JAHN–TELLER EFFECT ON IMPURITY CENTERS IN SEMICONDUCTORS

G. L. BIR

Institute of Semiconductors, Academy of Sciences, U.S.S.R.

The static Jahn–Teller effect on impurity centers in semiconductors is investigated. Interaction between the impurity center and lattice is regarded as an interaction with an elastic anisotropic medium. The nature and magnitude of splitting of the impurity-center ground state are derived for various types of symmetry centers in cubic crystals. The magnitude of the Jahn–Teller splitting increases with increasing ionization energy E of the impurity center and may be of the order of 0.01–0.002 eV for centers with $E_0 \sim 0.05$–0.1 eV.

IN 1937 Jahn and Teller have shown[1] that if the ground state of a polyatomic molecule is degenerate, then it is stable with respect to displacements of the atoms from symmetrical positions, leading in the general case to a lifting of the degeneracy of the electron level. Subsequently the Jahn–Teller effect was considered by Van Vleck, Öpik, and Pryce and by other authors for octahedral and tetrahedral complexes of ions in crystals.[2] Moffit et al.[3] considered the dynamic aspects of the Jahn–Teller effect and indicated that for low-symmetry stationary states due to the Jahn–Teller effect, to exist in molecules, it is necessary to satisy the condition $\Delta E > \hbar\omega$, where ΔE is the magnitude of the Jahn–Teller splitting of the degenerate state and ω is the characteristic oscillation frequency of the atoms.

We consider in this paper the Jahn–Teller effect for shallow impurity levels in semiconductors.

It is known that the ground state of shallow impurity centers in semiconductors has a degeneracy multiplicity which coincides with the degeneracy multiplicity of the band at the extremum point. Since the valence bands are degenerate in the elementary semiconductors Ge and Si, and also apparently in all semiconductors of the A_3B_5 type (InSb, GaSb, GaAs, etc.), we can expect the Jahn–Teller effect to take place for acceptor centers in such semiconductors. However, the method used by Van Vleck, Öpik, and Pryce and others to calculate the Jahn–Teller splitting is based on the quasi-molecular model of the complex in the crystal and is not applicable to semiconductors, since the wave function of the shallow acceptor center extends over many lattice constants. This circumstance, however, makes it possible to regard the interaction of the impurity center with the lattice as an interaction with an elastic anisotropic medium. In this case the analog of the Jahn–Teller displacement of the atoms in the molecule will be the occurrence of elastic deformations in the crystal. Since the form of the operator of interaction between the impurity center and the deformation is known,[4] we can obtain the magnitude and the character of the Jahn–Teller splitting of the impurity centers in semiconductors.

In this paper we consider the static Jahn–Teller effect for sufficiently shallow impurity centers in semiconductors, and obtain the character of the splitting of impurity centers of different symmetry in cubic semiconductors with the extremum of the band at the center of the Brillouin zone. It is shown that for orbitally non-degenerate centers (representations Γ_1, Γ_2, Γ_6, Γ_7) the interaction with the deformation leads to a certain lowering of the ground state, and for centers with orbital degeneracy (representations Γ_3, Γ_4, Γ_5, Γ_8) in additional splitting of the degenerate level of the impurity center takes place. The Jahn–Teller splitting of the impurity center differs in this case from the splitting of the degenerate impurity level for a specified external strain in that the stationary state corresponds only to the lower of the split levels. This gives rise to a different type of degeneracy, in which a finite number of states of the impurity center, differing in the strain direction (representation Γ_4, Γ_5), or even an infinite set of states, for which the direction of the strain changes continuously (representations Γ_3, Γ_8), correspond to the same energy. Estimates of the magnitude of the effect and of the criterion for its existence show that the static Jahn–Teller effect can be realized in semiconductors.

1. We consider a crystal at zero temperature,

with impurity center whose ground state is degenerate. In the effective-mass method the wave functions of the impurity center $\Psi^{(i)}$ ($i = 1, 2, \ldots, N$, where N is the multiplicity of the impurity-center degeneracy) are represented in the form of a product of slowly varying wave functions $f_t^{(i)}$ and Bloch functions $\varphi_{k_0}^{(s)}$, corresponding to the extremum of the band:[5]

$$\Psi^{(i)} = \sum_s f_s^{(i)} \varphi_{k_0}^{(s)}. \tag{1}$$

In (1), $s = 1, 2, \ldots, N_0$, where N_0 is the multiplicity of the degeneracy of the band at the extremum point k_0. The functions $f^{(i)}$, with N_0-components $f_s^{(i)}$ ($s = 1, 2, \ldots N_0$), can be written in the form of a column with N_0-components; in this case the operators acting on $f_s^{(i)}$ have the form of $N_0 \times N_0$ matrices.

In a crystal free of strains, $f_0^{(i)}$ is determined by the system of equations:[5]

$$H_l f_0^{(i)} = E_0 f_0^{(i)}, \qquad \sum_t (H_l)_{st} f_{0,t}^{(i)} = E_0 f_{0,s}^{(i)}, \tag{2}$$

where H_l is the energy operator of the impurity center in the effective-mass method. The explicit form of the operator H_l will not be needed here. The interaction between the impurity center and a slowly varying elastic deformation, described by a deformation tensor $\epsilon_{\alpha\beta} = \frac{1}{2}(\partial u_\alpha/\partial x_\beta + \partial u_\beta/\partial x_\alpha)$, where u is the displacement vector, is determined by the operator $H_{\epsilon l}$, which is linear in the deformation[6,5]

$$H_{\epsilon l} = \sum_{\alpha,\beta} D^{\alpha\beta} \varepsilon_{\alpha\beta}(r), \qquad (H_{\epsilon l})_{st} = \sum_{\alpha,\beta} D_{st}^{\alpha\beta} \varepsilon_{\alpha\beta}(r), \tag{3}$$

where $D_{st}^{\alpha\beta}$ are constants of the deformation potential, determining the splitting of the bottom of the band during the deformation. The form of the matrix $H_{\epsilon l}$ and the number of the constants of the deformation potential are determined uniquely by the symmetry of the functions $\varphi_{k_0}^{(i)}$. The presence of an interaction that is linear in the deformation causes the stationary states of the crystal with impurity center to correspond to a state with nonzero deformation, leading in the general case to the splitting of the initial degenerate impurity level. The energy density operator of the crystal in the presence of a strain takes the form

$$H = H_l + H_{\epsilon l} + E_\varepsilon, \tag{4}$$

where E_ϵ is the energy of the elastically deformed crystal:

$$E_\varepsilon = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \lambda_{\alpha\beta\gamma\delta} \, \varepsilon_{\alpha\beta}(r) \, \varepsilon_{\gamma\delta}(r); \tag{5}$$

Here $\lambda_{\alpha\beta\gamma\delta}$ is the elastic-constant tensor.

