

EFFECT OF SIZE AND TEMPERATURE ON THE ELECTRIC RESISTANCE OF ANTIMONY SINGLE CRYSTALS

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The electric resistance of square-cross-section antimony crystals of 9, 5, 3, 2, 1 and 0.7 mm thickness is measured. The crystallographic orientations of the crystals are the same, the axes being one of the directions of the binary axis $[11\bar{2}]$ and the two opposite faces coinciding with the (111) plane. The measurements are carried out at helium (1.5–5.2°K), hydrogen (13–23.6°K) and nitrogen (63.5–77.3°K) temperatures and also at 114, 273, and 293°K. For a 5-mm-thick crystal $R_0/R_{293} = 2.7 \cdot 10^{-4}$. The extrapolated value for a massive crystal at $T = 0$ is $R_0/R_{293} = 7 \cdot 10^{-5}$. It is shown that the ideal resistance of antimony varies as T^2 at $13 \leq T \leq 30^\circ\text{K}$ and as T^2 at $T \leq 10^\circ\text{K}$. The causes underlying this temperature dependence of the resistance are considered. It is suggested that for semimetals of the Sb or Bi type a temperature dependence of the resistance more rapid than cube-law cannot be observed. The size effect of the electric resistance is studied and it is found that $(\rho\lambda)_\perp = 3.7 \cdot 10^{-9} \Omega\text{cm}^2$ and the mean carrier free path $\lambda_{4.2} \approx 3.4$ mm and $\lambda_0 = 12$ mm. An effect of crystal thickness on resistance in weak longitudinal magnetic fields is observed at 4.2°K. From the estimated values of $\lambda_{4.2}$ and λ_0 it is possible to find the mean free path at 4.2°K, related to scattering of the carriers by phonons: $\lambda_{\text{ph}} = 4.5$ mm. This value exceeds by more than an order of magnitude the value obtained for antimony (of the same purity) in investigations of the high-frequency size effect. The causes of this large discrepancy are not clear.

INVESTIGATION of the electronic properties of antimony and the establishment of the form of its energy Fermi surface have been the subjects of many papers. It has been established by now that the Fermi surface of antimony consists of three "ellipsoids" for electrons and of six "ellipsoids" for holes (antimony, like bismuth, is a many-valley semi-metal), the volume of the three electronic "ellipsoids" being equal to the six hole "ellipsoids"^[1,2]. It follows therefore that the densities of the electrons and holes are equal. The carrier density $n_e = n_h = (5.6-4.3) \times 10^{19} \text{cm}^{-3}$ is practically independent of the temperature in the 1.5–400°K range: At $77^\circ \leq T \leq 400^\circ\text{K}$ we have $n \approx 4.3 \times 10^{19} \text{cm}^{-3}$, and at $T \leq 4.2^\circ\text{K}$ we have $n = (5-5.6) \times 10^{19} \text{cm}^{-3}$ ^[2-8]. The mobility of the holes is ≈ 1.4 times larger than the mobility of the electrons, and both mobilities increase by ≈ 6 times when the temperature is lowered from 300 to 77°K^[6,8].

Many features of the carrier-scattering processes at low temperatures have not been sufficiently investigated or have not been investigated at all. These include the dependence of the resistivity ρ on the temperature and on the thickness of the samples. The dependence of the resistivity on the temperature is one of the most sensitive methods of investigating the character of the scattering. Such investigations along the principal crystallographic directions—trigonal (ρ_{\parallel}) and binary (ρ_{\perp}) axes at high temperatures (750–77°K) were carried out by a number of workers^[6,8-10]. The anisotropy $\rho_{\perp}/\rho_{\parallel}$ is equal to 1.2–1.5 in the entire temperature interval and increases somewhat when the temperature is lowered from 300 to 77°K. It is noted in^[10] that $\rho \sim T^{1.9}$ at $T = 55-80^\circ\text{K}$ and $\rho \sim T^{1.4}$ at $T = 90-300^\circ\text{K}$.

