Electronic structure of group-V semimetals

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A theory of the electron spectrum of semimetals is developed on the basis of Peierls's idea that a metal with simple cubic lattice is unstable to doubling of the period. The translational symmetry is taken into account by using the approximation of tight binding to two nearest coordinate spheres. Expressions are obtained for the effective masses and for the spin splitting at the points T and L, as well as for the levels in Γ. The connection between rhombohedral deformation and the atom displacement due to doubling of the period is established, and the softening of the optical mode is investigated.

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1. INTRODUCTION

Semimetals of group V have been the subject of many studies. It is precisely for these substances that Peierls[1] first advanced the idea that metals with an odd number of electrons per unit cell can be unstable to a relatively small displacement of the atom, resulting in doubling of the lattice period. Abrikosov and one of us[2] considered the electron spectrum in the vicinity of those Brillouin points where the Peierls doubling lifts the electron-level degeneracy. It was found that the total energy acquires a term that is logarithmic in the small displacement, and it is this term which describes the instability of the metal to a transition into a dielectric (or semimetallic) state.

At the same time, many questions remained unanswered. Thus, the filling of the electronic states, considered in Ref. 2, corresponds to a metal with an even number of electrons per atom. To resolve the contradiction, Gordyunin and Gor'kov[3] analyzed the role of the electron and of the electron–phonon interactions and modified the Landau-Luttinger theorem. Next, besides the atom displacement that causes the doubling of the period, a small lattice deformation sets in and changes the angle between the elementary translation vectors. In experiment, the displacement and the deformation are of the same order, but the theory of Ref. 2 did not yield the connection between them. Finally, for the hole extremum (point T) in bismuth the spin splitting of the levels in a magnetic field is double the cyclotron splitting (the distance between the Landau levels), but in the theory of Ref. 2 these splittings are approximately equal (see the review articles[4]).

To answer these questions we must know the electron spectrum both in the vicinity of the conduction- and valence-band extrema, and in the entire Brillouin zone. The first to calculate the spectrum in symmetric directions was Mase,[5] who used the tight-binding method with only the nearest coordination sphere taken into account. However, the idea of the doubling of the period was not used, and no quantitative agreement with experiment was obtained.

The pseudopotential method was used to calculate the band structures of arsenic,[6] antimony,[7] and bismuth.[8] Pseudopotential calculations, however, do not lead to analytic results. Besides, the quantitative agreement of these calculations with experiment cannot be regarded as satisfactory. Thus, e.g., for bismuth the calculated effective masses differ by approximately a factor of 3 from the experimental ones. To reconcile them it is necessary to shift the calculated band positions for the point T by 0.3–1.2 eV.[9]

The situation is even more intricate for the L point, at which the electronic extremum is located. The forbidden gap between the conduction and valence bands in bismuth is here anomalously small (on the order of 0.01 eV). The velocity interband matrix element vanishes for some direction lying in the symmetry plane of the L point. This explains the great elongation of the equal-energy surface in the corresponding direction for which McClure and Choi[10] wrote out the higher-order terms within the framework of the two-band scheme previously proposed by Cohen.[11] A large number (17) of independent parameters were obtained, which could not be determined unambiguously in experiment.

Recently Pankratov and one of us[12] considered the band structure of IV–VI compounds, which have, like the group-V semimetals, ten valence electrons per unit cell. The body lattice of these compounds—which are of the rock-salt type—consists of two cubic face-centered sublattices, with the IV atoms at the sites of one of them and the VI atoms at the sites of the other. The parameter that distinguishes these sublattices, the ionicity, plays a role similar to the small displacement of the atoms in the lattice of the group-V semimetal. In both cases the "parent phase" is a simple cubic lattice, which is unstable to doubling of the period.

The use of the tight-binding approximation in Ref. 12 made it possible to obtain the energy spectrum in an analytic form suitable for the entire Brillouin zone. The basis of the wave functions consisted of three atomic p-orbitals. The requirement of the Landau-Luttinger theorem, that the number of states be conserved, is automatically satisfied in this case. The overlap integrals were regarded in Ref. 12 as free parameters determined by comparison with the experimental data. It turned out that to describe the available data on the electron spectra of all the cubic IV-VI semiconductors it suffices to use the two nearest coordination spheres.

It appears that the approximation used in Ref. 12 is effective for two reasons. The first is that allowance for only two nearest coordination spheres is sufficient to satisfy all the symmetry requirements. The second is the existence of a small parameter, the ratio of the crystal binding energy to the typical atomic energy. The order of magnitude of this

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parameter is given by the ratio of the boiling point (of the order of 10^3 K) to the ionization energy (5×10^4 K).

To determine the electronic structure of group-V semimetals we use in the present paper the idea of electronic instability of a simple cubic lattice and employ the tight-binding approximation on atomic p-orbitals. We present first the explicit form of the parent-phase spectrum. Next we consider its change as a result of the doubling of the period, and analyze the vicinities of points T, L, and Γ of the Brillouin zone. We then obtain the connection between the rhombohedral deformation and the shift of face-centered sublattices, and finally discuss the phonon-spectrum change, due to the doubling of the period, at the center of the new Brillouin zone.

2. ELECTRON SPECTRUM OF A METAL WITH A SIMPLE CUBIC LATTICE

The electron spectrum of the parent phase of group-V semimetals is made up, in analogy with Ref. 12, of three atomic p-states with wave functions $p_x\rangle$, $p_y\rangle$, $p_z\rangle$. The remaining two valence electrons are in deep s states and interact weakly with the p states. The Hamiltonian is a 3×3 matrix:

$$\hat{H}^0=\hat{\xi}+\hat{\eta}, \tag{1}$$

where $\hat{\xi}$ contains the overlap integrals for the first coordination sphere, and has only diagonal matrix elements of the type

$$\hat{\xi}_{xx}=\hat{\xi}_0\cos k_xa+\xi_1(\cos k_ya+\cos k_za), \tag{2}$$

and $\hat{\eta}$ are the overlap integrals for the second sphere

$$\eta_{xy}=\eta_0\sin k_xa\sin k_ya, \tag{3}$$

$$\eta_{xx}=\eta_1\cos k_ya\cos k_za+\eta_2\cos k_xa(\cos k_ya+\cos k_za). \tag{4}$$

We have introduced here the following overlap integrals

$$\begin{aligned}
&\xi_0=2\langle p_x(0,0,0)|H_0|p_x(a,0,0)\rangle,\\
&\xi_1=2\langle p_x(0,0,0)|H_0|p_x(0,a,0)\rangle,\\
&\eta_0=-4\langle p_x(0,0,0)|H_0|p_y(a,a,0)\rangle,\\
&\eta_1=4\langle p_x(0,0,0)|H_0|p_x(0,a,a)\rangle,\\
&\eta_2=4\langle p_x(0,0,0)|H_0|p_x(a,a,0)\rangle.
\end{aligned} \tag{5}$$

We use the coordinate axes of the simple cubic lattice, with a its period. The arguments of the wave function in (5) give the position of the atom chosen as the origin. The remaining elements of the matrix $\hat{H}_0$ are obtained from (2)–(4) by cyclic permutation of the indices.

Calculation[12] has shown that in the IV-VI case the overlap integrals for the nearest coordination sphere are of the order of $\xi_0\sim3$–4 eV and $\xi_1\sim-1$ eV, while for the second sphere $|\tilde{\eta}|\sim0.2$ eV. This estimate does not depend on the actual chemical composition of the IV-VI compound.

