha}e_{\nu\delta\gamma}\nabla_\beta\nabla_\delta G_{\alpha\gamma}(\mathbf{r}_i-\mathbf{r}_j). \tag{8}$$

It follows from considerations of homogeneity in connection with the nature of Eq. (5) [see note on p. 44 in Ref. 9] and directly from Eq. (4) that $H^{ij}\propto 1/r_{ij}^3$ and, therefore, it resembles the dipole-dipole interaction. However, in contrast to this interaction, the effect in question occurs also between centrally symmetric impurity centers when there are no dipole moments. It should be pointed out that in the case of the interaction via local rotations all the matrix elements H_2^{ij} vanish within the limits of degenerate states of centers i or j. This follows directly from Eq. (7) and it is due to the fact that the crystal field is the same for degenerate states and that local rotation is insensitive to the variations of this field. Correlation of local rotations occurs only if the states of each of the centers correspond to different eigenvalues of the crystal field operator.

3. GREEN TENSOR FOR CUBIC CRYSTALS

A general solution of an equation of the (5) type is obtained in Ref. 10 in an integral form for arbitrary anisotropic media. Here, in applying the solution of Lifshitz and Rozentsveĭg to specific calculations it is convenient to represent it in a somewhat different form. After the differentiation operations in Eqs. (4) and (8), the integrals are found and the expressions for H become simple analytic equations.

Following Lifshitz and Rozentsveĭg,[10] we shall use the integral transformation

$$G_{\alpha\gamma}(\mathbf{r})=\frac{1}{(2\pi)^3}\iiint G_{\alpha\gamma}(\mathbf{p})e^{-i\mathbf{pr}}\,d\mathbf{p} \tag{9}$$

to reduce the differential equation (5) to a system of nine algebraic equations. The solution of this system for cubic media is

$$\begin{aligned}G_{xx}(\mathbf{p})=[&b^2p^4+b(a+b+d)(p_y{}^2+p_z{}^2)p^2\\&+d(2a+2b+d)p_y{}^2p_z{}^2]/\Delta_1,\end{aligned} \tag{10}$$

$$G_{xy}(\mathbf{p})=G_{yx}(\mathbf{p})=-(a+b)p_xp_y[dp_z{}^2+bp^2]/\Delta_1,$$

where

$$\Delta_1=Ap^6+B(p_x{}^2p_y{}^2+p_x{}^2p_z{}^2+p_y{}^2p_z{}^2)p^2+Cp_x{}^2p_y{}^2p_z{}^2 \tag{11}$$

and the following notation is used:

$$\begin{gathered}a=\lambda_{xxxx},\quad b=\lambda_{xyxy},\quad d=\lambda_{xxxx}-\lambda_{xxyy}-2\lambda_{xyxy},\\A=b^2(a+2b+d),\quad B=bd(2a+2b+d),\quad C=d^2(3a+3b+d).\end{gathered} \tag{12}$$

The Fourier transforms of the Green function $G_{yy}(\mathbf{p})$, $G_{zz}(\mathbf{p})$, $G_{yz}(\mathbf{p})$, and $G_{xz}(\mathbf{p})$ are obtained from those given above by cyclic transposition of the indices x, y, and z. It is clear from Eqs. (10) and (11) that $G_{\alpha\gamma}(\mathbf{p})$ are homogeneous functions and the degree of homogeneity is 2. Consequently, when the inverse transformation is carried out in spherical coordinates, the δ Dirac function is obtained and the triple integrals reduce to single integrals. For example, in the case of G_{zz} and G_{xy}, we obtain

$$\begin{aligned}G_{zz}(\mathbf{r}_{ij})=\frac{n_z}{8\pi^2r_{ij}}\int_0^{2\pi}\frac{d\varphi}{n_z{}^2+n_\rho{}^2}\Big[&b^2+b(a+b+d)\frac{n_z{}^2}{n_z{}^2+n_\rho{}^2}\\&+d(2a+2b+d)\frac{n_z{}^4}{4(n_z{}^2+n_\rho{}^2)^2}\sin^2 2\varphi\Big]\frac{1}{\Delta_2},\end{aligned} \tag{13a}$$