Greatest interest attaches to study of the scattering of carriers in antimony at low temperatures (below that of liquid nitrogen). Such investigations were undertaken earlier^[4,11,12], but they are either insufficiently suitable, owing to the low purity of the metal, or incomplete. Indeed, antimony with a relative residual resistance $\delta_0 = R_0/R_{293} = 1.3 \times 10^{-3}$, which is larger by almost one order of magnitude than for the purest antimony presently available, was investigated in^[11] in the temperature interval 4.2–300°K. The helium temperature region could not be investigated with such antimony, since $\delta_{4.2} = \delta_0$ for this region. The authors have shown that $\rho \sim T^{2.8}$ at $T \leq 30^\circ\text{K}$. In^[4], using very pure antimony with $\delta_0 \approx 1 \times 10^{-4}$, only the helium temperature region ($\leq 4.2^\circ\text{K}$) was investigated, and it turned out that $\rho \sim T^{2.2}$. The resistance of antimony with $\delta_0 \approx 4.3 \times 10^{-4}$ was measured in^[12] not very thoroughly (3–4 points for each temperature region) at helium, hydrogen, and nitrogen temperatures, and it was stated (note near the plot on the figure) that at low temperatures $\rho \sim T^{2.3}$, without separating the helium and hydrogen temperature regions.

Carrier scattering from the surfaces of thin antimony samples with transverse dimensions commensurate with the mean free path λ of the carriers has not been investigated at all. Such investigations are of considerable interest, since for example, they can help estimate the mean free path, which must be known for many physical investigations at low temperatures.

SAMPLES AND EXPERIMENTAL TECHNIQUE

The measurements were performed on single-crystal samples of square cross section, grown by the

Bridgman method in molds of fine-grained graphite of special purity (OSCh), using brand Su-000 antimony of $\approx 99.999\%$ purity. The constructed graphite mold was roasted at $1000\text{--}1100^\circ\text{C}$ in a vacuum of 0.1 mm Hg for $\approx 20\text{ min}$, and then was "scrubbed" with pure antimony (two crystals, which were not used in the measurements, were grown). All the samples had the same orientation: the crystal axis coincided with the $[11\bar{2}]$ direction ($\mp 10^\circ$ —the binary axis, and the two flat faces of the crystal coincided with the (111) plane ($\pm 5^\circ$). The crystal-growing technique was described in detail earlier^[13]. The crystal dimensions are given below, and their thickness d was determined accurate to $\pm 0.02\text{ mm}$:

$d, \text{ mm}$:	9	5	3	2	1.5	1.1	1	0.83	0.7
$L, \text{ mm}$:	90	85	85	85	50	50	50	50	40

The samples were mounted on a rigid micarta plate 6 mm thick, on which were fastened eight spring-like needle-shaped potential contacts of stainless steel wire of 0.3 mm diameter. Such a number of contacts has made it possible to trace and eliminate the influence of the proximity of the potential contacts to the current contacts. To avoid possible cracking of the crystal by the pressure of the needle along the (111) plane, the needle-type contacts were pressed against that face of the crystal and not against the face perpendicular to it. Copper end pieces $10\text{--}15\text{ mm}$ long and of the same cross section as the sample were soldered to the ends of the thicker crystals ($d \geq 2\text{ mm}$) with POS-40 solder, and the current leads were soldered to those end pieces. This method of attaching the current lead was essential in order to avoid or to reduce considerably the influence of different distortions in the measurement of the resistance of Sb at helium temperatures¹⁾, as was observed in the case of Bi^[14]. The distances between the potential and the current contacts were $2\text{--}3d$ in the case of thick samples ($d = 9\text{ mm}$) and $6d$ in the case of samples with $d = 5\text{ mm}$.

In the case of thin samples ($d = 2\text{--}0.7\text{ mm}$), two or three thin spring-like wires were soldered to their ends to prevent possible deformation when the samples were cooled from room to helium temperature. The potential ends (wires of thickness 0.05 mm) were soldered by the spark method at a distance $5\text{--}10d$ from the current ends. None of the samples were subjected to special annealing after growing.

The relative resistance $\delta_T = R_T/R_{293}$ was measured throughout; this is much more accurate than measurement of the resistivity ρ_T . The resistances R_T and R_{293} were measured by a null method with sensitivity $\approx 7 \times 10^{-8}\text{ V}$. The measurement current at 293°K was $25\text{--}65\text{ mA}$. The value of this current at helium temperatures was chosen such that its influence

(that of the magnetic field of the current) on the resistance was small, and the resistance could be measured with sufficient accuracy²⁾. At helium temperatures, for thin samples ($d \leq 1\text{ mm}$) the current was 1 A , and with increasing d the current was increased and reached 11 A for $d = 9\text{ mm}$. The resistance-measurement error in the helium region was $4\text{--}5\%$ for the thicker samples and 1% for the thinner ones ($d \leq 2\text{ mm}$). To exclude significant time-dependent effects connected with the Peltier heat released from the antimony-copper junction as a result of flow of direct current, the voltage drop across the sample was measured at room temperature by passing several times a short-duration measurement current ($\tau = 1\text{--}2\text{ sec}$) through the sample, coming closer each time to the "instantaneous" value of the compensated potential difference.