The Hamiltonian H_0 in the spin coordinate is proportional to a unit matrix which we shall not write out hereafter. For the heavy elements of group V, however, account must be taken of the spin-orbit interaction

$$\hat{\Delta}=-\frac{i}{3}\Delta\begin{pmatrix}0&\sigma_z&-\sigma_y\\-\sigma_z&0&\sigma_x\\\sigma_y&-\sigma_x&0\end{pmatrix}, \tag{6}$$

where σ_a is a Pauli matrix. The quantity Δ is an intracenter matrix element. The corrections connected with all the overlap integrals can be left out here, since Δ is determined by small distances of the order of $1/Z$ (Ref. 13), where Z is the atomic number. For the same reason, the value of Δ corresponds to the spin-orbit splitting in an isolated atom (it is listed in the table, where the following notation is used: a_t (in Å is the lattice period, $a=2^{-1/2}(1-\varepsilon_{xy})a_t$ is the period of the cubic parent phase, α is the angle between the lattice vectors, $\varepsilon_{xy}=(\cos\alpha-1/2)/2$ is the strain-tensor component, x_t is the rhombohedral coordinate of the atom in the cell, $u=1/2-2x_t$ is the coordinate of the displacement vector of the fcc sublattice, and Δ is the spin-orbit splitting of the atomic p-levels).

The electron spectrum of the parent phase is given by the solution of the equation

$$\det(\hat{H}^0+\hat{\Delta}-\omega)=0.$$

3. CHANGE OF SPECTRUM ON DOUBLING OF THE PERIOD

For each semimetal atom there are three p-electrons, and the corresponding three bands of the simple cubic lattice are half-filled. If the small terms with η and Δ are left out of the Hamiltonian, the Fermi surface will consist of congruent sections that become superimposed on one another upon translation of any of the vectors

$$\mathbf{Q}_i=\frac{\pi}{a}(-1,1,1),\quad\frac{\pi}{a}(1,-1,1),\quad\frac{\pi}{a}(1,1,-1). \tag{7}$$

Therefore the simple cubic lattice is absolutely unstable (at zero temperature) to a relative shift of two face-centered sublattices in the [1, 1, 1] direction.

The elementary vectors of any face-centered sublattice are of the form

$$\mathbf{a}_i=a(0,1,1),\quad a(1,0,1),\quad a(1,1,0), \tag{8}$$

and the vectors of its reciprocal lattice are $\mathbf{Q}_i$ (7). The cubic coordinates of two atoms in the unit cell, after doubling of the period, are equal to $\pm a(1/2-u,\,1/2-u,\,1/2-u)$. In the initial lattice $u=0$, and the parameter u for semimetals is given in the table.

TABLE I.

	a_t	a	α	ε_{xy}	x_t	u	Δ, eV
As	4,131	2,796	54°10′	0,0427	0,226	0,048	0.30
Sb	4,507	3,118	57°6,5′	0.0215	0,233	0,034	0.64
Bi	4.746	3.289	57°19′	0.0200	0.234	0,032	1.61
	[14]		[14]		[14]		[15]

Corresponding to the doubling of the period is instability of optical oscillations with wave vectors (7). Their interaction with the electrons is given by

$$U=\mathbf{u}\nabla(V_A(\mathbf{r})-V_B(\mathbf{r}))\equiv\mathbf{u}\mathbf{O}(\mathbf{r}), \tag{9}$$

where V_A and V_B are the potentials of two fcc sublattices that are shifted by a vector $\mathbf{u}=ua(1,1,1)$ in opposite directions.

Doubling of the period transforms the lattice from cubic to rhombohedral. This lowering of the symmetry is of necessity accompanied by acoustic deformation described by the tensor ε_{ij}. In cubic axes, the tensor ε_{ij} has two independent components (ε_{xx} and ε_{xy}), one of which (ε_{xx}), which is responsible for the hyrostatic compression, can be set equal to zero. The deformation adds to the Hamiltonian a term

$$\mathscr{E}=\varepsilon_{ij}O_{ij}(\mathbf{r}), \tag{10}$$

which describes the interaction of the electrons with the acoustic phonons.

Without resorting to model representations it is impossible to write down the explicit forms of O_i and O_{ij}. In the calculation of the matrix elements of (9) and (19) on the tight-binding functions we shall therefore use only symmetry considerations that are dictated by the group of the simple cubic lattice.

The perturbation (10) has a nonzero intracenter matrix element

$$\varepsilon_0=\langle p_x(0,0,0)|\mathscr{E}|p_y(0,0,0)\rangle$$
$$=\varepsilon_{xy}\langle p_x(0,0,0)|O_{xy}|p_y(0,0,0)\rangle,$$

as well as the following matrix elements for the nearest neighbors:

$$\varepsilon_1=2\langle p_x(0,0,0)|\mathscr{E}|p_y(a,0,0)\rangle,$$
$$\varepsilon_2=2\langle p_x(0,0,0)|\mathscr{E}|p_y(0,0,a)\rangle:$$

Therefore the off-diagonal (in the index of the p-states) matrix element of the perturbation (10) takes the form

$$\mathscr{E}_{xy}=\varepsilon_0+\varepsilon_1(\cos k_xa+\cos k_ya)+\varepsilon_2\cos k_za, \tag{11}$$

or in shorter form

$$\hat{\mathscr{E}}=\hat{\varepsilon}_0+\hat{\varepsilon}_1+\hat{\varepsilon}_2.$$

The diagonal matrix element is proportional to the hydrostatic compression ϵ_{xx} and can therefore be discarded.

The matrix elements considered so far are diagonal in the quasimomentum $\mathbf{k}$. The perturbation (9), however, has the periodicity of a face-centered lattice and has matrix elements that connect the states $\mathbf{k}\rangle$ and $\mathbf{k}+\mathbf{Q}\rangle$ of the crystal, where $\mathbf{Q}$ is any of the vectors (7). To describe this situation it is necessary to introduce one more index, that of the doubling of I, such that the part of the Hamiltonian which is diagonal in this index is given by expressions (1), (6), and (11), while the off-diagonal one is connected with (9) and is proportional to the vector $\mathbf{u}$. Since any two vectors $\mathbf{Q}_i$ are equivalent in the initial cubic lattice, the index I can take on only two values and it suffices to consider the matrix elements for the transition $1,p_\alpha\rangle\equiv k,p_\alpha\rangle$ into the state $2,p_\alpha\rangle\equiv\mathbf{k}+\mathbf{Q},p_\beta\rangle$ with some definite $\mathbf{Q}$ from (7).