For a specified strain $\epsilon_{\alpha\beta}(r)$, the wave functions of the impurity center satisfy the system of equations

$$(H_l + H_{\epsilon l})_{is} f_s = (E - E_\varepsilon) f_i. \tag{6}$$

The strain should be determined here from the equilibrium condition, which in the stationary case is of the form

$$\sum_k \frac{\partial \sigma_{ik}}{\partial x_k} = 0, \tag{7}$$

where σ_{ik} are the components of the stress tensor. The stress tensor consists of a part proportional to the elastic strain, and of the stress $\sigma^{(e)}$ produced by the electrons of the impurity center

$$\sigma_{ik} = \sum_{l,m} \lambda_{iklm} \, \varepsilon_{lm}(r) + \sigma_{ik}^{(e)}, \tag{8}$$

where

$$\sigma_{ik}^{(e)}(r) = \frac{\delta \langle \mathbf{f} | H_{\epsilon l} | \mathbf{f} \rangle}{\delta \varepsilon_{ik}(r)} = \sum_{s,t} D_{st}^{ik} f_s^*(r) f_t(r). \tag{9}$$

Equations (6)–(9) constitute a complete system describing the interaction of the impurity-center electron with the static strain produced in the elastic medium.

The problem of determining the wave function of the impurity center is thus self-consistent, since the wave functions are determined by the strain as in (6), but the strain itself is determined by the wave function of (7)–(9). In this sense, the problem is similar to the case of large-radius polarons,[7] where a self-consistent polarization of the medium, leading to the occurrence of the polaron state, is likewise produced. Pekar and Deĭgen[8] considered the interaction of the conduction electron in a homopolar crystal from the point of view of the possible formation of a localized state of an electron–condenson. They have shown that, at any rate for states with sufficiently large radius, production of a condenson is impossible. Self-consistent interaction of the exciton with the lattice in molecular crystals was considered by Rashba.[9] In the present paper we are considering the splitting of the degenerate level of the impurity center due to interaction with the elastic strain produced in the crystal.

Let us consider the case when the level shift $\Delta E = E - E_0$ due to the interaction with the elastic strain is much smaller than the ionization energy

$$\Delta E / E_0 \ll 1. \tag{10}$$

In this case perturbation theory is valid and the wave functions $\mathbf{f}$ can be sought in the form of a linear combination of the functions $\mathbf{f}_0^{(i)}$

$$\mathbf{f} = \sum_i C_i \mathbf{f}_0^{(i)}, \quad f_s = \sum_i C_i f_{0,s}^{(i)}. \tag{11}$$

Substituting (11) in (9), we obtain for $\sigma_{ik}^{(e)}$:

$$\sigma_{ik}^{(e)} = \sum_{m,n} C_m C_n{}^* \Lambda_{ik}{}^{mn}, \quad \Lambda_{ik}^{mn} = \sum_{s,t} D_{st}^{ik} f_{0,s}^{*(n)} f_{0,t}^{(m)}. \tag{12}$$

The equilibrium equation (7), which determines the connection between the strain and the wave functions, is transformed into an inhomogeneous differential equation, in which the coefficients C_n and C_n^* play the role of parameters.

Let us show now in the general case that the presence of a strain leads to a lowering of the impurity-center energy, i.e., $\Delta E < 0$. From (6) in the approximation (10) we obtain for the energy E

$$E = E_0 + \frac{1}{2}\sum \lambda_{iklm}\int \varepsilon_{ik}\,\varepsilon_{lm}\,d\tau + \sum \int \sigma_{ik}^{(e)}\,\varepsilon_{ik}\,d\tau. \tag{13}$$

In (13), the second term is the elastic energy of the strained medium E_ϵ ($E_\epsilon > 0$), and the third term describes the interaction with the elastic strain.

To calculate $\sum\int \sigma_{ik}^{(e)}\epsilon_{ik}\,d\tau$ we multiply the equilibrium equation (7) by u_i, sum over i, and integrate over the entire volume. As a result we get

$$\sum_{i,k}\int \frac{\partial \sigma_{ik}}{\partial x_k} u_i = 0. \tag{14}$$

Integrating (14) by parts, using (8) and the symmetry of σ_{ik}, we obtain

$$\sum \lambda_{iklm}\int \varepsilon_{lm}\,\varepsilon_{ik}\,d\tau + \sum \int \sigma_{ik}^{(e)}\,\varepsilon_{ik}\,d\tau = 0$$

or

$$\sum \int \sigma_{ik}^{(e)}\varepsilon_{ik}\,d\tau = -2E_\varepsilon. \tag{15}$$

Thus, the energy of interaction between the impurity center and the elastic medium is negative and is exactly double the elastic energy of deformation. Therefore

$$\Delta E = -E_\varepsilon < 0. \tag{16}$$

We shall show further that in the case of orbital degeneracy of the state of the impurity center, this reduction in the energy is accompanied in general by a splitting of the impurity-center level.

To determine the strain from the equilibrium condition (8), we determine the displacement vector u, which is written in the form of an expansion in a Fourier integral

$$\mathbf{u}(r) = \int \mathbf{u}(q)e^{i\mathbf{q}\mathbf{r}}\,d^3q.$$

We resolve the vector $\mathbf{u}(q)$ along three mutually perpendicular unit vectors $\mathbf{e}^j$ (j = 1, 2, 3), which are conveniently chosen to be the polarization vectors of the elastic waves $\mathbf{e}^j = \mathbf{e}^j(q)$:

$$\mathbf{u}(r) = \sum_j \int \mathbf{e}^j(q)\gamma_{qj}\,e^{i\mathbf{q}\mathbf{r}}\,d^3q, \quad \varepsilon_{st}(r) = i\sum_j \tilde{\varepsilon}_{st}{}^j \gamma_{qj}\,e^{i\mathbf{q}\mathbf{r}}\,d^3q,$$

$$\tilde{\varepsilon}_{st}{}^j \equiv (e_s{}^j q_t + q_s e_t{}^j)/2. \tag{17}$$

We likewise expand $\sigma_{\alpha\beta}^{(e)}(r)$ in a Fourier integral:

$$\sigma_{\alpha\beta}^{(e)}(r) = \int \sigma_{\alpha\beta}^{(e)}(q)e^{i\mathbf{q}\mathbf{r}}\,d^3q$$

$$= \sum_{m,n} C_m C_n{}^* \int \Lambda_{\alpha\beta}{}^{mn}(q)e^{i\mathbf{q}\mathbf{r}}\,d^3q.$$