The resistance of the antimony was measured in a metallic cryostat in three temperature intervals: helium ($1.5\text{--}5.2^\circ\text{K}$), hydrogen ($13\text{--}23.5^\circ\text{K}$), and nitrogen ($63.5\text{--}77.3^\circ\text{K}$), and also at 114°K (liquid propane-butane mixture) and 0°C . The temperatures below the boiling point were obtained by pumping off vapor from over the liquid gas, and above the boiling point by producing an excess pressure (1.3 excess atm.). A constant pressure was maintained in the cryostat by means of a manostat, accurate to 0.002°K in the temperature interval $2.7\text{--}5.2^\circ\text{K}$, and accurate to $0.02\text{--}0.05^\circ\text{K}$ in the interval $1.5\text{--}2.7^\circ\text{K}$. In the nitrogen region and at 114°K , the temperature was monitored with a copper resistance thermometer with accuracy $0.2\text{--}0.4^\circ\text{K}$.

A magnetic field up to 2.5 kOe was produced with a solenoid having a large homogeneity region, $\approx 200\text{ mm}$. The measurements in the magnetic field were performed with elimination of the possible errors noted in^[15].

RESULTS

Dependence of δ on the Temperature

A study of the dependence of the resistance on the temperature was made on several antimony crystals with $d = 7\text{--}1\text{ mm}$ at helium, hydrogen, and nitrogen temperatures. Since the helium and hydrogen regions are of greatest interest, these results for a crystal with $d = 5\text{ mm}$ and $L = 90\text{ mm}$ are shown in Fig. 1. The general temperature dependence of the ideal relative resistivity $\delta(T) = \delta_T - \delta_0$, where $\delta_0 = 2.7 \times 10^{-4}$, is shown in Fig. 2³⁾. Since in many cases (for example, when calculation is compared with experiment) it is necessary to know most accurately the resistance at different temperatures, this information, which differs from the published data^[11], is partially listed in the table.

It is seen from Fig. 1 that for antimony with $\delta_0 = 2.7 \times 10^{-4}$ the resistance at 4.2°K is not the residual

¹⁾It was noted that even in the presence of copper end pieces on the crystal with $d = 5\text{ mm}$, the value of $\delta_{4.2}$ increased with increasing distance from the potential lead to the current lead. For example, $\delta_{4.2}$ increases by $\approx 16\%$ if the distance between the current and potential leads changes from 4 to $8d$. This indicates that the method of mounting the antimony samples can greatly alter the resistance in the helium region.

²⁾It was noted that at a measurement current of 11 A the resistance of a sample 1 mm thick at 4.2°K was $\approx 20\%$ higher than the resistance at 2 A .

³⁾In order not to clutter the figure, only half of the points from Fig. 1 have been plotted in the helium and hydrogen regions.

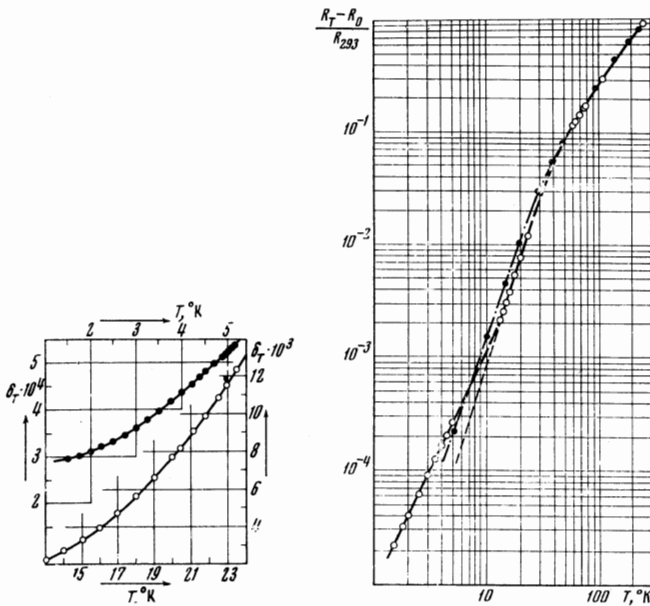


FIG. 1

FIG. 1. Dependence of the total resistance δ_T of an antimony single crystal of thickness 5 mm with $\delta_0 = 2.7 \times 10^{-4}$ on the temperature in the helium and hydrogen regions. The solid curves correspond respectively to $\delta_T \sim T^2$ and $\delta_T \sim T^3$. The upper curve pertains to the left-hand and upper coordinates, and the lower curve to the right-hand and lower coordinates.

