THE HEAT CAPACITY OF BISMUTH TELLURIDE AT LOW TEMPERATURES

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The heat capacity of p-type Bi_2Te_3 was measured between 1.37 and 65°K. At temperatures below 2.5°K the heat capacity can be described by a linear term with $\gamma = 17 \times 10^{-5}$ joule-deg^{-2} (g-atom)$^{-1}$ and a cubic term with $\Theta_0 = 155.5$°K. Between 2.5 and 8°K the heat capacity is proportional to a power of the temperature greater than three. The heat capacity of the laminar Bi_2Te_3 lattice is not consistent with the calculations performed for lattices with a larger difference between the elastic moduli in the layer and between the layers. Data are presented on measurements of the Hall effect and resistivity of Bi_2Te_3 at a number of temperatures between 2° and 300°K. The linear term of the heat capacity is ascribed to holes. The hole mass is estimated as $1.46 m_0$.

INTRODUCTION

THE intermetallic compounds Bi_2Te_3, Bi_2Se_3 and Sb_2Te_3 are semiconductors with lattices which have strong layer characteristics. This property makes a study of their heat capacity especially interesting

An investigation of the heat capacity of cadmium halides at low temperatures[1] showed that its temperature dependence for these layer lattices is considerably different from that characteristic of less anisotropic structures. The attempt at a quantitative comparison with theory was unsuccessful because the anisotropy of CdI_2, $CdBr_2$, and $CdCl_2$ is not as great as the theory requires.[2,3]* In addition, a temperature range was found for all three salts in which the heat capacity varied with temperature according to a power greater than three. This was ascribed to the effect of soft optical branch modes, corresponding to inter-layer interactions.

In the last 3 or 4 years Bi_2Te_3 has become a much studied substance.[4-9] However, there are only the data of Gul'tyaev and Petrov[10] on the heat capacity in the temperature region attainable with liquid nitrogen. We have undertaken a study of bismuth telluride to widen the investigation of the heat capacity of layer lattices.

1. THE COMPOUND AND METHOD OF MEASUREMENT

Bismuth telluride has a typical layer lattice, which consists of five-chain layers, with the monatomic networks alternating in the order Te-Bi-Te-Bi-Te. The bonding between such layers is produced by van der Waals forces. Within the weakly bound layers the atoms are held considerably more strongly by covalent (with an ionic component) forces.[11-13]

The Semiconductor Institute of the Academy of Sciences kindly prepared the p-type Bi_2Te_3 for us. The alloy was recrystallized twice to increase the purity and was not analyzed for purity. A cylinder consisting of large crystals was cast from this material and pieces were cleaved from the top and bottom for measurements of resistivity, thermal emf and Hall constant. These measurements, made at room temperature in the Semiconductor Institute, gave the following results: for the upper part of the casting the conductivity $\sigma = 470\ \Omega^{-1}\,cm^{-1}$, thermal emf $\alpha = 37.7\ \mu v/deg$ and Hall constant $R = 0.965\ cm^3/coul$; for the lower part $\sigma = 173\ \Omega^{-1}\,cm^{-1}$, $\alpha = 30.5\ \mu v/deg$ and $R = 1.06\ cm^3/coul$. The upper and lower surfaces of the cylinder were drilled and a cylindrical hole bored along the axis for the thermometer. The weight of the specimen was 567.6 g.

The outside of the cylinder was coated with polymer varnish BF-2, and enamelled constantan wire wound on as a heater of resistance ~180 ohms at 4.2°K. The measurements were made in the calorimetric apparatus described previously.[1] The cylinder was hung on three caproic threads in a vacuum jacket. The high heat capacity of the specimen above 20°K (20.34 joule/deg at 20.8°K and 68.92 joule/deg at 64.8°K), together with the good vacuum obtained with the adsorption pump, made it possible to carry out measurements without any further adiabatic arrangements up to

*It was shown by Itskevich and Kontorovich[3] that graphite shows the required anisotropy.