Then Eq. (7) yields

$$i\sum_{j',\beta\gamma\delta} \lambda_{\alpha\beta\gamma\delta}\tilde{\varepsilon}_{\gamma\delta}^{j'}q_\beta\gamma_{qj'} + \sigma_{\alpha\beta}^{(e)}(q)q_\beta = 0. \tag{18}$$

We multiply both sides of (18) by e_α^j and sum over α:

$$i\sum_{j',\alpha\beta\gamma\delta} \gamma_{qj}\lambda_{\alpha\beta\gamma\delta}\tilde{\varepsilon}_{\gamma\delta}^{j'}\tilde{\varepsilon}_{\alpha\beta}^{j} + \sigma_{\alpha\beta}^{(e)}(q)\tilde{\varepsilon}_{\alpha\beta}^{j} = 0. \tag{19}$$

Using an identity readily obtained from the equations for elastic oscillations of the medium

$$\sum_{\alpha\beta\gamma\delta} \lambda_{\alpha\beta\gamma\delta}\tilde{\varepsilon}_{\gamma\delta}^{j'}\tilde{\varepsilon}_{\alpha\beta}^{j} = \rho\omega_{qj}^2\,\delta_{jj'}, \tag{20}$$

where ω_{qj} is the oscillation frequency of the j-branch and ρ is the density of the medium, we obtain

$$\gamma_{qj} = i\sum \frac{\sigma_{\alpha\beta}^{(e)}(q)\tilde{\varepsilon}_{\alpha\beta}^{j}}{\rho\omega_{qj}^2} \equiv i\frac{\Gamma^j(q)}{\rho\omega_{qj}^2},$$

$$\Gamma^j(q) = \sum_{\alpha\beta} \sigma_{\alpha\beta}^{(e)}(q)\tilde{\varepsilon}_{\alpha\beta}^{j} = \sum_{m,n\alpha\beta} C_m C_n{}^* \Lambda_{\alpha\beta}^{mn}(q)\tilde{\varepsilon}_{\alpha\beta}^{j}. \tag{21}$$

Thus, $\Gamma^j(q)$ is a quadratic function of C_m. Substituting γ_{qj} in $\epsilon_{\alpha\beta}$, we obtain ΔE:

$$\Delta E = -E_\varepsilon = \frac{1}{2}\sum \int \sigma_{\alpha\beta}^{(e)}\varepsilon_{\alpha\beta}\,d\tau$$

$$= -(2\pi)^3\sum_j \int \frac{|\Gamma^j(q)|^2}{2\rho\omega_{qj}^2}\,d^3q. \tag{22}$$

ΔE contains the coefficients C_m, which actually determine the character of the splitting of the impurity-center level.

To determine the coefficients C_m it is necessary to solve the Schrödinger equation (6), which in the approximation (10), (11) takes the form

$$\sum_{s,k} (\mathbf{H}_{el})_{is} C_k f_{0,s}^{(k)} = 2\Delta E \sum_n C_n f_{0,i}^{(n)}. \tag{23}$$

Multiplying both sides of (23) by $f_{0,i}^{*(n)}$, summing over i, and integrating over the volume we obtain a system for determining the coefficients C_n:

$$W_{nk}C_k = 2\Delta E C_n, \qquad (24)$$

where

$$W_{nk} = \sum_{is} \int f_{0,i}^{*(n)} (\mathbf{H}_{\varepsilon l})_{is} f_{0,s}^{(k)} \, d\tau$$

$$= i(2\pi)^3 \sum_{j,\alpha\beta} \Lambda_{\alpha\beta}^{*nk}(q) \gamma_{qj} \tilde{\varepsilon}_{\alpha\beta}{}^j \, d^3q$$

$$= -(2\pi)^3 \sum_{jml\alpha\beta\gamma\delta} C_m C_l^* \int \Lambda_{\alpha\beta}^{*nk}(q) \Lambda_{\gamma\delta}^{ml}(q) \frac{\tilde{\varepsilon}_{\alpha\beta}{}^j \tilde{\varepsilon}_{\gamma\delta}{}^j}{\rho\omega_{qj}^2} \, d^3q.$$

$$(25)$$

Thus, each matrix element W_{nk} is a quadratic function of the coefficients C_m. Therefore, to determine the coefficients C_m we must solve the nonlinear system (24). The nonlinearity of the system is connected with the self-consistency of the problem in question: the wave functions are determined by the strain, but the strain itself is determined by the form of the wave function, i.e., by the coefficients C_m. The level splitting differs in this case from the level splitting for a specified external strain,[4] when the number of the splitting levels is equal to the number of the different roots of the corresponding secular equation. In our case, for each permissible type of strain there is possible only one (lower) state corresponding to the equilibrium condition.

It is easy to understand physically and to verify directly that the system (24) is exactly equivalent to the problem of finding the minimum of ΔE in independent variation with respect to C_n and C_n^* and under the normalization condition $\sum_n |C_n|^2 = 1$. Equations (24) and (25) yield the solution of the problem on the deformation Jahn–Teller splitting of the degenerate levels of impurity centers in semiconductors. For a concrete calculation of the character and magnitude of the Jahn–Teller splitting it is necessary to know the wave functions $f_{0,k}^{(s)}$ of the impurity center.

2. It is known that the multiplicity of the degeneracy and the symmetry of the impurity center (ground state) coincide in the effective-mass method with the multiplicity of the degeneracy and symmetry of the wave functions of the carriers at the extremum point. We shall consider below cubic crystals with an extremum of the band at the center of the Brillouin zone ($k_0 = 0$). The wave functions of the acceptor centers in crystals of the type Ge and Si were considered in the paper of Kohn and Schechter.[10] Bearing in mind a determination of the character of the splitting and an estimate of the magnitude of the effect, we shall make a simplifying assumption with respect to the form of the wave functions of the impurity center, which

is factually equivalent to the hydrogen-like model for the degenerate impurity center. Namely, from among all the functions $f_{0,k}^{(s)}$, we retain only one— the spherically symmetrical function φ_0. From this we obtain for $f_{0,k}^{(s)}$

$$f_{0,k}^{(s)} = \varphi_0 \delta_{sk}. \qquad (26)$$

Indeed, from (1) we get $\Psi^{(i)} = \varphi_0 \varphi_{k0}^{(i)}$, i.e., $\Psi^{(i)}$ transforms like $\varphi_{k0}^{(i)}$. It is clear that the approximation (26) can only change slightly the magnitude of the splitting, but not its character or order; however, it does simplify greatly the result and makes it possible to obtain it in closed form.