The intracenter matrix elements U (9) are equal to zero, since this perturbation is odd in the inversion $\mathbf{r}\to-\mathbf{r}$. In the next higher approximation the matrix elements $\langle 1,p_\alpha|U|2,p_\beta\rangle\equiv U_{\alpha\beta}$ take the form

$$\begin{gathered}U_{xx}=i[u_1\sin k_xa+{}^1/{}_2u_2(\sin k_ya+\sin k_za)],\\ U_{xy}={}^1/{}_2iu_3(\sin k_xa+\sin k_ya),\end{gathered} \tag{12}$$

where

$$u_1=2ua\langle p_x(0,0,0)|O_x|p_x(a,0,0)\rangle,$$
$$u_2=4ua\langle p_x(0,0,0)|O_y|p_y(0,a,0)\rangle,$$
$$u_3=4ua\langle p_x(0,0,0)|O_y|p_y(a,0,0)\rangle.$$

In the derivation of (12) we used the relations

$$\langle p_x(0,0,0)|O_y|p_x(0,a,0)\rangle=\langle p_x(0,0,0)|O_z|p_x(0,0,a)\rangle,$$
$$\langle p_x(0,0,0)|O_y|p_y(a,0,0)\rangle=\langle p_x(0,0,0)|O_x|p_y(0,a,0)\rangle,$$

the first of which is the consequence of the invariance of the matrix element to the symmetry transformation $y\rightleftarrows z, x\to x$ of the simple cubic lattice. To prove the second, we effect the transformation $x\rightleftarrows y, z\to z$. Then

$$\langle p_x(0,0,0)|O_x|p_y(0,a,0)\rangle\to\langle p_y(0,0,0)|O_y|p_x(a,0,0)\rangle.$$

We next carry out the shift $x\to x+a$, $y\to y$, $z\to z$, in which the sublattices A and B change places, and consequently $O_y\to-O_y$ [see (9)],

$$\langle p_y(0,0,0)|O_y|p_x(a,0,0)\rangle\to-\langle p_y(-a,0,0)|O_y|p_x(0,0,0)\rangle.$$

It remains to carry out the reflection $x\to-x$, $y\to y$, $z\to z$, whereby $O_y\to O_y$, $p_x(0,0,0)\to-p_x(0,0,0)$, $p_y(-a,0,0)\to p_y(a,0,0)$, and we return to the left-hand side of the second relation.

The total Hamiltonian

$$\hat{H}=\hat{H}^0+\hat{\Delta}+\hat{\mathscr{E}}+\hat{u} \tag{13}$$

is a 12×12 matrix. We write it out relative to the doubling index

$$\begin{array}{ccc} \mathrm{I}= & 1 & 2\\ \hat{H}= & \multicolumn{2}{c}{\begin{pmatrix}\hat{\xi}+\hat{\eta}+\hat{\Delta}+\hat{\varepsilon}_0+\hat{\varepsilon}_1+\hat{\varepsilon}_2 & i\hat{u}\\ -i\hat{u} & -\hat{\xi}+\hat{\eta}+\hat{\Delta}+\hat{\varepsilon}_0-\hat{\varepsilon}_1-\hat{\varepsilon}_2\end{pmatrix},}\end{array} \tag{14}$$

where each term is a 6×6 matrix in the index p_α and in the spin variable; the imaginary unity is explicitly separated in the matrix $\hat{u}$ (12).

To determine the electronic spectrum $\omega(k)$ in the self-consistent field approximation it is necessary to solve the secular equation

$$\det(\hat{H}-\omega)=0. \tag{15}$$

Inasmuch as inversion is preserved in the crystal also after the doubling of the period, the eigenvalues $\omega(\mathbf{k})$ in the common point **k** are doubly degenerate. The spectrum determined by expressions (1), (6), (11) and (12) is specified in the Brillouin zone of the undeformed fcc lattice. This is as it should be, even though the lattice is deformed. Its unit vectors $\mathbf{a}_i'$ are connected with the initial rectangular basis $\mathbf{a}_i'$ via the strain tensor

$$\mathbf{a}_i' = (\delta_{ij} + \varepsilon_{ij})\,\mathbf{a}_j^0,$$

where the nonzero component ε_{xy} is determined by the angle between the elementary translation vectors and is given in the table. Transformation to the undeformed basis is implied in the derivation of (11) and (12), since it is needed for the elimination of the sizeable displacement of the remote atoms. For this purpose it is necessary to carry out in the Hamiltonian an appropriate coordinate transformation that returns the atoms to the original position.[16]

4. ELECTRON SPECTRUM IN THE VICINITY OF HIGH-SYMMETRY POINTS

We consider the spectrum in the vicinity of the most symmetrical points T and Γ, as well as L, the latter being the location of the electronic extremum of all the semimetals of group V.

4.1 The point $T = \frac{1}{2}\sum_i Q_i$

The cubic coordinates of this point are $(1,1,1)\pi/2a$. The Hamiltonian terms with $\xi_0, \xi_1, \eta_1, \eta_2, \varepsilon_1$ and ε_2 vanish at the point T. We therefore carry out the unitary transformation

$$\hat{\mathscr{P}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ -i & -1 \end{pmatrix}, \tag{16}$$

where the elements, just as in (14), are 6×6 matrices. The transformation $\hat{\mathscr{P}}$ corresponds to a transition to functions of definite parity $P = \pm 1$ at the point T. We obtain

$$\begin{array}{cc} P= & \begin{array}{cc} -1 & \qquad\qquad +1 \end{array} \\ \hat{\mathscr{P}}^{-1}\hat{H}\hat{\mathscr{P}} = & \begin{pmatrix} \hat{\eta} + \hat{\Delta} + \hat{\varepsilon}_0 + \hat{u} & i(\hat{\xi} + \hat{\varepsilon}_1 + \hat{\varepsilon}_2) \\ -i(\hat{\xi} + \hat{\varepsilon}_1 + \hat{\varepsilon}_2) & \hat{\eta} + \hat{\Delta} + \hat{\varepsilon}_0 - \hat{u} \end{pmatrix}. \end{array} \tag{17}$$

To obtain the spectrum in T, it is necessary to diagonalize the matrices $\hat{\eta}_0 + \hat{\Delta} + \hat{\varepsilon}_0 \pm \hat{u}$. With the aid of (3), (4), (11), and (12) we get

$$\hat{\eta}_0 + \hat{\varepsilon}_0 + \hat{u} = \begin{pmatrix} c_1 & c_2 & c_2 \\ c_2 & c_1 & c_2 \\ c_2 & c_2 & c_1 \end{pmatrix}, \tag{18}$$

where

$$c_1 = u_1 + u_2, \quad c_2 = \eta_0 + \varepsilon_0 + u_3 \tag{19}$$

at $\mathbf{k} = T$. The matrix (18) is reduced to the diagonal form

$$\hat{\mathscr{T}}^{-1}(\hat{\eta}_0 + \hat{\varepsilon}_0 + \hat{u})\mathscr{T} = \begin{pmatrix} c_1 - c_2 & 0 & 0 \\ 0 & c_1 - c_2 & 0 \\ 0 & 0 & c_1 + 2c_2 \end{pmatrix} \tag{20}$$

with the aid of the transformation

$$\hat{\mathscr{T}} = \begin{pmatrix} 0 & 2/\sqrt{6} & 1/\sqrt{3} \\ -1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \\ 1/\sqrt{2} & -1/\sqrt{6} & 1/\sqrt{3} \end{pmatrix}, \tag{21}$$

which reduces to a rotation of the coordinate frame. The new axes are chosen as follows: $01 \equiv [0, -1, 1]$ along the twofold symmetry axis of the point T, and $03 \equiv [1,1,1]$ along the threefold symmetry axis. The eigenfunctions of the operator (20), which we designate $1\rangle$, $2\rangle$, and $3\rangle$, are connected in the usual manner with $p_\alpha\rangle$. For example,

$$1\rangle = \mathscr{T}_{\alpha 1}\,|\,p_\alpha\rangle.$$

The spin-orbit interaction (6) is written in invariant form, so that to transform to the new axes it suffices to make the change of variables $x, y, z \to 1, 2, 3$. As already noted, Kramers degeneracy takes place in this case. We designate the eigenfunctions of the spin projection operator by $\uparrow\rangle$ and $\downarrow\rangle$. The two sets of functions corresponding to the Kramers states take then the form

$$\begin{aligned} \psi &= 2^{-1/2}(1 - i2)\downarrow\rangle, \quad 2^{-1/2}(1 + i2)\downarrow\rangle, \quad 3\uparrow\rangle, \\ \varphi &= 2^{-1/2}(1 + i2)\uparrow\rangle, \quad 2^{-1/2}(1 - i2)\uparrow\rangle, \quad -3\downarrow\rangle. \end{aligned} \tag{22}$$

