# Crystal structures and symmetry of the electron spectrum of IV–VI semiconductors

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The structures of the crystalline modifications of IV–VI compounds are regarded as distorted cubic lattices of the NaCl type. The instability of the cubic phase is attributed to a specific feature of the electron spectrum, whereby the Fermi surface of the "parent" phase with primitive cubic lattice becomes completely or partially congruent with itself under certain translations in reciprocal space. It is shown that different degrees of doping can result in ferroelectric structures with different symmetries. Restructuring into an antiferromagnetic phase with rhombic symmetry is considered within the framework of the phenomenological theory of structure transitions. The possibility of the onset of an inhomogeneous structure in this phase, due to the noncommensurability of the displacement wave with the period of the initial lattice, is indicated. The influence of doping, which stabilizes the commensurate structure, is examined. A number of experimental data on phase transitions in IV–VI compounds are discussed on the basis of the proposed model.

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## 1. INTRODUCTION

The crystal structures of IV–VI semiconductors, meaning compounds of elements of group IV and group VI of the periodic table, can be one of three systems, cubic, rhombic, and rhombohedral. The crystals of lead chalcogenide Pb(S, Se, Te) and of the high-temperature modifications of GeTe and SnTe have a cubic lattice of the NaCl type. The structures of the compounds Ge(S, Se) and Sn(S, Se) belong to the rhombic system.[1] With changing temperature and pressure, phase transitions between the indicated crystalline modifications take place in the IV–VI compounds.[1] Thus, when the temperature of GeTe is decreased, depending on the deviation of the composition from stoichiometric (which determines the carrier density in IV–VI semiconductors[1]), transitions are observed from the cubic to the rhombohedral phase[2] or to the rhombic phase.[3] In SnTe, a structure transition is observed only into the rhombohedral phase,[4] although there are experimental indications that another phase transition is possible.[5]

In the present study we attempted to connect the observed crystal structures of the semiconductors of the IV–VI group with the general symmetry properties of their electron spectrum. We shall use here the known analogy between IV–VI compounds and the elements of group V (Bi, Sb, As),[6] an analogy which is apparently due to the fact that in all these substances each atom has on the average two *s* and three *p* valences electrons. The crystal structures of the different modifications of the IV–VI semiconductors can be regarded as NaCl lattices, deformed in a definite fashion, in analogy with the Abrikosov and Fal'kovskiĭ[2] treatment of the structure of the elements of the bismuth group by starting from a primitive cubic lattice.

The dependence of the critical temperature of the transition, especially in SnTe (Ref. 4) and of the symmetry of the low-temperature phase in GeTe (Refs. 2 and 3) on the carrier density indicates that the structural transition is due to instability in the electronic subsystem, due to electron–electron and electron–phonon interactions. This instability can arise in a metal in the presence of congruent sections of the Fermi surface,[6] in a semimetal that has electron and hole Fermi surface of almost the same shape,[9] or in a semiconductor with sufficiently narrow forbidden band.[10] These three cases can be treated in unified fashion by assuming the initial state to be metallic. Simultaneously with the "collective" gap in the electron spectrum, it is necessary to take into account the semiconducting gap,[11] as well as the structural rearrangement with the corresponding change of the Brillouin zone. This approach should be based on an analysis of the electron spectrum of the initial phase.

## 2. ELECTRON SPECTRUM OF IV–VI SEMICONDUCTORS IN THE TIGHT-BINDING APPROXIMATION

1. From among the IV–VI compounds, the most fully investigated is the band structure of lead chalcogenides.[12,13] It has been established that the extrema of the electron and hole bands are located at *L* points of the Brillouin zone (Fig. 1). A similar electron spectrum is possessed by the semiconductors SnTe (Ref. 14) and GeTe. Experiments on photoemission[15] offer evidence of a similar band structure also for compounds with orthorhombic lattice such as Ge(S, Se) and Sn(S, Se). Thus, one can speak of an electron spectrum that is typical of semiconductors of the IV–VI group.

The forbidden band widths are ≈0.1 and ≈0.18 eV for GeTe and SnTe, respectively, and ≈0.3 eV in lead chalcogenides[1] (300 K). The situation considered in Refs. 10 and 11 is thus realized, and it might seem that the structural realignment should be connected

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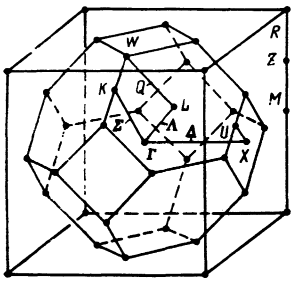

FIG. 1. Brillouin zones for primitive cubic lattice with period $a$ (see Fig. 2) and for an fcc lattice with period $2a$.

with the electron instability in the vicinity of the $L$ points. It can be shown, however (see Ref. 16 and the Appendix) that the instability at the $L$ points should lead to a transition into a structure with tetragonal symmetry,[1)] whereas a rhombohedral distortion of the lattice is observed in experiment. Consequently, the instability is due to some other states and it is necessary to consider the formation of the electron spectrum in the entire Brillouin zone. We use for this purpose the tight-binding approximation.

Regarding the interaction integrals as the parameters of the fit, it is possible to account in this approximation for the real band structures with good accuracy.[17] At the same time, the symmetry of the electron spectrum is taken into account automatically and does not depend on these parameters.

2. We start with a primitive cubic lattice with period $a$ (Fig. 2), in which each atom contains three valence $p$ electrons. The chemical non-equivalence of neighboring atoms will be subsequently taken into account by introducing the ionicity $v(\mathbf{r})$, as was done by Gordyunin and Gor'kov.[18] The Brillouin zone for the considered primitive and fcc lattices are respectively a cube and a polyhedron (Fig. 1). Since the atomic $s$ levels form a deep-lying narrow band,[12] we confine ourselves to $p$ electrons only.

Thus, our initial approximation agrees with the hypothetical phase of the elements of the bismuth group, which has a primitive cubic lattice, and corresponds to a metal with a Fermi surface of large area.

In the tight-binding approximation the atomic states $|p_i\rangle$ lead to bands $\varepsilon_i(\mathbf{k})$ ($i=x, y, z$ with $|p_x\rangle = xf(|\mathbf{r}|)$ etc.). The corresponding Bloch functions are

$$|\mathbf{k}, i\rangle = \frac{1}{\sqrt{N}}\sum_n \exp(i\mathbf{k}\mathbf{R}_n)\varphi_i(\mathbf{r}-\mathbf{R}_n), \tag{1}$$

where the summation is over the sites of the primitive cubic lattice, $N$ is the number of sites, $\varphi_i(\mathbf{r})$ is the atomic wave function of the state $|p_i\rangle$. Taking into account the interaction integrals for the three coordination spheres, the energy spectrum takes the form[17]

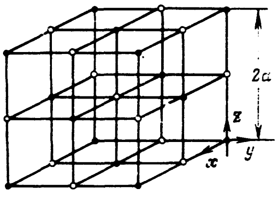

FIG. 2. Crystal lattice of the NaCl type. This structure can be obtained from the primitive cubic lattice with period $a$ by making the neighboring atoms nonequivalent.

$$\begin{aligned}\varepsilon_x^{(0)}(\mathbf{k}) &= \alpha\cos k_x a + V_{xx}(0,1,0)(\cos k_y a + \cos k_z a)\\ &+ V_{xx}(1,1,0)(\cos k_x a\cos k_y a + \cos k_x a\cos k_z a)\\ &+ V_{xx}(0,1,1)\cos k_y a\cos k_z a + V_{xx}(1,1,1)\cos k_x a\cos k_y a\cos k_z a.\end{aligned} \tag{2}$$

Similar expressions are obtained also for $\varepsilon_y$ and $\varepsilon_z$. The interaction integrals are

$$V_{ij}(p, q, r) = \int d^3\mathbf{r}\,\varphi_i^*(\mathbf{r})\hat{H}\varphi_j(\mathbf{r}-p\mathbf{a}_x-q\mathbf{a}_y-r\mathbf{a}_z),$$

where $\mathbf{a}_i$ are the basis vectors of the cubic lattice.