FIG. 2. Ideal relative resistance of antimony from 1.5 to 293°K: \circ —our experimental points, \bullet —data from White's paper [11]. The dashed curve shows the slope of the plot $\delta(T) \sim T^3$.

value, but decreases by another ~ 1.7 times, since the lattice resistance at 4.2°K for antimony is $\delta_{4.2} = 1.83 \times 10^{-4}$ (see the table). We note that for Su-0 antimony (99.9% pure) we have $\delta_{4.2} = \delta_0 = 5.5 \cdot 10^{-2} \gg \delta(4.2)$, and for antimony with $\delta_0 \approx 1 \times 10^{-4}$ we have $\rho_{4.2}/\rho_0 \approx 2.6$ [4]. Thus, the purer the antimony, the larger the difference between $\delta_{4.2}$ and δ_0 , and the more accurately is it possible to investigate $\delta(T)$ as a function of T in the helium temperature region.

After reducing our experimental data, we established the following temperature dependence of the resistance: at $T \leq 5^\circ\text{K}$ we have $\delta(T) = 1.0 \times 10^{-5} T^2$, and at $13 \leq T \leq 23.5^\circ\text{K}$ we obtain $\delta(T) = 9.55 \times 10^{-7} T^3$. From the common part of the curves on Fig. 2 we can assume that the quadratic dependence begins not with 5°K but somewhere near 10°K, while the cubic dependence begins with 30°K. The interval between 10 and 13°K is a transition region where the ideal resistance is apparently described as a function of the temperature by the relation

$$\delta(T) = \alpha T^2 + \beta T^3, \quad (1)$$

although we were unable to verify this.

To verify the degree of influence of the thickness on the temperature dependence of the resistance, the latter was investigated in the helium region on eight crystals with $d = 1, 1.5, 2,$ and 3 mm. It turned out that for all values of d , $\delta(T) \sim T^n$, where $n = 2.05 \pm 0.1$, indicating that the thickness does not influence the temperature dependence of the antimony. This is in-

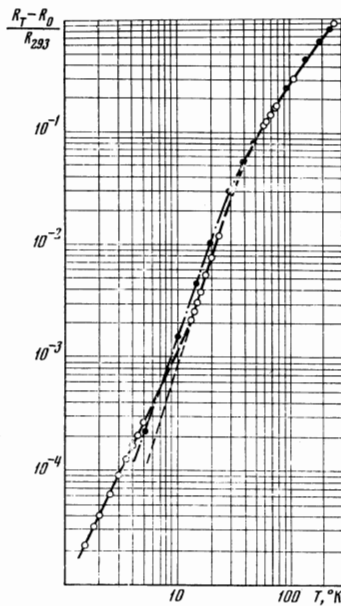


FIG. 2

$T, ^\circ\text{K}$	$\delta_T \cdot 10^4$	$(\delta_T - \delta_0) \cdot 10^4$	$T, ^\circ\text{K}$	$\delta_T \cdot 10^4$	$(\delta_T - \delta_0) \cdot 10^4$
0	2.70	0	5.14	5.35	2.65
1.50	2.96	0.26	13.0	22.3	19.6
2.00	3.10	0.40	15.0	33.0	30.3
2.50	3.32	0.62	17.0	47.5	44.8
3.00	3.60	0.90	19.0	66.6	63.9
3.50	3.96	1.26	20.4	82.4	79.7
4.22	4.53	1.83	21.8	99.6	96.9
4.52	4.84	2.14	23.6	124	121.3

direct proof that the carrier scattering by the sample surface is diffuse, for it is precisely in this case that no difference is observed in the temperature dependence of the resistance in accord with [16].

Attention is called to the fact that the curve drawn through the experimental points of [11] coincides with our points at $T > 50^\circ\text{K}$ and is close to our dependence in the hydrogen temperature region. Investigations in the helium region [4] on very pure antimony also give results close to ours. It should be noted that the investigations in [4, 12] were made on small antimony crystals, and this can lead to certain errors in the exponent of T , owing to failure to take into account the proximity of the current and potential contacts, something the authors themselves do not discuss.