For Λ^{mn} we obtain

$$\Lambda_{ih}^{mn} = D_{nm}^{ik} \varphi_0^2(r).$$

From this we get the values of W_{nk}, which determine the system (24):

$$W_{nk} = -(2\pi)^3 \sum C_m C_l^* D_{nk}^{\alpha\beta} D_{lm}^{\gamma\delta} \int \frac{\Phi_0^2(q) \tilde{\varepsilon}_{\gamma\delta}{}^j \tilde{\varepsilon}_{\alpha\beta}{}^j \, d^3q}{\rho\omega_{qj}^2},$$

$$(27)$$

where

$$\Phi_0(q) \equiv \frac{1}{(2\pi)^3} \int \varphi_0^2(r) e^{-i\mathbf{q}\mathbf{r}} \, d\tau.$$

Inasmuch as $\varphi_0(x)$ is a continuous function, the values of q which are essential for the integration are sufficiently small in the integral with respect to d^3q in (27), so that $w_{qj}^2 = C_{qj}^2 q^2$, where C_{qj} is the speed of sound. In this case W_{nk} can be written in the form

$$W_{nk} = -\langle \varphi_0^4 \rangle \sum C_m C_l^* D_{nk}^{\alpha\beta} D_{lm}^{\gamma\delta} S_{\alpha\beta\gamma\delta}, \qquad (28)$$

where

$$\langle \varphi_0^4 \rangle \equiv \int \varphi_0^4(r) \, d\tau, \qquad S_{\alpha\beta\gamma\delta} \equiv \frac{1}{4\pi} \sum_j \int \frac{\tilde{\varepsilon}_{\gamma\delta}{}^j \tilde{\varepsilon}_{\alpha\beta}{}^j}{\rho\omega_{qj}^2} \, d\Omega_q. \qquad (29)$$

In (29) $d\Omega_q$ is a solid-angle element. The tensor $S_{\alpha\beta\gamma\delta}$ is perfectly analogous in its symmetry properties to the elastic-constant tensor, and has for cubic crystals three independent components:

$$S_{xxxx} \equiv S_{11}, \quad S_{xxyy} \equiv S_{12}, \quad S_{xyxy} \equiv S_{44}\ldots \qquad (30)$$

We represent the matrix $\mathbf{D} = \Sigma D^{\alpha\beta}\varepsilon_{\alpha\beta}$ in the form

$$\mathbf{D} = a\,\mathrm{Sp}\,\varepsilon I_0 + \mathbf{D}'^{\alpha\beta}\varepsilon_{\alpha\beta}, \qquad D_{st}^{\alpha\beta} = a\delta_{\alpha\beta}\delta_{st} + D_{st}'^{\alpha\beta}, \qquad (31)$$

where I_0 is a unit matrix, $\mathrm{Tr}\,\varepsilon = \varepsilon_{xx} + \varepsilon_{yy} + \varepsilon_{zz}$ describes the change of the volume due to the strain, and a is a constant of the deformation potential, determining the shift of the band as a whole under hydrostatic deformation. Thus, only the matrix $\mathbf{D}'$ determines the splitting of the band in the

case of uniaxial deformation. The trace of the matrix D' is equal to zero, and since D' = 0 under hydrostatic deformation, we have $\Sigma_\alpha D'^{\alpha\alpha}_{st} = 0$.

Using (28)–(31) for ΔE and W_{nk}, we easily obtain, after simple transformations

$$\Delta E = -\tfrac{1}{2}\langle\varphi_0^4\rangle 3a^2(S_{11} + 2S_{12})$$
$$- \tfrac{1}{2}\langle\varphi_0^4\rangle\Sigma C_s^* C_n C_t C_m[(S_{11} - S_{12})P^{(nm,\,st)} + S_{44}Q^{(nm,\,st)}]$$
$$\equiv -\tfrac{1}{2}\langle\varphi_0^4\rangle 3a^2(S_{11} + 2S_{12}) + \Delta E',$$

$$W_{nk} = -\langle\varphi_0^4\rangle 3a^2(S_{11} + 2S_{12})\delta_{nk} - \langle\varphi_0^4\rangle\Sigma C_m C_l^*$$
$$\times [(S_{11} - S_{12})P^{(nk,\,lm)} + S_{44}Q^{(nk,\,lm)}]$$
$$\equiv -3a^2\langle\varphi_0^4\rangle(S_{11} + 2S_{12})\delta_{nk} + W_{nk}', \tag{32}$$

where

$$P^{(nk,\,lm)} = \sum_\alpha D_{nk}'^{\alpha\alpha}D_{lm}'^{\alpha\alpha} = D_{nk}'^{xx}D_{lm}'^{xx} + D_{nk}'^{yy}D_{lm}'^{yy}$$
$$+ D_{nk}'^{zz}D_{lm}'^{zz},$$

$$Q^{(nk,\,lm)} = \sum_{\alpha\neq\beta} D_{nk}'^{\alpha\beta}D_{lm}'^{\alpha\beta} = D_{nk}'^{xy}D_{lm}'^{xy} + D_{nk}'^{xz}D_{lm}'^{xz}$$
$$+ D_{nk}'^{yz}D_{lm}'^{yz}. \tag{33}$$

In the approximation (26), the strain $\epsilon_{\alpha\beta}(r)$ is simply proportional to $\varphi_0^2(r)$:

$$\epsilon_{\alpha\beta}(r) = a\varphi_0^2(r)(S_{11} + 2S_{12})\delta_{\alpha\beta}$$
$$- \varphi_0^2(r)\sum_{mn,\,\gamma\delta} C_m C_n^* D_{nm}'^{\gamma\delta} S_{\alpha\beta\gamma\delta} \ldots \tag{34}$$

The average value of the strain $\bar\epsilon_{\alpha\beta} \equiv \int \epsilon_{\alpha\beta}(r)$ $\times \varphi_0^2(r)\,d\tau$ is

$$\bar\epsilon_{\alpha\beta} = -a\langle\varphi_0^4\rangle(S_{11} + 2S_{12})\delta_{\alpha\beta}$$
$$- \langle\varphi_0^4\rangle\sum_{m,\,n,\,\gamma\delta} C_m C_n^* D_{nm}'^{\gamma\delta} S_{\alpha\beta\gamma\delta}.$$

It follows from (29) that

$$S_{11} + 2S_{12} = \frac{1}{12\pi}\sum_j \int \frac{(e^j q)^2}{\rho\omega_{qj}^2}\,d\Omega_q. \tag{35}$$