The degeneracy of the bands $\varepsilon_i(k)$ along the $\Lambda$ axis is partially lifted if account is taken of the off-diagonal matrix elements $W_{ij}$ (hybridization of the bands (2)):

$$\begin{aligned}W_{xy}(\mathbf{k}) &= V_{xy}(1,1,0)\sin k_x a\sin k_y a\\ &- V_{xy}(1,1,1)\sin k_x a\sin k_y a\sin k_z a.\end{aligned} \tag{3}$$

The electron spectrum is determined by the roots of the secular equation

$$\det\|[\varepsilon-\varepsilon_i^{(0)}(\mathbf{k})]\delta_{ij}-W_{ij}(\mathbf{k})\|=0. \tag{4}$$

It is seen from (2)–(4) that if we neglect the interaction integrals corresponding to the second coordination sphere, then the electron spectrum $\varepsilon_j(\mathbf{k})$ ($j=1, 2, 3$) satisfies the condition

$$\varepsilon_j(\mathbf{k}+\mathbf{Q}) = -\varepsilon_j(\mathbf{k}), \tag{5}$$

where $\mathbf{Q} = (\pi/a)(1,1,1)$. The Fermi surface defined by Eq. (4) for $\varepsilon = 0$ would then coincide with itself following a translation by the vector $\mathbf{Q}$. If the violation of the condition (5) on account of integrals of the type $V_{ij}(1,1,0)$, is not too strong, then the crystal lattice may turn out to unstable and the crystal acquires a periodicity characterized by the wave vector $\mathbf{Q}$.[8,19]

A strikingly illustrative picture can be obtained by discarding in (2) all the terms except the first. As a result we have three purely one-dimensional bands which can be regarded as the "zeroth" approximation Fermi surface consists of three pairs of planes passing through the centers of the lines $\Delta$ (see Fig. 1). This surface becomes congruent with itself when shifted by the vector $\mathbf{Q}$.

The hybridization (3) leads to splitting of the zeroth-approximation Fermi surface into surfaces of three types. At the center of the Brillouin zone $\Gamma$ is located a hole surface which is close in shape (with measure $W_{ij}$) to a cube. At the vertices $R$ there are electron pockets. Finally, there is an open Fermi surface being shown in Fig. 3. On the $\Lambda$ axis this surface is tangent to the central whole cube, a fact that is patently of symmetry origin.

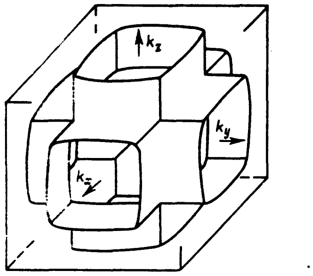

FIG. 3. Open Fermi surface in the metallic "original phase" with the cubic lattice. The surface was constructed in the limit of small hybridization for quasi-one-dimensional bands (2).

Inasmuch as bismuth becomes metallic under pressure,[20] and probably has then a primitive cubic lattice,[21] one can hope to observe the open Fermi surface in experiment. We note also that the existence of this very Fermi surface was proposed by Arbikosov[22] to reconcile his theory of the electron spectrum of bismuth[7] with the Luttinger theorem.[23]

3. The initial spectrum (2) is transformed into a spectrum of the semiconductor type if account is taken of the ionicity $v(\mathbf{r})$—a potential with the symmetry of a face-centered lattice with period $2a$. The interaction of the electrons with this potential in the representation of the tight-binding Bloch functions (1) is of the form

$$\hat{H}_{ion}=\sum_{i,j}\sum_{\mathbf{k}} v_{ij}(0,\mathbf{k})a^{+}_{\mathbf{k},i}a_{\mathbf{k},j}+\sum_{i\neq j}\sum_{\mathbf{k}} v_{ij}(\mathbf{Q},\mathbf{k})a_{\mathbf{k}+\mathbf{Q},i}a_{\mathbf{k},j},$$
$$+\sum_{i}\sum_{\mathbf{k}} v_{ii}(\mathbf{Q},\mathbf{k})a^{+}_{\mathbf{k}+\mathbf{Q},i}a_{\mathbf{k},i}, \qquad (6)$$

where $a^{+}_{\mathbf{k},i}$ is the operator of creation of an electron in the state (1) (we omit the spin indices). The summation over k in (6) is within the limits of the Brillouin zone of the cubic lattice. If the vector $\mathbf{k}+\mathbf{Q}$ lies outside its limits, it must be replaced by the vector into which it is transformed when referred to the first Brillouin zone. The matrix elements are obtained in the form

$$v_{ij}(\mathbf{Q},\mathbf{k})=\sum_{n}\exp(i\mathbf{k}\mathbf{R}_n)\sum_{\mathbf{B}}v(\mathbf{B}+\mathbf{Q})\int d^3\mathbf{r}\exp(i(\mathbf{B}+\mathbf{Q})\mathbf{r})\varphi_i^{*}(\mathbf{r})\varphi_j(\mathbf{r}-\mathbf{R}_n), \qquad (7)$$

where $v(\mathbf{B}+\mathbf{Q})$ are the Fourier components of the potential $v(\mathbf{r})$, $\mathbf{R}_n$ are the vectors of the primitive cubic lattice sites, and $\mathbf{B}$ are the vectors of the corresponding reciprocal lattice. The matrix elements (7) satisfy the condition

$$v_{ij}(Q,k)=v_{ij}^{*}(Q,k+Q),$$

which guarantees hermiticity of the operator $H_{ion}$.

The interaction corresponding to the first term in (6) reduces simply to replacement of the integrals $V_{ij}(p,q,r)$ in (2) and (3) by the quantities $V_{ij}(p,q,r)=V_{ij}(p,q,r)+v_{ij}(p,q,r)$, where

$$v_{ij}(p,q,r)=\int d^3\mathbf{r}\,\varphi_i^{*}(\mathbf{r})\sum_{\mathbf{B}}v(\mathbf{B})e^{i\mathbf{B}\mathbf{r}}\varphi_j(\mathbf{r}-p\mathbf{a}_x-q\mathbf{a}_y-r\mathbf{a}_z).$$

We denote the electron spectrum and the hybridization matrix elements, with allowance for this interaction, by $\bar{\xi}_i^{(0)}(\mathbf{k})$ and $W_{ij}(\mathbf{k})$. Far from the degeneracy line of the $\Lambda$ bands $\bar{\xi}_i^{(0)}(\mathbf{k})$, the hybridization $W_{ij}(\mathbf{k})$ and the second term in the interaction with ionicity (6) can be taken into account by perturbation theory:

$$\varepsilon_i(\mathbf{k})=\bar{\xi}_i^{(0)}(\mathbf{k})+\sum_{j\neq i}\left[\frac{|W_{ij}(\mathbf{k})|^2}{\xi_i^{(0)}(\mathbf{k})-\xi_j^{(0)}(\mathbf{k})}-\frac{|v_{ij}(\mathbf{Q},\mathbf{k})|^2}{\xi_i^{(0)}(\mathbf{k})+\xi_j^{(0)}(\mathbf{k})}\right]. \qquad (8)$$

It is implied here that in the energy correction, the matrix elements and the energy denominators were calculated with account taken only of the first nonvanishing interaction integrals. Then $\xi_i^{(0)}(\mathbf{k})$ is the sum of the first two terms of (2) and satisfies the condition (5). Inasmuch as in this approximation we also have

$$|W_{ij}(\mathbf{k}+\mathbf{Q})|=|W_{ij}(\mathbf{k})|,\quad |v_{ij}(\mathbf{Q},\mathbf{k}+\mathbf{Q})|=|v_{ij}(\mathbf{Q},\mathbf{k})|,$$

the second-order correction does not violate the requirement (5).

