L. A. Fal'kovskiĭ. *The origin of electron spectra of group V semimetals.* It is well known that the lattice of group V semimetals can be obtained from a simple cubic lattice by a small shift of atoms. This fact was already used[1] for the calculation of the carrier spectrum in bismuth, in which carriers occupy the small neighborhoods around the symmetical points of a Brillouin zone.

Here we suggest to consider group IV–VI semiconductors[2] and group V semimetals[3] within the framework of a single theory that makes it possible to determine the electron structure throughout the entire Brillouin zone and to calculate various other properties. The substance of the method can be presented in the following way. Of the five valence electrons in group V metals, two are in the deep s-states, and three are in the p-states with higher energy. The overlapping of nearest neighbor wave functions transforms these p-states into energy bands of the following type

$$\xi = \xi_0 \cos k_x a + \xi_1 (\cos k_y a + \cos k_z a), \qquad (1)$$

where $\xi_0 \approx 3.5$ eV, $\xi_1 \approx -1.1$ eV, and a is the period of a simple cube. Two other bands can be obtained from this expression by cyclical permutation of the indices $x \to y \to z$. It is important that the hybridization of these three bands occurs only as a result of the overlapping of wave functions of more distant neighbors and is described by energies of the order of $\eta \approx 0.2$ eV. Thus the p-bands turn out to be quasi-one-dimensional. If one takes into account that three valence p-electrons can fill these bands only half-way, one can see that the state under consideration is unstable to such small atomic shifts for which a Brillouin zone decreases by a factor of 2 and becomes completely filled. The so-called Peierls transition with period-doubling will occur. In semimetals such transitions actually happen as the result of a small shift u of alternating atomic layers in the direction perpendicular to the third order axis C_3. In IV–VI group semiconductors the role of the shift is played by a chemical difference between metal and chalcogenide atoms that stabilizes the cubic lattice. A factor that, together with hybridization of η, prevents the Peierls transition from occurring is the spin-orbital interaction Δ which is greatest for heavy atoms. For example, for bismuth the intensity of this interaction is characterized, according to atomic calculations, by the value $\Delta/3 = 0.53$ eV, and for its neighbor in the periodic table, polonium, the only metal in nature with a simple cubic lattice, by

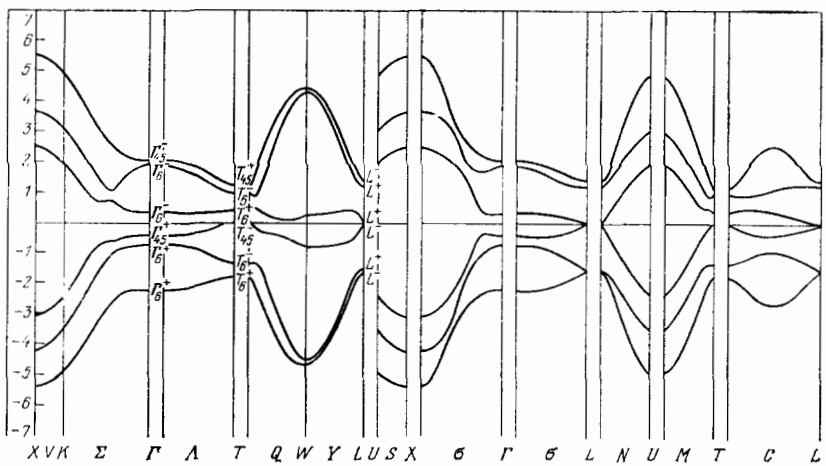

FIG. 1. Energy band structure of bismuth.

TABLE I. Carrier parameters in bismuth.

Carriers		Experiment	Theoretical results		
			[4]	[5]	[6]
Holes	m_3	0,0639±0,0003	0,0655	0,17	0,10
	$m_{1,2}$	0,212±0,0005	0,225	0,65	0,38
	S_3	6,76±0,01	6,42	18,4	7,66
	$S_{1,2}$	22,49±0,02	22,05	65,2	28,9
	γ	1,87 or 2,13	1,74	1,9	—
	ε_F	11,5	10,7	11,6	8
Electrons	m_x	0,119±0,0005	0,115	0,11	0,161
	m_y	0,088±0,002	0,100	0,091	0,148
	m_z	0,0082±0,00005	0,0087	0,018	0,015
	S_x	19,23±0,05	16,76	17,29	18,0
	S_y	14,48±0,04	14,79	14,6	14,4
	S_z	1,300±0,003	1,33	2,88	1,27
	θ	96,38	96,74	100	98,2
	ε_g	11,2	11,4	5,4	16

The values of the cyclotron masses m are given in units of m_0; the measurement units for the sections S are 10^{-42} g^{2}cm^2/s^2, for the Fermi-energy ε_F measured from the extremum, and for the forbidden energy gap ε_g they are meV; for the angle θ between the C_3 axis and the normal to the minimal cross-section they are deg.

$\Delta/3 = 0.7$ eV. It is not surprising that the shift u, as it turned out, has in semimetals a value $u \lesssim 0.5$ eV in energy units.

Together with the shift one must also take into account a rhombohedral deformation that accompanies a Peierls transition. By calculating the electron contribution to the total energy and minimizing it, it is possible to find that the value of the deformation tensor ε_{ij} is related to the shift vector: $\varepsilon_{ij} \sim u_i u_j \ln(\xi_0/u)$. This estimate is in agreement with crystallographic data, and in energy units gives $\varepsilon_{xy}\xi_0 \approx 0.15$ eV.

In order to determine precise values of the spectrum parameters that were estimated above, the following measured and calculated characteristics of carriers were compared: cyclotron masses, extremal sections of the Fermi-surface and the spin splitting factor γ (the ratio of the spin-splitting of energy levels in a magnetic field to cyclotron splitting).