In the new basis, the spin-orbit interaction has no matrix elements for the transition between the states ψ and φ: $\langle\psi|\varDelta\,|\varphi\rangle = 0$. The matrix $\hat{\varDelta}$ is of the same form for transitions within each set:

$$\langle\psi\,|\,\hat{\Delta}\,|\,\psi\rangle = \langle\varphi\,|\,\hat{\Delta}\,|\,\varphi\rangle = \begin{pmatrix} \dfrac{\Delta}{3} & 0 & 0 \\ 0 & -\dfrac{\Delta}{3} & -\dfrac{\sqrt{2}}{3}\Delta \\ 0 & -\dfrac{\sqrt{2}}{3}\Delta & 0 \end{pmatrix}, \tag{23}$$

and the matrix (20) remains unchanged. The eigenvalues of the sum of these two matrices can be easily obtained:

$$T_{45}^{-} = c_1 - c_2 + {}^1/_3\Delta, \tag{24}$$

$$T_6^{-}(1, 2) = c_1 + {}^1/_2(c_2 - {}^1/_3\Delta) \pm [{}^1/_4(c_2 + \Delta)^2 + 2c_2^2]^{1/2}. \tag{25}$$

The even terms are obtained from (24) and (25) by reversing the signs of the terms u_i in c_1 and c_2 (19). The subscripts in (24) and (25) are standard. Thus, the term T_{45} corresponds to two one-dimensional complex conjugate representations of a two-valued group.

If the inequality $\varDelta \gg 2^{3/2}|c_2|$ is satisfied, Eq. (25) is simplified:

$$T_6^{-}(1) = c_1 + c_2 + {}^1/_3\Delta, \qquad T_6^{-}(2) = c_1 - {}^2/_3\Delta.$$

The schematic arrangement of the levels at the point T is shown in the figure for the case $|c_1|, |c_2| \ll \varDelta$. The sixfold degenerate (in a simple cubic lattice) p-state is split by the spin-orbit interaction into two terms with respective total angular momenta $j = 3/2$ and $1/2$. This splitting is equal to $\varDelta$. The acoustic deformation ε_{xy} together with the cubic crystal field η_0 splits the states with different values of the projection m_j in the term $j = 3/2$. Doubling of the period causes us to join the three terms obtained for the point T with the same terms for the point $-T$. The optical shift u splits the resultant degeneracy while retaining the twofold Kramers degeneracy of all the terms. We note that the relative arrangement of the four upper levels can be arbitrary, depending on the ratio of c_1 and c_2. The relative position of the two lower levels is determined by the sign of the sum $u_1 + u_2$.

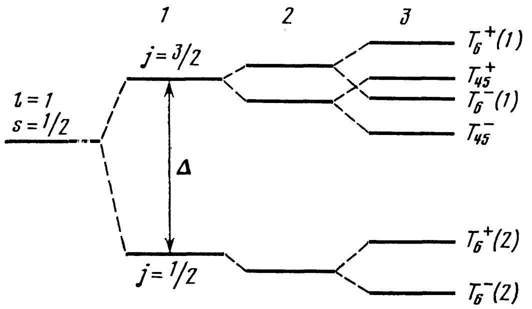


FIG. 1. Splitting of atomic p-term under the influence of: 1) the spin-orbit interaction (Δ), 2) of the cubic crystal field (η) and of the acoustic deformation (ε_{xy}), 3) of the doubling of the lattice period (u).

Let us calculate the effective masses at the point T, applying to (17) the usual kp scheme. To this end we subject $\hat{\xi}$, $\hat{\eta}$, and $\hat{\varepsilon}$ to the same transformations as in the derivation of relations (24) and (25). We transfer the origin to the point T, expand all the matrices in powers of k and rotate the axes with the aid of (21). The matrix $\hat{\xi}$ (1) (2) takes in the basis of the coordinate functions $2^{-1/2}(1+i2)\rangle$, $2^{-1/2}(1-i2)\rangle$, $3\rangle$ used in (22) the form

$$\hat{\xi}=-\frac{a}{\sqrt{3}}(\xi_0+2\xi_1)k_3\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}-\frac{a}{\sqrt{6}}(\xi_0-\xi_1)\begin{pmatrix}0&ik_+&k_-\\-ik_-&0&k_+\\k_+&k_-&0\end{pmatrix}, \tag{26}$$

where $k_\pm=k_1\pm ik_2$.

The quantity $\xi_0+2\xi_1$ is substantially smaller than $\xi_0-\xi_1$ (estimates of ξ_0 and ξ_1 were given in the Introduction). We retain therefore in $\hat{\varepsilon}$ and $\hat{\eta}$ only the terms with k_3

$$\hat{\varepsilon}_1+\hat{\varepsilon}_2=-\frac{a}{\sqrt{3}}(\varepsilon_2+2\varepsilon_1)k_3((-1,-1,2)), \tag{27}$$

$$\hat{\eta}={}^1/_3a^2k_3^2((\eta_0+\eta_1+2\eta_2,\ \eta_0+\eta_1+2\eta_2,\ -2\eta_0+\eta_1+2\eta_2)), \tag{28}$$

where the parentheses contain the diagonal elements of the matrix; the off-diagonal elements vanish in this approximation.

Rewriting (17) in the basis of the functions (22), we use the transformation C that diagonalizes the Hamiltonian at the point T. With the aid of (20) and (23) we obtain for the basis of the functions with definite spin (ψ and φ) and parity

$$\hat{C}(-1)=\begin{pmatrix}1&0&0\\0&s&c\\0&c&-s\end{pmatrix}, \tag{29}$$

where

$$s\equiv\sin\theta=\frac{c_1+2c_2-T_6^-(1)}{\left\{[c_1+2c_2-T_6^-(1)]^2+\frac{2}{9}\Delta^2\right\}^{1/2}}, \tag{30}$$

$$c\equiv\cos\theta.$$

To obtain $\hat{C}(+1)$ it suffices the reverse the sign of u_j in (19) and (25); the corresponding values will be marked by a tilde; $\hat{C}$ does not change sign on reversal of the spin.

We obtain thus a spectrum in the vicinity of each of the extrema at the point T:

$$\omega=\omega(T)+k_3^2/2m_3+k_\perp^2/2m_\perp,$$

and the longitudinal and transverse masses m_3 and $m_\perp$ are:

for the level T_6^- (1)

$$\frac{1}{2m_3}=\frac{(\mu s\tilde{s}+\mu_1c\tilde{c})^2}{T_6^-(1)-T_6^+(1)}+\frac{(\mu s\tilde{c}-\mu_1c\tilde{s})^2}{T_6^-(1)-T_6^+(2)}+\frac{a^2}{3}\left[\eta_1+2\eta_2-\frac{(u_1+u_2)}{2}+(-2+3s^2)\left(\eta_0+\frac{u_3}{2}\right)\right],$$

$$\frac{1}{2m_\perp}=\frac{a^2}{6}(\xi_0-\xi_1)^2\left[\frac{1}{T_6^-(1)-T_{45}^+}+\frac{\sin^2(\theta-\bar{\theta})}{T_6^-(1)-T_6^+(1)}+\frac{\cos^2(\theta-\bar{\theta})}{T_6^-(1)-T_6^+(2)}\right]; \tag{31}$$

for the level T_{45}^-

$$\frac{1}{2m_3}=\mu^2(T_{45}^--T_{45}^+)^{-1}+\frac{a^2}{3}\left[\eta_0+\eta_1+2\eta_2-\frac{(u_1+u_2-u_3)}{2}\right],$$

$$\frac{1}{2m_\perp}=\frac{a^2}{6}(\xi_0-\xi_1)^2[(T_{45}^--T_6^+(1))^{-1}+(T_{45}^--T_6^+(2))^{-1}], \tag{32}$$

where

$$\mu=3^{-1/2}a(\xi_0+2\xi_1-\varepsilon_2-2\varepsilon_1),$$

$$\mu_1=3^{-1/2}a(\xi_0+2\xi_1+2\varepsilon_2+4\varepsilon_1).$$

The corresponding expressions for the remaining terms are obtained from (31) and (32) by the obvious permutation of the indices.