$$G_{xy}(\mathbf{r}_{ij})=-\frac{(a+b)n_z{}^3}{8\pi^2r_{ij}}\int_0^{2\pi}\frac{d\varphi}{(n_z{}^2+n_\rho{}^2)^2}\left(b+d\frac{n_\rho{}^2}{n_z{}^2+n_\rho{}^2}\right)\frac{\sin 2\varphi}{2\Delta_2}, \tag{13b}$$

where

$$\Delta_2=A+B\frac{n_z{}^2}{(n_z{}^2+n_\rho{}^2)^2}\left(n_\rho{}^2+n_z{}^2\frac{\sin^2 2\varphi}{4}\right)+C\frac{n_z{}^4n_\rho{}^2\sin^2 2\varphi}{4(n_z{}^2+n_\rho{}^2)^3} \tag{14}$$

and the following notation is used:

$$n_z=\cos\theta_r,\quad n_\rho=\sin\theta_r\cos(\varphi-\varphi_r).$$

When the angles θ_r and φ_r that define the direction of the vector $\mathbf{r}_{ij}$ relative to the selected coordinate system vanish, i.e., when the points i and j are located on the z axis, Eq. (13a) reduces to that obtained by Lifshitz and Rozentsveĭg.[10] In another special case defined by $d\ll a$ and $d\ll b$, the integrals of Eq. (13) are found in their general form. The result obtained

$$\begin{aligned}G_{\alpha\gamma}(\mathbf{r})=\frac{(a+b)}{8\pi(a+2b)r^3}\Big\{&\left(\frac{a+3b}{a+b}\right)r^2\delta_{\alpha\gamma}+x_\alpha x_\gamma\\&+\frac{3d}{2b}\Big[\left(\frac{a-b}{3a+3b}\right)(r^2-x_\alpha{}^2)\delta_{\alpha\gamma}-\frac{(2r^2-x_\alpha{}^2-x_\gamma{}^2)x_\alpha x_\gamma}{r^2}\Big]\Big\}\end{aligned} \tag{15}$$

is again identical with that given by Lifshitz and Rozentsveĭg.[10] if $d=0$, then the Green tensor of weakly anisotropic cubic media (15) reduces to the familiar[4] form applicable to isotropic media. Substituting Eq. (13) into Eqs. (14) and (8), we can obtain the explicit form of the interaction operator for arbitrary elastic moduli.

4. INTERACTION OF IMPURITY CENTERS IN AN ISOTROPIC MEDIUM

The case of weak anisotropy is encountered quite frequently. For example, in perovskite-type or rocksalt crystals the values of d/a and d/b are ≈ 0.1. This case is also interesting because calculations carried out on the basis of theory of elasticity for $d = 0$ yield results which can be compared directly with those of quantum-mechanical calculations reported in Refs. 6 and 7. If $d = 0$, then without allowance for local rotations, we find that

$$H_1^{ij} = \frac{(a+b)}{8\pi b r^3 (a+2b)} \Big[15\sigma_{\alpha\beta}{}^i \sigma_{\gamma\delta}{}^j \frac{x_\alpha x_\beta x_\gamma x_\delta}{r^4} + 6(4\sigma_{\alpha\beta}{}^i\sigma_{\gamma\alpha}{}^j + \sigma_{\alpha\alpha}{}^i\sigma_{\gamma\beta}{}^j + \sigma_{\gamma\beta}{}^i\sigma_{\alpha\alpha}{}^j)\frac{x_\gamma x_\beta}{r^2} - 2\sigma_{\alpha\beta}{}^i\sigma_{\alpha\beta}{}^j - \sigma_{\alpha\alpha}{}^i\sigma_{\beta\beta}{}^j \Big] + \frac{1}{4\pi b r^3}\Big(3\sigma_{\alpha\beta}{}^i\sigma_{\gamma\alpha}{}^j\frac{x_\gamma x_\beta}{r^2} - \sigma_{\alpha\beta}{}^i\sigma_{\alpha\beta}{}^j\Big), \tag{16}$$