The energy bands have the highest symmetry at the center of the Brillouin zone, where the wave vector group coincides with the total cubic group. If spin is disregarded, there are in a cubic crystal five irreducible representations Γ_i (i = 1, 2, 3, 4, 5), of which two are one-dimensional (Γ_1 and Γ_2), one is two-dimensional (Γ_3), and two are three-dimensional (Γ_4, Γ_5). If spin and spin-orbit interaction are taken into account, the band symmetry is characterized by the irreducible representation of the double cubic group Γ_6, Γ_7, and Γ_8, where Γ_6 and Γ_7 are two-dimensional and Γ_8 is a four-dimensional representation. These representations are derived from the representations Γ_i (i = 1, ..., 5) of the cubic group by expansion of the direct product $\Gamma_i \times D^{(1/2)}$, where $D^{(1/2)}$ is the irreducible

representation of the rotation group with weight $1/2$:

$$\Gamma_1 \times D^{(1/2)} = \Gamma_6, \quad \Gamma_2 \times D^{(1/2)} = \Gamma_7, \quad \Gamma_3 \times D^{(1/2)} = \Gamma_8,$$
$$\Gamma_4 \times D^{(1/2)} = \Gamma_6 + \Gamma_8, \quad \Gamma_5 \times D^{(1/2)} = \Gamma_8 + \Gamma_7. \tag{36}$$

Thus, in the limiting case of weak spin-orbit interaction it is necessary to consider the representations Γ_i (i = 1, ..., 5), and in the case of a strong one—the representations Γ_6, Γ_7, and Γ_8. As follows from the theorem on time reversal, interaction with a strain cannot lift the Kramers degeneracy; therefore the energy shift ΔE for the doubly degenerate levels Γ_6 and Γ_7 coincides with ΔE for orbitally non-degenerate levels Γ_1 and Γ_2. We shall consider below three main cases which can be realized in cubic crystals: 1—orbitally non-degenerate levels Γ_1, Γ_2, Γ_6, and Γ_7, 2—doubly degenerate level Γ_3, 3—triply degenerate levels Γ_4 and Γ_5, and 4—fourfold degenerate level Γ_8.

1. In the case of non-degenerate bands D' = 0 and the entire interaction with the strain reduces to the first term in (32). Therefore for non-degenerate bands the decrease in the level energy due to the interaction with the strain is equal to

$$\Delta E = -\tfrac{3}{2}a^2\langle\varphi_0^4\rangle(S_{11} + 2S_{12}). \tag{37}$$

If we go over to the approximation of an elastically isotropic medium, i.e., replace the elastic constants C_{11}, C_{12}, and C_{44} by the mean values $\bar C_{11}$, $\bar C_{12}$, $\bar C_{44}$, for which the conditions of elastic isotropy are satisfied:

$$\bar C_{11} - \bar C_{12} = 2\bar C_{44}, \tag{38}$$

then we can easily obtain for S_{11}, S_{12}, and S_{44}

$$S_{11} = \frac{1}{5}\left(\frac{1}{\bar C_{11}} + \frac{2}{3}\frac{1}{\bar C_{44}}\right); \quad S_{12} = \frac{1}{15}\left(\frac{1}{\bar C_{11}} - \frac{1}{\bar C_{44}}\right),$$
$$S_{44} = \frac{1}{10}\left(\frac{1}{\bar C_{44}} + \frac{2}{3}\frac{1}{\bar C_{11}}\right). \tag{39}$$

From this we get $S_{11} + 2S_{12} = 1/3\bar C_{11}$. From the isotropy condition (38) follows a similar relation between $S_{11} - S_{12}$ and S_{44}:

$$S_{11} - S_{12} = 2S_{44}. \tag{40}$$

2. In the case of a doubly degenerate band Γ_3, the matrix D' in the basis of the functions that transform like $\sqrt3\,(x^2 - y^2)/2$ and $z^2 - (x^2 + y^2)/2$ is of the form

$$\mathbf{D'} = \frac{b}{2}\begin{pmatrix}\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz} & \sqrt3(\varepsilon_{yy} - \varepsilon_{xx})\\ \sqrt3(\varepsilon_{yy} - \varepsilon_{xx}) - (\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz})\end{pmatrix}, \tag{41}$$

where b is the constant of the deformation potential and describes the splitting of the band upon deformation in the (100) direction. From (41 we obtain

$$D_{11}'^{xx} = D_{11}'^{yy} = -D_{22}'^{xx} = -D_{22}'^{yy} = \frac{b}{2};$$

$$D_{11}'^{zz} = -D_{22}'^{zz} = -b, \quad D_{12}'^{yy} = -D_{12}'^{xx} = \frac{\sqrt{3}}{2}b.$$

Using (32) and (33) we get

$$\Delta E = -\frac{3a^2}{2}(S_{11} + 2S_{12})\langle\varphi_0{}^4\rangle - \frac{3b^2}{4}\langle\varphi_0{}^4\rangle(S_{11} - S_{12}). \quad (42)$$

Thus, in the case of the representation Γ_3 the value of ΔE does not depend on the coefficients C_1 and C_2; in this case (23) is satisfied identically for arbitrary coefficients C_1 and C_3.

For the level Γ_3, in accordance with (34), there arise besides hydrostatic deformation also components of shear deformation

$$\bar\varepsilon_{xx} - \bar\varepsilon_{yy} = 2\sqrt{3}C_1C_2\langle\varphi_0{}^4\rangle(S_{11} - S_{12})b,$$

$$\bar\varepsilon_{xx} + \bar\varepsilon_{yy} - 2\bar\varepsilon_{zz} = -\langle\varphi_0{}^4\rangle 3b(C_1{}^2 - C_2{}^2)(S_{11} - S_{12}), \quad (43)$$

which depend on the coefficients C_1 and C_2. They satisfy one condition:

$$(\bar\varepsilon_{xx} - \bar\varepsilon_{yy})^2 + (\bar\varepsilon_{xx} - \bar\varepsilon_{zz})^2 + (\bar\varepsilon_{yy} - \bar\varepsilon_{zz})^2$$
$$= {}^9\!/_2 \langle\varphi_0{}^4\rangle^2 (S_{11} - S_{12})^2 b^2, \quad (44)$$

and are arbitrary in all other respects. Thus there remains a unique degeneracy in the strain direction, when the magnitude of the shear deformation is determined by formula (44), but its direction is arbitrary.

