INVESTIGATION OF THE EFFECT OF UNIFORM COMPRESSION ON THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY OF BISMUTH

D. BALLA and N. B. BRANDT

Moscow State University

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The effect of uniform compression on the temperature dependence of the electrical conductivity ρ of bismuth single crystals was investigated, in the region of pressures up to 25 000 atm and at temperatures of 2—300°K, along the trigonal axis and perpendicular to it. It was found that, irrespective of the orientation of the current with respect to the crystallographic axes, a maximum appeared in the $\rho(T)$ curves of compressed samples. At pressures exceeding 20 000 atm, this maximum shifted toward the region of the residual resistance, the value of which increased reversibly by a factor of 290 at $T = 2°K$ and about 24 000 atm. The dependences of the carrier density on pressure, in the residual-resistance region, and on temperature, at various pressures, were obtained. It is shown that at a pressure $p_c \approx 26\ 000$ atm the constant energy surfaces of bismuth contract to become points and that at low temperatures bismuth becomes a dielectric. The pressure-induced transformation of bismuth into a dielectric is, as far as the authors are aware, the first experimental observation of a phase transition of the type $2\frac{1}{2}$, predicted by I. M. Lifshitz.[8]

INTRODUCTION

In a study of the effect of about 1600 atm pressure on the electrical resistance ρ of bismuth and alloys of bismuth with lead and tin, carried out over a wide range of temperatures T,[1,2] it was found that the pressure gives rise, at 30—40°K, to a reversible maximum in the $\rho(T)$ curve of bismuth alloys and that a slight irregularity appears in the $\rho(T)$ curve of bismuth in the same range of temperatures.

A maximum in the $\rho(T)$ curve also appears in bismuth under the action of acceptor impurities (lead and tin)[3] when the current is oriented parallel to the trigonal axis. The amplitude of the maximum increases with increase of the lead and tin concentration and its position shifts toward the region of higher temperatures. The effect is considerably weaker when the current is oriented at right angles to the trigonal axis.

A method has recently been developed for investigating the electrical conductivity of metals and semiconductors at low temperatures and quite high uniform pressures,[4,5] and therefore it seemed of interest to determine the nature of the change in the temperature dependence of the resistance of bismuth at considerable pressures.

This problem is also of interest for the following reasons.

Under uniform pressure, the density of electrons and holes in bismuth decreases. At liquid helium temperatures, a pressure of 7500 atm reduces the electron and hole densities by about 50%,[6] and we may expect that at pressures exceeding 20 000 atm the carrier density may drop to zero in bismuth. The transition of bismuth to the "metal" modification Bi III in the liquid helium range of temperatures occurs only at pressures of about 45 000 atm.[7] Therefore, we might expect that the phase transition Bi I → Bi III at helium temperatures is preceded by a phase transition of the "intermediate" type,[6] as a result of which bismuth becomes a dielectric and retains this state at low temperatures in the pressure region 20 000—45 000 atm. Obviously, this effect may be observed only at sufficiently low temperatures, since at high temperatures it is masked by the thermal liberation of electrons and holes.

MEASUREMENT METHOD AND SAMPLES

The pressure was established using an improved variant of the method described earlier.[4] The general appearance of the apparatus is shown in Fig. 1. The lower part of the pressure booster with a working bore of 3.5 mm diameter was made of refined beryllium bronze. The value of the

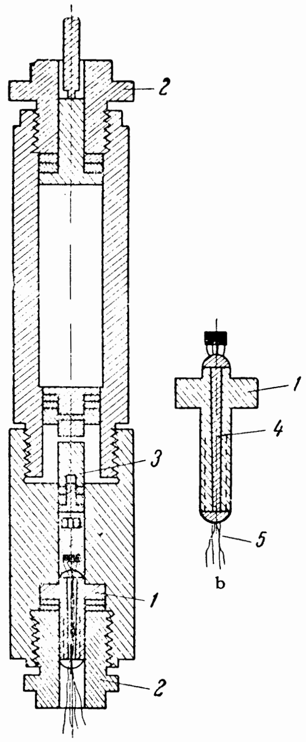

FIG. 1. a) General view of the pressure booster: 1) flanged plug; 2) screw plug; 3) piston plunger. b) Plug 1 with sample mounted on it: 4) Araldite resin; 5) electrical leads.