where for the sake of brevity the indices of the modulus and Cartesian coordinates $\mathbf{r}_{ij}$ are omitted. Equation (16) generalizes a series of special expressions obtained earlier. The longitudinal and transverse velocities of sound are $v_l = [(a+2b)/\rho]^{1/2}$ and $v_t = (b/\rho)^{1/2}$, respectively. Assuming, as in Ref. 6, that these velocities are equal, we find that after elementary transformations Eq. (16) reduces[2)] to that obtained by Aminov and Kochelaev if the retardation effects are ignored. Our result differs only in respect of the sign of some of the terms from that expression obtained in Ref. 7 where an allowance is made for the fact that $v_t \neq v_l$ and a specific orientation of a pair ($x_{ij} = y_{ij} = 0$) is considered. For the same special case of $x_{ij} = y_{ij} = 0$ our result is in full agreement with that of Ref. 1, where it was obtained using the theory of elasticity but by a more cumbersome method. If the operators $\sigma_{\alpha\beta}$ in Eq. (16) are simplified only to their diagonal parts, we obtain the result of Ref. 3.

The second part of the Hamiltonian (4) due to local rotations is

$$H_2^{ij} = -\frac{1}{32\pi b r_{ij}^3}\Big\{[L_\alpha{}^i V_{\mathrm{cr}}{}^i][L_\alpha{}^j V_{\mathrm{cr}}{}^j] - 3\frac{[L_\alpha{}^i V_{\mathrm{cr}}{}^i]x_\alpha x_\beta[L_\beta{}^j V_{\mathrm{cr}}{}^j]}{r_{ij}^2}\Big\}. \tag{17}$$

To some extent this expression reminds us of the usual dipole-dipole interaction. Only the shear modulus occurs in the expression. The minus sign is to be expected because the energy of the interaction is minimal when the local rotations of different centers are opposite.

5. INTERACTION OF IMPURITY CENTERS IN CUBIC CRYSTALS

The general expression for the interaction energy is quite cumbersome. For this reason we shall consider only two special cases.

Ions with twofold orbital degeneracy located along fourfold axes. The operator (1) is usually employed in the form[13]

$$H^i = \sigma_\alpha{}^i(e_{xx}+e_{yy}+e_{zz}) + \sigma_\theta{}^i(2e_{zz}-e_{xx}-e_{yy})/2 + \sqrt{3}\sigma_\varepsilon{}^i(e_{xx}-e_{yy})/2, \tag{18}$$

where σ_a, σ_θ, and σ_ε are the effective operators in the space of an orbital doublet. In particular, in the case of ions located along the z axis, we have[3)]

$$H_{E-E}^{ij} = \frac{1}{4\pi b r_{ij}^3}[\Phi_{13}(\sigma_a{}^i\sigma_\theta{}^j + \sigma_a{}^j\sigma_\theta{}^i) + \Phi_{22}\sigma_\varepsilon{}^i\sigma_\varepsilon{}^j + \Phi_{33}\sigma_\theta{}^i\sigma_\theta{}^j], \tag{19}$$

where

$$\Phi_{13} = \frac{2dcb^2}{B^2} - \frac{b^2}{[A(A+B/4)]^{3/2}}\Big[dc\frac{A^2(2A+3B/4)}{B^2} - Ad\Big(\frac{3A}{2}+\frac{B}{2}\Big) + b\Big(\frac{AC}{8} + 3A^2 + \frac{3AB}{2} + \frac{B^2}{8}\Big)\Big], \tag{19a}$$