3. For the triply degenerate band Γ_4 and Γ_5, the matrix $\mathbf{D}'$ is the same and takes the form[6]

$$\mathbf{D}' = \begin{pmatrix} b(\varepsilon_{zz} + \varepsilon_{yy} - 2\varepsilon_{xx}) & d\sqrt{3}\varepsilon_{xy}, & d\sqrt{3}\varepsilon_{xz} \\ d\sqrt{3}\varepsilon_{xy}, & b(\varepsilon_{xx} + \varepsilon_{zz} - 2\varepsilon_{yy}), & d\sqrt{3}\varepsilon_{yz} \\ d\sqrt{3}\varepsilon_{xz} & d\sqrt{3}\varepsilon_{yz}, & b(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}) \end{pmatrix}, \quad (45)$$

where b and d are the constants of the deformation potential and determine the splitting of the bottom of the band upon deformation along the directions (100) and (111). From (45) we get $D'^{\alpha\beta}_{st}$:

$$D_{11}'^{yy} = D_{11}'^{zz} = D_{22}'^{xx} = D_{33}'^{xx} = -D_{11}'^{xx}/2$$

$$= -D_{22}'^{yy}/2 = -D_{33}'^{zz}/2 = b$$

$$D_{12}'^{xy} = D_{13}'^{xz} = D_{23}'^{yz} = d\sqrt{3}. \quad (46)$$

From (46) we obtain a system of equations for determining the coefficients C_i and ΔE:

$$C_1[C_1{}^2(3b^2(S_{11} - S_{12}) - 2d^2S_{44}),$$
$$+ 2d^2S_{44} - b^2(S_{11} - S_{12})] = -\frac{2}{3}\frac{\Delta E'C_1}{\langle\varphi_0{}^4\rangle}. \quad (47)$$

The remaining two equations are obtained by cyclic permutation of the indices 1, 2, and 3.

Let us consider the solutions of the system (47) for the case

$$3b^2(S_{11} - S_{12}) \neq 2d^2S_{44}. \quad (48)$$

In this case the system (47) has three types of solutions:

a) $C_1 \neq 0$, $C_2 \neq 0$, $C_3 \neq 0$. From (47) we get $C_1^2 = C_2^2 = C_3^2 = \frac{1}{3}$, altogether four solutions having the same energy ΔE:

$$\Delta E = -\frac{3a^2}{2}\langle\varphi_0{}^4\rangle(S_{11} + 2S_{12}) - 2d^2S_{44}\langle\varphi_0{}^4\rangle. \quad (49)$$

Solution a) corresponds, in addition to hydrostatic

deformation, also to the shear deformations ϵ_{xy}, ϵ_{xz}, and ϵ_{yz}

$$\bar\varepsilon_{xy} = -2C_1C_2\langle\varphi_0{}^4\rangle\sqrt{3}dS_{44} \quad (50)$$

etc. Thus, case a) corresponds to a deformation in the (111) direction.

b) $C_1 = 0$, $C_2 \neq 0$, $C_3 \neq 0$. It follows from (47) that in this case $C_2^2 = C_3^2 = \frac{1}{2}$ or, in particular, $C_2 = C_3 = 1/\sqrt{2}$. We obtain altogether six solutions of this type with energy ΔE:

$$\Delta E = -\frac{3a^2}{2}\langle\varphi_0{}^4\rangle(S_{11} + 2S_{12})$$
$$- \frac{3}{2}\langle\varphi_0{}^4\rangle\left(d^2S_{44} + \frac{b^2}{2}(S_{11} - S_{12})\right). \quad (51)$$

In case b), besides the hydrostatic deformation, the following deformation components differ from zero:

$$\bar\varepsilon_{yy} = \bar\varepsilon_{zz}, \quad \bar\varepsilon_{xx} - \bar\varepsilon_{yy} = -{}^3\!/_2 b(S_{11} - S_{12})\langle\varphi_0{}^4\rangle, \quad (52)$$
$$\varepsilon_{yz} = -\langle\varphi_0{}^4\rangle d\sqrt{3}S_{44}$$

(the remaining five solutions are obtained by permutation of the indices), corresponding to deformation of the crystal in the (011) direction.

c) $C_1 = C_2 = 0$, $C_3 = 1$. There are three types of such solutions with energies

$$\Delta E = -{}^3\!/_2 a^2\langle\varphi_0{}^4\rangle(S_{11} + 2S_{12}) - 3b^2(S_{11} - S_{12})\langle\varphi_0{}^4\rangle. \quad (53)$$

For the solution c) the non-zero strains are

$$\bar\varepsilon_{xx} = \bar\varepsilon_{yy}, \quad \bar\varepsilon_{xx} - \bar\varepsilon_{zz} = -3b\langle\varphi_0{}^4\rangle(S_{11} - S_{12}), \quad (54)$$

which correspond to deformation of the crystal along the (001) direction.

These three types of solutions correspond to the three cases of Jahn–Teller splitting of an octahedral complex, as obtained by Öpik and Pryce.[2] Thus, the number of levels with different energy, arising as a result of the Jahn–Teller splitting, is determined by the number of different types of deformation which can exist in stationary manner in the crystal. This gives rise to a specific degeneracy, when several levels with different deformations have the same energy. Thus, for the levels Γ_4 and Γ_5, cases a), b), and c) correspond, in accordance with the cubic symmetry of the crystal, to groups of 4, 6, and 3 levels with identical energy. This degeneracy is outwardly analogous to the "many-valley" degeneracy of the extrema of bands in semiconductors.

We have considered the case when $3b^2(S_{11} - S_{12}) \neq 2d^2S_{44}$. If $3b^2(S_{11} - S_{12}) = 2d^2S_{44}$, then the system (47) has a solution for arbitrary coefficients C_1, C_2, and C_3 and the energy ΔE is in this case equal to

$$\Delta E = -{}^3/_2 a^2 \langle \varphi_0{}^4 \rangle (S_{11} + 2S_{12}) - 2d^2S_{44} \langle \varphi_0{}^4 \rangle.$$

In this case the energy ΔE for the cases a), b), and c) coincide and are equal to this value. An "accidental" degeneracy in the strain arises, wherein the energy does not depend at all on the direction of the strain. The condition $3b^2(S_{11} - S_{12}) = 2d^2S_{44}$ corresponds to "isotropy" of the Jahn–Teller effect and is realized, for example, in the case of elastic isotropy of the crystal, when $S_{11} - S_{12} = 2S_{44}$, and the "isotropy" of the constants of the deformation potential $b^2 = 3b^2$.[6] It corresponds to the case when the splitting of the band does not depend on the direction of the stress.

4. Fourfold degenerate level Γ_8. If we choose as the basis functions $\varphi_m^{(3/2)}$ ($m = \pm{}^3/_2, \pm{}^1/_2$), then the matrix D' takes the form[6]

$$\mathbf{D}' = \begin{pmatrix} D_{11}' & D_{12}' & D_{13}' & 0 \\ D_{12}'{}^* & -D_{11}' & 0 & D_{13}' \\ D_{13}{}^* & 0 & -D_{11}' & -D_{12}' \\ 0 & D_{13}'{}^* & -D_{12}'{}^* & D_{11}' \end{pmatrix},$$ (55)

where

$$D_{11}' = {}^1/_2 b(\varepsilon_{xx} + \varepsilon_{yy} - 2\varepsilon_{zz}), \quad D_{12}' = -d(\varepsilon_{yz} + i\varepsilon_{xz}),$$
$$D_{13}' = {}^1/_2\sqrt{3}b(\varepsilon_{xx} - \varepsilon_{yy}) - id\varepsilon_{xy};$$ (56)

$\mathbf{D}'$ is determined in the same way as in the case of the representations Γ_4 and Γ_5, by two constants of the deformation potential b and d.