In the case of bismuth it is known that holes and electrons occupy small neighborhoods of the points T and L in a Brillouin zone. For this reason, in general theoretical formulas a quadratic expansion near the extremum was utilized for holes, and a closely located valence band was taken into consideration for electrons. After thus determining the parameters that enter the theory, we have constructed[4] electron dispersion curves for a number of symmetric directions (Fig. 1). The degree of agreement between the measured and calculated characteristics of carriers can be seen from Table I. Moreover, the values of direct gaps between different energy bands in Fig. 1 also agree with the results of optical measurements. Let us also note that the parameters that characterize the cubic paraphase, such as ξ_0, ξ and η, turned out to be close to their values in Group IV–VI semiconductors, and the spin-orbital constant was simply taken from atomic spectra. Table I gives also the results of pseudopotential calculations.[5,6] Poor agreement with the data for holes is noticeable. One should keep in mind that the pseudopotential calculations require a large amount of computer time and that they do not lead to analytical results.

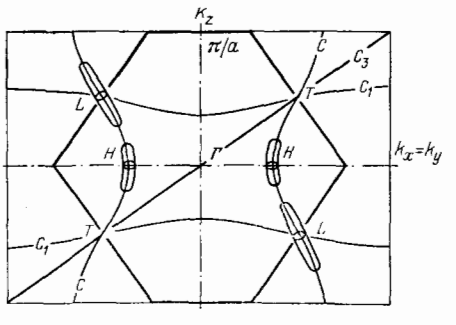

FIG. 2. σ-plane. The hexagon represents the Brillouin zone (BZ) of antimony, the deformed rectangle—BZ of the cubic "parent phase"; the "ellipsoids" represent the Fermi-surfaces of electrons and holes.

In the case of arsenic and antimony the situation is more complicated. Although the electrons in this case occupy, as in bismuth, the neighborhood of the point L, the maximum size of their Fermi-surface is comparable with the size of the Brillouin zone itself. As for the holes, it is only known that their extremum lies at a point of common position that belongs to the symmetry plane σ. For this reason, it is necessary to study in greater detail the Fermi-surface of the cubic paraphase in order to establish the location of holes. As can be seen from (1), this Fermi-surface (it corresponds to $\xi = 0$, while $\xi_0 \gg |\xi_1|$) consists of three slightly corrugated planes which, roughly speaking, are parallel to the faces of a simple cube. These planes intersect the diagonal plane σ along the curves c and c_1 shown in Fig. 2. The energy is constant along the curves in a simple cube and starts changing at a rate proportional to u only after the Peierls transition. In the direction perpendicular to any of these curves, the rate of the energy change is of the order of ξ_0, i.e., is rather large. For this reason the isoenergetic surface in a semimetal must be elongated in the direction of the discussed curves. From experiments it is known, for example, that for antimony the angle between the direction of Fermi-surface elongation and the C_3 axis is 53.0° for holes and 87.7°

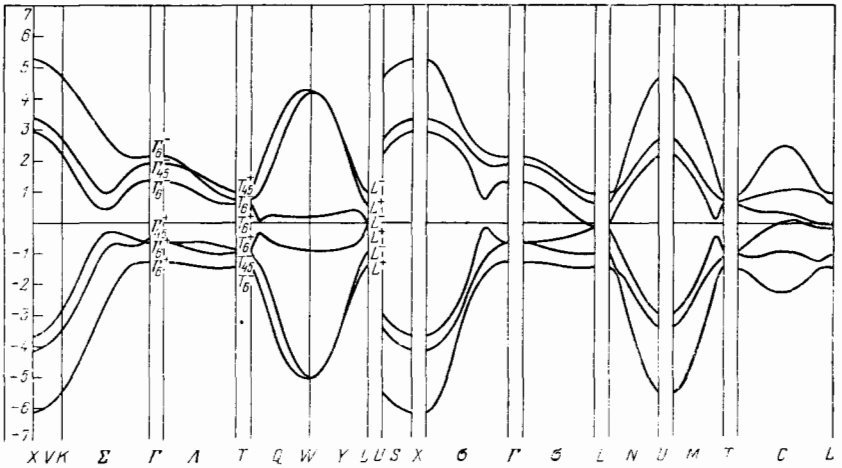

FIG. 3. Energy band structure of antimony.

for electrons. Calculating with the help of (1) the angle between the curve c and the C_3 axis, we can find that the angle θ_H is arccos $(1/\sqrt{3}) = 54.7°$ at the point $H(k_z = 0)$ and $\theta_L = 54.7° - \text{arctg}[\sqrt{2}\xi_1/(\xi_0 + \xi_1)] = 86.6°$ at the point $L(k_z = -\pi/2a)$. In this way, our attention is drawn to the curve c. Taking into account that the size of the Fermi surface in the direction perpendicular to the curve c is 1/10 of the size of the Brillouin zone, simple analytical expressions for cyclotron masses and extremal sections were obtained.[7] By comparing these expressions with experimental data, it was possible to find theoretical parameters for antimony, and then to calculate the electron structure in symmetric directions (Fig. 3). The most significant difference between the bismuth and antimony spectra is evident in the extreme right sides of Figs. 1 and 3, which show the dispersion along the curve c along the path from L to T. It can be seen that in making the transition from bismuth to antimony the hole extremum shifts from T towards L in such a way that the electron and hole valleys become separated in k-space by a rather narrow barrier.

The proposed method allows one to study different phenomena in semimetals: the probabilities and frequencies of optical transitions,[4] specifics of the phonon spectra,[3] dielectric[8] and magnetic susceptibilities, dopant and surface states.

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