$$\Phi_{22} = \frac{3b}{8[A(A+B/4)]^{3/2}}\Big[A^2\Big(\frac{c}{d} + 2bd - 4b^2\Big) - \frac{B^2b^2}{2} - Ab\Big(\frac{Cb}{2} + 5Bb + Ba\Big)\Big], \tag{19b}$$

$$\Phi_{33} = 2\Big(\frac{3a+3b+d}{2a+2b+d}\Big)^2 - \frac{1}{2[A(A+B/4)]^{3/2}}\Big[\frac{A^2}{2}(3A+B) - Ab^2a\Big(\frac{9A}{2}+\frac{5B}{4}\Big) + b^3\Big(\frac{AC}{8} - 3A^2 - \frac{AB}{4} + \frac{B^2}{8}\Big) - \frac{b^2cdA^2}{B^2}\Big(2A+\frac{3B}{4}\Big) - 6(a+b)A^2bd\Big(A+\frac{B}{4}\Big)\frac{1}{B}\Big]. \tag{19c}$$

In the particular case $d = 0$, Eqs. (19a)–(19c) reduce to the familiar expressions of Ref. 1. An attempt made in Ref. 1 to find the form of $H_{E\text{-}E}$ for cubic media in a dimensional analysis was not successful. Our result has nothing in common with the predictions of Ref. 1. On the other hand, in the case of a weak cubic anisotropy Eqs. (19a)–(19c) reduce to expressions obtained on the basis of the Lifshitz-Rozentsveĭg tensor of Eq. (15).

Ions with threefold orbital degeneracy. In this case the operator (18) is supplemented by the expression

$$\sigma_4{}^i e_{xy} + \sigma_5{}^i e_{xz} + \sigma_6{}^i e_{yz}, \tag{20}$$

where σ_4, σ_5, and σ_6 are the operators in the space of the effective orbital momentum $L = 1$ (Ref. 13). When the interacting ions are located along the z axis, Eq. (19) must be supplemented by

$$\frac{1}{br_{ij}^3}[\Phi_{44}\sigma_{xy}{}^i\sigma_{xy}{}^j + \Phi_{55}\sigma_{yz}{}^i\sigma_{yz}{}^j + \Phi_{66}\sigma_{xz}{}^i\sigma_{xz}{}^j], \tag{21}$$

where

$$\Phi_{44} = \frac{A}{[A(A+B/4)]^{3/2}}\Big[\frac{B^2}{8} - A^2 + \frac{(2A+B)Bb}{4d} - \frac{(2b+d)}{8d}AC\Big], \tag{21a}$$

$$\Phi_{55} = \Phi_{66} = \frac{2Bb^3 - B^2 + AC + 2(a+b)b^3d(2b+d)}{B[A(A+B/4)]^{1/2}} - \frac{bd(6a+6b+d)+c}{B}. \tag{21b}$$

If $d = 0$, then Eqs. (21a) and (21b) reduce to the expression familiar for isotropic media. In the case of cubic media, these expressions differ from that given in Ref. 1. The terms allowing for local rotations are not included because of the simplicity of the general expression (7).

6. SOME MANIFESTATIONS OF THE INTERACTION VIA THE DEFORMATION FIELD IN THE CASE OF JAHN-TELLER CENTERS

By way of example, we shall consider some manifestations of the interaction of orbitally degenerate ions with a partly filled $3d$ shell in cubic crystals. A direct substitution of the elastic moduli into Eqs. (19) and (21) using the empirical values of the deformation potential parameters shows that the interaction via the deformation field predominates over the interaction of electrostatic multipoles. For example, in the case of the $\mathrm{Cu}^{2+}(^2E_g)$ at distances $r_{ij} \approx 8$ Å for $C_{11} = \lambda_{xxxx} = 13.45$, $C_{44} = \lambda_{xyxy} = 3.81$, and $C_{12} = \lambda_{xxyy} = 5.27$ (all in units of 10^{11} dyn/cm^2), both for a $\mathrm{KZnF_3}$ crystal[15] and for $\sigma_\theta \approx 20\,000$ cm^{-1} (Ref. 13), we have $H_{E\text{-}E} \approx 125$ cm^{-1}. The interaction of electric quadrupoles at these distances does not exceed 10 cm^{-1}. Such a strong interaction indicates that in some cases it should be allowed for even before solution of the vibronic problem[14] for each of the centers.