pressure in the bore was determined by means of a superconducting tin gauge, in which the transition to the superconducting state was recorded electronically by an induction method at a frequency of 20 cps. A single-crystal sample of 0.8—1 mm diameter and 2.5 mm length with welded copper-wire (50 μ diameter) electrodes was mounted at a distance of 3 mm from a flanged plug. Copper wire of 0.2 mm diameter, insulated by enamel and silk, was used to provide electrical leads. Four wires, representing the current and potential electrodes, were introduced into the high-pressure chamber through a conical aperture of 0.6 mm diameter in the flanged plug and were sealed with an Araldite resin, polymerized at 200°C in 30 min. This arrangement of the electrical leads was found to be very convenient and worked reliably up to pressures of the order of 25 000—30 000 atm.

The pressure was established in four ways:

1) by freezing water—alcohol solutions in the upper channel of the pressure booster and using silver chloride as the pressure-transmitting medium;

2) by the same method as above, but using a 50% solution of oil in dehydrated kerosene instead of silver chloride;

3) by slow compression, at room temperature, in the lower part of the pressure booster of a 50% solution of oil in kerosene using a rod placed in the upper part of the booster and a screw plug 2; [5]

4) by preliminary compression, at room temperature, of a 50% solution of oil and kerosene up to a pressure in the range 7000—10 000 atm and additional compression by freezing water—alcohol solutions in the upper part of the pressure booster.

The first method unavoidably gave rise to considerable plastic deformation of the sample and damaged the crystal. However, it made it possible to reach easily pressures up to 30 000 atm. From the point of view of pressure uniformity, the third method was the best. Good results were obtained by the second and fourth methods.

Single-crystal samples of 99.9999% pure bismuth, with a trigonal axis at right angles and parallel to the current, were used. The potential difference across the sample was measured with the usual potentiometric circuit.

Temperatures below 4.2°K were determined from helium vapor pressure; above 4.2°K - with a carbon thermometer and a copper—constantan thermocouple. The measurements were carried out during slow heating of the apparatus which lasted for 5—6 hours and guaranteed sufficient accuracy in the determination of the temperature.

RESULTS OF MEASUREMENTS

Figures 2 and 3 show the temperature dependence of the electrical resistance of bismuth for two orientations of the samples at various pressures. When pressure was established by methods 1) and 2), the compression occurred in the temperature region near 250°K. In this region, the resistance of bismuth rose.

Measurements of ρ of bismuth under pressure at room temperature have been carried out by several workers.[9,10] The values of ρ, obtained by extrapolation to 300°K, and making a correction for the temperature dependence of pressure,[5] are given in Fig. 4 for various pressures and sample orientations. In spite of the roughness of the extrapolation, these data agree well with the results given in the work of Sekoyan and Likhter.[10]

It is evident from Figs. 2 and 3 that at pressures exceeding 10 000 atm the curves show a clear maximum preceded, on the high-temperature side, by a semiconducting-type region. The amplitude of the maximum rises rapidly on increase of pressure and its position shifts toward lower temperatures. At pressures exceeding 20 000 atm, the nature of the $\rho(T)$ curves