The Size Effect

The dependence of the relative resistance on the thickness of the antimony samples is shown in Fig. 3. The values of d are averages obtained by measuring the thickness at 3–5 spots along the crystal between two pairs of opposite faces. The horizontal "whiskers" indicate the maximum scatter in the values of $1/d$, owing to the fact that the thickness is not constant over the length of the crystal (the inaccuracy in the construction of the graphite mold), something that affects thin samples in particular. The error in the measurement of $\delta_{4.2}$ lies within the dimensions of the experimental point. It is seen from Fig. 3 that the experimental points fit well a straight line that intercepts the ordinate axis at $\delta_{4.2} = 2.5 \times 10^{-4}$, which corresponds to the value of the resistance for a bulky sample ($d = \infty$).

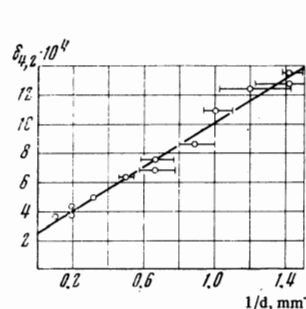


FIG. 3

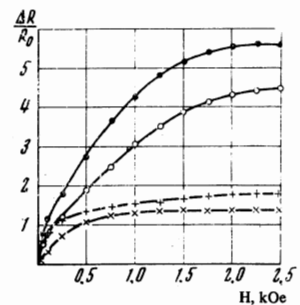


FIG. 4

FIG. 3. Variation of the relative resistance at 4.2°K with the reciprocal thickness of single-crystal antimony.

FIG. 4. Relative variation of the resistance of antimony single crystals with different thicknesses in a longitudinal magnetic field: \bullet — 9×9 mm, 2°K; \circ — 9×9 mm, 4.2°K; $+$ — 5×5 mm, 4.2°K; \times — 1×1 mm, 4.2°K.

The resistance of wires of square cross section, assuming the electron reflection from the surface to be completely diffuse, is described by the following equations for two limiting cases^[17]:

$$\delta_d = \delta_\infty (1 + 0.897 \lambda/d) \text{ for } \lambda \gg d,$$

$$\delta_d = \delta_\infty (1 + 0.75 \lambda/d) \text{ for } \lambda \ll d,$$

where λ is the mean free path of the conduction electrons. The validity of the assumption that the electron reflection from the surface is completely diffuse in the case of antimony follows (besides the fact that the sample thickness does not influence the temperature dependence) also from the circumstance that the sample was not treated in any manner to improve its quality (after removal from the graphite mold). Moreover, as follows from^[16], a perfect surface, which leads at helium temperatures to a partly specular reflection, can be obtained so far only for single-crystal "whiskers" of Zn, Cd, and Cu, and for all the other rather bulky metallic samples it was apparently possible to regard the reflection from the surface as completely diffuse.

The slope of the line in Fig. 3 is $\tan \varphi = 7.5 \times 10^{-4}$ mm. Then, assuming that $\lambda \gg d$, we can find $\lambda_{4.2} = \tan \varphi / 0.897 \delta_\infty = 3.4$ mm. At such a large value of $\lambda_{4.2}$, the section of the curve corresponding to the other extreme case $\lambda \ll d$ will begin somewhere at $1/d < 0.2 \text{ mm}^{-2}$. As a result of allowance for this small region at $\lambda \ll d$, the value of $d_{4.2\infty}$ increases somewhat and becomes equal to $\approx 2.7 \times 10^{-4}$. Knowing $\lambda_{4.2}$ and $\rho_{4.2\infty} = \delta_{4.2\infty} \rho_{293} = 2.7 \cdot 10^{-4} \times 42.5 \cdot 10^{-6} \Omega \text{cm} = 11.3 \times 10^{-9} \Omega \text{cm}$, we found the product $(\rho\lambda)_\perp = 370 \times 10^{-11} \Omega \text{cm}^2$, corresponding to a crystallographic direction perpendicular to [111]. We note that for Sb, just as for Bi^[41], $(\rho\lambda)_\perp$ is larger by two orders of magnitude than for ordinary metals, a fact that remains so far unexplained.