Let us assume that, for example, we are dealing with a pair of octahedrally coordinated Cu^{2+} ions separated by distances $r_{ij} \sim 8$ Å along the fourfold axis. Averaging the interaction operator (19) over electron variables and allowing for the corrections due to the anharmonicity, we can represent the adiabatic potential of a pair in the form

$$V = \beta_1 \cos 3\varphi_1 + \beta_2 \cos 3\varphi_2 + K_\theta (\cos \varphi_1 + \cos \varphi_2) + K_{\theta\theta} \cos \varphi_1 \cos \varphi_2 + K_{\varepsilon\varepsilon} \sin \varphi_1 \sin \varphi_2. \tag{22}$$

Here, β_1 and β_2 are the anharmonicity parameters amounting to 300 cm^{-1} (Ref. 13); the angles φ_1 and φ_2 have their usual meaning[13]; K_θ, $K_{\theta\theta}$, and $K_{\varepsilon\varepsilon}$ are quantities which represent the interaction of the centers. It follows from the results of specific calculations given in Table I that $K_{\theta\theta} > 0$, $K_{\varepsilon\varepsilon} < 0$, and $K_{\theta\theta} > |K_{\varepsilon\varepsilon}|$. The quantity K_θ is governed by two coupling constants: the constant describing the interaction between one center and a totally symmetric vibration and that representing the interaction of another center with a tetragonal mode. Therefore, this quantity differs from crystal to crystal also in respect of the sign.

It is known that without allowance for the interaction the adiabatic potential minima in the range $\beta < 0$ correspond to dilatation of each of the octahedra along one of the fourfold axes ($\varphi = 0, 2\pi/3, 4\pi/3$). Impurity centers may have the tetragonal symmetry. An analysis of the adiabatic potential (22) as a function of the angles φ_1 and φ_2 readily shows that if the interaction is included, then self-localized distortions of a new type may appear. The principal minima of (22) in the range $K_{\theta\theta} > K_\theta$ correspond to two equivalent configurations of a "bioctahedron" of the orthorhombic symmetry. Naturally, such self-localized pairs with a new symmetry can be detected experimentally only when the frequency of observation is higher than the frequency of tunneling between equivalent minima of the adiabatic potential of Eq. (22).[4)] Similar behavior has recently been reported for a tetragonal $\mathrm{K_2ZnF_4{:}Cu^{2+}}$ crystal with centers exhibiting the JT pseudoeffect.[16] A series of experiments involving an increase in the concentration of magnetic ions was carried out and the ESR method applied at $T < 77$ K revealed the appearance of centers with correlated distortions at distances exceeding the radius of the superexchange interaction. In this example the interaction via the deformation field resulted in "freezing" of the tunneling and self-localization of static distortions at each of the centers.

7. CONCLUDING REMARKS

These examples of a strong manifestation of the interaction via the deformation field do not exhaust all the possibilities. The interaction plays an important role in the transfer of energy quanta in the acoustic range[5)] between various impurity centers. For example, the Stark splitting of rare-earth ions is frequently $\approx$ 10–100 cm^{-1}. A direct calculation shows that in this case the probabilities of energy transfer over distances ≈ 10 Å are higher than because of the quadrupole-quadrupole interactions. This result is readily understood on the basis of the following qualitative considerations. It is clear from Eqs. (7) and (17) that the energy of the interaction due to local rotations depends weakly on the values of the deformation potential parameters; it is governed by the splitting and elastic properties of the medium. In more rigorous calculations we then face the problem of validity of tackling energy transfer within the framework of the theory of elasticity. As illustrated above in the example of an isotropic medium, an analysis based on the theory of elasticity corresponds to just an allowance for the interaction via acoustic phonons and complete neglect of the retardation effects. On the other hand, it is quite clear that an analysis based on the theory of elasticity suggests a method for compact formulation of complete quantum-mechanical expressions allowing for the retardation effects.[6] In particular, the complete operator representing the interaction via acoustic phonons in an isotropic medium can be represented

TABLE I. Values of elastic moduli (10^{11} dyn/cm^2) and of constants $\Phi_{\alpha\beta}$ of some crystals.