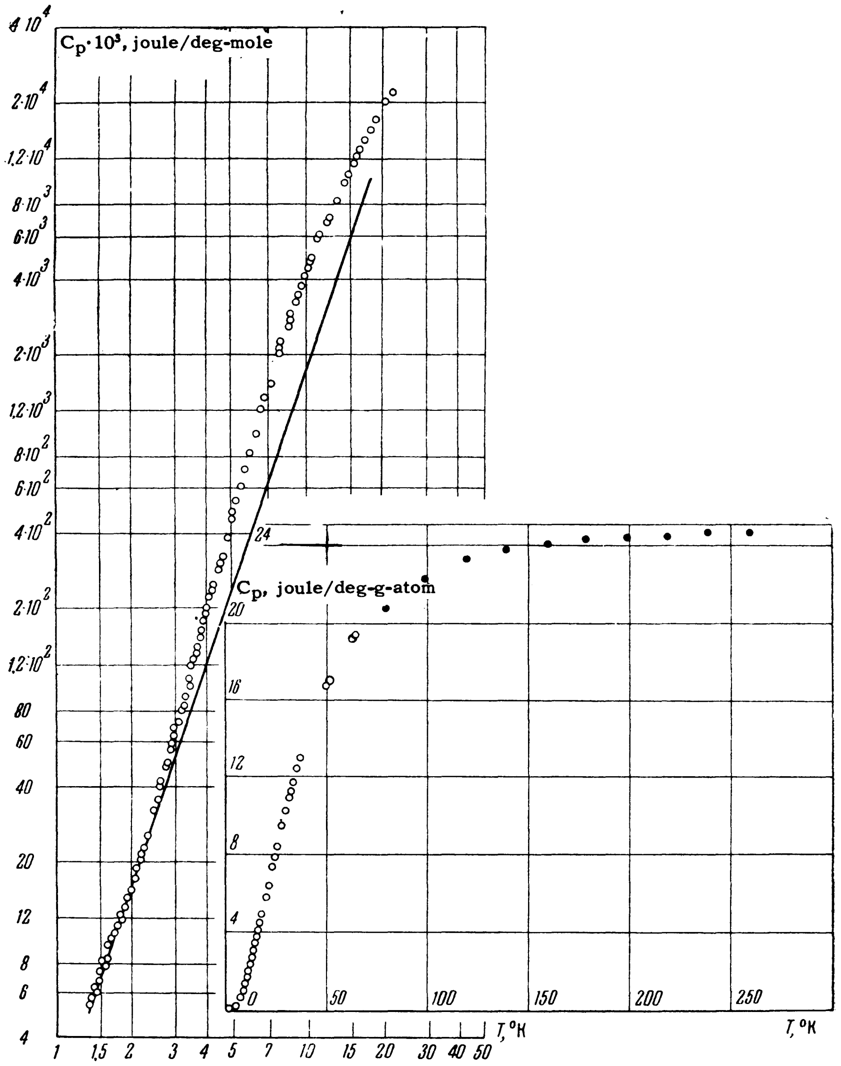

FIG. 1. Heat capacity of p-type bismuth telluride. The straight line corresponds to the law $C_p \sim T^3$. Below right; data of the author (open circles) and the values obtained by Gul'tyaev and Petrov[10] (full circles).

65° K, using liquid and gaseous hydrogen as coolant and heat exchange medium above 20° K. At 30° K the temperature drift was 5×10^{-4} deg/min and at 65° K it was 4×10^{-3} deg/min. A platinum resistance thermometer was used at hydrogen temperatures, a bronze thermometer in the helium range (1958 scale) and a carbon thermometer between 3.5 and 16.3° K. The thermometer construction and calibration and the measuring procedure have been described.[1] Thermal equilibrium was established rapidly in the specimen. Calculation showed that apart from the copper and BF-2 varnish, the heat capacity of all components of the heater and thermometer could be neglected at all temperatures. Corrections were made for the copper and varnish, calculated from the data of Corak et al.[14] and of Kalinkina,[15] extrapolated according to the Debye law above helium temperatures. At all temperatures the total correction was less than 1% of the measured heat capacity and only reached 1.5% below 2° K, so that any error in determining the correction could be neglected.

