Variation of the electronic spectrum of As with pressure up to 120 kbar

Yu. A. Pospelov and G. S. Grachev

Sergo Ordzhonikidze Moscow Control Institute

The variation of the electronic spectrum (ES) and As due to the action of pressure is calculated. The overlap of the valence band and of the conduction band varies nonmonotonically and has a minimum at $p \sim 40$ kbar. The influence of pressure on the ES of all semimetals of the Bi group is compared with the experiment.

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It is known that the semimetals of the Bi group (Bi, Sb, and As) at a pressure $p = 1$ bar have isostructural crystal lattices (D_{3d} point group), and under the influence of hydrostatic pressure their lattices approach a cubic lattice, so that the rhombohedral deformation of the lattices is reduced. On the basis of the small rhombohedral deformation of the lattices of the Bi group, an attempt was made[1] to construct a model of the ES of these semimetals. This approach was successful for Bi, but for Sb and As,

which have large charge-carrier densities, it did not give an adequate empirical picture of the ES. The semimetallic nature of the ES of crystals of the Bi group was substantiated by qualitative crystallo-chemical analyses in Ref. 2, and an identical behavior was predicted in Ref. 3 for their ES due to the action of hydrostatic pressure.

It became clear,[4] however, that the relation of the ES of these semimetals to their crystal lattices is much more complicated. It was shown in Ref. 4 that the changes of the ES of the semimetals of the Bi group due to the action of hydrostatic pressure (up to pressures $p \sim 30$ kbar) are not charaterized by the predicted "parallelism," i. e., the charge carrier density $N(p)$ in Bi and As decreases with pressure, while it increases in Sb.

Using the computational methods developed previously,[5] we calculated the variation of overlap of the valence band and of the conduction band $\Delta(p)$ for As, $\Delta = \max_{k}$ $\{E_5(\mathbf{k})\} - \min_{k}\{E_6(\mathbf{k})\}$, due to the action of a hydrostatic pressure up to 120 kbar. After the computational methods[5] had been successfully applied to calculations of the ES of Sb,[7] it was reasonable to calculate the variation of the As ES due to pressure. Interest in this was especially high since the curious fact of nonmonotic variation of the charge-carrier density in As with pressure had recently been discovered.[8]

The Bi-type lattice (see Fig. 1) can be defined by specifying three numbers: the edge a of the rhombohedron, the angle α between the basis vectors of the lattice, and the parameter s, so that the distance between the two atoms in the unit cell along the C_3 axis (CC' in Fig. 1) is equal to the fraction $2s$ ($s < 0.25$) of the body diagonal of the rhombohedron. We obtain for the distances R_1 to the nearest neighbor and R_2 to the next nearest neighbor

$$R_1 = (2a/\sqrt{3})[\sin^2 \alpha/2 + (3S - 1/2)^2 (1 + 2\cos\alpha)]^{1/2}, \tag{1}$$

$$R_2 = (2a/\sqrt{3})[\sin^2 \alpha/2 + (3s - 1)^2 (1 + 2\cos\alpha)]^{1/2}. \tag{2}$$

For $s = 0.25$ $R_1 = R_2$. As retains the rhombohedral structure up to pressures $p \sim 140$ kbar. In the calculations we used McWhan's data[9] for the parameters a and α for different values of the bulk modulus $\Delta V/V$, Bridgman's data[10] for the relationship

FIG. 1

$$\begin{array}{l} N\,(p)\,/\,N\,(0)-1 \\ \varDelta\,(p)\,/\,\varDelta\,(0)-2 \end{array}$$

1,4

1,2

1,0

0,8
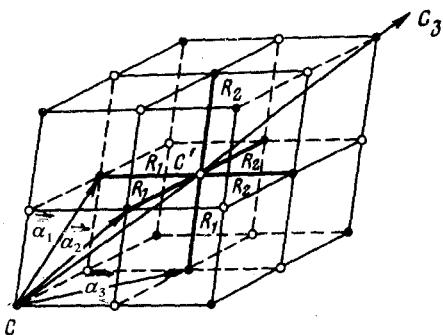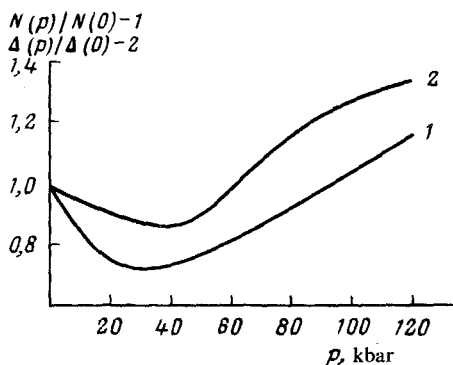
20 40 60 80 100 120

p, kbar

FIG. 2

between $\varDelta V/V$ and p for As, and x-ray diffraction data[11] for the initial (up to $p \sim 3$ kbar) variation of the parameter s with pressure.

