Variation of the electronic structure of Sb with pressure in the pseudopotential method

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The electronic structure of Sb and its variation as a result of different lattice deformations were calculated on the computer. An improvement of the accuracy of calculation of the energies of the terms up to $\sim 10^{-5}$ hartree and of the cross-sectional areas of the isoenergetic surfaces up to $\sim 1\%$ produced essentially a good agreement between the calculated variation with pressure of the electronic structure of Sb and the experiment. The main results of the calculations, their comparison with the experiment, and discussion are present.

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The semimetals of the Bi group (As, Sb, Bi) have attracted attention for a long time, especially after the work of Abrikosov and Fal'kovskiĭ,[1] who attempted to construct from first principles their electronic structure on the basis of their identical crystal lattices (which differ slightly from the cubic lattices). This approach was successful for Bi; however, for As and Sb, which have large concentrations of the current carriers, this method did not produce experimentally satisfactory spectrum. A number of other studies (see, for example, Ref. 2) with essentially a similar goal of constructing the electronic spectrum of these semimetals on the basis of the "small letter parameter" was conducted. It should not be ruled out, however, that the electronic structure of these semimetals is determined by "small numerical parameters." Therefore, the results of a numerical calculation of their electronic structure are of particular interest. This approach, however, caused some difficulties. If the electronic structures of Sb and As can be accurately described by the Falikov-Lin[3,4] pseudopotentials (PP) at a normal pressure, then Falikov's[5] determination of the dependence of the electronic structure of the Bi group on the hydrostatic pressure (HP) will bring all three semimetals to the semiconducting state under the influence of HP, which, as it turned out, cannot be confirmed experimentally. In the experiment of Brandt *et al.*,[6] which was confirmed by a number of subsequent experiments (see, for example, Ref. 7) it was shown that such behavior of the electronic structure is valid for As and Bi but not for Sb, in which the concentration of the current carriers $N(p)$ increases with HP. Thus, the pseudopotential approach for Sb (Ref. 3) was discredited for the most part.

In this paper we show that the discrepancy between the experiment and the calculation does not follow from the pseudopotential.[3] If the lattice deformation and the electronic structure of Sb are calculated more precisely (this is apparently particularly important for semimetals whose existence is due to a certain "smallness"), then the pseudopotential,[3] without any fitting of the parameters, increases $N(p)$ with hydrostatic pressure, in agreement with experiment.

We briefly summarize the calculation technique. The Fourier transform $v(q)$ of

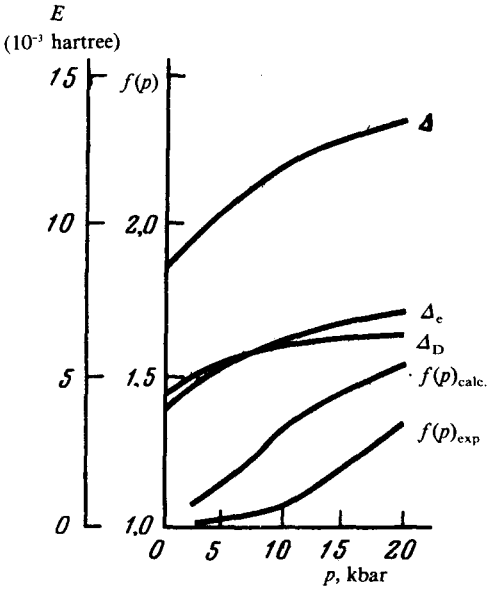

FIG. 1.

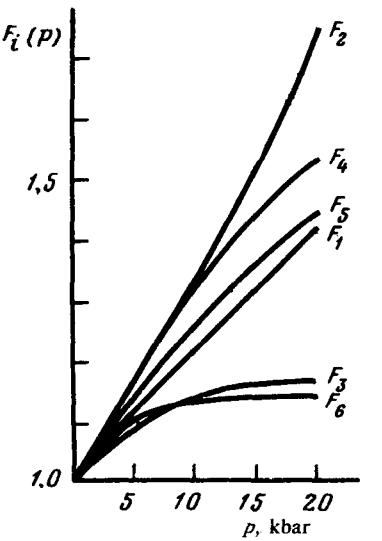

FIG. 2.

the pseudopotential[13] descreases rapidly according to the modulus with increasing wave vector **q**. Therefore, the problem of determining the electronic structure with any accuracy can be correctly formulated in terms of this pseudopotential by diagonalizing on the computer the finite secular matrices $n \times n$. Since, for comparison with experiment,[8,9] the cross-sectional areas of the isoenergetic surfaces must be calculated with an accuracy of several percent, we can easily see ($dS \sim m_c^* dE$) that the error in calculating the energies must be $dE \sim (10^{-4} - 10^{-5})$ hartree.[1] According to the calculations, the matrices of order 100×100 should give this accuracy. This was confirmed by an analysis of the convergence as a function of n (up to the 130×130 matrices). It is much more difficult (for the given accuracy of calculation) to calculate in a reasonable time on the computer the cross sections of the isoenergetic surfaces, the volume of the **q** space occupied by the current carriers, and the Fermi level (from the condition of electroneutrality). To solve these problems, we developed algorithms for direct methods of constructing isoenergetic contours, giving particular attention to their optimization.[2]

We give the most important physical results obtained by us.