The measurements made between 3.5 and 4.1° K using both the bronze and carbon thermometers, and those between 12.2 and 16.3° K with the carbon and platinum thermometers almost coincide; there may be an insignificant systematic difference between the data obtained between 12° and 14° K with the two thermometers, which does not influence the final result.

2. RESULTS

A total of 135 measurements was made between 1.37 and 64.8° K. The range between 1.37 and 38.6° K was covered continuously and no phase transition was found. Figure 1 shows the results from 1.37 to 20.0° K. Our data from 1.4 to 65° K are also shown together with the smoothed data of Gul'tyaev and Petrov[10] between 80 and 300° K.

Below 2.3° K the results can be fitted by the expression

$$C = \gamma T + 464.5\,(T/\Theta_0)^3, \qquad (1)$$

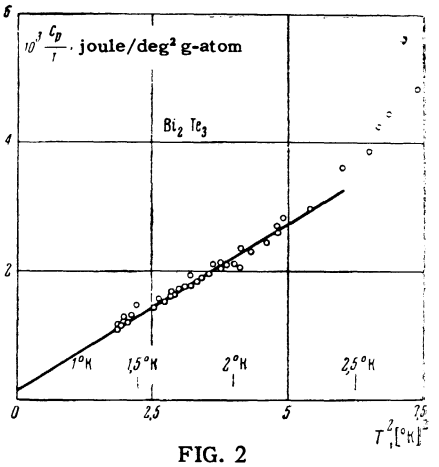

FIG. 2

with $\gamma = (17 \pm 8) \times 10^{-5}$ joule-deg^{-2}/g-atom and $\Theta_0 = (155.5 \pm 3)\,^\circ$K — the Debye temperature at absolute zero. It can be seen from Fig. 2 that the linear term in (1) shows up clearly and at 1.5° K contributes 12% of the measured heat capacity.

The exponent of the temperature dependence of the heat capacity increases considerably above 2.5 — 3° K (see Fig. 1). In this region the contribution of the linear term is negligible (it comprises 4% at 3° K, and this rapidly falls off with increasing temperature). The experimental points fit a dependence $C = aT^{3.6}$ up to 8° K. Above 8° K the power falls monotonically and again goes through a region of cubic dependence. This can easily be seen in Fig. 3, where there is a minimum in the $\Theta_D(T)$ curve between 8 and 11° K. The greatest deviation from the curve corresponding to Eq. (1) is greater than 200%. There is no extension of the linear and quadratic dependence found previously.[1]

We estimate that the overall mean error in the results is 1% above 20° K and between 2 and 3% below 20° K.

3. DISCUSSION OF THE FORM OF THE HEAT CAPACITY OF THE BISMUTH TELLURIDE LATTICE

It can be seen from Fig. 1 that the heat capacity curve for the Bi_2Te_3 lattice is considerably different from that of the cadmium halides:[1] the cubic law for Bi_2Te_3 (allowing for the linear term below 2.3° K) agrees with Blackman's requirement that it should hold for $R < \Theta_D/50$; the square