It is of interest to calculate the splitting ω_s of a Kramers doublet in a magnetic field H parallel to the C_3 axis. The ratio of ω_s to the distance between the Landau levels ω_c is called the spin-splitting factor $Y=|\omega_s/\omega_c|$.

In a magnetic field, the components k_+ and k_- in (26) are operators that satisfy the commutation relation

$$\{k_+,\ k_-\}=2eH/c\hbar.$$

By tracking the sequence of the operators k_+ and k_- we obtain within the framework of the employed kp method

$$\gamma=[(A-B)^2+C^2]^{1/2}/|A+B|, \tag{33}$$

where we have for the T_6^- (1) level

$$A=[T_6^-(1)-T_{45}^+]^{-1},$$

$$B=\frac{\sin^2(\theta-\bar{\theta})}{T_6^-(1)-T_6^+(1)}+\frac{\cos^2(\theta-\bar{\theta})}{T_6^-(1)-T_6^+(2)}, \tag{34}$$

$$C=0$$

and for the T_{45}^- level

$$A=\frac{\tilde{c}^2}{T_{45}^--T_6^+(1)}+\frac{\tilde{s}^2}{T_{45}^--T_6^+(2)},$$

$$B=\frac{\tilde{s}^2}{T_{45}^--T_6^+(1)}+\frac{\tilde{c}^2}{T_{45}^--T_6^+(2)}, \tag{35}$$

$$C=2\tilde{s}\tilde{c}[(T_6^+(1)-T_{45}^-)^{-1}-(T_6^+(2)-T_{45}^-)^{-1}].$$

It can be seen from (33) that γ can be noticeably larger than unity if A and B have opposite signs and are comparable in magnitude.

4.2 The point L

This is any of the points $\mathbf{Q}_i/2$ (7). Let, for the sake of argument, $L = \mathbf{Q}_i/2 = (-1,1,1)\pi/2a$. Following the transformation $\mathscr{P}$(16), the Hamiltonian is again written in the form (17), while $\hat{\xi}$, $\hat{\xi}_1$, and $\hat{\varepsilon}_1$, and $\hat{\varepsilon}_2$ vanish at the point L itself. At the same point, the matrix is

$$\hat{\eta}_0 + \hat{\varepsilon}_0 + \hat{u} = \begin{pmatrix} -u_1 + u_2 & -\eta_0 + \varepsilon_0 & -\eta_0 + \varepsilon_0 \\ -\eta_0 + \varepsilon_0 & u_1 & \eta_0 + \varepsilon_0 + u_3 \\ -\eta_0 + \varepsilon_0 & \eta_0 + \varepsilon_0 + u_3 & u_1 \end{pmatrix}. \tag{36}$$

We transform to the axes of the point L, choosing 01 along the twofold axis $[0,-1,1]$ and 03 along $\Gamma L = [1,1,1]$, and transforming the matrix (36) with the aid of

$$\hat{\mathscr{L}} = \begin{pmatrix} 0 & 2/\sqrt{6} & -1/\sqrt{3} \\ -1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \\ 1/\sqrt{2} & 1/\sqrt{6} & 1/\sqrt{3} \end{pmatrix}. \tag{37}$$

At the point L we obtain

$$\hat{\mathscr{L}}^{-1}(\hat{\eta}_0 + \hat{\varepsilon}_0 + \hat{u})\hat{\mathscr{L}} \equiv \hat{w} \tag{38}$$

with nonzero elements

$$\begin{gathered} w_{11} = -\eta_0 - \varepsilon_0 + u_1 - u_3, \quad w_{22} = -\eta_0 + (5\varepsilon_0 - u_1 + 2u_2 + u_3)/3, \\ w_{23} = (2\varepsilon_0 + 2u_1 - u_2 + u_3)\sqrt{2}/3, \\ w_{33} = 2\eta_0 + (-2\varepsilon_0 + u_1 + u_2 + 2u_3)/3. \end{gathered} \tag{39}$$

We designate the basis functions of the matrix (38) by $1\rangle$, $2\rangle$, and $3\rangle$ and choose the basis in spin space to be the eigenfunctions $\uparrow\rangle$ and $\downarrow\rangle$ of the projection of the spin σ_1 on the 01 axis. The Kramers-doublet function is of the form

$$\begin{aligned} \psi &= 2^{-1/2}(3 - i2)\downarrow\rangle, \quad 2^{-1/2}(3 + i2)\downarrow\rangle, \quad 1\uparrow\rangle, \\ \varphi &= 2^{-1/2}(3 + i2)\uparrow\rangle, \quad 2^{-1/2}(3 - i2)\uparrow\rangle, \quad -1\downarrow\rangle \end{aligned} \tag{40}$$

and satisfies the requirements

$$\langle\psi|\hat{\Delta}|\varphi\rangle = \langle\psi|\hat{w}|\varphi\rangle = 0, \quad \langle\varphi|\hat{w}|\varphi\rangle = \langle\psi|\hat{w}|\psi\rangle^*,$$

as well as relation (23). In the new basis (40) the matrix $\langle\psi|w|\psi\rangle \equiv h_{ij}$ has the following nonzero elements:

$$\begin{gathered} h_{11} = h_{22} = (w_{22} + w_{33})/2, \\ h_{12} = (w_{33} - w_{22})/2 + iw_{23}, \quad h_{33} = w_{11}, \quad h_{21} = h_{12}^*. \end{gathered} \tag{41}$$

To find the levels at the point L it is necessary to diagonalize the sum $\eta_0 + \varepsilon_0 + \hat{u} + \Delta$. With the aid of (23) and (41) we arrive at the cubic equation

$$\begin{aligned} &\omega^3 - \omega^2 \operatorname{Sp} w + \omega\left[w_{22}w_{33} + w_{11}(w_{22} + w_{33}) - w_{23}^2 - {}^1/_3\Delta^2\right] \\ &\quad - w_{11}(w_{22}w_{33} - w_{23}^2) \\ &\quad + {}^1/_9\Delta^2(\operatorname{Sp} w + {}^2/_3\Delta) = 0, \end{aligned} \tag{42}$$

which yields three states $L^+(j)$. The odd states L^- are obtained by reversing the signs of the terms u_i in (39).

