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Fig. 1

Figure 1: Fig. 1

Abstract

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THE EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF BISMUTH TELLURIDE

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The study of layered crystals at high pressures is an important problem. The crystal lattices of the intermetallic compounds Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3 are layered in character, and their investigation over a wide pressure range up to 100 kbar may be expected to yield interesting results. The fact that these compounds are semiconductors with a comparatively small forbidden-band width E_g ([1]) makes it possible to use, for their investigation, the method most accessible in the region of such high pressures—measurement of electrical resistance.

In the present article the results of a study of bismuth telluride are presented.

On the basis of the data of Chi, Yu-li, Ruoff, and Spencer, who measured the effect of hydrostatic pressure up to 30 kbar on the value of E_g for n-type Bi_2Te_3 ([2]) (E_g decreases from 0.171 to 0.104 eV), it may be assumed that at pressures approximately twice as high Bi_2Te_3 should undergo a transition to the metallic state. On the other hand, a significant decrease in the interlayer distance under pressure, by analogy with layered lattices of the graphite type, may lead to a polymorphic transition and to the appearance of a noticeable amount of a new phase after removal of the pressure.

Fig. 1. Effect of hydrostatic pressure on the electrical resistance of Bi_2Te_3 at room temperature.
a, —I sample of p-type; , —II sample of p-type; , —sample of n-type; a, , —direct run; , , —reverse run.

We used a high-pressure chamber designed by L. F. Vereshchagin and co-workers, which makes it possible to obtain a quasihydrostatic pressure of 200,000 kg/cm^2 ([3]). Catlinite was used as the pressure-transmitting medium; in the appropriate cavity of it the specimen was placed, compacted with a mixture of kaolin and water glass. To determine the temperature dependence of the resistance at

Fig. 2

Figure 2: Fig. 2

various pressures, a graphite heater placed inside the high-pressure chamber was used.

Single-crystal samples of p- and n-type Bi_2Te_3 had the form of plates parallel to the basal plane, of size 4×2 mm and thickness from 0.1 to 0.3 mm. The current was passed through the sample by means of two copper ribbons introduced into the high-pressure chamber and mechanically pressed against the plane of the sample at its ends. Immediately outside the chamber the electrode was divided into current and potential leads. The resistance of the electrode without the sample–

was measured up to 90 kbar and proved to be approximately two orders of magnitude lower than the minimum value of the sample resistance. Temperature measurements were carried out only up to 40°; at higher temperatures it was not possible to obtain stable values of the electrical resistance–it changed with time without a tendency toward saturation. We believe that this is associated with an increase in the plasticity of the sample, under which quasihydrostatic conditions are no longer sufficient. Calibration of the chamber for pressure was carried out from the jumps in the electrical resistance of Bi, Tl, Ba ([4]). Temperature calibration was carried out using a copper-constantan thermocouple introduced through the electrical lead into the high-pressure chamber. The dependence of the temperature at the center of the chamber on the power supplied to the heater was measured. The calibration was performed at various pressures up to 90 kbar; no systematic dependence on pressure was observed.

For measuring the temperature dependence of the resistance under hydrostatic pressure, a fixed-pressure steel bomb, described in ([5]), was used. After pressure fixation, the bomb was placed in an oil thermostat, where resistance measurements were carried out. The temperature was determined from the readings of a copper-constantan thermocouple pressed against the bomb. The Bi_2Te_3 samples used were only longer than the preceding ones (length 10 mm); current and potential leads were soldered to the ends of the plates.

Fig. 2. Dependence of the electrical resistance of Bi_2Te_3 on temperature at various constant hydrostatic pressures. **1, 2, 3** –sample I of p-type at pressures respectively atmospheric, 5870 and 10365 bar; **4, 5, 6** –sample II of p-type at pressures respectively atmospheric, 8340 and 11150 bar; **7, 8, 9** –n-type sample at pressures respectively atmospheric, 8290 and 11650 bar.

Figure 1 presents the results of measurements of the electrical resistance of two Bi_2Te_3 samples of p-type and one sample of n-type as a function of pressure between 1 and 15,000 bar, carried out under hydrostatic conditions. The results for all samples practically coincide. The mean piezoresistance coefficient for this pressure region is

Fig. 3. Dependence of the electrical resistance of Bi2Te3 on quasi-hydrostatic pressure in the range 20–95 kbar at room temperature.

Figure 3: Fig. 3. Dependence of the electrical resistance of Bi2Te3 on quasi-hydrostatic pressure in the range 20–95 kbar at room temperature.

$$\frac{1}{R}\frac{\partial R}{\partial p} = -3.5 \cdot 10^{-5} \text{ bar}^{-1}.$$

Figure 2 shows the temperature dependences of the resistance of these same samples at several fixed pressures in the range 20–80°.