It was observed for the strongly anisotropic metals Sn, Zn, Cd^[14], Hg^[18], and Ga^[19] that the product $(\rho\lambda)_\infty$, or, what is the same, the slope of the straight lines plotted in coordinates δ and $1/d$ along the maximum-symmetry axis, is smaller by a factor 2–3.5 than in a perpendicular direction. Such a difference in the slopes is connected with the anisotropy of the Fermi surface^[20]. We can therefore expect $(\rho\lambda)_\parallel$ for antimony along the [111] direction also to be smaller than $(\rho\lambda)_\perp$ by a factor 2–3^[4].

Let us estimate λ_0 , the mean free path at 0°K, which is determined by the scattering from impurities. For an antimony crystal at $d = 5$ mm we have $\Delta\delta = \delta_{4.2} - \delta_0 = (4.5 - 2.7) \cdot 10^{-4} = 1.8 \cdot 10^{-4}$. Therefore, assuming the slopes of the straight lines at 0 and 4.2°K to be the same (this assumption is perfectly valid on the basis of the experimental data for In, Sn, Cd, Ga, Hg, and Tl), and also taking into account the fact that the dimensions do not influence the temperature dependence of δ_T on T , we find that $\delta_{0\infty} = (2.5 - 1.8) \cdot 10^{-4} = 7 \cdot 10^{-5}$. This value is smaller by a factor 3.5 than $\delta_{4.2\infty}$; therefore the value of λ_0 in-

creases by the same factor, and becomes equal to ≈ 12 mm. The values $\lambda_0 \approx 12$ mm and $\lambda_{4.2} \approx 3.4$ mm indicate that in the region of the residual resistance (1.5–2°K) the samples of antimony (having $\delta_{0\infty} = 7 \times 10^{-5}$) of thickness 10 mm cannot be regarded as bulky for a number of physical investigations.

An additional indication that λ is indeed very large in antimony crystals is provided by measurements of the resistance in a longitudinal magnetic field, shown in Fig. 4. It is known that the magnetoresistance curves should exhibit saturation even in parallel fields that are not very strong, but $\Delta R/R$ depends on the purity of the metal, on the crystallographic orientation, and on the thickness of the sample if $\lambda \geq d$ ^[21]. In the latter case, in diffuse reflection, the ratio $\Delta R/R$ is the smaller, the larger the inequality $\lambda > d$, and at $\lambda \gg d$ there is even observed a decrease of $\Delta R/R$ with increasing H after passing through a certain maximum value. In Fig. 4, the value of $\Delta R/R$ corresponding to saturation is three times larger for a sample with $d = 9$ mm than for a sample with $d = 1$ mm, and is 2.5 times larger than for a sample with $d = 5$ mm. It is thus seen both from $(\Delta R/R)_{\text{sat}}$ and from the character of the curves (the slope at the same value of the field H) that for the samples with $d = 1$ and 5 mm we have $\lambda_{4.2} \gg d$, and for $d = 9$ mm we have $\lambda_{4.2} < d$. A confirmation of the latter inequality is the curve for the sample with $d = 9$ mm at 2°K. From a comparison of this curve with the curve for the same sample at 4.2°K we see clearly that the magnetoresistance effect predominates over the influence of the dimensions with decreasing temperature^[21].

It should be noted that for an antimony crystal with $d = 9$ mm, $(\Delta R/R)_{H=2.5}$ is 3–4 times larger at both temperatures than given by Steel^[22]. This apparently is connected with the much higher purity of our samples (the value of δ_0 is not given in Steel's paper, but the purity of the metal is reported, namely 99.997%). In longitudinal magnetic fields $H \gg 2.5$ kOe there should be observed in our samples with $d = 1.5$ mm, without doubt, a decrease of $\Delta R/R$ with increasing field above a certain value H_{max} . Moreover, for our samples H_{max} should be smaller than the $H'_{\text{max}} = 8$ kOe (at $T = 4.2$ and 1.5°K) for Steel's samples. The decrease of $\Delta R/R$ at $H > H_{\text{max}}$ is due to the increase of λ_{eff} as a result of the twisting of the electron trajectory by the magnetic field.