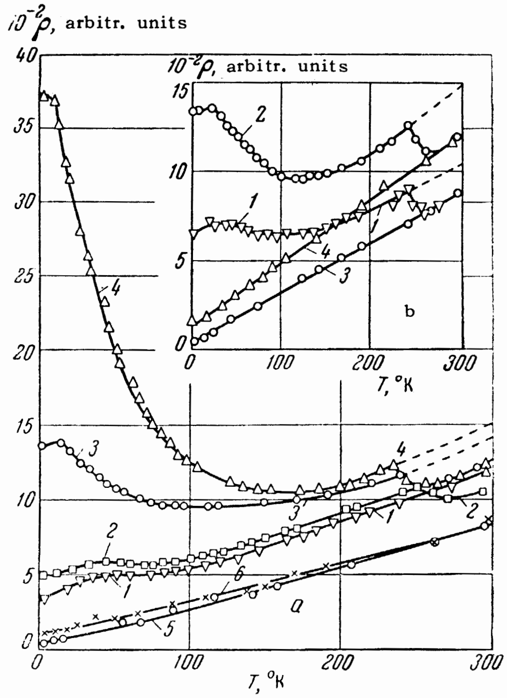

FIG. 2. Temperature dependence of the electrical resistance ρ (in arbitrary units, common to all figures) of bismuth. a) Current parallel to the trigonal axis: sample No. 1, curve 1 – p_1 = 8600 atm (3), curve 4 – p_4 = 20 600 atm (4); sample No. 2, curve 2 – p_2 = 12 600 atm (4); sample No. 3, curve 3 – p_3 = 17 800 atm (4); curve 5 – pressures p_1, p_2, p_4 removed; curve 6 – pressure p_3 removed. b) Current perpendicular to the trigonal axis: sample No. 1, curve 1 – p_1 = 13 000 atm (2); curve 3 – pressure p_1 removed; sample No. 2, curve 2 – p_2 = 15 000 atm (2); curve 4 – pressure p_2 removed. The numbers in parentheses denote the method of establishing pressure.

changes. Instead of a maximum on cooling, we observe a sharp resistance rise which goes over directly into the residual resistance. At a pressure of about 24 000 atm, this transition occurs at 2.3°K, and the value of the residual resistance at this pressure exceeds, by a factor of 290, the residual resistance after the removal of pressure. The effect disappears completely when the pressure is removed but full reversibility of the results is not observed if the pressure is established by methods 1) and 2). The reason for the irreversibility is a small plastic deformation of the samples which is produced mainly during the application of the pressure.

It is interesting to note that the amplitude and the nature of the maximum in the $\rho(T)$ curve depend on the degree of plastic deformation of the sample. The closer the compression to hydrostatic conditions (which can be judged by the degree of reversibility of the results on removal of pressure) the lower the amplitude of the maximum. This circumstance is associated with the reduction of the temperature dependence of the

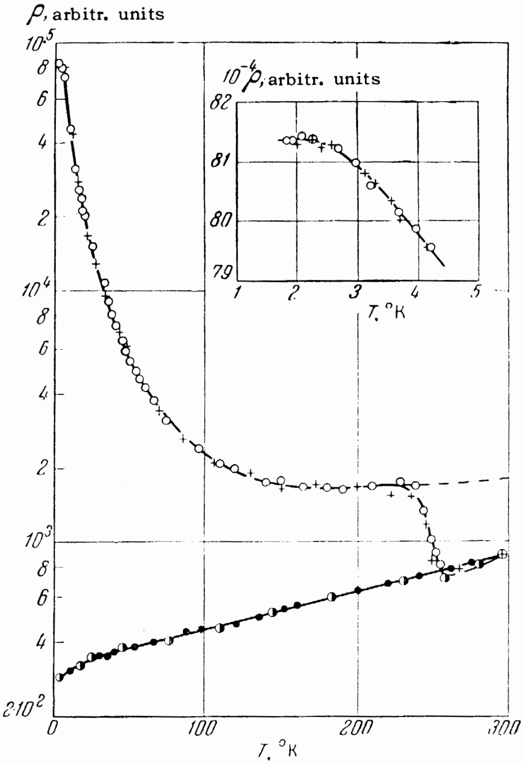

FIG. 3. Temperature dependence of the electrical resistance ρ of bismuth at high pressures. Sample No. 1, o – p_1 = 24 500 atm (1), ◐ – pressure p_1 removed; sample No. 2, + – p_2 = 24 200 atm (1), ● – pressure p_2 removed.