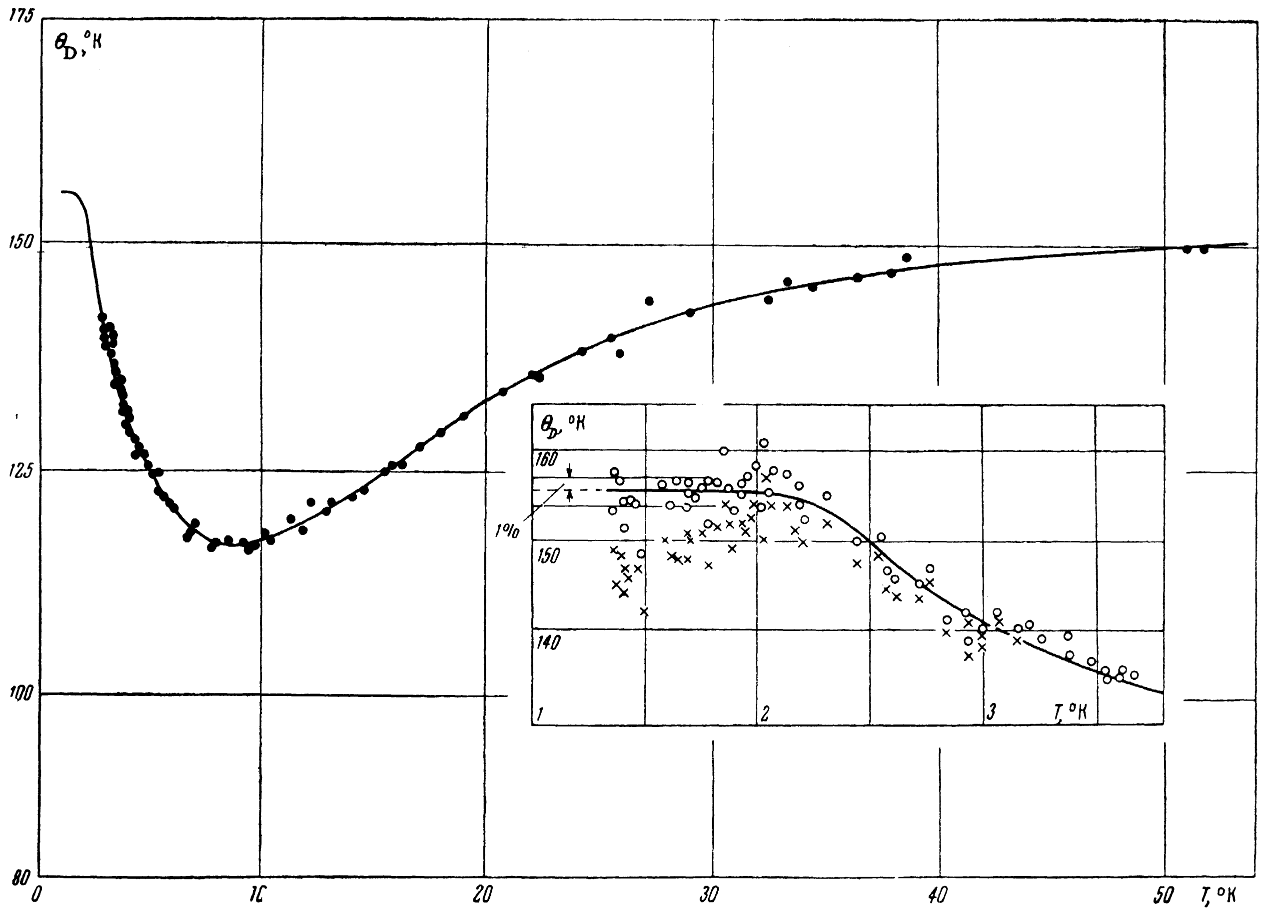

FIG. 3. Characteristic Debye temperature for Bi_2Te_3 between 1.37 and 50°K, derived from the experimental data. The region below 3.5°K is shown separately and corresponds to the portion of the main figure which has no points. The crosses indicate the value of Θ_D calculated on the assumption that the whole measured heat capacity is due to the lattice.

and linear regions are clearly absent; there is a larger interval in which the temperature dependence is greater than cubic and the exponent has a greater maximum value.

Figure 3 shows the $\Theta_D(T)$ curve below 3.5°K and also over a wide temperature range. (The Debye temperature is calculated from the data on C_p. The difference between C_p and C_v is negligible over the whole range; it is 1% at 90°K and rapidly decreases at lower temperatures.) The linear term can be separated out from the trend of the Θ_D points below 2°K. Both this curve and Fig. 2 lead to the conclusion that $\Theta_0 = \Theta_D(0) = (155.5 \pm 3)$°K. Θ_D decreases above 2.3°K, corresponding to a more rapid C-T relation. There is a broad minimum ($\Theta_{D\,min} = 117$°K) at 8 — 11°K, reminiscent of Blackman's pseudo-cubic region,[16] after which there is a more gradual rise: between 30 and 65°K, Θ_D only increases from 144 to 151°K. The dependence of $\Theta_D(T)$ for the cadmium halides is qualitatively similar. Other crystals show a similar variation, and in particular this curve resembles de Sorbo's for bismuth.[17]