DISCUSSION

Temperature Dependence of $\rho(T)$

The observed quadratic dependence of $\rho(T)$ on T in the helium-temperature region is in full agreement with the results of investigations of the high-frequency size effect on antimony of the same purity ($\delta_{4.2} \approx 3.7 \times 10^{-4}$)^[23], where it is shown that the mean free path of the carriers scattered by the phonons is $\lambda_{\text{ph}} \sim T^{-2}$ (or $\rho \sim T^2$) in the same temperature interval. The theoretical estimate given in the same paper shows that the quadratic dependence of λ_{ph} on T^{-1} cannot be connected with electron-electron scattering, as was already noted earlier for bismuth^[24]. Moreover, it has been shown that the quadratic dependence is due to

⁴⁾By taking a certain value $(\rho\lambda)_{\text{av}}$, equal to $\approx (2/3)(\rho\lambda)_\perp \approx 250 \times 10^{-11}$ cm, just as in the case of Sn and Zn^[14], we can get the value $\lambda_{4.2} \approx 2.5$ mm corresponding to a polycrystalline sample. This value of $\lambda_{4.2}$ is more correct than $\lambda_{4.2} = 3.4$ mm.

scattering of electrons (or holes) by the phonons and should be observed in experiment in a sufficiently broad temperature interval. This is connected with the large anisotropy of the Fermi surface of Sb (the major axis of the ellipsoid is ≈ 4 times larger than the minor axis), as a result of which the momentum of the scattering thermal phonon in the helium temperature region, $p \sim kT/s$ (s is the speed of sound), is comparable with the minor semiaxis of the electronic ellipsoid but is smaller than the major semiaxis. As a result, the principal role in the scattering is played by electrons with large momenta close in magnitude to the largest semiaxis of the ellipsoid.

The cubic dependence of the resistance on the temperature in the interval 13–30°K is apparently connected with the increasing role of the intervalley scatterings of electrons (and holes) in antimony, which at these temperatures become decisive in the electron-scattering process. The intervalley collisions are highly effective, since they lead to a strong change of the momentum and energy of the electrons. Therefore the frequency ν_{ph} of the collisions with the phonon is proportional for Sb (and for Bi) to their number, or $\nu_{ph} \sim (T/\Theta)^3$, without the additional factor $(T/\Theta)^2$, which is characteristic of metals and is due to the low efficiency of electron-phonon collisions, which leads in final analysis to the Bloch-Gruneisen law $\rho \sim T^5$.

It also follows from the experimental curve of Fig. 2 that the $\rho \sim T^5$ law, which holds for many metals in the "pure" form or with an additional term containing T to a lower power, never comes into play for semimetals of the type of Sb (or Bi) with further increase of purity (decrease of δ_0) of the antimony (or bismuth)⁵⁾. In fact, the value of δ_0 already exerts practically no influence on the cubic dependence of $\rho(T)$ on T (at 13°K we have $\rho_0/\rho_{13} \approx 14\%$, and at 23.5°K $\rho_0/\rho_{23.5} \approx 1\%$), and it can influence the quadratic dependence only insignificantly (to the extent that the impurities influence $\rho(T)$ or that the Matthiessen rule is violated).

Evidence in favor of the argument that at low temperatures there should exist in antimony two processes of inelastic scattering by phonons is found in the existence of two effective Debye temperatures: $\Theta^*_1 = 25^\circ\text{K}$ and $\Theta^*_2 = 100^\circ\text{K}$. The former temperature corresponds to small-angle scattering of the carriers by long-wave phonons (intervalley scattering), and the latter to scattering at large angles by short-wave phonons (intervalley scattering)^[12,26]. It is interesting to note that the temperatures at which the quadratic ($T \approx 10^\circ\text{K}$) and cubic ($T \approx 30^\circ\text{K}$) dependences become visible on Fig. 2 are $\Theta^*_1/3 \approx 8^\circ\text{K}$ and $\Theta^*_2/3 \approx 33^\circ\text{K}$.

It should be noted that the results and the foregoing statements must be confirmed by a suitable theoretical calculation of the dependence of $\rho(T)$ on T at low temperatures, something not yet performed. We note that the corresponding calculation with allowance for the deviation of the electron dispersion law from parabolicity was carried out only for Bi at 80–350°K^[27] and agrees well with experiment.

The Size Effect

The very large value $\lambda_0 \approx 12$ mm for antimony calls for a certain amount of caution, since such a large value of λ_0 is possessed only by W and Ga^[28], which are no less than 10 times purer than our antimony. To estimate the correctness of our estimate of λ it would therefore be necessary to compare it with data obtained by studying other physical phenomena, but there are no such direct data. Thus, in^[29] it is reported that investigations of the absorption of ultrasound in a magnetic field at helium temperatures by 99.9999% pure antimony yield the estimate $\lambda_{1,2} = 1$ mm, which is smaller by one order of magnitude than the $\lambda_0 = 12$ mm obtained from our measurements. The authors note in this case that the useful signal at 1.2°K is much stronger than that at 4.2°K, thus evidencing the high purity of the antimony. However, they do not give the values of $\delta_{1,2}$ and $\delta_{4,2}$, and therefore a detailed comparison with our data is impossible.

