EFFECT OF PRESSURE ON THE SHUBNIKOV–DE HAAS EFFECT IN ANTIMONY

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The effect of hydrostatic pressure up to 14 kbars on quantum oscillations of the magnetoresistance in Sb is investigated. A reversible decrease with pressure is observed (for p = 14.3 kbar, by 10%) of the period of oscillations associated with the hole part of the Fermi surface. Under the assumption of an isotropic change in the Fermi surface with pressure, this corresponds to an increase in the concentration of current carriers by 15.5%, which is in complete agreement with data given by the integral method.[5] A change with pressure of the angle of inclination of the hole ellipsoids has not been observed.

INTRODUCTION

A large number of papers have been devoted to the effect of pressure on the galvanomagnetic and oscillation properties of metals; however, the most frequently studied in this connection have been only the typical semimetal, Bi. At the present time, it has been established[1-3] that, under the action of pressure, the amount of overlap of the fifth and sixth zones in Bi and the corresponding concentration of current carriers decrease, while the hole and electron parts of the Fermi surface of Bi change, in first approximation, similar to themselves.

The first experimental data on the effect of pressure on the energy spectrum have been obtained very recently for two other semimetals—Sb and As. With the help of a new method,[4] which allows us to determine the relative change of concentration of the current carriers in semimetals under pressure, it has been shown[5] that the concentration of current carriers in As as well as in Bi, decreases under compression (at p ≈ 30 kbar, by a factor of 1.7), and increases for Sb, and at a pressure ~40 kbar, it increases by a factor of 1.8. The latter result is unexpected, since, as a consequence of the similarity of the crystalline structure and the common origin of the energy spectrum, it was natural to expect the same type of behavior for all semimetals under pressure. From this point of view, the study of the effect of pressure on the oscillatory effects in Sb is of interest. These not only allow the direct determination of the volume of the Fermi surface, but give more complete information on the change in the energy spectrum with pressure than could be obtained with the help of the method suggested in[4].

We recall that the Fermi surface of Sb[6] consists of three electron and six hole distorted "ellipsoids" in which one of the short axes coincides with the binary axis, and which transform into one another upon rotation by 120° around the trigonal axis. The angle of inclination of the "ellipsoids" to the basis plane is equal to 2.3 and 37°, for electrons and holes respectively. The concentration of current carriers is $n_e = n_h = (5.36 \pm 0.06) \times 10^{19}\ \text{cm}^{-3}$. The location of the hole "ellipsoid" relative to the crystallographic axes is shown in Fig. 1. The arrow indicates the direction of the magnetic field corresponding to minimum cross section. The location of the electron "ellipsoid", with the exception of the value of the angle of inclination to the plane C_1C_2, is similar to that of the hole "ellipsoid" (C_1, C_2, C_3 are the bisector, binary and trigonal axes, respectively). The deformation of the ellipsoid is not shown in the drawing.

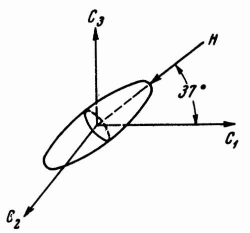

FIG. 1. Position of the hole "ellipsoid" of the Fermi surface of Sb relative to the crystallographic axes.

METHOD OF MEASUREMENT

The bomb described in the work of Brandt and Ponomarev was used to produce the pressure, with the diameter of the working space 4 mm.[7] Application of a composite plunger of refined bronze and weakly magnetic tempered steel, and also an "opposing pinch" apparatus comprising plunger and shutter made it possible to obtain a pressure of up to 22 kbar in the bombs of such construction. As in the work of Itskevich,[8] the pressure in the working space was produced by the slow compression which transmitted the pressure of the medium at room temperature, after which the bomb was cooled to the temperature of liquid helium.

A new aspect in the method of pressure production is the use of a mixture of 40% oil with pentane as the pressure-transmitting medium. This has a significantly greater degree of hydrostatic usefulness than the 50% mixture of oil and kerosene previously used. This is connected with the fact that, in contrast to kerosene, which solidifies at p ~ 20 kbar, as a result of which the oil mixture is considerably thickened at pressures above 10–12 kbar, pentane remains liquid to 30 kbar. Moreover, the mixture with pentane has a very low solidification temperature (~−140°C at p = 0) which lowers the chance of deformation of the sample upon cooling.