Figure 3 gives the results of measurements of the dependence of the electrical resistance of 7 Bi_2Te_3 samples of p-type and 2 samples of n-type on quasihydrostatic pressure. Qualitatively the curves resemble one another. Three regions can be distinguished on the plotted curves. In the first region, at initial pressures, there is a steep drop in resistance with increasing pressure. The temperature dependence of the resistance for p-type samples, which was determined between 10–40° at each pressure point, has a semiconducting character in this region. The vertical line on the curves for samples **1, 1a, 2, 3, 7** in Fig. 3 separates the semiconducting region-

temperature dependence of the resistance to the region of "metallic" dependence. The latter corresponds to a qualitatively different character of the dependence $R(p)$ in Fig. 3. In samples 4, 5, and 6 the semiconducting character of the resistance was retained over the entire range of measurements; in the horizontal part of the curves, as a rule, the same form of the dependence $R(T)$ is preserved as in the preceding pressure interval. All the curves in Fig. 3 begin at a pressure of 20 kbar, since in the pressure-generation method used quasi-hydrostatic conditions set in approximately in this region. At pressures below 20 kbar the sample undergoes considerable deformation, and therefore separate measurements at low pressures were carried out. For n-type samples, a metallic character of the conductivity was observed over the entire pressure range.

Fig. 3. Dependence of the electrical resistance of Bi_2Te_3 on quasi-hydrostatic pressure in the region 20–95 kbar at room temperature. 1–7—p-type samples; 8, 9—n-type samples. Samples 1 and 2 were cut from one single crystal; samples 3, 4, 5, 6, 7—from another. All curves were obtained while increasing the pressure, except 1a, measured while decreasing the pressure.

From the temperature dependence of the electrical resistivity, the band-gap values E_g were calculated for p-type Bi_2Te_3 samples in the region of semiconducting conductivity. Our n-type samples, in measurements below 40°, are not yet in the region of intrinsic conductivity, and therefore it is impossible to calculate E_g.

Figure 4 shows the obtained values of E_g. All series of points above 25 kbar

Fig. 4. Effect of pressure on E_g for p-type Bi_2Te_3.

Figure 4: Fig. 4. Effect of pressure on E_g for p-type Bi_2Te_3.

show a sharp decrease of E_g with increasing pressure. The values of E_g for samples 1 and 3 lie along one curve, which ends at $E_g < 0.01$ eV. The higher absolute values of E_g for samples 2, 4, and 7, as well as the maxima obtained for them and for sample 1 in the dependence $E_g(p)$ below 25 kbar, are difficult to explain. It is possible that they are caused by tensile stresses of the samples during the initial deformation in measurements by the quasi-hydrostatic method. E_g, calculated from measurements under hydrostatic conditions, does not show the increase with pressure that occurs in the curves with a maximum. The real dependence $E_g(p)$, apparently, may be represented by the solid curve in Fig. 4. Above 25 kbar the average value is $\partial E_g/\partial p = -6 \cdot 10^{-6}$ eV/bar. At a pressure of 40-45 kbar, E_g becomes zero; evidently, Bi_2Te_3 passes into the metallic state, and the change at the indicated pressure in the character of the dependence $R(p)$ (Fig. 3) and in the signs of $\partial R/\partial T$ corresponds to this transition. Below the transition pressure, the average value of the piezoresistance coefficient is

$$\frac{1}{R}\frac{\partial R}{\partial p} = 0.4 \cdot 10^{-5} \text{ bar}^{-1},$$

which corresponds to the value usually observed in metals. The difference in the transition pressures for different samples and the quantitative difference in the curves $R(p)$ (Fig. 3) are evidently also caused by tensile stresses. As for $E_g(p)$, one may consider curve 1 in Fig. 3 closest to the truth. The transition to the metallic state, as curve 1a in Fig. 3 shows, is reversible. At temperatures 40-50° in Bi_2Te_3, despite

because of its layered structure, no appreciable amount of the metastable metallic high-pressure phase is obtained. This fact is indicated by Debyegrams taken by us from some samples that had remained for several tens of hours at pressures up to 100 kbar. Nevertheless, it is apparently precisely the layered structure of Bi_2Te_3 that leads to a gradual transition to the metallic state as a result of a monotonic decrease in the interlayer distance.

Fig. 4. Effect of pressure on E_g for p-type Bi_2Te_3. The numbers on the curves correspond to the samples in Fig. 3. a—measurements by the hydrostatic method; b—(dash-dotted curve)—data of ([2]).

The authors intend in the near future to consider this transition in greater detail. We also still find it difficult to explain whether the horizontal section of the $R(p)$ curves in Fig. 3 has independent significance, and the absence of metallic conductivity in $R(T)$ for some samples, although the latter may be attributed to an incomplete transition of the sample into the new state.

In conclusion, the authors consider it their pleasant duty to express their grati-

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REFERENCES

1. J. Black, E. W. Conwell, L. Seigle, C. W. Spencer, J. Phys. Chem. Solids, **2**, 240 (1957).

2. CheJu-Li, A. L. Ruof, C. W. Spencer, J. Appl. Phys., **32**, No. 9, 1733 (1961).

3. L. F. Vereshchagin, A. A. Semerchan et al., DAN, **136**, No. 2, 320 (1961).

4. G. C. Kennedy, P. N. La Mori, *Progress in Very High Pressure Research*, N. Y.—London, 1961, p. 304.

5. E. S. Itskevich. *Pribory i tekhn. eksp.*, No. 4 (1963).

Note: Figure translations are in progress. See original paper for figures.