It remains now to determine how the third term in $\hat{H}_{ion}$ (6) transforms the spectrum (8). We note that since $2\mathbf{Q}$ is the reciprocal-lattice vector, in the most general case the spectrum $\varepsilon_i(\mathbf{k})$ can be represented in the form

$$\varepsilon_i(\mathbf{k})=\xi_i(\mathbf{k})+\eta_i(\mathbf{k}), \qquad (9)$$

where

$$\xi_i(\mathbf{k}+\mathbf{Q})=-\xi_i(\mathbf{k}),\quad \eta_i(\mathbf{k}+\mathbf{Q})=\eta_i(\mathbf{k}).$$

Concrete expressions for $\xi_i(\mathbf{k})$ and $\eta_i(\mathbf{k})$ are easy to obtain from formulas (2) and (8). The electron spectrum is defined by the equation

$$\begin{vmatrix}\varepsilon_i(\mathbf{k})-E & v_{ii}(\mathbf{Q},\mathbf{k})\\ v_{ii}^{*}(\mathbf{Q},\mathbf{k}) & \varepsilon_i(\mathbf{k}+\mathbf{Q})-E\end{vmatrix}=0,$$

whose solution, with allowance for (9), is of the form

$$E_i(\mathbf{k})=\eta_i(\mathbf{k})+\operatorname{sign}\,\xi_i(\mathbf{k})[\xi_i^2(\mathbf{k})+|v_{ii}(\mathbf{Q},\mathbf{k})|^2]^{1/2}. \qquad (10)$$

The dispersion law $E_i(\mathbf{k})$ along any direction is characterized by a dielectric gap, and a discontinuity in $E_i(\mathbf{k})$ takes place on the surface $\xi_i(\mathbf{k})=0$. Since this surface satisfies exactly the congruence condition for the vector $\mathbf{Q}$, when $E_i(\mathbf{k})$ is reduced to the Brillouin zone of an fcc lattice it is "matched" exactly on the $\xi_i(\mathbf{k})=0$ surface, so that the energy in the reduced band is continuous.

The term $\eta_i(\mathbf{k})$ in (10), which violates the congruence condition for the spectrum (9), leads to two consequences. First, inasmuch as $\nabla_{\mathbf{k}}\eta_i(\mathbf{k})\neq 0$ on the surface $\xi_i(\mathbf{k})=0$, the extrema of the upper and lower bands shift away from this surface in opposite directions. As a result, an indirect gap is produced near the surface $\xi_i(\mathbf{k})=0$. Quantitative calculations of the band structure[12,13] indeed lead to the existence of a large indirect gap near the midpoint of the line $\Gamma X$. Second, $\eta_i(\mathbf{k})$ can lead to overlap of bands at different points of k-space if

$$\max\eta_i(\mathbf{k})-\min\eta_i(\mathbf{k})>\min|v_{ii}(\mathbf{Q},\mathbf{k})|.$$

In order for the spectrum $E_i(\mathbf{k})$ to correspond to a semiconductor it is therefore necessary that the "noncongruent" term $\eta_i(\mathbf{k})$ not exceed the ionicity matrix element.

## 3. ELECTRON-PHONON INTERACTION AND STRUCTURAL INSTABILITY. FERROELECTRIC PHASES

An analysis of the electron spectrum allows us to conclude that the structural instability in IV–VI compounds is apparently connected with the approximate congruence of the Fermi surface following a shift by the vector $\mathbf{Q}=(\pi/a)(1,1,1)$. We have in mind here the Fermi surface of a hypothetical structure with a primitive cubic lattice.

We consider the interaction of electrons with a wave of static displacements:

$$\mathbf{u}(\mathbf{R}_n)=\mathbf{u}\cos\mathbf{QR}_n. \tag{11}$$

Here $\mathbf{u}(\mathbf{R}_n)$ is the displacement of the ion in the site $\mathbf{R}_n$. In a cubic lattice of a IV–VI semiconductor (Fig. 2) this wave corresponds to doubling in the system of planes (111), which contain only the atoms $A$ and $B$; in other words, it corresponds to a relative shift of two fcc sublattices of atoms $A$ and $B$ by a vector $\mathbf{u}$. The perturbation connected with the wave (11) takes the form

$$\delta V(\mathbf{r})=-\sum_n \nabla_{\mathbf{r}} v_1(\mathbf{r}-\mathbf{R}_n)\mathbf{u}(\mathbf{R}_n), \tag{12}$$

where $v_1(\mathbf{r}-\mathbf{R}_n)$ is the potential of the ion at the site $\mathbf{R}_n$. The matrix element of the perturbation (12) in the wave functions (1), with allowance for the first nonvanishing overlap integrals, is

$$\langle \mathbf{k}i|\delta V|\mathbf{k}'j\rangle=2i\mathbf{u}\sum_{\alpha=x,y,z} I_{ij}(\mathbf{a}_\alpha)\sin k_\alpha a\sum_{\mathbf{B}}\delta(\mathbf{k}-\mathbf{k}'+\mathbf{Q}+\mathbf{B}),$$

where

$$I_{ij}(\mathbf{a}_\alpha)=\int d^3\mathbf{r}\,\nabla v_1(\mathbf{r})\,[\varphi_i(\mathbf{r}-\mathbf{a}_\alpha)\varphi_j(\mathbf{r})+\varphi_j(\mathbf{r}-\mathbf{a}_\alpha)\varphi_i(\mathbf{r})],$$

$\mathbf{a}_\alpha$ are the basis vectors of the primitive cubic lattice.

We confine ourselves to the integrals $I_{ii}(\mathbf{a}_i)=I\mathbf{a}_i/a$, which are the largest because of the anisotropy of the atomic $p$ functions. Then the interaction of the electrons with the displacement wave (11), in the representation of the tight-binding functions (1), is of the form

$$\hat{H}_{int}=i\sum_i\sum_{\mathbf{k}} g_i(\mathbf{k})a^+_{\mathbf{k}+\mathbf{Q},i}a_{\mathbf{k},i}, \tag{13}$$

where $g_i(\mathbf{k})=I\sin k_i a$ and the region of summation over $\mathbf{k}$ is limited to the Brillouin zone of the cubic lattice; the vector $\mathbf{k}+\mathbf{Q}$, just as in (6) is assumed to be the reduced one.

The electron spectrum in the deformed lattice is similar to the spectrum (10):

$$E_i(\mathbf{k})=\eta_i(\mathbf{k})+\operatorname{sign}\xi_i(\mathbf{k})\,[\xi_i^2(\mathbf{k})+|v_{ii}(\mathbf{Q},\mathbf{k})|^2+|g_i(\mathbf{k})u_i|^2]^{1/2}. \tag{14}$$

At zero temperature, the energy of the system can be written in the form

$$E=2\sum_i\left[\int\frac{d^3\mathbf{k}}{(2\pi)^3}E_i(\mathbf{k})\Theta(\mu-E_i(\mathbf{k}))+\frac{1}{2}\omega_0^2u_i^2\right], \tag{15}$$

where the last term corresponds to the energy of the elastic deformation of the lattice; $\Theta(x)=1$ at $x>0$ and $\Theta(x)=0$ if $x<0$. We take into account here the possibility of doping the semiconductor, which leads to a deviation from half-filled bands. The chemical potential $\mu$ is defined by the equation

$$2\sum_i\int\frac{d^3\mathbf{k}}{(2\pi)^3}[\Theta(\mu-E_i(\mathbf{k}))-\Theta(-E_i(\mathbf{k}))]=N, \tag{16}$$

where $N$ is the concentration of the "excess" electrons. The coefficient 2 in (15) and (16) is due to summation over the spin.