The pseudopotential parameters, taken from Ref. 6, were assumed to be constant, except for the scale parameter A_1, which varied in such a way[6] that its product with the atomic volume remained constant. For $p = 1$ bar and $T = 4.2$ K the parameters were as follows (the atomic system of units is used throughout this paper):

$$A_1 = 0.0883, \quad A_2 = 2.68, \; A_3 = 2.53, \; A_4 = 3.4.$$

Figure 2 depicts the dependence $\varDelta\,(p)/\varDelta\,(0)$, calculated by us for As, as well as the dependence $N\,(p)/N\,(0)$ obtained in Ref. 8. A comparison of the curves basically shows that they both have a minimum. The curves do not coincide on the Y axis, because N is not directly proportional to $\varDelta$ and is not determined by the overlap alone. The fact that the minima do not coincide on the X axis is apparently due to imprecise information about the variation of a, α, and s with pressure. The data for a and α in Ref. 9 have a large spread; an even larger error is probably due to the linear[11] $s = s(p)$ dependence used in the calculations. As our calculations of the Sb ES showed,[12] the linear dependence of s on p in the Sb case can be used to a pressure $p \sim 30$ kbar, and with a closer approach to the phase transition in SB ($p \sim 70$ kbar) the calculation of its ES becomes very sensitive to small variations of the lattice parameters. The bend on the calculated $\varDelta\,(p)/\varDelta\,(0)$ dependence is apparently due to the imprecise s values for As at $p > 70$ kbar.

What can be the physical cause of the nonmonotonic behavior of the $\varDelta = \varDelta\,(p)$ dependence? As noted elsewhere,[12] the quantity R_1 varies anomalously with pressure in As: the distance between the nearest neighbors in As increases with pressure because of an increase of the angle α and of s (Fig. 1) up to a pressure $p \sim 40$ kbar. We can see a bend on the dependence $\alpha = \alpha(\varDelta V/V)$ in Ref. 9 in the region $\varDelta V/V \sim (0.05-0.06)$, which corresponds to a pressure $p \sim (30-40)$ kbar, beyond which the rate of increase of the angle α decreases with pressure; this also stops the increase of R_1 with pressure. In many discussions of the variation of the ES of semimetals of the Bi group with hydrostatic pressure reasons were given for a possible correlation between this variation with pressure and that of the parameter s (which is determined from the intensity of x-ray lines, which is more difficult to measure in the experiments). These considerations, in

TABLE I.

	p, kbar	T, K	R_1, at. units	R_2, at. units
As	10^{-3}	78	4,7559	5,8580
	10^{-3}	4,2	4,7562	5,8508
	10	4,2	4,7733	5,7033
Sb	10^{-3}	78	5,4876	6,3201
	10^{-3}	4,2	5,4854	6,3178
	10	4,2	5,4690	6,2240
Bi	10^{-3}	78	5,7871	6,6424
	10^{-3}	4,2	5,7881	6,6378
	10	4,2	5,7962	6,4880

the words of the authors, stimulated the measurements[11] of the $s = s(p)$ dependences for the Bi group. But it turned out that the initial variation of the parameter s with pressure is identical for the entire group; it increases due to the action of hydrostatic pressure. An unusual $s = s(p)$ dependence was suggested[8] for As at high pressures, which can also cause a nonmonotonic $N = N(p)$ dependence. However, the variations of the lattice parameters are important. This also increases the distance between the nearest atoms in the As lattice due to the action of hydrostatic pressure (up to $p \sim 40$ kbar). It is physically clear, however, that the variation $R_1 = R_1(p)$ is much more important than the $s = s(p)$ dependence for the variation of the crystal properties with pressure.[1]

It is curious that the distance R_1 increases due to the action of the hydrostatic pressure for Bi (although a comparison of its ES with the ES of As and Sb is obscured by the large spin-orbital interaction). Table I gives the $R_1(p)$ and $R_2(p)$ dependences calculated from Eqs. (1) and (2) by using the data of Refs. 11 and 13, and also the variations of R_1 and R_2 in the 78–4.2 K temperature interval, in which the most precise measurements of the lattice parameters exist for the entire group of Bi-type semimetals.[13]

Thus, we can see a direct relationship between the $R_1 = R_1(p)$ dependences for the crystal lattices of the Bi group of semimetals and the variation of their ES due to the action of pressure. This relationship is most clearly evident in the pressure dependence of the As ES, which produces the nonmonotonic curve in Fig. 2. Beyond $p \sim 40$ kbar, apparently, no new charge-carrier regions appear in As (this was hypothesized in Ref. 8), but the variation of the volumes of the charge-carrier "packets" in As occurs nonmonotonically with pressure. At $p \lesssim 40$ kbar these volumes decrease with pressure, which is analogous to the Bi case; at $p \gtrsim 40$ kbar they increase with pressure, which is analogous to the Sb case.

[1]We are dealing, of course, with the change in the parameters at some distance from the structural transitions.

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