As a consequence of the low viscosity of the pentane-oil mixture, the requirements for sealing in the working space of the bomb are considerably increased, espec-

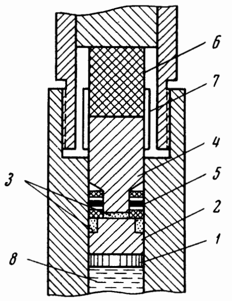

FIG. 2. Cross section of the plunger seal: 1 – thin washer, 2 – layer of beryllium bronze, 3 – oil cushion, 4 – bronze part of plunger, 5 – packing, 6 – steel part of plunger, 7 – cloth sleeve, 8 – pentane-oil oil-mixture.

ially on the side of the moving plunger. This difficulty was overcome by the creation of an oil cushion 3 near the plunger, separated from the oil-dissolving working medium 8 by the layer 2 and the tin washer 1 (Fig. 2). Since the pressurization of the oil cushion is achieved by means of a small compression of the tin washer, it is important that the layer rest at its base on the packing of the previously "pressed" and fixed plunger-stopper, without at the same time damaging its own vacuum seal. Use of the oil cushion allowed us to obtain pressures up to 14 kbar consistently.

The excellent reversibility of the residual resistance of the sample upon removal of pressure, and the high amplitude of the Shubnikov–de Haas (ShdH) oscillations at maximum pressures served as a criterion for the hydrostatic behavior of the apparatus. It should be noted that in a kerosene-oil mixture, the ShdH oscillations in Sb almost completely disappeared at a pressure of about 3 kbar. Data on the change in the residual resistance of the sample, after removal of pressure, with the use of the pentane-oil mixture as the pressure-transmitting medium are shown in Table 1 (samples Sb I and Sb II). In this same table, similar data with the use of a kerosene-oil mixture are shown for comparison (sample Sb III).

The pressure in the working space of the bomb at room temperature was determined by a manganin resistance manometer, connected in series with the potential applied to the sample. At temperatures of liquid helium, the pressure was measured by the shift in the temperature of the superconducting transition of the tin washer, which served at the same time for pressurization of the oil cushion. The transition of the tin to the superconducting state was recorded by an electronic method at a frequency of 22 Hz. The accuracy of determination of the pressure amounted to ~0.2 kbar.

The quantum oscillations of the resistance were measured at a constant current of 100 mA by the usual modulation method. The magnetic field was modulated sinusoidally by a signal with a frequency of 22 Hz and maximum amplitude ~80 Oe. The signal from the sample was recorded on an x-y recorder with continuous variation of the magnetic field, the value of which was recorded on the x coordinate in the scale of 1/H.

The measurements were made on samples cut by an electric spark method along the binary axis from a single crystal in the form of parallelopipeds of dimensions 1 × 1 × 5 mm. The initial single crystal was grown by the Bridgman method from Sb of purity 99.9999% and was characterized by the resistance ratio $R_{300}/R_{4.2}$ ≈ 2500 (see Table 1). The orientation of the crystal was determined by the direction of the cleavage planes. The total error in orientation of the samples in the bomb was no greater than 2–3°.

Table I

Sb I			Sb II			Sb III		
p, kbar	$R_{4.2} \times 10^6$, ohms	$\frac{R_{300}}{R_{4.2}}$	p, kbar	$R_{4.2} \times 10^6$, ohms	$\frac{R_{300}}{R_{4.2}}$	p, kbar	$R_{4.2} \times 10^6$ ohms	$\frac{R_{300}}{R_{4.2}}$
0	0.645	2685	0	0.844	2325	0	3.245	844
14.3	0.631	3010	11.9	—	—	15.4	4.18	680
0	0.720	2415	0	0.843	2300	0	5.21	508
			13.9	0.810	2445			
			0	0.921	2105			

RESULTS OF MEASUREMENTS

The effect of hydrostatic pressures up to 14 kbar on the ShdH oscillations in Sb was studied at temperatures of 3.3 and 1.65°K in magnetic fields up to 19 kOe on two samples at the orientations: current $I \parallel C_2$, magnetic field H in the C_1C_3 plane.