From the condition $\partial/\partial u_i(E-\mu N)=0$ (it is convenient here to assume $\mu$ fixed and to obtain the derivative $\partial N/\partial u_i$ by differentiating (16)) we obtain equations for the equilibrium values of the order parameters $u_i$:

$$u_i\frac{\omega_0^2}{2}=-u_i\int\frac{d^3\mathbf{k}}{(2\pi)^3}\frac{g_i(\mathbf{k})}{E_i(\mathbf{k})-\eta_i(\mathbf{k})}\Theta(\mu-E_i(\mathbf{k})). \tag{17}$$

We note that the equations for the different $i$ are connected by the condition (16), so that the displacements $u_i$ in different directions are not independent. Each equation of (17) coincides with the typical self-consistency equation that appears, for example, in the problem of electron–hole pairing.[9-11] This equation has been studied in quite a number of papers.[24] We are interested in effects connected with "spillover" of the carriers from one band to the other, which makes the order parameters $u_i$ interdependent and, in final analysis, causes the symmetry of the restructured lattice. We therefore simplify to the utmost Eqs. (16) and (17), putting $g_i(\mathbf{k})=g=\text{const}$, $v_{ii}(\mathbf{Q},\mathbf{k})=v=\text{const}$, $\eta_i(\mathbf{k})=0$. The integration in (16) and (17) will be carried out in standard fashion, introducing the effective state density on the Fermi surface $N(0)$. As a result we obtain from (17)

$$\begin{gathered}\Delta_i^2=\Delta_0(2\mu-\Delta_0)-v^2 \text{ if } \mu>(v^2+\Delta_i^2)^{1/2},\\ \Delta_i^2=\Delta_0^2-v^2 \text{ if } \mu<(v^2+\Delta_i^2)^{1/2}, \text{ or } \Delta_i=0.\end{gathered} \tag{18}$$

The condition (16) takes the form

$$\sum_i(\mu^2-v^2-\Delta_i^2)^{1/2}\Theta[\mu-(v^2+\Delta_i^2)^{1/2}]=3(\mu_0^2-v^2)^{1/2}=3n. \tag{19}$$

We have introduced here the order parameter $\boldsymbol{\Delta}=g\mathbf{u}$ and $\mu_0=\mu(\boldsymbol{\Delta}=0)$,

$$n=N/6N(0);\ \Delta_0=2\alpha\exp(-\omega_0^2/2g^2N(0)).$$

From (15), using (18) and (19), we can obtain an expression for the change $\delta E$ of the system energy due to restructuring:

$$\frac{\delta E}{N(0)}=-\frac{1}{2}\sum_i\Delta_i^2+3n(\mu-\mu_0)$$
$$+v^2\left[(3-M)\ln\frac{\mu+(\mu^2-v^2)^{1/2}}{\mu_0+(\mu_0^2-v^2)^{1/2}}-M\ln\frac{\mu_0+(\mu_0^2-v^2)^{1/2}}{\Delta_0}\right].$$

Here $M$ is equal to the number of bands in which $\Delta_i\neq 0$.

Equations (18) and (19) admit of five types of solutions with different symmetries. We present expressions for the order parameter and the energy in the case $v=0$. Neglect of ionicity does not affect the qualitative results but simplifies very greatly the formulas. For the concentration of electrons and for the energy gain we introduce the dimensionless quantities:

$$x=n/\Delta_0,\quad W=2|\delta E|/3\Delta_0^2N(0).$$

Thus, the following solutions are possible:

$$\Delta_x^2=\Delta_y^2=\Delta_z^2=\Delta_0^2(1-2x);\quad W=(1-2x)^2.$$

This solution corresponds to a shift of the sublattices along the threefold axis [111] and to rhombohedral symmetry

$$\Delta_x=\Delta_y=\Delta_0,\quad \Delta_z^2=\Delta_0^2(1-6x);\quad W=(1-2x)^2+4x^2.$$

This solution corresponds, generally speaking, to triclinic symmetry. With increasing doping $x$, the polarization vector $\boldsymbol{\Delta}$ rotates in the plane (110) from the [111] axis to the twofold axis [110].

$$\Delta_x^2=\Delta_y^2=\Delta_0^2(1-3x),\quad \Delta_z=\Delta_0;\quad W=(1-2x)^2+x^2.$$

Here the symmetry is likewise triclinic, but with increasing $x$ the vector $\boldsymbol{\Delta}$ rotates in the (110) plane from [111] to the fourfold axis [001].

$$\Delta_z=0,\quad \Delta_x^2=\Delta_y^2=\begin{cases}\Delta_0^2, & W={}^2/_3(1-6x^2)\ \text{if}\quad x<{}^1/_3\\ 3\Delta_0^2(1-2x), & W=2(1-2x)^2\ \text{if}\quad x>{}^1/_3\end{cases}.$$

The sublattices shift here along [110] and the symmetry is rhombic

$$\Delta_z=\Delta_0,\quad \Delta_x=\Delta_y=0;\quad W={}^1/_3(1-3x^2).$$

The sublattices along [001] and the symmetry is tetragonal.

Figure 4 shows the dependence of the energy gains on the carrier density for all five solutions. At zero doping, the rhombohedral phase is energywise favored. This situation is realized in elements of the bismuth group, whose crystal structure is obtained from the cubic by shifting the fcc sublattices along a threefold axis.[20] When structural transitions take place in GeTe and SnTe, the sublattices of the different atoms shift in eactly the same way.[1] In all these substances, the shift of the sublattices is accompanied by acoustic deformation along the same [111] axis; these deformations can be attributed to anharmonicity of the type $\varepsilon u^2$, where $\varepsilon$ is the acoustic deformation. Indeed, measurements of the elastic constants near the phase-transition point in GeTe - SnTe alloys[25] point to an anomalously strong coupling of the acoustic phonons with the soft optical mode.

It is seen from Fig. 4 that at arbitrarily small doping the rhombohedral solution becomes triclinic. This does not occur in GeTe or SnTe, owing to the presence of a reservoir for the carriers in the vicinity of the $L$ points, where the gap between the electron and holes bands is anomalously small. Therefore, up to concentrations $N\approx 10^{19}-10^{20}$ cm$^{-3}$, when this reservoir turns out to be filled, on large sections of the Fermi surface there are no "excess" electrons, and the semiconductor must be regarded as "undoped." In our simplified model, the rhombohedral, triclinic (2), rhombic, and tetragonal solutions replace each other in sequence with increasing carrier density. Transitions (with increasing $x$) from the rhombohedral phase to the triclinic (2) and from the triclinic (2) to the rhombic are of second order. The transition from the rhombic to the tetragonal phase is of first order, since the derivative $\partial E/\partial n$ is discontinuous. The triclinic (3) solution goes over continuously into the tetragonal solution, but it can be only metastable.

All the obtained solutions correspond to instability of a phonon with $\mathbf{Q}=(\pi/a)$ (1, 1, 1) (point $R$, Fig. 1), and have different polarizations of the unstable oscillations. The lattice deformation can be represented as a doubling in the system of (111) planes, each of which contains only atoms of one sort. Therefore, owing to the ionicity, electric polarization is produced in the structural transition, i.e., the obtained phases are ferroelectric. One can expect repolarization and stabilization of the metastable phases in the electric field.

It appears that up to now only a rhombohedral ferroelectric phase has been observed in IV-VI compounds (see, however, Ref. 5). The rhombic phase, into which GeTe goes over when the carrier density is increased, is similar to the structure of the compounds Ge(S, Se) and Sn(S, Se), and is antiferroelectric.