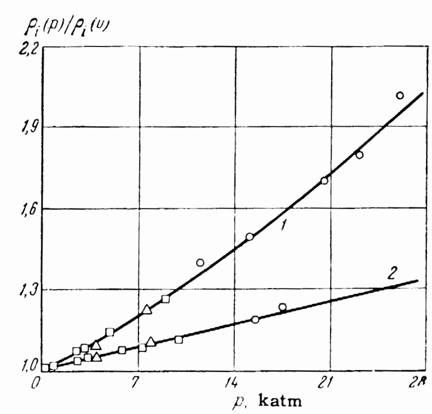

FIG. 4. Relative change of the resistance of bismuth on compression at T = 300°K: 1) current parallel to the trigonal axis, 2) current perpendicular to the trigonal axis; □ – data from[10], Δ – data from[9]; o – present work.

carrier mobility in plastically deformed crystals, as a result of which the effect due to changes in the carrier density appears very clearly.

Another interesting property of the results is that the magnitude of the effect depends weakly on the orientation of the current with respect to the crystallographic axes of the sample (curves 2 and 3 in Fig. 2a, and curves 1 and 3 in Fig. 2b). This indicates that the mechanisms of the influence of lead type impurities and of pressure on the electrical conductivity of bismuth are basically different.

DISCUSSION OF RESULTS

1. Dependence of the electrical conductivity and carrier density n_0 in bismuth on pressure at $T = 0°K$. The pressure dependence of the electrical conductivity σ_0 in the residual-resistance region is shown in Fig. 5. To determine from this curve the nature of the variation of the carrier density n_0 with compression, we can use the formula

$$n_0(p) = \xi\sigma_{0\parallel}(p) \approx \xi\sigma_{0\perp}(p) \quad (1)$$

(ξ is the coefficient which represents a change in the average value of the carrier mobility in the residual-resistance region due to any elastic deformation of the crystal) and the data taken from a study of the influence of uniform compression on quantum oscillation effects in bismuth and a determination of the pressure depenence of n_0 up to 7500 atm.[6]

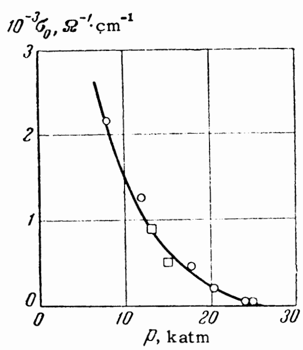

FIG. 5. Dependence, on uniform pressure, of the electrical conductivity σ_0 of bismuth in the residual-resistance region: o – current parallel to the trigonal axis; □ – current perpendicular to the trigonal axis (the experimental points represent different samples).

The coefficient ξ may be selected in such a way that the values of n_0, calculated using Eq. (6) and taken from [6], coincide in a comparable pressure region. If we now assume that, in the first approximation, ξ is independent of pressure at $p > 8000$ atm, then the dependence of n_0 on p is given by the curve shown in Fig. 6. Obviously, the use of the same value of ξ in different tests and at different pressures is not valid. ξ should rise with increase of pressure and, therefore, the true values of the carrier density n_0 at $p > 15\ 000$ atm may lie somewhat higher than the curve in Fig. 6.

From the nature of the dependence of σ_0 and n_0 on pressure, we may expect that at some critical pressure p_c the value of the band overlap ΔE in bismuth becomes zero and bismuth becomes a dielectric at low temperatures. As shown in [6], the reduction of ΔE of bismuth on compression is associated with the reduction of the anisotropy of the c/a ratio of its crystal lattice. Since, at helium temperatures, the parameter c/a is a monotonic function of pressure from zero to $\approx 45\ 000$ atm, ΔE near $p = p_c$ may be expanded as a series in powers of $(p_c - p)/p_c$. In the first approximation

$$\Delta E(p) = \alpha(1 - p/p_c).$$

In the quadratic-dispersion-law approximation, we have $n_0 \propto [\Delta E(0)]^{3/2}$, so that