Preliminary orientation of the sample in the magnetic field was carried out by the rotation rosettes. The direction of the trigonal axis was determined more accurately from the intersection of the two branches of periods of oscillation (see Fig. 4 below) associated with the hole part of the Fermi surface. Because of the complexity of the Fermi surface of Sb, the oscillating dependences of the derivative dR/dH on H are as a rule superpositions of two and more frequencies and only in narrow ranges of angles are single-period curves observed. In the presence of two frequencies for the analysis of the curves the formula $P_2 = P_1P_b/(P_1 \pm P_b)$ was used, where P_1 is the period of the frequency with the larger amplitude and P_b is the period of the beat. The indeterminacy in sign was removed by comparison with the known model of the Fermi surface. In more complicated cases, one could almost always separate the regions where only two frequencies are present. This was possible because of the different dependence on the field of the amplitudes of the separate components on the curves of the dependence of dR/dH on H. The accuracy of determination of the oscillation period depended on the complexity of the curve being analyzed and the number of observed oscillations, and amounted to 1–3%. Usually the computations of the period were extended over 30–40 oscillations.

Measurements have shown that under the action of the pressure the amplitude of the oscillations decreases in inverse fashion while the period decreases. Figure 3 shows three curves of the dependence of dR/dH on H for one and the same direction of the magnetic field at pressures p = 0, p = 13.9 kbar, and p = 0 after removal of a pressure of 13.9 kbar. The decrease of the period is clearly seen from the change with pressure of the number of oscillations in a definite range of values of the magnetic field.

Attention is turned to the complete reversibility of the amplitude of the oscillations after removal of the pressure. The angular dependence of the periods of oscillation P on φ for one of the samples (Sb II) at various pressures is shown in Fig. 4 (φ is the angle between the direction of the magnetic field and the trigonal axis of the sample). The continuous lines are drawn through the experimental points of the present research; the dashes indicate the angular dependence of the period of oscillations measured for Sb at p = 0 by

Windmiller and Preistley.[6] Branches A, B and C correspond to the hole, and D, E and F to electron "ellipsoids." The values of the periods of oscillation for p = 0 agree with the data of[6] to within 1%.

The reversible increase with pressure of the minimum cross section of the hole "ellipsoid" $S^h_{min} = eh/cP^h_{min}$ (maximum of branch A), shown in Fig. 4, was also observed on sample Sb I at pressures of 9.6 and 14.3 kbar. The data on the change of S^h_{min} under pressure for both samples are given in Table 2.

To find cyclotron effective masses $m^*_{S_m}$ correspond-

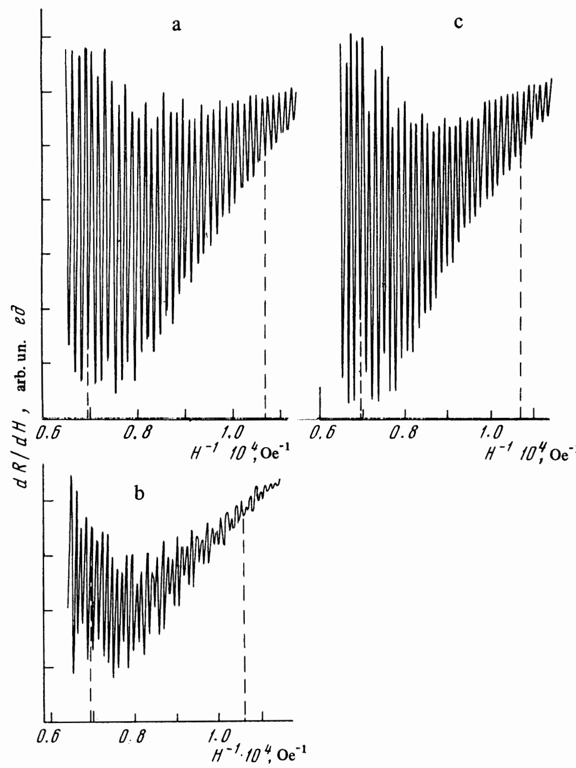

FIG. 3. Change of amplitude and period of Shubnikov – de Haas oscillations in Sb under pressure ($\varphi = 17°$): a – p = 0; b – p = 13.9 kbar, c – p = 0 (pressure of 13.9 kbar removed). Common ranges of field are indicated by the dashed lines.