## 4. RHOMBIC PHASE. NONCOMMENSURABILITY

The structure of the rhombic modification of the IV-VI compounds can be obtained from the cubic one with aid of the atom displacements shown in Fig. 5. The relative displacements of the sublattices made up of different atoms in the (001) planes are directed along the twofold axis [110] and have different signs for neighboring two pairs of planes. In addition, planes with identical directions of the displacements come closer together, and a layered structure is produced along the [001] axis. In accordance with the preceding section, we can call this structure antiferroelectric.[2)]

If the atoms of the initial lattice are assumed to be equivalent, the displacements on Fig. 5 denote a quadrupling of the period of the initial primitive cubic lattice along [001] and doublings along [100] and [010]. This corresponds to instability of the phonon with wave vector $\mathbf{Q}_z=(\pi/a)$ (1, 1, $\frac{1}{2}$) (point $Z$ on Fig. 1) and with

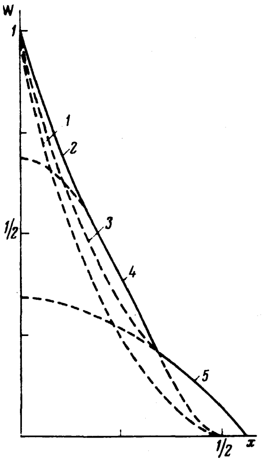

FIG. 4. Dependence of the energy gain on going into ferroelectric phases of various symmetry: 1—rhombohedral phase, 2, 3—triclinic, 4—rhombic, 5—tetragonal.

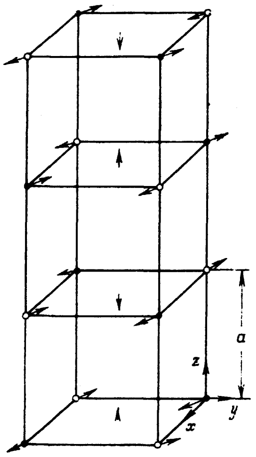

FIG. 5. Atom displacements that cause a cubic structure to become antiferroelectric with rhombic symmetry.

polarization along [110], and to a phonon $\mathbf{Q}_x=(\pi/a)(0, 0, 1)$ (point $X$) with polarization along [001].

In the model of three purely one-dimensional bands, the Fermi surface that consists of planes is made partially congruent with itself by a displacement by any of the vectors that join the point Γ with a point on the surface of the cubic Brillouin zone. One can therefore expect softening of all the phonons with such wave vectors, particularly at the points $X$ and $Z$ (see Fig. 1).

Let us examine a structural transition from the cubic phase into the rhombic phase with the aid of the Landau expansion for the free energy[28] near the critical temperature. We assume that the transition is connected with the instability of the phonon at the point $Z$ (we note that when an hcp lattice is reduced to the Brillouin zone, this point goes over into a point at the middle of the Δ axis). The star of the vector $\mathbf{Q}_z$ contains six vectors. The displacement vector in the (110) plane is transformed in accordance with the two-dimensional irreducible representation of the small group $C_{4v}$ of the vector $\mathbf{Q}_z$. Consequently, the phase transition should be characterized by 12 order parameters. Bearing in mind the crystal structure in Fig. 5, we restrict our analysis to two vectors $(\pi/a)(1, 1, \pm\frac{1}{2})$ of the star $\{\mathbf{Q}_z\}$. The direction [110] of the displacement is assumed given. Then the transition is characterized only by two order parameters, $u_s$ and $u_c$, which have the meaning of the amplitudes of sine and cosine electron-density waves:

$$\delta\rho_s\propto u_s\cos\pi x\cos\pi y\,\sin(\pi z/2),\quad \delta\rho_c\propto u_c\cos\pi x\,\cos\pi y\,\cos(\pi z/2). \tag{20}$$

Here $x$, $y$, and $z$ are the coordinates along the cubic axes, measured in units of the period of the cubic lattice. Doubling in the system of planes (001) corresponds to the wave

$$\delta\rho_x\sim u_x\cos\pi z. \tag{21}$$

By making up invariants out of functions that transform in accordance with (20) and (21), we obtain for the free energy the expansion

$$F=\alpha(u_s^2+u_c^2)+{}^1/_2\beta_1(u_s^4+u_c^4)+\beta_2u_s^2u_c^2+\gamma u_su_cu_x+au_x^2. \tag{22}$$

Minimization of this expression yields: 1) at $\beta_2-\beta_1-\gamma^2/4a>0$

$$u_s^2=-\alpha/\beta_1,\quad u_c=u_x=0.$$

This solution is obviously of no interest to us; 2) at $\beta_2-\beta_1-\gamma^2/4a<0$

$$u_s^2=u_c^2=-\alpha/(\beta_1+\beta_2-\gamma^2/4a),\quad u_x=-\gamma u_su_c/2a. \tag{23}$$

Owing to the presence in (22) of a third-order invariant, the appearance of $u_{s,c}\neq 0$ induces a displacement $u_x$, so that the antiferroelectric phase becomes automatically layered. An analogous situation is realized in impurity ferroelectrics, where the spontaneous polarization is induced by the true order parameter.[29] We note that the sign of $\gamma$ determines the phase of the wave (21): the layers that come close together have the same displacement directions along [110] at $\gamma<0$ (as in Fig. 5), and opposite directions at $\gamma>0$.

The small group $C_{4v}$ of the vector $\mathbf{Q}_z$ does not have a central point. Therefore the homogeneous solution (23) is generally speaking unstable, and the order parameters become functions of the coordinate $z$.[28] The expression for the free energy (22) must be supplemented by invariants that contain arbitrary $u'_{s,c}=du_{s,c}/dz$. Instead of (22) we have the functional

$$\begin{gathered}F=\alpha\langle u_s^2+u_c^2\rangle+{}^1/_2\beta_1\langle u_s^4+u_c^4\rangle+\beta_2\langle u_s^2u_c^2\rangle\\ +s^2\langle u_s'^2+u_c'^2\rangle+\sigma\langle u_su_c'-u_cu_s'\rangle;\quad \langle u^2\rangle=\frac{1}{L}\int_0^L u^2(z)\,dz.\end{gathered} \tag{24}$$

Here $L$ is the crystal dimension. In (24) we have omitted the connection with the $X$ phonon, which is inessential for subsequent analysis of the transition into the inhomogeneous phase.[3)] Equating the variational derivatives $\delta F/\delta u_{s,c}$ to zero, we obtain the system of equations

$$\begin{gathered}\alpha u_s+\sigma u_c'-s^2u_s''+\beta_1u_s^3+\beta_2u_su_c^2=0,\\ \alpha u_c-\sigma u_s'-s^2u_c''+\beta_1u_c^3+\beta_2u_cu_s^2=0.\end{gathered} \tag{25}$$

For the complex-conjugate order parameters $u_\pm=u_c\pm iu_s$, Eqs. (25) take the form

$$\begin{gathered}\alpha u_++i\sigma u_+'-s^2u_+''+B_1u_-u_+^2+B_2u_-^3=0,\\ \alpha u_--i\sigma u_-'-s^2u_-''+B_1u_+u_-^2+B_2u_+^3=0,\end{gathered}$$

where $B_1=(3\beta_1+\beta_2)/4$, $B_2=(\beta_1-\beta_2)/4$. These equations reduce to an integral equation

$$\begin{gathered}u_+(z)=-\int_{-\infty}^{\infty}dz'G_+(z-z')[B_1u_-(z')u_+^2(z')+B_2u_-^3(z')],\\ u_-(z)=u_+^*(z).\end{gathered} \tag{26}$$