$$n_0(p) = \beta(1 - p/p_c)^{3/2}. \quad (2)$$

Equation (2) is in satisfactory agreement with the experimental data shown in Fig. 6 in the region of pressures exceeding 15 000 atm provided $\beta = 1.65 \times 10^{17}\ cm^{-3}$ and $p_c = 26\ 000$ atm. At this pressure, the electron and hole constant energy surfaces contract to become points. Bismuth becomes a dielectric. The gap between the valence and conduction bands of dielectric bismuth at $p \geq p_c$ is a function of pressure and varies from zero at $p = p_c$ to a value of the order of 0.02 eV at $p \approx 45\ 000$ atm, estimated from the variation of the parameter c/a with pressure.

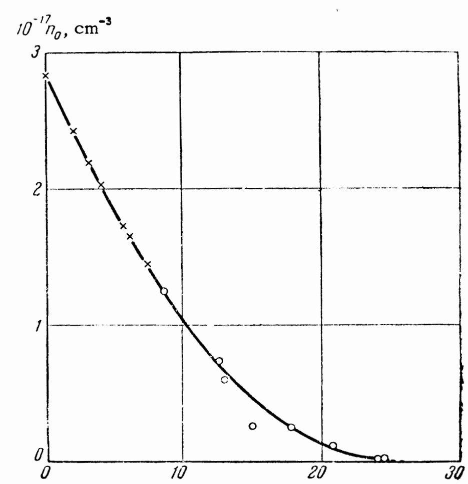

FIG. 6. Pressure dependence of the carrier density n_0 in bismuth in the residual-resistance region: × – data from[6], o – data of the present work for different samples and different orientations of the current.

Unfortunately, it is not possible to study the properties of dielectric bismuth in the pressure region from 26 000 to $\approx 45\ 000$ atm using the method employed here. In the tests described, the pressure is established in the region of temperatures close to 273°K. At these temperatures, bismuth transforms into the superconducting metal modifications Bi II and Bi III at pressures of about 25 000 and 27 000 atm, respectively. As pointed out above, the phase-transition pressure increases on cooling and at T = 0°K the transition from Bi I to Bi III takes place at a pressure of about 45 000 atm. Therefore, if at temperatures of about 273°K, the pressure exceeds 25 000 atm, the modifications Bi II and Bi III are formed, which, as shown in [11], are usually retained at low temperatures in the supercooled state when the apparatus is cooled.

Figure 7 shows the temperature dependence of the electrical resistance of bismuth compressed by 27 600 atm. The sharp reduction of ρ at $T \approx 240$°K corresponds to the formation of the modifications Bi II and Bi III. A further reduction of the resistance on cooling corresponds to the modification Bi III with a small admixture of Bi II. Two resistance jumps at 7 and 3.8°K correspond to the superconducting transitions of Bi III at the critical temperature $T_c = 7$°K (at 27 000 atm < p < 31 000 atm) and of Bi II at $T_c = 3.92$°K (at p = 25 000 atm).[11] Bearing in mind that $\partial T_c/\partial p$ of Bi II is equal to 3.2×10^{-5} deg/atm, we obtain excellent agreement between the values of T_c determined from the resistance jumps in Fig. 7 and the results of induction measurements.[11]

To study the dielectric phase of bismuth at low temperatures at pressures above 25 000 atm, we need a method by means of which the sample can be compressed at temperatures below 200°K.