The figure presented above can be used to elucidate the arrangement of the levels at the point L, paying attention only to the parity symbol. The two lower levels $L^+(3)$ and $L^-(3)$ split off by the spin-orbit interaction are relatively deep in the case of bismuth (where Δ is large). The distances between the four upper levels should be of the order of $E_g \sim \varepsilon_{xy}\xi_0$, i.e., of the order of 0.2–0.4 eV. For the T point in bismuth this estimate is confirmed by the experimental data.[9] All that is known about the terms in L is that in bismuth the levels $L^+(2)$ and $L^-(2)$ are close, the distance ε_g between them not exceeding 0.015 eV. According to pseudopotential calculations,[8] the lower and upper pair of levels are about 1 eV away from the middle one, but we know, with the T point as the example, that the results of these calculations can be subject to a correction amounting to 0.3–1.2 eV.

For energies $|\omega - L(2)| \ll E_g$ one can construct a two-band approximation that describes the levels $L^\pm(2)$. To this end we write down the matrix $\hat{\xi}$ in the vicinity of the point L, using the basis (40):

$$\begin{aligned} \langle\psi, +1|\hat{\xi}|\psi, -1\rangle &= -\frac{ak_3}{\sqrt{3}}(\xi_0 + 2\xi_1)\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ &+ \frac{ak_2}{2\sqrt{6}}(\xi_0 - \xi_1)\begin{pmatrix} 1 & -1 - i2^{3/2} & 0 \\ & 1 & 0 \\ \text{c.c.} & & -2 \end{pmatrix}, \end{aligned} \tag{43}$$

$$\langle\psi, +1|\hat{\xi}|\varphi, -1\rangle = \frac{ak_1}{\sqrt{6}}(\xi_0 - \xi_1)\begin{pmatrix} 0 & 0 & 1 + i2^{-1/2} \\ & 0 & 1 - i2^{-1/2} \\ -1 - i2^{-1/2} & -1 + i2^{-1/2} & 0 \end{pmatrix}.$$

We retain in the matrices $\hat{\varepsilon}$ and $\hat{\eta}$ only the terms with k_3:

$$\langle\psi, +1|\hat{\varepsilon}|\psi, -1\rangle = \frac{ak_3}{\sqrt{3}}(\varepsilon_2 + 2\varepsilon_1)\begin{pmatrix} -{}^1/_2 & {}^7/_6 - i2^{3/2}/3 & 0 \\ & -{}^1/_2 & 0 \\ \text{c.c.} & & 1 \end{pmatrix}, \tag{44}$$

$$\langle\psi, +1|\hat{\eta}|\psi, +1\rangle$$

$$= \frac{a^2k_3^2}{3}\begin{pmatrix} -{}^1/_2\eta_0 + \eta_1 + 2\eta_2 & -{}^3/_2\eta_0 + 2^{3/2}i(\eta_2 - \eta_1)/3 & 0 \\ & -{}^1/_2\eta_0 + \eta_1 + 2\eta_2 & 0 \\ \text{c.c.} & & \eta_0 + \eta_1 + 2\eta_2 \end{pmatrix}. \tag{45}$$

The matrices $\hat{\xi}$, $\hat{\varepsilon}$, and $\hat{\eta}$ satisfy the relations

$$\langle\varphi|\ldots|\varphi\rangle=\langle\psi|\ldots|\psi\rangle^*,\quad \langle\varphi|\ldots|\psi\rangle=-\langle\psi|\ldots|\varphi\rangle^*.$$

Finally, we transform the Hamiltonian (17), diagonalizing it at the point L itself. The functions with definite parity and spin are then transformed, as we have already seen, only in terms of one another. The matrix elements of the corresponding unitary transformation $\hat{C}(\psi, +1)$ can be expressed with the aid of (41) and (23) in the form

$$\begin{gathered} c_{1j}=h_{12}(h_{33}-L^+(j))/N_j,\\ c_{2j}=(L^+(j)-h_{33})(h_{11}+\Delta/3-L^+(j))/N_j,\\ c_{3j}=\sqrt{2}\Delta(L^+(j)-\Delta/3-h_{11})/3N_j, \end{gathered} \tag{46}$$

where N_j is determined by the normalization condition

$$\sum_i |c_{ij}|^2=1.$$

The matrix $\hat{C}(\varphi, +1)$, with the aid of which are transformed the functions of the second set (40), are obtained from (46) by the complex conjugation $\hat{C}(\varphi, +1)=\hat{C}(\psi, +1)$, and to transform to the odd functions it is necessary to reverse the sign of u_i in (39).

We obtain thus the effective Hamiltonian of the two-band approximation

$$H=\begin{pmatrix} L^+(2,k) & 0 & v_{222}k_2+v_{322}k_3 & v_{122}k_1\\ 0 & L^+(2,k) & v^*_{122}k_1 & -v^*_{222}k_2-v^*_{322}k_3\\ v^*_{222}k_2+v^*_{322}k_3 & v_{122}k_1 & L^-(2,k) & 0\\ v^*_{122}k_1 & -v_{222}k_2-v_{322}k_3 & 0 & L^-(2,k) \end{pmatrix}, \tag{47}$$

where

$$\begin{aligned} v_{1ij}={}&i\frac{a}{\sqrt{6}}(\xi_0-\xi_1)\left[\left(1+\frac{i}{\sqrt{2}}\right)(c_{1i}^*\tilde{c}_{3j}^*-\tilde{c}_{1j}^*c_{3i})\right.\\ &\left.+\left(1-\frac{i}{\sqrt{2}}\right)(c^*_{2i}\tilde{c}_{3j}^*-\tilde{c}_{2j}^*c_{3i}^*)\right],\\ v_{2ij}={}&i\frac{a}{\sqrt{6}}(\xi_0-\xi_1)\left\{\left[\frac{1}{2}c_{1i}^*-\left(\frac{1}{2}-i\sqrt{2}\right)c_{2i}^*\right]\tilde{c}_{1j}\right.\\ &\left.+\left[\frac{1}{2}c_{22}^*-\left(\frac{1}{2}+i\sqrt{2}\right)c_{1i}^*\right]\tilde{c}_{2j}-c_{3i}^*\tilde{c}_{3j}\right\},\\ v_{3ij}={}&-3^{-1/2}ia\{(\xi_0+2\xi_1)(c_{1i}^*\tilde{c}_{2j}+c_{2i}^*\tilde{c}_{2j}\\ &+c_{3i}^*\tilde{c}_{3j})-(\varepsilon_2+2\varepsilon_1)[(-{}^1/{}_2c_{1i}^*+({}^7/{}_6+i2^{3/2}/3)\\ &\times c_{2i}^*)\tilde{c}_{1j}+(({}^7/{}_6-i2^{3/2}/3)c_{1i}^*-{}^1/{}_2c_{2i}^*)\tilde{c}_{2j}+c_{3i}^*\tilde{c}_{3j}\}. \end{aligned} \tag{48}$$

Contributions to the diagonal terms are made by the terms with η, (45) and (12), as well as by the levels $L(1)$ and $L(3)$ in second-order perturbation theory:

$$\begin{aligned} L^+(2,k)={}&L^+(2)+\frac{(ak_3)^2}{2}\left[\left(-\frac{\eta_0}{4}+\eta_1+2\eta_2-\frac{u_2}{4}-\frac{u_3}{4}\right)\right.\\ &(|c_{12}|^2+c_{22}^2)\\ &+\left(\eta_0+\eta_1+2\eta_2-\frac{u_1}{2}+\frac{u_3}{2}\right)c_{32}^2\\ &+\left(-3\eta_0-\frac{u_1}{3}+\frac{u_2}{6}-\frac{u_3}{6}\right)c_{22}\operatorname{Re}c_{12}\\ &\left.+\frac{\sqrt{2}}{3}(-2u_1+u_2-u_3)c_{22}\operatorname{Im}c_{12}\right]\\ &+\sum_{i=1,3}|v_{22i}k_2+v_{32i}k_3|^2/(L^+(2)-L^-(i)). \end{aligned} \tag{49}$$