From everything described here it is evident that the layer lattice of Bi_2Te_3 is so different from the lattice for which the formula of the Lifshitz theory[2] applies, that we will not attempt to derive quantitative results, as for graphite. It is probable that the increase in the power of the temperature dependence above three is related, as was suggested in the case of the cadmium halides, to the inclusion in the heat capacity of soft optical branches, corresponding to weak inter-layer interactions.

4. HALL EFFECT AND RESISTIVITY OF BISMUTH TELLURIDE AT LOW TEMPERATURES

From the Hall-effect measurements mentioned above, it follows that our specimen had a hole conductivity at room temperature. However, to determine the type of carrier responsible for the linear term in the heat capacity it is necessary to measure the Hall effect at low temperatures. If the conductivity is produced by charge carriers of one sign, their concentration could be deduced from such measurements. From the concentration and the coefficient of the linear term in the heat capacity, if it is assumed that the Fermi surface is an ellipsoid, the limiting Fermi energy can be derived and the effective mass, if it is assumed isotropic.

There are data on the Hall effect in p-type Bi_2Te_3 in several papers in recent years (e.g., references 4 — 9), but the measurements only extend down to nitrogen temperature.* All measurements on Bi_2Te_3 specimens show a slight decrease in the absolute value of the Hall constant on going from room temperature to nitrogen temperature.

Stil'bans and Vlasova[4] found that for a hole specimen with 0.2% bismuth in excess of the stoichiometric proportion, the Hall constant fell sharply with decreasing temperature and was close to zero at 82°K. On this basis, they suggested that there might be a change of sign and an unfilled impurity band with electronic conductivity near 0°K.

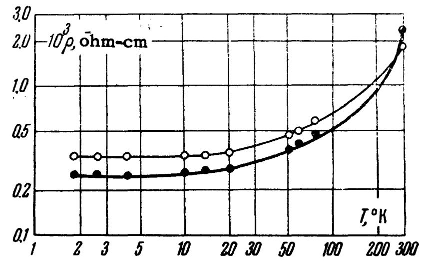

FIG. 4. Resistivity of p-type Bi_2Te_3 between 2 and 300°K: ● – specimen No. 1, ○ – specimen No. 2.

We measured the resistance and Hall effect at low temperatures (helium, hydrogen and nitrogen). The resistance measurements were made on two polycrystalline circular rods, made from the upper and lower parts of the specimen used for the heat capacity measurements. One of these rods was then polished down to a disc for determining the Hall emf. The measurements were made by a null method, and for this, current and potential leads were attached to the ends of the rod. The resistance was compared with a 0.01-ohm standard. The specimens were joined in series and were placed close together in a Dewar vessel containing the appropriate liquid. Temperatures below the boiling point were obtained by pumping. The results are shown in Fig. 4 and in Table I.

TABLE I. Resistance of two specimens of p-type Bi_2Te_3 at low temperatures

T, °K	Specimen No. 1		Specimen No. 2	
	R, Ω	σ, $\Omega^{-1}\cdot cm^{-1}$	R, Ω	σ, $\Omega^{-1}\cdot cm^{-1}$
1.9	0.0057	3880	0.0037	2950
2.6	0.0057	3880	0.0037	2950
4.2	0.0056	3950	0.0037	2950
10.2	0.0059	3780	0.0037	2950
14.0	0.0059	3760	0.0038	2910
20.4	0.0061	3630	0.0040	2760
52	0.0082	2700	0.0051	2140
59	0.0088	2520	0.0054	2020
78	0.0104	2130	0.0064	1700
room temperature	0.052	420	0.020	550

*See the next footnote.