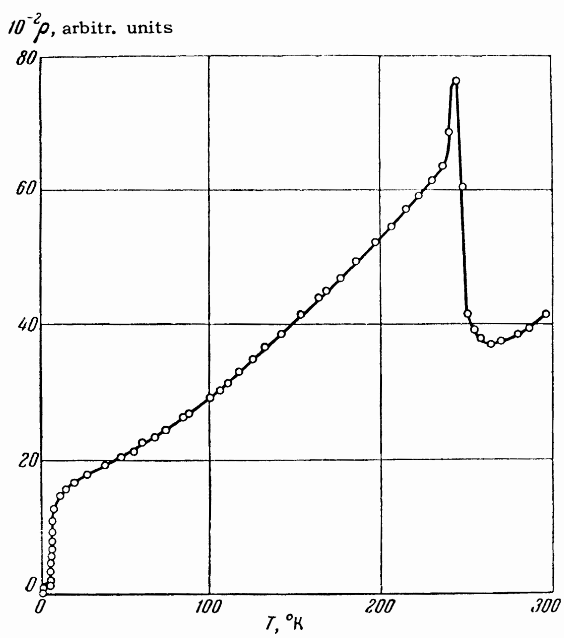

FIG. 7. Temperature dependence of the electrical resistance of bismuth at p = 27 600 atm.

The pressure-induced transition of bismuth to the dielectric state, as far as we know, is the first experimental observation of a special phase transition of type $2\frac{1}{2}$, predicted by I. M. Lifshitz [8] and associated with a basic change of the electron energy spectrum of metals on compression.

2. Temperature dependence of the carrier density. To determine the temperature dependence of the carrier density of compressed bismuth samples from curves shown in Figs. 2 and 3, it is necessary to bear in mind that the temperature dependence of ρ is associated with a change in the carrier density and mobility. Without additional galvanomagnetic measurements, it was possible to separate these two changes in compressed bismuth samples only by making the following assumptions:

a) the temperature dependence of the carrier density of uncompressed bismuth samples is little affected by slight plastic deformation during compression;

b) elastic deformation does not change basically the temperature dependence of the carrier mobility, except in the residual resistance region, i.e., the temperature dependences of the mobility of samples during compression and after the removal of pressure are similar.

The dependence of n on T at p = 0 for bismuth, taken from the published data [12–16], is shown in Fig. 8. The data presented in Fig. 6 allow us, if the assumptions made are valid, to determine from the $\rho(0, T)$ and $\rho(p, T)$ curves the temperature dependence of the average mobility for bismuth samples after the removal of pressure and for samples subjected to uniform pressure, and to deduce the temperature dependence of the carrier density.

Figure 9 shows an example of the separation of the dependences n(T) and τ/m on T. Curve 2 is the result of the simultaneous change in the carrier density and mobility in a bismuth sample

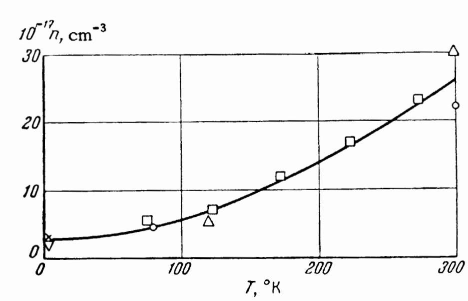

FIG. 8. Temperature dependence of the carrier density n(T) in bismuth according to various workers: × – [12]; ▽ – [13]; o – [14]; Δ – [15]; □ – [16].

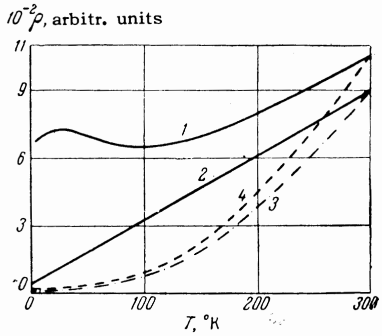

FIG. 9. Method of separating the effects of the temperature dependence of the carrier density and the mobility on the variation of the resistance of bismuth: 1) p = 13 000 atm; 2) pressure removed; 3) the change in ρ due to a change in the average mobility of bismuth after the removal of pressure at a constant value of the carrier density n(T) = n(T = 300°K); 4) the same as 3) for a compressed sample.