The Green's function is given by

$$G_+(z)=\int_{-\infty}^{\infty}\frac{dq}{2\pi}\frac{e^{iqz}}{\alpha(q)+i\delta}, \tag{27}$$

where $\delta\to+0$ and

$$\alpha(q)=\alpha-\sigma q+s^2q^2. \tag{28}$$

The direction of circling around the poles in (27) is determined by the requirement that the exact solution of (26) at $B_2=0$ be of the form

$$u_\pm=u_qe^{\pm iqz}, \tag{29}$$

where

$$u_q^2=-\alpha(q)/B_1. \tag{30}$$

The function $G_+(z)$ satisfies the condition

$$\int_{-\infty}^{\infty}dz'G_+(z-z')e^{ikz'}=e^{ikz}/\alpha(k). \tag{31}$$

Equation (26) can be solved by successive approximations, using relation (31). The first iteration is the solution of (29), (30). As a result of successive iterations, the solution of (26) will assume the form of a series in odd powers of $u_q$, containing odd harmonics. For example, accurate to third order we have

$$u_+(z)=\left(u_q+\frac{3B_2^2}{2B_1\alpha(-3q)}u_q^3\right)e^{iqz}-\frac{B_2}{\alpha(-3q)}u_q^3e^{-3iqz}.$$

Near the transition temperature $T_c$, which is defined by the equality $\alpha(q)=0$, a value $q_m=\sigma/2s^2$ is realized at which $\alpha(q)$ has a minimum. The inequalities

$$|\alpha(q_m)|<\alpha(-3q_m)<\alpha(5q_m)<\alpha(-7q_m)<\ldots \tag{32}$$

are then satisfied, and the series in powers of $u_2$ converges rapidly, so that the first harmonic (29) suffices. If the coefficient $\alpha$ has the usual temperature dependence $\alpha=\alpha_0(T-T_0)$, then equating $\alpha(q)$ (28) to zero, we get

$$T_c=T_0+\sigma^2/4s^2\alpha_0.$$

At a temperature below $T_c$, atom displacements are produced in the crystal and are characterized by the values

$$u_s(z)=u_{q_m}\sin q_m z,\qquad u_c(z)=u_{q_m}\cos q_m z. \tag{33}$$

Since the period $2\pi/q_m$ of the superstructure is generally speaking not a multiple of the period $a$ of the cubic lattice, the system becomes inhomogeneous. It is of interest to note that x-ray diffraction studies of the rhombic modification of GeTe (Refs. 1, 3) indicate that the atoms are shifted somewhat from the ideal positions of the rhombic lattice. This can be attributed to the presence, in the GeTe rhombic phase, of a superstructure that is not commensurate with the fundamental period.

Substituting (33) in (24), we obtain the change of the free energy on going to an inhomogeneous antiferroelectric phase

$$\delta F_{\text{inh}}=-2\alpha^2(q_m)/(3\beta_1+\beta_2). \tag{34}$$

Equations (25) admit also of a homogeneous solution:

$$u_s^2=u_c^2=-\alpha/(\beta_1+\beta_2), \tag{35}$$

and the corresponding gain in the free energy is

$$\delta F_{\text{hom}}=-\alpha^2/(\beta_1+\beta_2). \tag{36}$$

Since $T_c>T_0$, the transition into the inhomogeneous phase occurs before a transition into a homogeneous antiferroelectric becomes possible. However, with further decrease of the temperature, the homogeneous phase may turn out to be more convenient than the inhomogeneous one. Using (28), (34), and (36), we obtain

$$\left|\frac{\delta F_{\text{inh}}}{\delta F_{\text{hom}}}\right|=\frac{2(\beta_1+\beta_2)}{3\beta_1+\beta_2}\left(\frac{T_c-T}{T_0-T}\right)^2. \tag{37}$$

Therefore at $\beta_1>\beta_2$, when the coefficient of the temperature factor in (37) is less than unity, at the temperature

$$T_1=T_0\frac{B-T_c/T_0}{B-1} \tag{38}$$

(here $B^2=(3\beta_1+\beta_2)/2(\beta_1+\beta_2)$, the free energies of the homogeneous and inhomogeneous phases become comparable and the system should go over, via a first-order transition, into a commensurate phase. Of course, all these arguments are valid only if the temperatures $T_0$, $T_c$, and $T_1$ are close enough to one another, so that the Landau expansion is valid in the entire considered temperature region, and the condition (32) is not violated.

We have assumed that the transition to the rhombic phase is of second order. It is possible, however, to advance arguments in favor of the assumption that the coefficient $\beta_1$ of the fourth-order invariant in (22) is negative, and consequently a first-order transition into a commensurate phase is possible. The expansion (24) of the free energy is no longer valid in this case.

We turn now to model with a Fermi-surface consisting of planes. Displacement by a vector **Q** makes congruent two pairs of planes perpendicular to the axes $x$ and $y$. This leads to a logarithmic singularity of the coefficient $\alpha$ at $T=0$ and to a reversal of its sign at $T=T_0$. The third pair of planes perpendicular to the $z$ axis is made congruent by a displacement by a vector $2\mathbf{Q}_z$. Therefore, if account is taken, in the electron–phonon interaction (12), of the next term of the expansion, which is proportional to the square of the displacement, the coefficient $\beta_1$ for this interaction will behave in analogy with the coefficient $\alpha$ for a first-order interaction. (We note that in the model of plane sections there is no interaction linear in the displacement at all for the $\varepsilon_z$ band.) Consequently, at $T=0$ the coefficient $\beta_1<0$ and has a logarithmic singularity. It is possible that $\beta_1<0$ also at $T=T_0$. In this case the system, bypassing the noncommensurate phase, becomes jumpwise restructured into a commensurate phase.

The negative $\beta_1$ can, however, be compensated for by "excess" carriers. Indeed, in the presence of doping, the appearance of order parameters $u_{s,c}\neq 0$ is accompanied by a shift of the chemical potential $\mu$, which is determined by the mean values $\langle u_{s,c}^2\rangle$. The coefficients of the expansion (24) are functions of $\mu$, and can therefore be expanded in powers of $\langle u_{s,c}^2\rangle$. As a result, the following invariants are added to the functional (24):

$$\tfrac{1}{2}\gamma_1[\langle u_s^2\rangle^2+\langle u_c^2\rangle^2]+\gamma_2\langle u_s^2\rangle\langle u_c^2\rangle. \tag{39}$$

Minimizing $F$ and taking (39) into account, we obtain in place of (30)

$$u_q^2=-\alpha(q)/[B_1+(\gamma_1+\gamma_2)/2].$$

Thus, in the case of sufficiently strong doping, we can have $B_1+(\gamma_1+\gamma_2)/2>0$ and the structural transition is of second order.

The foregoing arguments make it possible to interpret qualitatively the results of an investigation of the phase transition in the ternary compound[30] $\mathrm{Pb}_{1-x}\mathrm{Sn}_x\mathrm{Se}$. In this compound, at sufficiently large $x\approx 0.5$, one should expect a structural transition from the cubic phase, which is typical of PbSe, into the rhombic phase into which SnSe crystallizes. From the dependence of the resistivity on the temperature we can conclude that a first-order transition takes place in samples with sufficiently low carrier density. With increasing carrier density, a second-order transition is observed, probably into a noncommensurate phase. With further cooling, a jump of the resistance takes place—the system becomes realigned, via a first-order transition, into a commensurate phase. In samples with still larger carrier density, only a continuous change of the resistance is observed, inasmuch as the transition to the homogeneous phase is already completely suppressed.

## 5. CONCLUSION

Among the elements of the fifth group, a rhombic structure, analogous to that considered above, is realized for black phosphorus and for the rhombic modification of arsenic. In this case, just as for the rhombic modifications of IV–VI compounds, the displacements of the atoms from their positions in the cubic lattice are quite large. Therefore a theory based on expanding the free energy in powers of the displacements can claim only qualitative results.

In IV–VI semiconductors, the essential factor that suppresses the phase transition is the ionicity. An analogous role is played by spin–orbit interaction, since it splits the triply degenerate atomic $p$ term and consequently, upsets the congruence of the Fermi surfaces. This is particularly large in lead chalcogenides, and must be taken as the reason why no structural transitions are observed in them. An investigation of the phonon spectrum, however, shows that there is a strong softening of the optical phonon at the point $\Gamma$.[13] In elements of the fifth group, owing to the lack of ionicity, the instability of the cubic lattice manifests itself much more strongly and they crystallize immediately into distorted cubic structures.