TABLE II. Absolute values of emf and Hall constant, R, for p -type bismuth telluride (specimen No. 1)

T, °K	emf at H=10.2 koe, μv	R, cm³/coul	T, °K	emf at H=10.2 koe, μv	R, cm³/coul
1.9	31.2	+0.182	78.0	37.7	+0.223
4.2	31.8	+0.186	room temperature	50.9	+0.306
20.4	33.7	+0.192			

The results show our specimen to have a metallic type conductivity, starting from the lowest temperatures. The conductivity is independent of temperature below 10° K, which is probably to be explained by the presence of a large impurity concentration. The impurity could be bismuth atoms produced, as Satterthwaite and Ure have shown,[8] by the exact stoichiometric proportions in the liquid not giving rise to the same proportions in the crystals.

The Hall emf was measured on specimen No. 1 at liquid helium temperatures and at the boiling points of hydrogen and nitrogen using a KL-48 potentiometer. Our magnet made measurements possible up to fields of 10,200 oe. The direction of the field was reversed by rotating the specimen. Measurements were made in different fields at each temperature, and no field dependence of the Hall constant, R, was found (in the range 2.0 to 10.2 koe). The results are shown in Table II and in Fig. 5.*

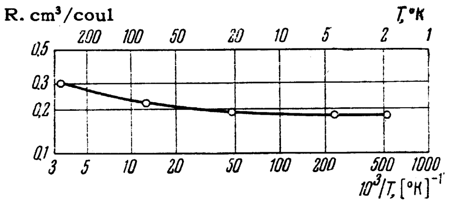

FIG. 5. Hall constant of p-type Bi_2Te_3 between 2 and 300°K.

The Hall constant is always positive, which does not bear out the suggestion of Stil'bans and Vlasova[4] about a change in sign, and the conductivity of our Bi_2Te_3 is by holes at all temperatures. We can deduce the hole concentration at helium temperatures and possibly at hydrogen temperatures, where the Hall constant is practically independent of temperature. Using the formula $R = 3\pi/8ne$ or $n = 7.35 \times 10^{18} R^{-1}$, we obtain $n = 4.0 \times 10^{19}$ cm^{-3} for our sample.

Since the Hall constant increases, although slowly, with increasing temperature, we can presume that one or more further groups of charge carriers come into evidence above hydrogen temperatures. Our data on the temperature dependence of resistance and Hall constant do not fit into the simple scheme with an unfilled impurity band, proposed by Vlasova and Stil'bans.

*We recently learned of Yates' work[18] on the measurement of electrical resistance and Hall effect in Bi_2Te_2 between 1.3 and 660°K. Our results are in satisfactory agreement with Yates' results.

5. DISCUSSION OF THE RESULTS ON THE HEAT CAPACITY OF THE HOLES IN BISMUTH TELLURIDE

On the assumption that in p -type Bi_2Te_3 near 0° K there is one group of holes in a large concentration, giving the main contribution to the linear term in the heat capacity and to the Hall emf, we can deduce their effective mass at 2° K from their concentration and heat capacity.

The atomic heat capacity of a highly degenerate gas of holes is

$$C_v = \gamma T = 3.86 \cdot 10^{-13} V n^{1/3} (m/m_0) T \text{ cal/g-atom-deg}, \tag{2}$$

where V is the atomic volume, n the number of holes per unit volume, and m/m_0 the ratio of the effective hole mass to the mass of the electron. This relation applies for $T \ll T_F$, where T_F is the Fermi temperature:[19]

$$T_F = 4.2 \cdot 10^{-11} n^{2/3} m_0 / m.$$

In our case the Fermi temperature comes out to be 336° K, so that Eq. (2) is applicable, and from it we obtain $m/m_0 = 1.46$.

Since the Hall constant changes little between 2 and 300° K it is possible that the activation energy for the impurities in our Bi_2Te_3 is close to zero.

In conclusion, the author considers it a pleasant duty to express his sincere appreciation to Academician P. L. Kapitza for making it possible to carry out this work in the Institute for Physical Problems of the Academy of Sciences and to Professor P. G. Strelkov for his constant interest in the work and for valuable advice.

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