The functions $\varphi_m^{(3/2)}$ were chosen such[5] that under time reversal Θ they go over into another as follows:

$$\Theta\varphi_{3/2}^{(3/2)} = \varphi_{-3/2}^{(3/2)}, \quad \Theta\varphi_{1/2}^{(3/2)} = -\varphi_{-1/2}^{(3/2)},$$
$$\Theta\varphi_{-1/2}^{(3/2)} = -\varphi_{1/2}^{(3/2)}, \quad \Theta\varphi_{-3/2}^{(3/2)} = -\varphi_{3/2}^{(3/2)}.$$ (57)

We see that the matrix $\mathbf{D}'$ is invariant to such a transformation of the basis functions, and therefore for any deformation double degeneracy of the levels remains when Ψ and $\Theta\Psi$ describe a state with one energy. The operation Θ corresponds to the following transformation of the functions f_i:

$$f_1 \to -f_4{}^*, \quad f_2 \to f_3{}^*, \quad f_3 \to -f_2{}^*, \quad f_4 \to f_1{}^*.$$ (58)

Since in our case $f_S = \varphi_0 C_S$ and φ_0 is real, this transformation corresponds to the following transformation of the coefficients C_i:

$$C_1 \to -C_4{}^*, \quad C_2 \to C_3{}^*, \quad C_3 \to -C_2{}^*, \quad C_4 \to C_1{}^*.$$ (59)

As a result of the remaining double degeneracy of the level, the system (24) cannot determine the coefficients C_i uniquely, and it is therefore more convenient to consider in this case ΔE in place of the system (24). Using (32) and the form of the matrix $\mathbf{D}'$ for ΔE, we can obtain

$$\Delta E = -{}^3/_2 a^2 (S_{11} + 2S_{12}) \langle \varphi_0{}^4 \rangle$$
$$- {}^3/_4 b^2 \langle \varphi_0{}^4 \rangle (S_{11} - S_{12})(\alpha^2 + \beta^2)$$
$$- {}^1/_2 d^2 \langle \varphi_0{}^4 \rangle S_{44}(\gamma^2 + |\delta|^2),$$ (60)

where

$$\alpha \equiv |C_1|^2 + |C_4|^2 - |C_2|^2 - |C_3|^2,$$
$$\gamma \equiv 2\mathrm{Im}(C_1{}^*C_3 + C_2{}^*C_4),$$
$$\beta \equiv 2\mathrm{Re}(C_1{}^*C_3 + C_2{}^*C_4), \quad \delta \equiv 2(C_1{}^*C_2 - C_3{}^*C_4).$$ (61)

As expected, ΔE is determined not by all the coefficients C_i and $C_i{}^*$, but only by certain combinations (61) that are invariant to the transformation (59).

Minimizing ΔE with respect to α, β, γ, and δ under the normalization condition

$$\sum_i |C_i|^2 = \alpha^2 + \beta^2 + \gamma^2 + |\delta|^2,$$

we obtain two solutions. The first is of the form $\alpha^2 + \beta^2 = 1$, $\gamma = \delta = 0$,

$$\Delta E = -{}^3/_2 a^2 (S_{11} + 2S_{11}) \langle \varphi_0{}^4 \rangle - {}^3/_4 b^2 \langle \varphi_0{}^4 \rangle (S_{11} - S_{12}),$$ (62)

i.e., the quantities α and β are not determined uniquely, and their ratio can be arbitrary. This case corresponds to the deformation

$$\overline{\varepsilon_{xx}} - \overline{\varepsilon_{yy}} = -\langle \varphi_0{}^4 \rangle (S_{11} - S_{12})\sqrt{3}b\beta,$$
$$\overline{\varepsilon_{xx}} + \overline{\varepsilon_{yy}} - 2\overline{\varepsilon_{zz}} = -3\langle \varphi_0{}^4 \rangle b(S_{11} - S_{12})\alpha.$$ (63)

The second solution has the form

$$\gamma^2 + |\delta|^2 = 1, \quad \alpha = \beta = 0,$$
$$\Delta E = -{}^3/_2 a^2 (S_{11} + 2S_{12}) \langle \varphi_0{}^4 \rangle - {}^1/_2 d^2 \langle \varphi_0{}^4 \rangle S_{44}.$$ (64)

For this case the shear components of the deformation differ from zero

$$\bar{\varepsilon}_{xy} = d\langle\varphi_0^4\rangle S_{44}\gamma, \quad \bar{\varepsilon}_{yz} = d\langle\varphi_0^4\rangle \,\mathrm{Re}\,\delta,$$
$$\bar{\varepsilon}_{xz} = -\langle\varphi_0^4\rangle S_{44}d\,\mathrm{Im}\,\delta. \tag{65}$$

Both solutions for the level Γ_8 correspond to a crystal deformation whose magnitude is specified by means of the relations

$$(\bar{\varepsilon}_{xx} - \bar{\varepsilon}_{yy})^2 + (\bar{\varepsilon}_{xx} - \bar{\varepsilon}_{zz})^2 + (\bar{\varepsilon}_{yy} - \bar{\varepsilon}_{zz})^2$$

$$= {}^9\!/_2\, b^2 \langle\varphi_0^4\rangle^2 (S_{11} - S_{12})^2,$$

$$\bar{\varepsilon}_{xy}^{\,2} + \bar{\varepsilon}_{xz}^{\,2} + \bar{\varepsilon}_{yz}^{\,2} = d^2\langle\varphi_0^4\rangle^2 S_{44}^2,$$

but whose direction is arbitrary and is determined by the relation between α, β, or γ, $\mathrm{Re}\,\delta$, $\mathrm{Im}\,\delta$. Thus, here, as in the case of the levels Γ_4 and Γ_5, a specific degeneracy in the strain sets in, but unlike the levels Γ_4 and Γ_5, where a finite number of states corresponds to each energy, there is a continuous set of states with one energy, having different strain directions. This case is similar to the case of a "ring" or "sphere" in the band structure, when the extremum of the band is realized not at isolated points of the Brillouin zone, but along an entire line or even along the surface of the extrema. If the condition $2d^2S_{44} = 3b^2(S_{11} - S_{12})$ is satisfied, then again the energies for both solutions coincide, and the splitting is thus independent of the type of deformation.