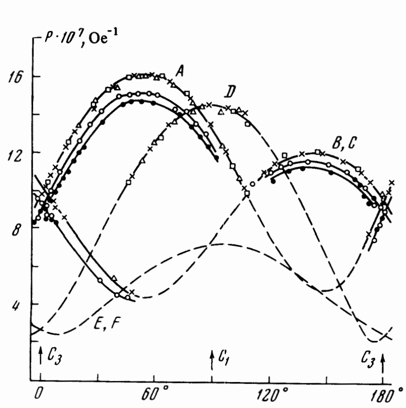

FIG. 4. Angular dependence of the period of the Shubnikov – de Haas oscillations for Sb under pressure: ○ – p = 11.9 kbar, ● – p = 13.9 kbar and without pressure, □ – before application of pressure, × – after removal of p = 11.9 kbar, Δ – after removal of p = 13.9 kbar.

Table II

Sample	p, kbar	$\frac{S^h_{min}(p)}{S^h_{min}(0)}$	$\frac{N(p)}{N(0)}$
Sb I	9.2	1,04	1.06
Sb II	11.9	1.07	1.11
Sb II	13.9	1,09	1.14
Sb I	14.3	1.10	1.155

ing to the extremal cross sections of the Fermi surface S_m, the temperature dependence of the amplitude of oscillations A(T) was studied. The absolute value of the amplitude of the oscillations of dR/dH could be obtained by using the expression of Adams and Holstein[9] for the oscillating part of the transverse conductivity in a magnetic field and differentiating only the oscillating factor cos $(2\pi F/H)$ which varies rapidly with time (F is the frequency of the oscillations) which, for $T_2 = 2T_1$, leads to the formula

$$m^*_{S_m} = \frac{e\hbar}{c}\frac{\operatorname{Arch}\,[A(T_1)/A(T_2)]}{2\pi^2 kT_1}H.$$

(We note that the expression for the ratio $A(T_1)/A(T_2)$ is identical with the formula for the absolute values of the amplitudes in the de Haas–van Alphen effect.)

The results of the measurements of $m^*_{S_m}$ for p = 0 and p = 11.9 kbar are given in Table 3. For comparison, the data of Datars[10] on the cyclotron resonance are also shown. The error of the measurement of the effective mass, ~3%, is determined as the mean square value of the scatter of the values of $m^*_{S_m}$, obtained for different values of the magnetic field. It should be noted that $m^*_{S_m}$ can be calculated sufficiently accurately only when one frequency or the clear beats of only two frequencies are observed. Therefore, for Sb even at p = 0 one can determine $m^*_{S_m}$ from the oscillating curves only for separate ranges of angles. As a consequence of this, data are given in Table 3 only for a small range of angles, which refer to the hole "ellipsoid" (A, Fig. 4) and which are regarded as very reliable by us.

DISCUSSION OF THE RESULTS

The study of the effect of pressure on the quantum oscillations of resistance in Sb is a much more difficult problem than in Bi. This circumstance is connected with the fact that in Sb the volume of the Fermi surface is approximately 200 times greater than of Bi, and the effective masses for some directions are almost 10 times greater. The distance between the Landau levels $\Delta = e\hbar H/m^*c$ in Sb is an order of magnitude smaller than in Bi for the same H. Therefore, the requirements for the hydrostatic character of the applied pressure

Table III

deg	$\left(\frac{m^*_S}{m_0}\right)_{p=0}$	$\left(\frac{m^*_S}{m_0}\right)'_{p=0}$	$\left(\frac{m^*_S}{m_0}\right)_{p=11,9}$	$\frac{m^*}{m_0}$ [10]
6	0.096±0,003	0.086±0,004	—	0.09±0,01
26	0.068±0,002	0.068±0,002	—	0.072±0,01
29	—	—	0.084±0,003	0.07±0,01
36	0.071±0,002	0.068±0,002	—	0.069±0,01
39	—	—	0.084±0,007	0.067±0,01
76	0.081±0,003	0.081±0,002	—	0.07±0,01

Note. 1) The values of $(m^*S/m_0)'_{p=0}$ are obtained after removal of the pressure p = 11.9 kbar.
2) A large error in the determination of small effective masses in [10] appears as the result of the splitting of the resonance peaks.

are sharply increased, whereas the effects observed under pressure are much less because of the greater volume of the Fermi surface.