Let us estimate the value of λT starting from the known electron concentration at helium temperatures, $n = 5 \times 10^{19} \text{ cm}^{-3}$ ^[2-8] and the measured resistance δT (see the table), using the theory of free electrons and the relation

$$(\rho\lambda)^{-1} = \left(\frac{8\pi}{3}\right)^{1/2} \frac{e^2}{h} n^{1/2} = 7.85 \cdot 10^{-3} n^{1/2}. \quad (2)$$

From this we obtain $\lambda_{4,2} \approx 0.9$ mm and $\lambda_0 \approx 3$ mm, which is smaller by 3–4 times than the values obtained by us. This difference can be decreased by a factor 1.5 by excluding the influence of the anisotropy of the size effect (see footnote 4). The agreement might then seem to be satisfactory. But this is not quite so.

Indeed, using the dependence of the ideal resistance of antimony on the temperature (see the table) $\delta(T) = 10^{-5} T^2$ (or $\rho(T) = 4.25 \times 10^{-10} T^2$), $n = 5 \times 10^{19} \text{ cm}^{-3}$, and the relation (2), we can find the connection between λ_{ph} and the temperature, namely $\lambda_{ph} = 2.2 T^{-2} \text{ cm}$. Similar relations for electrons and holes were obtained by Gantmakher: $\lambda^{el} = 0.22 T^{-2} \text{ cm}$ and $\lambda^{hole} = 0.68 T^{-2} \text{ cm}$ ^[23]. We see that our coefficients of T^{-2} are larger than Gantmakher's by 10 and 3 times, respectively. All the carriers take part in the resistance size effect, and therefore the value of λ estimated from this effect is a certain average value for the electrons and the holes.

Let us estimate λ_{ph} at $T = 4.2^\circ\text{K}$ from the resistance size effect, knowing $\lambda_0 = 12$ mm, the total $\lambda = 3.3$ mm, and assuming the relation $1/\lambda = 1/\lambda_0 + 1/\lambda_{ph}$ to hold. The obtained value $\lambda_{ph} = 4.5$ mm is larger by ≈ 37 times than the $\lambda_{ph}^{el} = 0.12$ mm and ≈ 12 times larger than the $\lambda_{ph}^{hole} = 0.38$ mm that follow from the Gantmakher relations.

This large difference increases by another three times if it is assumed that at 4.2°K the reflection of the carriers from the surface is partly specular ($\approx 50\%$) and not diffuse. As already noted above, in our samples there cannot be even partly specular reflection. Therefore the character of the reflection and its dependence on the temperature^[16] cannot explain this discrepancy.

One of the possible reasons for such a large disparity in the values of λ may be the fact that in anti-

⁵⁾It follows from the experimental data on the dependence of ρ on T ^[11,25] that $\rho \sim T^3$ for Bi in the temperature region 5–15°K, and at helium temperatures we should have $\rho \sim T^2$ ^[24].

mony the size effect is determined not by the intravalley but by the intervalley scattering of the carriers. Intervalley scattering is characterized by a mean free path L much larger than the intravalley λ (for Bi, for example, they differ by a factor of 5), and by a diffuse character of reflection from the surface, although its probability is much lower than that of the intravalley scattering. Resistance size effects in semimetals are considered in^[30,31], in which the experimental results on the size effect in Bi^[32,27] receive a new treatment; in particular, it is stated that Price's conclusion^[33] that the size effect accompanies specular reflection in Bi (a highly nontrivial result) is incorrect. In addition to a different treatment of the two plateaus observed on the plot of ρ against the thickness of the semimetal plate, as observed in experiments on Bi, it is shown in^[30,31] that intervalley scattering leads to the appearance of the third plateau in the region of very large thicknesses $d \gg L$. To estimate the degree of the contribution from intervalley scattering, it is necessary to know the relaxation time of the intravalley and intervalley transitions in antimony, which is as yet unknown.

In any case, the question of the large differences between the λ determined from the resistance size effect and from the high-frequency size effect still remains open. Its solution will also explain the anomalously large values of $\rho\lambda$ for Sb and Bi that are determined from the resistance size effect.

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