3. Let us consider the order of magnitude of the Jahn–Teller effect in semiconductors and the criteria for the applicability of the obtained results. For estimates, let us consider the solution a) for levels Γ_4 and Γ_5 at $\alpha = 0$ and in the isotropic approximation (39). From (49) we have for $\Delta E'$ when $\bar{C}_{44} \sim \bar{C}_{11}$

$$\Delta E' = - 2d^2S_{44}\langle\varphi_0^4\rangle \approx -\frac{d^2}{3\bar{C}_{44}}\langle\varphi_0^4\rangle = -\frac{d^2\gamma_0\alpha_0^3}{3\bar{C}_{44}}, \tag{66}$$

where $\alpha_0 = 1/\bar{r}$ and $\bar{r}$ is the average radius of the electron state. The dimensionless factor γ_0 depends on the detailed form of the wave function $\langle\varphi_0^4\rangle$. From (66) we see that the magnitude of the effect increases strongly, like r^{-3}, with decreasing radius of the electronic state, i.e., the Jahn–Teller effect is maximal for the deepest levels. For an order-of-magnitude estimate of $\Delta E'$ we obtain from (66), recognizing that $\bar{C}_{44}\Omega_0$ and d are of the order of the atomic energy (Ω_0 is the unit-cell volume),

$$\Delta E \sim \frac{d}{3}\frac{\Omega_0}{V_0}, \tag{67}$$

V_0 is the volume occupied by the wave function of the impurity center.

Let us consider first the criteria for the applicability of the results. We used in the calculations the effective-mass method, the theory of elasticity, and also perturbation theory, requiring satisfaction of the inequalities

$$a_0 a_0 \pi^{-1} \ll 1, \quad \Delta E / E_0 \ll 1, \tag{68}$$

a_0 is the lattice constant. In our analysis the interaction between the impurity ion and the lattice was regarded as an interaction with an elastic anisotropic medium which is under stationary conditions. In this approximation we found that in the general case a Jahn–Teller splitting of the degenerate level of the impurity center always takes place. It is known, however, that owing to the presence of zero-point oscillations, even at absolute zero temperature, the approximation of the immobile lattice is not always valid. The lattice oscillation frequencies that are important in our problem are of the order of ω_{α_0}. The immobile-lattice approximation is valid in the case when the frequency of the electron of the impurity center $\Delta E/\hbar$ greatly exceeds ω_{α_0}, i.e., the adiabaticity criterion must be satisfied:

$$\Delta E / \hbar\omega_{\alpha_0} \gg 1. \tag{69}$$

The lattice vibrations give rise to transitions of the electrons both between different equivalent configurations (with one value of ΔE) and between states with different types of deformation (with different values of ΔE). Such transitions are accompanied by reorientation of the deformation, and if their intensity is sufficiently large, they can lead to a strong mixing of the states with different deformation and in final analysis to a vanishing of the Jahn–Teller effect. However, for the re-orientation of the deformation even within an equivalent configuration, the energy required is of the order of ΔE, and therefore the transition probability $\tilde{w}$ is exponentially small when condition (69) is satisfied: $\tilde{w} \sim \exp(-\Delta E/\hbar\omega_{\alpha_0})$. In this connection, the adiabaticity condition (69) ensures the existence of a static Jahn–Teller coefficient for a sufficiently low temperature.

A unique situation arises when states exist with continuous distribution of the deformations, for example in the case of the levels Γ_3 and Γ_8. In this case arbitrarily close states are possible, with arbitrarily low re-orientation energy. For such close states, the adiabaticity condition is not satisfied and the transitions between them are not exponentially small. Therefore intense transitions take place between such states and a continuous re-orientation of the deformation takes place inside the states belonging to the same energy ΔE. However, under the condition (69) the phonons cannot destroy the entire aggregate of states as a whole, for this calls for, as before, an energy on the order

of ΔE, and the probability of such a process is exponentially small, therefore in this case under condition (69) there exists a Jahn–Teller splitting of the impurity centers.

We note also that condition (69) is simultaneously also the criterion for a strong coupling of the impurity-center electrons with the lattice. If $\Delta E/\hbar\omega_{\alpha_0} < 1$, then the coupling is weak and the electron-phonon interaction can be considered by perturbation theory. We note in this connection that this situation here recalls to a certain degree the case of large-radius polarons in the strong-coupling approximation,[7] where satisfaction of a criterion of the type (69) is also required, and the role of ΔE is played by the polaron shift.

Let us consider now the satisfaction of the adiabaticity criterion (69) for semiconductors. The ionization energy E_0 in semiconductors ranges from 0.1 to 0.2–0.3 eV. Taking a value $E_0 \sim 0.08$ eV and estimating α_0 from the hydrogenlike model, $\alpha_0 = 2\epsilon E_0/e^2$ (where ϵ is the dielectric constant, $\epsilon \sim 10$), we obtain $\alpha_0 \sim 10^7$ cm^{-1}; for $d \sim 5$ eV, $\gamma_0 \sim 0.2$, $C_l \sim 3 \times 10^5$ cm/sec, and $\rho \approx 2$ g/cm^3 we have $\Delta E/\hbar\omega_{\alpha_0} \approx 8$. These values of the parameters correspond to $\Delta E' \sim 0.015$ eV for $a = 0$. We see also that under these conditions the criteria (68) are also satisfied. The foregoing estimates point to a real possibility of the existence of a Jahn–Teller effect in semiconductors.

In conclusion the author thanks G. E. Pikus for a discussion of the work and for reviewing the manuscript, and V. L. Gurevich for a discussion of the work.

---

[1] H. A. Jahn and E. Teller, Proc. Roy. Soc. **A161**, 220 (1937).

[2] J. H. Van Vleck, J. Chem. Phys. **7**, 72 (1939); U. Öpik and H. M. L. Pryce, Proc. Roy. Soc. **A238**, 425 (1957).

[3] W. Moffit and A. D. Liehr, Phys. Rev. **106**, 1195 (1957); W. Moffit and W. Thorson, Phys. Rev. **108**, 1251 (1957).

[4] W. H. Kleiner and L. Roth, Phys. Rev. Lett. **2**, 334 (1959); G. L. Bir, E. I. Butikov, and G. E. Pikus, J. Phys. Chem. Solids **24**, 1467 (1963).

[5] M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[6] G. E. Pikus and G. L. Bir, FTT **1**, 1642 (1959), Soviet Phys. Solid State **1**, 1502 (1960).

[7] S. I. Pekar, Issledovaniya po elektronnoĭ teorii kristallov (Research on the Electron Theory of Crystals), Gostekhizdat, 1961.

[8] M. F. Deĭgen and S. I. Pekar, JETP **21**, 803 (1951).

[9] E. I. Rashba, Optika i spektroskopiya **2**, 75 and 88 (1957).

[10] W. Kohn and D. Schechter, Phys. Rev. **99**, 1903 (1955); D. Schechter, J. Phys. Chem. Solids **8**, 216 (1959).