measured after the removal of pressure. Curve 3 represents the variation of ρ with temperature at zero pressure, which is solely due to a change in the mobility at a constant value of n(0, T) = (0, 300°K). Curve 1 shows the result of measurement of the dependence of ρ on T for a sample subjected to 13 000 atm. Curve 4 is similar to curve 3; it represents the change in the resistance ρ(p, T) due to a change in the mobility at a constant value of n(p, T) = n(p, 300°K). Therefore

$$n(p, T) = n(p, 300^\circ\,\mathrm{K})\rho_4(p, T)\,/\,\rho_1(p, T), \qquad (3)$$

where ρ_1 and ρ_4 are the values of the resistance at temperature T calculated, respectively, from curves 1 and 4. Some examples of the dependences ln[n(p, T)/n(p, 300°K)] on ln T at various pressures and sample orientations are given in Fig. 10a.

The temperature dependence of the carrier density of bismuth may be due to three mechanisms:

1) a change in the anisotropy of c/a of the crystal lattice;

2) thermal excitation of electrons from a lower to an upper energy band;

3) thermal excitation of carriers through energy gaps in the spectrum of bismuth.

According to x-ray-diffraction data [17], the change in the anisotropy of c/a of the bismuth lattice on cooling from 300 to 4.2°K amounts to 0.2%. The lattice parameter a is practically unaffected by such cooling. The resultant change in the carrier density is equivalent to a pressure of 2000 atm. Obviously, this effect is not important if the carrier density is high. With a reduction in the carrier density, the role played by the thermal contraction of the bismuth lattice parameters in-

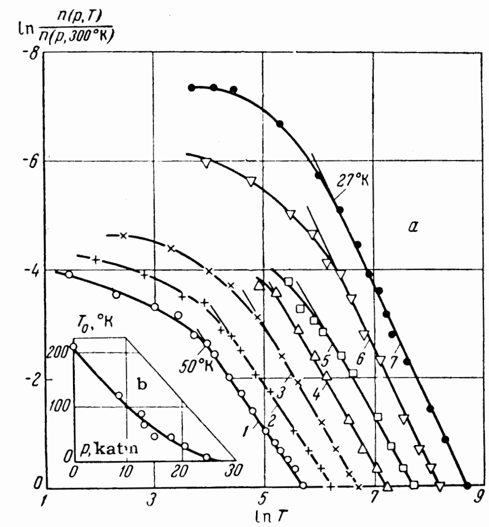

FIG. 10. a) Temperature dependence of the carrier density n(T) in bismuth at various pressures: 1) p = 8600 atm; 2) p = 12 600 atm; 3) p = 13 000 atm; 4) p = 15 000 atm; 5) p = = 17 800 atm; 6) p = 20 600 atm; 7) p = 24 500 atm. Curves 2 – 7 are shifted with respect to curve 1 along the ln T axis by 0.5, 1, 1.5, etc., respectively. b) Approximate pressure dependence of the degeneracy temperature for electrons in bismuth.

creases considerably but it can still be neglected in those cases when the resistance varies most strongly at low temperatures, where the change in c/a is small.

The overlap of the upper and lower energy bands means that a finite number of carriers is present in bismuth at T = 0°K. When the temperature increases, additional electron transitions from a lower to an upper band take place, as a result of which the number of carriers increases. It has been shown by Elcock [18] and by Zil'berman and Itskovich [19] that this effect should lead to dependences of the type

$$\begin{aligned} n(T) &\approx n_0 + \eta T^2 \quad \text{when} \quad T \ll E_0, \\ n(T) &\approx n_0 T^{3/2} \quad \text{when} \quad T \gg E_0. \end{aligned} \qquad (4)$$

Figure 10b shows the approximate pressure dependence of the degeneracy temperature T_0 = E_0/k for bismuth, calculated for a quadratic dispersion law. It is evident from Figs. 10a and 10b that at T > T_0 the $T^{3/2}$ law is satisfied quite well in the pressure region from zero to 18 000 atm. At higher pressures, the temperature dependence of the carrier density becomes stronger and approaches a dependence of the T^2 type at 25 000 atm. It is possible that the stronger dependence of n on T is associated with the thermal reduction of the anisotropy of c/a of the bismuth lattice, the importance of which increases in the region of high pressures due to the considerable reduction of the carrier density. Moreover, at high pressures, the region in which n (p, T) $\propto T^{3/2}$ shifts toward lower temperatures. However, from the form of the $T_0(p)$ curve (Fig. 10b), we might expect that in compressed samples the $T^{3/2}$ law is satisfied to considerably lower temperatures than, in fact, is observed.