With the aid of (47) we obtain the spectrum of the two-band approximation

$$(L^+(2,k)-\omega)(L^-(2,k)-\omega)=|v_{122}|^2k_1^2+|v_{222}k_2+v_{322}k_3|^2. \tag{50}$$

By rotating the coordinate axes in the (2,3) plane

$$03=z_1\cos\varphi-y_1\sin\varphi,\quad 02=z_1\sin\varphi+y_1\cos\varphi,\quad 01=x_1$$

we diagonalize the right-hand side of (50)

$$Q_{xx}^2k_{x1}^2+Q_{yy}^2k_{y1}^2+Q_{zz}^2k_{z1}^2,$$

where

$$\begin{gathered} Q_{xx}^2=|v_{122}|^2,\quad Q_{yy}^2=|v_{222}\cos\varphi-v_{322}\sin\varphi|^2,\\ Q_{zz}^2=|v_{222}\sin\varphi+v_{322}\cos\varphi|^2,\\ \operatorname{tg}2\varphi=2\operatorname{Re}(v_{322}v^*_{222})/(|v_{322}|^2-|v_{222}|^2). \end{gathered}$$

We note that for bismuth $Q_{zz}{}^2/Q_{yy}{}^2\sim10^{-2}$, and according to the estimate given above $|v_{3ij}/v_{2ij}|^2\sim10^{-1}$. The additional smallness appears if v_{222} and v_{322} are simultaneously real or pure imaginary [see (50)]. This condition is realized, for example, in the limiting case $|u_i|\ll\max\{|\eta_0|, |\epsilon_0|\}$ [see (39)]. Then the values of $\tilde{c}_{ij}$ and c_{ij} differ little, and v_{222} and v_{322} in (48) are almost pure imaginary. In this case there exists a direction z_1 in which $\omega(k)$ remains practically unchanged, i.e., the corresponding Q_{zz} is small. At small Q_{zz} the two-band approximation is not very accurate for directions close to k_{z1}, since the contributions of the higher orders of perturbation theory are substantial (their relative magnitude is $v_{3ij}(\omega-L(2))/Q_{zz}E_g$).

4.3. The point Γ

This point is the center of the Brillouin zone. We are interested here only in the term arrangement known from optical measurements. At $\mathbf{k}=\Gamma$ the matrix u vanishes from the Hamiltonian (14), and the parity of the states is uniquely determined by the doubling index. With the aid of relations (2)–(4) and (11) we see that the matrix $\hat{\xi}+\hat{\eta}+\hat{\varepsilon}_0+\hat{\varepsilon}_1+\hat{\varepsilon}_2$ has a structure similar to the matrix (18) with a diagonal element $b_1=\xi_0+2\xi_1+\eta_1+2\eta_2$ and an off-diagonal one $b_2=\varepsilon_0+2\varepsilon_1+\varepsilon_2$. We can therefore use Eqs. (24) and (25):

$$\Gamma_{45}^-=b_1-b_2+{}^1/{}_3\Delta, \tag{51}$$

$$\Gamma_6^-(1,2)=b_1+\frac{1}{2}\left(b_2-\frac{\Delta}{3}\right)\pm\left[\left(\frac{b_2+\Delta}{2}\right)^2+2b_2^2\right]^{1/2}, \quad (52)$$

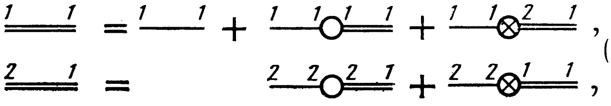
where the parity index is determined with allowance for the translational functions of the crystal functions $|\Gamma\rangle$ and $|\Gamma+Q\rangle$. The even terms, as can be seen from (14), are obtained by substitution in (51) and (52):

$$b_1\rightarrow-\xi_0-2\xi_1+\eta_1+2\eta_2, \quad b_2\rightarrow\varepsilon_0-2\varepsilon_1-\varepsilon_2.$$

5. CONNECTION BETWEEN RHOMBOHEDRAL DEFORMATION AND SUBLATTICE SHIFT

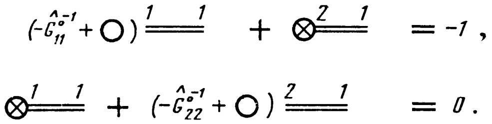
So far, the rhombohedral deformation ε_{xy} and the sublattice shift u were regarded by us as independent quantities. Actually, however, they are connected by the condition that the new phase be at equilibrium. To find this connection we use the Green-function technique.

We denote the p-electron Green function $\hat{G}_0(k)$ in the parent phase by $\hat{G}_{11}^0$, and the corresponding value of $G_0(k+Q)$ shifted by some vector $\mathbf{Q}$ (7) will be designated $\hat{G}_{22}^0$. These functions are matrices in the index $\alpha=x, y, z$, which numbers the basis p-states. When the period is doubled, anomalous mean values of $\hat{G}_{12}$ appear. In the mean-field approximation we obtain the equations



(53)

where a circle corresponds to the interaction (11), and a cross to (12). Multiplying the first equation from the left by the matrix G_{11}^{0-1}, and the second by $\hat{G}_{22}^{0-1}$, we obtain



(54)

It can be seen from these equations that the poles of the exact functions $\hat{G}_{11}$ and $\hat{G}_{21}$ are determined by the eigenvalue equation (15) for the Hamiltonian (14).

We obtain the self-consistency equations by noting that the vertices of the equations (53) are proportional to the small shift of the atoms:

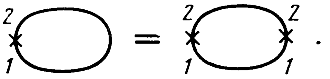
(55)

where phonon Green functions were introduced for the parent phase at the frequency $\omega=0$. The wavy line corresponds to the acoustic limit $k\rightarrow0$, and the dashed one to $k\rightarrow Q$. The structure of the vertices g in the right-hand side of (55) can be explained with the aid of (9) and (10), namely, to obtain g it is necessary to exclude from the interaction the factors that correspond to the phonon shifts.

To solve (54) and (55) we proceed as follows. We retain during the first stage only the principal terms with ξ. The electron spectrum breaks up then into three quasi-one-dimensional bands of the type

$$\omega_x(k)=\xi_0\cos k_xa+\xi_1(\cos k_ya+\cos k_za), \quad (56)$$

and the Green function G_{12} is determined by second-order perturbation theory in U (12):



(57)

After integration with respect to frequency, this loop diagram contains the denominator $\omega_\alpha(k)-\omega_\beta(k+Q)$. The integral over the occupied states diverges logarithmically if $\alpha=\beta$. The divergence is a consequence of the congruence condition $\omega_\alpha(k+Q)=-\omega_\alpha(k)$, because of which the integrand becomes infinite on the Fermi surface (at $\xi_1=0$ this surface consists of the planes $k_\alpha a=\pm\pi/2$). We note that the threefold degeneracy at the point T (or L) is completely lifted only if the spin-orbit interaction and the hybridization η are simultaneously turned on (see Fig. 1). For the parent phase to be unstable it suffices therefore to have only one of them small compared with ξ_0.