Besides the congruent sections of the Fermi surface, an additional (although not a principal) contribution to the lattice instability is made also by electronic states near the $L$ points of the Brillouin zone. The maximum contribution of this state should be expected at the minimal value of the energy gap at the $L$ point. It is known[1] that in the triple compound $Pb_{1-x}Sn_xSe$ the width of the forbidden band decreases to zero with increasing $x$, and then begins to increase. Measurement of the frequency of the soft optical phonon[31] shows in fact that a noticeable additional softening occurs in the region of compositions with minimum forbidden band against the background of a monotonic decrease of the frequency with increasing $x$.

The microscopic model of the transition into the ferroelectric phase was investigated by us at zero temperature of the transition is determined by anharmonicities, which, incidentally, are also of electronic origin,[32] and cannot be obtained in the Hartree–Fock approximation.

## APPENDIX

We consider a structural transition under the assumption that it is connected with electron instability at the $L$ points of the Brillouin zone. The order parameter $\mathbf{u}$ is the vector of the relative displacement of two fcc sublattices, each of which contains only atoms of one sort. The Landau expansion in this case, with allowance for the cubic symmetry, is well known[29]

$$F=-\alpha\sum_i u_i^2+\frac{1}{2}\beta_1\sum_i u_i^4+\frac{1}{2}\beta_2\sum_{i\neq j}u_i^2u_j^2 \qquad (A.1)$$

where $i, j=x, y, z$. Minimization of this expression leads to the equations

$$\alpha u_i=[\beta_1u_i^2+\beta_2(u_j^2+u_k^2)]u_i, \quad i\neq j\neq k, \qquad (A.2)$$

which admit of the following nontrivial solutions:

1) $u_x^2=u_y^2=\alpha/(\beta_1+\beta_2)$, $u_z=0$ is the sublattice shift along the [110] axis, rhombic symmetry. This solution corresponds to an energy gain. $F_1=-\alpha^2/(\beta_1+\beta_2)$.

2) $u_x=u_y=0$, $u_z^2=\alpha/\beta_1$, $F_2=-\alpha^2/2\beta_1$ is the shift along the [001] axis, tetragonal symmetry.

3) $u_x^2=u_y^2=u_z^2=\alpha/(\beta_1+2\beta_2)$, $F_3=-3\alpha^2/2(\beta_1+2\beta_2)$ is the shift along the [111] axis, rhombohedral symmetry.

From a comparison of $F_1$, $F_2$, and $F_3$ it follows that the tetragonal solution (2) is realized at $\beta_1<\beta_2$, and the rhombohedral solution (3) is realized at $\beta_1>\beta_2$. Thus, the symmetry of the low-temperature phase is determined by the ratio of the coefficients $\beta_1$ and $\beta_2$ in the expansion (A.1). To find this ratio, we turn to the microscopic model.

The symmetry group $D_{3d}$ of the $L$ point has four one-dimensional ($L_1$, $L_1'$, $L_2$, $L_2'$) and two two-dimensional ($L_3$, $L_3'$) representations.[33] Assume that in each of the four nonequivalent $L$ points there are two levels, upper ($a$) and lower ($b$), belonging to the representations $a$ and $b$. The interaction of the electrons with the sublattice displacement is of the form

$$\hat{H}_{int}=\sum_{j=1}^{4}\sum_{\mathbf{k}}\sum_{\mu,\nu}(\mathbf{u}\mathbf{g}_{\mu\nu}^{j})a_{j\mathbf{k}}^{(\mu)+}b_{j\mathbf{k}}^{(\nu)}+\text{h. c.}, \qquad (A.3)$$

where $\mathbf{g}_{\mu\nu}^{j}$ is the matrix element of the gradient of the crystal potential $V(\mathbf{r})$

$$\mathbf{g}_{\mu\nu}^{j}=\int\psi_\mu^{*(a)}(\mathbf{r})\nabla V(\mathbf{r})\psi_\nu^{(b)}(\mathbf{r})d^3\mathbf{r}; \qquad (A.4)$$

the subscripts $\mu$ and $\nu$ number the basis functions of the representations $a$ and $b$, and the superscript $j$ labels the nonequivalent $L$ points. The operator $a^{(\mu)+}$ produces an electron in a state $\psi_\mu^{(a)}e^{-i\mathbf{k}\mathbf{r}}$, where the quasimomentum $\mathbf{k}$ is reckoned from the $j$-th $L$ point. Actually we are using the Luttinger–Kohn representation with allowance of only the two nearest energy levels, as was done in Ref. 11.

There are three possible variants: 1) both levels $a$ and $b$ are nondegenerate, i.e., they belong to one-dimensional representations; 2) one of the levels is doubly degenerate; 3) both levels are doubly degenerate. We consider these possibilities in succession. We introduce first four unit vectors $\mathbf{n}_j$ directed along the axes $\Lambda_j$:

$$\mathbf{n}_1=\frac{1}{\sqrt{3}}(1,1,1),\quad \mathbf{n}_2=\frac{1}{\sqrt{3}}(1,-1,1),$$
$$\mathbf{n}_3=\frac{1}{\sqrt{3}}(-1,-1,1),\quad \mathbf{n}_4=\frac{1}{\sqrt{3}}(-1,1,1). \qquad (A.5)$$

1) In the case of one-dimensional representations $a$ and $b$ it follows from symmetry considerations that the matrix element (A.4) is of the form $g\mathbf{n}_j$, where $g$ is a constant. Putting $g\mathbf{u}=\mathbf{\Delta}$, we express the interaction (A.3) in the form

$$\hat{H}_{int}=\sum_{j=1}^{4}(\mathbf{\Delta}\mathbf{n}_j)\sum_{\mathbf{k}}a_{j\mathbf{k}}^{+}b_{j\mathbf{k}}+\text{h.c.} \qquad (A.6)$$

We assume for simplicity that the electron spectrum at the $L$ point is symmetrical: $\varepsilon_a(\mathbf{k}) = -\varepsilon_b(\mathbf{k}) = \varepsilon(\mathbf{k})$. When account is taken of the interaction (A.6), the energy spectrum is determined by the equation

$$\begin{vmatrix} \varepsilon(\mathbf{k})-E & (\Delta\mathbf{n}_j) \\ (\Delta\mathbf{n}_j) & -\varepsilon(\mathbf{k})-E \end{vmatrix} = 0,$$

from which we get

$$E(\mathbf{k}) = \pm[\varepsilon^2(\mathbf{k}) + (\Delta\mathbf{n}_j)^2]^{1/2}.$$

The energy of the ground state consists of the energy of the elastic deformation and the energy of the electrons in the valence band (we assume that there is no doping):

$$F(\Delta) = \frac{\omega_0^2}{2g^2}\Delta^2 - 2\sum_{j=1}^{4}\int\frac{d^3\mathbf{k}}{(2\pi)^3}\{[\varepsilon^2(\mathbf{k}) + (\Delta\mathbf{n}_j)^2]^{1/2} - \varepsilon(\mathbf{k})\}.$$

From the condition $\partial F/\partial\Delta_x = 0$ we obtain

$$\frac{\omega_0^2}{2N(0)g^2}\Delta_x = \sum_{j=1}^{4}(\Delta\mathbf{n}_j)n_{jx}\int\frac{d^3\mathbf{k}}{(2\pi)^3N(0)}[\varepsilon^2(\mathbf{k}) + (\Delta\mathbf{n}_j)^2]^{-1/2}. \qquad (A.7)$$

Taking into account the smallness of $\Delta$, the integral in the right-hand side can be represented in the form of the expansion $a + b(\Delta\mathbf{n}_j)^2$. We then obtain from (A.7)

$$\frac{\omega_0^2}{2N(0)g^2}\Delta_x = \sum_{j=1}^{4}[an_{jx}(\Delta\mathbf{n}_j) + bn_{jx}(\Delta\mathbf{n}_j)^3]. \qquad (A.8)$$