At $T < T_0$, the difference between the densities $n(T) - n_0$ varies more slowly than T^2. Obviously, a dependence of the T^2 type occurs only in the region of very low temperatures where the accuracy of the experimental data is insufficient for quantitative analysis.

Abrikosov [20] has shown that bismuth has several (at least four) closely spaced energy bands. Therefore, one would expect that, on heating, the electrons will undergo transitions from filled to empty bands, which would lead to the appearance of an exponential term in the temperature dependence of the electrical resistance. However, it follows from Abrikosov's work that these transitions cannot make much contribution to the electrical conductivity of bismuth. This theoretical conclusion is in good agreement with the experimental data, since the obtained dependences of n (T) are not, in any temperature region, given by the formula of the semiconducting type

$$n(T) \sim T^{3/2} \exp(-E_g / 2kT), \qquad (5)$$

where E_g is the energy gap between the bands.

Thus the principal mechanism which determines the temperature dependence of the carrier density in bismuth at $T > T_0$ is the thermal excitation of carriers due to the small overlap of the energy bands.

In conclusion the authors take the opportunity to thank A. I. Shal'nikov for his interest in this work and A. A. Abrikosov for discussing the results.

[1] N. E. Alekseevskiĭ and N. B. Brandt, JETP **28**, 379 (1955), Soviet Phys. JETP **1**, 384 (1955).

[2] Alekseevskiĭ, Brandt, and Kostina, DAN SSSR **105**, 46 (1955).

[3] N. Thompson, Proc. Roy. Soc. (London) **155A**, 111 (1936).

[4] N. B. Brandt and D. Balla, PTÉ No. 6, 135 (1962).

[5] E. S. Itskevich, PTÉ No. 4, 148 (1963).

[6] Brandt, Gaĭdukov, Itskevich, and Minina, JETP **47**, 455 (1964), Soviet Phys. JETP **20**, 301 (1965).

[7] N. B. Brandt and N. I. Ginzburg, PTÉ No 5, 161 (1962).

[8] I. M. Lifshitz, JETP **38**, 1569 (1960), Soviet Phys. JETP **11**, 1130 (1960).

[9] P. W. Bridgman, The Physics of High Pressure (Russ. Transl., ONTI, 1935).

[10] S. S. Sekoyan and A. I. Likhter, FTT **2**, 1940 (1960), Soviet Phys. Solid State **2**, 1748 (1961).

[11] N. B. Brandt and N. I. Ginzburg, JETP **39**, 1554 (1960), Soviet Phys. JETP **12**, 1082 (1961).

[12] Brandt, Dolgolenko, and Stupochenko, JETP **45**, 1319 (1963), Soviet Phys. JETP **18**, 908 (1964).

[13] R. N. Zitter, Phys. Rev. **127**, 1471 (1962).

[14] B. Abeles and S. Meiboom, Phys. Rev. **101**, 544 (1956).

[15] T. Okada, J. Phys. Soc. Japan **12**, 1327 (1957).

[16] G. A. Ivanov, FTT **6**, 938 (1964), Soviet Phys. Solid State **6**, 720 (1964).

[17] C. S. Barrett, Australian J. Phys. **13**, 209 (1960).

[18] E. W. Elcock, Proc. Roy. Soc. (London), **A222**, 239 (1954).

[19] G. E. Zil'berman and F. Itskovich, JETP **32**, 158 (1957), Soviet Phys. JETP **5**, 119 (1957).

[20] A. A. Abrikosov, JETP **44**, 1632 (1963), Soviet Phys. JETP **17**, 1099 (1963).

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234