Figure 1 shows the dependence on hydrostatic pressure of the function $f(p) = N(p)/N(0)$, of the Δ overlap of the valence and the conduction bands, Δ_D and Δ_E "partial" chemical potentials (i.e., the distance between the Fermi level and the absolute extrema of the fifth and sixth bands), and $f(p)_{exp}$ from Refs. 6 and 8.

Figure 2 shows the dependences of all the main extremal cross sections of the Fermi surface (FS) on hydrostatic pressure. The cross sections are numbered in a sequential order: first the holes, then the electrons S_{min}, S_{max}, S_{bin}; $F_i(p) = S_i(p)/S_i(0)$.

At $p \approx 3$ kbars, we observed a transition in symmetry of the T_6 and T_7 terms (the

TABLE I.

	η_1	η_2	η_3	η_4
Calculation	− 8	− 4	− 7	16
Experimental data (Ref. 9)	− 5.5	− 4	− 6.5	12

sixth and seventh levels at the T center of the hexagonal face of the Brillouin zone near which the holes are located.

For a flat loading (experiment of Ref. 9): as a result of stretching along the binary axis C_2 and along the bisectrix axis C_1, the variation of the Fermi surface is reduced to redistribution of the current carriers between the nonequivalent valleys that result from these loads without changing (within the limits of accuracy of the calculation) the total concentration of the current carriers. The variation, in percent, of the four main cross sections of the Fermi surface (for which experimental data are available[9]) as a result of stretching with a force $F = 13.5$ kg directed along C_2 is given in Table I; $\eta_i = 100\ \Delta S_i/S_i(0)$, the cross sections are given in the same order as above and the holes are represented by a decreasing "ellipsoid" and the electrons by an increasing "ellipsoid."

We compared the data in Fig. 2 with the experiment.[8] Brandt *et al.*[8] determined that the cross sections S_2 and S_3 increase monotonically with pressure, the cross section S_1 initially decreases and then increases, passing through the minimum near $p = 3$ kbars, and the cross section S_4 decreases monotonically (up to the limiting measured pressure of $p \approx 14$ kbars). Although final data on the other two main electronic cross sections are not available, it was noted in Ref. 8 that if these cross sections increase, the increase will be too insignificant for the compensated sample.

The hole cross sections apparently are determined by the spin-orbit interaction, which is not taken into account in the pseudopotential.[3] At $p \approx 3$ kbars, the variation in the symmetry of the terms at point T undoubtebly will change the spin-orbit interaction between the fifth and sixth terms, which can lead to a nonmonotonic variation with pressure of the maximum of the fifth band, which, in turn, will influence to the largest extent the variation of S_1 with pressure. This can explain also the slower initial increase of the $f(p)_{\text{exp}}$ function compared with $f(p)_{\text{calc}}$.

As for the electronic cross sections, they have yet to be explained experimentally and theoretically. It is conceivable, for example, that the electronic ellipsoid acquires the shape of a strongly compressed cigar at the center, but then an additional oscillation period connected with the noncentral extreme cross section will be observed in the experiment. As the calculation shows, the terms are bunched near the minimum of the sixth band and the spin-orbit interaction gives a large correction, but it is difficult to draw a definite conclusion without calculating precisely the effect of the spin-orbit interaction on this group of levels. In the light of the above discussion, it is clear that for the physics of semimetals it is important to determine the pressure dependence of the electronic part of the Fermi surface of Sb, for which new, carefully conducted

TABLE II.

	$(m_c)_1$	$(m_c)_2$	$(m_c)_3$	$(m_c)_4$	$(m_c)_5$	$(m_c)_6$
Experimental data (Ref. 10)	− 0.069	− 0.18	− 0.215	0.084	0.325	0.32
Calculation (Ref. 3)	-	-	~−0.3	-	-	~0.2
Present calculations	− 0.064	− 0.22	− 0.23	0.086	0.32	0.30

experiments and calculation of the effect of the spin-orbit interaction on the electronic structure of Sb are highly desirable.

We note that the computational methods developed by us gave a better agreement of the calculated characteristics of the Fermi surface of Sb at a normal pressure with the experiment. Table 2 gives the effective cyclotron masses of the current carriers.

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[1)]The errors in calculating the energies of the terms in Ref. 3 are $\sim 10^{-3}$ hartree.
[2)]The corresponding algorithms will be published.

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