The principal logarithmic contribution is made by the region $|U/\xi_0|\ll|k_\alpha a\pm\pi/2|\ll1$, where U determines the band splitting due to doubling of the period. This contribution can be written in the form

$$(6/\pi a^3\xi_0)\overline{U_{xx}g_Q}\ln|4\xi_0/U|. \quad (58)$$

The coefficient 6 corresponds to weak spin-orbit interaction, when the three bands of (56) make equal contributions, and the factor 4 under the logarithm sign arises when $|2U|$ coincides exactly with the gap between the one-dimensional bands; the bar denotes averaging over the Fermi surface. It is the fact that distances far from the Fermi surface are significant in (57), as well as that the splitting U has little effect on the result, which justifies the perturbation theory in $1/\xi$ which is used here. With allowance for (6), the second equation of (35)

$$U\sim(6g_Q^2u/\pi Ma^2\Omega_Q^2\xi_0)\ln|4\xi_0/U| \quad (59)$$

determines the equilibrium shift of the sublattices

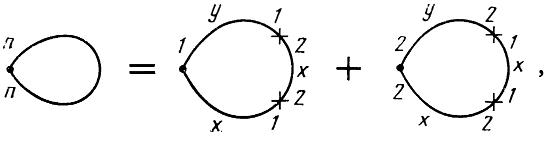
$$U=4\xi_0\exp(-1/\lambda_Q),$$

where

$$\lambda_Q\sim6g_Q^2/\pi Ma^2\Omega_Q^2\xi_0\sim6\xi_0/\pi Ma^2\Omega_Q^2, \quad (60)$$

M is the mass of the atom, Ω_Q is the frequency of a phonon with $k=Q$ in the parent phase. The observed value $|U/\xi_0|\sim1/20$ leads to $\lambda_Q=1/\ln|4\xi_0/U|\sim1/4$. We obtain this value from (60) using the data known[17] for bismuth: $\Omega_Q\approx1.5\cdot10^{13}$ rad/sec, $M=3.47\cdot10^{-22}$ g.

The connection between the rhombohedral deformation and the shift of the sublattices is determined by the first equation of (55). The loop in it arises in third-order perturbation theory



(61)

where we show by way of example the one configuration of the band indices x and y which makes the largest contribution. These indices were arranged with account taken of the fact that the interaction (11)with the acoustic phonons contains only off-diagonal elements. In diagram (61) the term with ε_0 [see (11)] is cancelled and in the logarithmic approximation the integral is equal to

$$(6/\pi a^3\xi_0^2)\overline{U_{xx}U_{xy}g_0}\ln|4\xi_0/U|.$$

The first equation of (55) reduces therefore to the condition

$$\xi_0\varepsilon_{xy}\sim(6g_0^2U^2/\pi M\Omega_0^2\xi_0^2)\ln|4\xi_0/U|, \tag{62}$$

where Ω_0 is the frequency of the acoustic phonon as $k\to 0$ in the parent phase. Recognizing that $g_0\sim\xi_0 k$, we rewrite (62) in the form

$$\varepsilon_{xy}\sim(6U^2/\pi Ms^2\xi_0)\ln|4\xi_0/U|, \tag{63}$$

where s is the speed of sound in the parent phase.

We see that the rhombohedral deformation is proportional to a large logarithm that compensates for the extra power of the sublattice shift u. Substituting in (63) the speed of sound in bismuth $s = 1.5\cdot 10^5$ cm/sec we get $\xi_0/Ms^2\sim 1$, which agrees with the observed value. We emphasize that an important role in the estimate of ε_{xy} was played by the difference between the constants of the coupling with the optical ($k\to Q$) and acoustic ($k\to 0$) phonons.

The present results cast light on the question of the softening of the optical mode at the center of the Brillouin zone, i.e., of the oscillation with wave vector Q in the parent phase. Instability of a cubic lattice corresponds to vanishing of the frequency of the oscillations with vector Q. To find the frequency of these oscillations in the restructured lattice, it suffices to note that the self-consistency conditions (55) constitute requirements that the total energy be a minimum as a function of the phonon displacements. However, the second derivative of the total energy yields directly the square of the phonon frequency. Thus, the second equation of (55), which can be rewritten with the aid of (59) and (60) in the form

$$U-\lambda_Q U\ln|4\xi_0/U|=0, \tag{64}$$

allows us to calculate the frequency of the optical oscillations as $k\to 0$. Differentiating the left-hand side of (64), we obtain the square of the frequency

$$\Omega^2=\Omega_Q^2(1-\lambda_Q\ln|4\xi_0/U|+\lambda_Q).$$

Taking the equilibrium condition (64) into account, we get

$$\Omega=\Omega_Q(\ln|4\xi_0/U)^{-1/2}.$$

Thus, the optical frequencies as $k\to 0$ are approximately half the frequency Ω_Q of the acoustic oscillations in the parent phase with wave vector Q. The dimension of that region near the Brillouin-zone center where the optical frequencies have a dip is not literally small—it is small only compared with the dimensions of the zone itself.

6. CONCLUSION

Our results for quantitative comparison with experimental data. This should be done in two stages. First, using the well-known parameters of the electrons and holes, we determine the overlap integrals. The equations given above are next used to reconstruct the electronic spectrum in the entire Brillouin zone. Let us list the parameters involved in the theory: the overlap integrals ξ_0 and ξ_1 for the first coordination sphere and η_0, η_1, and η_2 for the second coordination sphere in the cubic parent phase, the energy Δ of the spin-orbit interaction, the three parameters ε_0, ε_1, and ε_2 that characterize the rhombohedral deformation, and the three parameters u_1, u_2, and u_3 of the shift of the face-centered sublattices. From among the listed 12 quantities, Δ is known from the splitting of the atomic levels (see the table), while ξ and η should go over into the corresponding values for IV–VI compounds with allowance for the correction for the change of the interatomic distance.

We note that electrons and holes, say in bismuth, are described at present by at least 12 quantities (two masses and the spin splitting for holes; three interband effective masses, the energy gap, the slope of the "ellipsoid," as well as the Fermi energy for the electrons). The experimental information on the electronic spectrum is, of course, much more extensive. Measurements were made also of the different frequencies and of the probabilities of the optical transitions, e.g., at the Γ point, of the deformation potentials, and of other quantities that are directly described by the proposed theory.

The relation obtained here between the acoustic deformation and the shift of the sublattices is valid also for the rhombohedral modifications of IV–VI semiconductors, as well as to hexagonal helical structures of Te and Se. For this reason, the "vibronic model" of Konsin and Kristoffel' (Ref. 18), constructed under the assumption that the decisive role is played by a small vicinity of the L points of the Brillouin zone, and in which the topology of the parent-phase Fermi surface is neglected, is not an adequate description of the structural transitions in IV–VI.

In conclusion, we assess the role of the Coulomb interaction. Keldysh and Kopaev, in an analysis of a model of an excitonic dielectric,[19] have shown that Coulomb interaction can also lead to structural instability if the Fermi surface has congruent sections. In the case of group-V metals, however, one deals with a transition that conserves the spatial inversion wherein two face-centered sublattices exchange place. The order parameter that describes this transition is pure imaginary [see (12)]. In this case the Hartree diagrams similar to those shown in (55) but with a Coulomb line in place of a phonon line, are cancelled out by complex conjugation. What are left are diagrams of the type of the electron self-energy, which contain an internal Coulomb line. This line has in the long-wave limit a small factor that is inversely proportional to the dielectric constant. In semimetals the latter is of the order of 10^2. To consider the contribution of short distances, we replace the Coulomb interaction by point interaction. In this case we verify again that the complex-conjugate diagrams cancel out. The Coulomb interaction is thus suppressed under the given conditions.

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