Crystal	C_{11}	C_{12}	C_{44}	Φ_{22}	Φ_{33}	Φ_{12}
KCl	4.53	0.54	0.66	2.639	−0.094	2.136
MgO	2.89	0.88	1.55	3.732	−1.206	2.601
$\mathrm{KMgF_3}$	13.2	3.96	4.85	3.481	−0.578	2.136
$\mathrm{CaF_2}$	17.4	5.6	3.58	3.281	−0.181	1.750
$\mathrm{BaF_2}$	9.81	4.48	2.54	3.657	−0.364	1.596

as follows:

$$H^{ij}=\sum a^{+}_{m_i}a_{n_i}a^{+}_{n_j}a_{m_j}\langle n_i|\sigma_{\alpha\beta}{}^{i}|m_i\rangle \langle m_j|\sigma_{\gamma\delta}{}^{j}|n_j\rangle\nabla_{\beta}{}^{i}\nabla_{\delta}{}^{i}T_{\alpha\gamma}(\mathbf{r}_{ij}), \tag{23}$$

$$T_{\alpha\gamma}(\mathbf{r})=\frac{1}{4\pi\rho}\left\{\frac{\delta_{\alpha\gamma}}{v_t^2 r}\cos\left(\frac{\omega_{nm}r}{v_t}\right) +\nabla_\alpha\nabla_\gamma\frac{1}{\omega_{nm}{}^2 r}\left[\cos\left(\frac{\omega_{nm}r}{v_t}\right)-\cos\left(\frac{\omega_{nm}r}{v_l}\right)\right]\right\}. \tag{24}$$

We can see that, in the limit $(\omega_{nm}r/v)\rightarrow 0$, Eq. (24) becomes exactly identical with the classical expression (15) corresponding to $d=0$. It should be stressed that an explicit separation of the operations of differentiation in Eq. (23) not only leads to a compact expression, but it also simplifies greatly the quantum-mechanical calculations of the Green functions. In other words, the classical (elastic field) and quantum-mechanical (phonon field) approaches complement one another.

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1)We are stressing this circumstance because there have been several later treatments based on the theory of the indirect interaction via a phonon field in which this passage to the limit is not carried out. The results of such investigations should apparently be regarded as incorrect.

2)Some inaccuracies in Eq. (5) of Ref. 6 were pointed out in Refs. 11 and 12. In the old edition[4] and in Ref. 2 the plus sign should be replaced with minus in the case of the Green tensor inside the parentheses.

3)It is assumed here that $A>0$ and $B>-A$. In the opposite case the integrals of Eq. (13) should be recalculated. We are not aware of any cases when these conditions are not obeyed in the case of real crystals.

4)It should be pointed out that this self-localization of distortions of new symmetry may not occur if the kinetic energy of ion motion is greater than β and $K_{\theta\theta}$.

5)The treatment in Ref. 17 deals with the transfer of an energy Δ in the optical range via a phonon field but it suffers from some misunderstandings. If the phonon energy is $h\omega_{as}<\Delta$, the interaction ceases to depend on the phonon dispersion law and vanishes. In the case of centers occupying nonequivalent positions in a unit cell this can be demonstrated by using the relationship describing the orthogonality of the polarization vectors $\Sigma_s l^{(s)}_{ak} l^{*(s)}_{\beta l}=\delta_{\alpha\beta}\delta_{kl}$, where the index s labels the vibration branches, and k and l are the numbers used to label various sites within one unit cell.

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