With the aid of (A.5) we can verify the validity of the following expressions:

$$\sum_{j=1}^{4}n_{jx}(\Delta\mathbf{n}_j) = \frac{4}{3}\Delta_x, \quad \sum_{j=1}^{4}n_{jx}(\Delta\mathbf{n}_j)^3 = \frac{4}{9}\Delta_x(\Delta_x^2 + 3\Delta_y^2 + 3\Delta_z^2),$$
$$\sum_{j=1}^{4}(\Delta\mathbf{n}_j)^2 = \frac{4}{3}(\Delta_x^2 + \Delta_y^2 + \Delta_z^2). \qquad (A.9)$$

Using these equalities, we can transform (A.8):

$$\frac{\omega_0^2}{2N(0)g^2}\Delta_x = \frac{4}{3}a\Delta_x + \frac{4}{9}b\Delta_x[\Delta_x^2 + 3(\Delta_y^2 + \Delta_z^2)]. \qquad (A.10)$$

It suffices now to compare (A.10) with (A.2), and we obtain $\beta_1/\beta_2 = \frac{1}{3}$, from which it follows that in this case a tetragonal solution is realized.

2) Let one of the representations, $a$ or $b$, be two-dimensional. Using the symmetry, we can show that the interaction (A.3) takes in this case the form

$$\hat{H}_{int} = \sum_{j=1}^{4}\sum_{\mathbf{k}}[(\Delta_{x_j} + i\Delta_{y_j})\overset{+}{a}_{j\mathbf{k}}b_{j\mathbf{k}}^{(1)} + (\Delta_{x_j} - i\Delta_{y_j})\overset{+}{a}_{j\mathbf{k}}b_{j\mathbf{k}}^{(2)}] + \text{h.c.} \qquad (A.11)$$

Here $\Delta_{x_j}$ and $\Delta_{y_j}$ are the projections of the vector $\Delta$ on the axes $x_j$ and $y_j$ of a coordinate system whose $z_j$ axis is directed along the vector $\mathbf{n}_j$. The spectrum is determined by the equation

$$\begin{vmatrix} \varepsilon - E & \Delta_x + i\Delta_y & \Delta_x - i\Delta_y \\ \Delta_x - i\Delta_y & -\varepsilon - E & 0 \\ \Delta_x + i\Delta_y & 0 & -\varepsilon - E \end{vmatrix} = 0,$$

from which we get

$$E_1 = \varepsilon, \quad E_{2,3} = \pm[\varepsilon^2 + 2(\Delta^2 - (\Delta\mathbf{n}_j))^2]^{1/2}.$$

Further calculations are analogous to those performed earlier for the case of nondegenerate bands. As a result we obtain $\beta_1/\beta_2 = \frac{2}{3}$, so that in this case a tetragonal solution is realized.

3) In the case when both levels $a$ and $b$ are doubly degenerate, the interaction of the electrons with the sublattice displacement takes the form

$$H_{int} = \sum_{j=1}^{4}\sum_{\mathbf{k}}[\Delta_z a_{j\mathbf{k}}^{(1)+}b_{j\mathbf{k}}^{(1)} + \Delta_z^* a_{j\mathbf{k}}^{(2)+}b_{j\mathbf{k}}^{(2)} + \Delta_- a_{j\mathbf{k}}^{(1)+}b_{j\mathbf{k}}^{(2)} + \Delta_-^* a_{j\mathbf{k}}^{(2)+}b_{j\mathbf{k}}^{(1)} + \text{h.c.}],$$

where

$$\Delta_z = ig_z u_z, \quad \Delta_- = g_-(u_x + iu_y),$$

where $u_{z_j}$, $u_{x_j}$, and $u_{y_j}$ are the projections of the vector $\mathbf{u}$ on the axes of the coordinate system for the $j$-th $L$ point with $z_j$ axis along the vector $\mathbf{n}_j$.

Solving the corresponding secular equation, we obtain the electron spectrum:

$$E = \pm[\varepsilon^2 + (|\Delta_z| \pm |\Delta_\perp|)^2]^{1/2}.$$

Using this spectrum to calculate the energy of the ground state with the aid of the procedure described above, we get

$$\frac{\beta_1}{\beta_2} = \frac{g_z^4 + 12g_z^2g_\perp^2 + 4g_\perp^4}{3(g_z^4 + 2g_\perp^4)}.$$

In the interval $(3-\sqrt{8})^{1/2} < g_\perp/g_z < (3+\sqrt{8})^{1/2}$ the ratio of the coefficient is $\beta_1/\beta_2 > 1$. If the ratio of the coupling constants $g_\perp/g_z$ does not fall in this interval, then $\beta_1/\beta_2 < 1$.

Consequently, in this case the rhombohedral solution turns out to be possible, but only in a definite range of the values of the ratio $g_\perp/g_z$.

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1) In Ref. 16 it was assumed, in accordance with the band calculation[12,13], that the "interacting" zones belong to one-dimensional representations $L_1$ and $L_2$ of the group $D_{3d}$ of the point $L$. Consequently, the electrons at a point $L_i$ interacts only with the relative displacements of the atom sublattices A and B (Fig. 2) along the $\Lambda_i$ axis (Fig. 1). The spin—orbit interaction mixes the states $L_1$ and $L_2$ with two-dimensional representations $L_3$ and $L_{3'}$.[12] As a result, the matrix elements for the displacements perpendicular to $\Lambda_i$ differ from zero. However, as shown in the Appendix, even if the bands were to belong entirely to the representations $L_3$ and $L_{3'}$, a rhombohedral structure can appear only if the inequality $3-\sqrt{8} < (g_\perp/g_z)^2 < 3+\sqrt{8}$ is satisfied, where $g_\perp$, $z$ are the coupling constants.

2) In real structures, neighboring pairs of planes with identical displacements along [110] are shifted relative to each other along the same direction by half the diagonal of the (110) face of the cubic lattice. This shift can be attributed to the fact that the charge-density waves in the neighboring pairs of planes tend to become aligned in counterphase.[26] The structure described above is physically the structure of black phosphorus and of the corresponding modification of arsenic.[27] In the lattice of rhombic modifications of the compounds IV—VI there are additional small distortions,[1,27] which are due to the difference between the masses of the atoms and to the electrostatic interaction.

3) Rearrangement into a rhombic structure can in principle be due to instability of the $X$ phonon if the coefficient $a$ has a critical temperature dependence. In this case the question of the transition to an inhomogeneous phase does not arise, since the small group of the vector $\mathbf{X}$ contains a central point.

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# Electric-field effect in electron–nuclear double resonance of $Cr^{3+}$ ions in ruby

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External static electric fields up to 800 kV/cm were applied in a study of the linear effect of these fields on the spectra of electron–nuclear double resonance of $(^{53}\mathrm{Cr})^{3+}$ impurity ion nuclei and "distant" $^{27}$Al nuclei in ruby. The measured splitting of the spectral lines was used to find the electric-field-induced changes in the hyperfine interaction parameter of the impurity ions and in the electric field gradients at the $^{53}$Cr and $^{27}$Al nuclei. The results indicated that the mechanisms responsible for the changes in the electric-field gradients were the same for both nuclei. Estimates were obtained of the orbital contribution and the contribution of the polarization of the ion cores to the change in the hyperfine interaction parameter. The change in the electron $g$ factor of the impurity ions was estimated.

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## INTRODUCTION

The capabilities of the electron-nuclear double resonance (ENDOR) method in investigations of paramagnetic centers in crystals can be greatly extended by the use of external agencies and, in particular, by the application of static electric fields.[1,2] High fields of $10^5$–$10^6$ V/cm intensity are needed to observe and measure the elec-