According to the results of Table 1, the ratio $R_{300}/R_{4.2}$ decreases for the observed samples of Sb I and Sb II, and the absolute value of the resistance $R_{4.2}$, after removal of the pressure $p \sim 14$ kbar, increases by at most 9–10%. With the use of the kerosene-oil mixture, similar changes amounted to 60–65% (sample Sb III). Here it should be noted that the samples Sb I and Sb II are more nearly perfect single crystals than Sb III and therefore are more sensitive to deformation.

The fundamental result of the research is the angular dependence of the period of the ShdH oscillations, obtained for different pressures (Fig. 4). The chosen orientation $I \parallel C_2$ and H in the C_1C_3 plane is convenient for the study of pressure effects, since the minimal cross section of the hole "ellipsoid" observed in it is very slightly sensitive to possible changes in the orientation of the sample in the bomb under compression. The relative change in the extremal cross sections $S_m = e\hbar/cP$ (P is the period of oscillations) of the hole "ellipsoid" A at p = 13.9 kbar in the range of angles $\varphi = 170°-0°-90°$ is shown in Fig. 5.

In first approximation, it can be assumed that the corresponding extremal cross sections of the Fermi surface in this region change in a way that is similar to the original cross section. For hole "ellipsoids" B, C the dependences $P(\varphi)$ are obtained in a narrower range of angles and are calculated with less accuracy, because of the more complex character of the oscillation curves. However, the existing data allow us to estimate the relative increase with pressure of their extremal cross sections, which amounts to 1.075 on the average for a pressure of 11.9 kbar, and which agrees well with the value of 1.07 for "ellipsoid" A.

Since the measured dependence of $P(\varphi)$ spans a wide range of angles and refers not only to the minimal but also to the mean cross sections of the hole "ellipsoid", on the basis of the data given above, one can evidently assume that the volume of this part of the Fermi surface of Sb increases, isotropically with the pressure in first approximation. The changes in the concentration of current carriers in Sb with pressure $N(p)/N(0) = [S^h_{min}(p)/S^h_{min}(0)]^{3/2}$, computed under this assumption (Table 2), agree well with the results of[5]. Figure 6 shows the curve of the dependence $N(p)/N(0)$ on pressure, taken from[5]. The values of $N(p)/N(0)$ obtained in the present research are indicated by black circles. The excellent agreement of the oscillation data with the results of[5] confirms the conclusion on the similar change of the hole "ellipsoids" of the Fermi surface of Sb in compression.

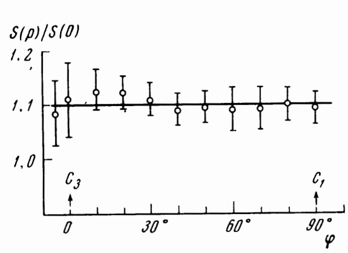

FIG. 5. Relative change in the extremal cross sections of the hole isoenergetic surface in the measured orientation, p = 13.9 kbar.

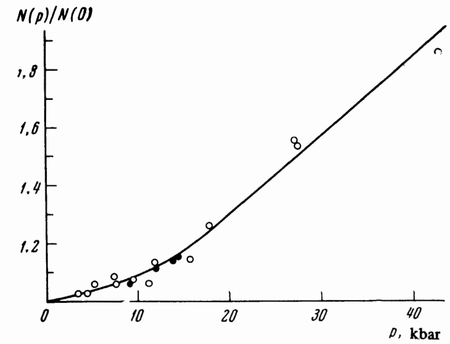

FIG. 6. Relative change in the concentration of current carriers with pressure in Sb: ○ – data of [5], ● – data of present research.

One can also conclude from the analysis of the curves of $P(\varphi)$ that the angle of inclination of the hole "ellipsoid" in the studied region of pressures does not change within the limits of error of measurement (±1°), since the position of the minimal cross section (the dome of curve A) does not change relative to the trigonal axis (Fig. 4).

Unfortunately, it has not been possible to observe under pressure periods connected with the electron part of the Fermi surface. However, because of the equality of concentration of electrons and holes, the volume of the electron part of the isoenergetic surface in Sb should change in the same way as the volume of the hole "ellipsoids."

The data of Fig. 3 testify to the significant reversible increase of the effective mass with pressure (by 20% at p = 11.9 kbar), which shows the strong non-quadratic character of the hole dispersion law for Sb. However, these data should be regarded as only preliminary.

In conclusion, we express our deep gratitude to N. B. Brandt for constant interest in the research and valuable advice, and also to E. I. Skidan for help with obtaining the pressure.

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