INFLUENCE OF PRESSURE ON OSCILLATION EFFECTS IN BISMUTH

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Submitted to JETP editor March 17, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) 47, 455-463 (August, 1964)

A study was made of the effect of uniform compression on the quantum oscillations of the magnetic susceptibility (at pressures of 1300—1600 kg/cm^2) and the electrical resistance (at 3000—7500 kg/cm^2) in bismuth at liquid helium temperatures. A reduction of the oscillation frequency, amounting to 37% at 7500 kg/cm^2, was observed. The possibility of transforming bismuth into a dielectric at low temperatures is discussed.

INTRODUCTION

In a recent work [1] two of the present authors reported on investigation of the effect of uniform compression on the quantum oscillations of the electrical resistance (Shubnikov-deHaas effect) of zinc. This study revealed a monotonic increase of the frequency of the lowest-frequency oscillations under pressure, in contrast to the earlier observations of a nonmonotonic decrease of the frequency of oscillations of the magnetic susceptibility (deHaas-van Alphen effect) under the influence of pressure.[2] The effect in both cases was sufficiently large to discount the possibility of experimental error. Therefore, it was interesting to investigate the influence of uniform compression on the deHaas-van Alphen and Shubnikov-deHaas effects in another metal exhibiting anisotropic compressibility, for example bismuth. The influence of uniform compression on the quantum oscillations of the electrical resistance of bismuth has not yet been investigated although the fact that the oscillations were retained under pressure was established back in 1955.[3] The influence of pressure on the quantum oscillations of the magnetic susceptibility of bismuth has been investigated on several occasions (for example, [4,5]) but the results of different authors are not in good agreement.

It follows from the theories of Jones [6], Cohen, [7] and Abrikosov and Fal'kovskiĭ [8] that the characteristic features of the electron energy spectrum of bismuth are associated with the characteristic features of its crystal lattice. The formation of the crystal lattice in bismuth can be represented as the result of a mutual displacement of two cubic face-centered sublattices by a vector **u** in the direction of the space diagonal and a small rhombohedral deformation γ of each sublattice along the direction of **u**. As a result of the deformation γ, the right angles of the sublattices become 92°34′ and 87°26′. The consequent changes of the lattice period and the doubling of the number of electrons in a unit cell are the basic reason for the appearance of electron and hole groups containing few carriers. The volume and shape of the corresponding constant-energy surfaces are governed, as shown in [8], by several a priori unknown parameters and, therefore, they cannot be predicted theoretically with certainty simply on the basis of data on the crystal structure of bismuth.

The same difficulties are met with in the prediction of the nature of changes of the energy spectrum of bismuth under uniform compression although we may assume that the energy spectrum of bismuth should be very sensitive to changes in the parameters **u** and γ.

In the present paper we used the model of the Fermi surface of bismuth consisting of one hole and three electron ellipsoids.[9,10]

MEASUREMENT METHOD. SAMPLES

To investigate the influence of pressure on the deHaas-van Alphen effect we used a torsional magnetic balance with an automatic compensation of the torque acting on the sample.[11] A magnetically uniform high-pressure chamber was suspended from the balance in a uniform magnetic field; it contained a special sample holder. The most successful construction of the sample holder was that described in [5]. Other types of holder gave rise to stronger plastic deformation and did not ensure sufficient uniformity of the elastic stresses in the compression sample. To apply the pressure, we used aqueous solutions of raw alcohol.[12] The pressure in the chamber was measured with a superconducting manometer by a radio-frequency method.[13]

To investigate the influence of uniform compression on the quantum oscillations of the electrical resistance, we used the method described earlier.[14] The samples were compressed in a special high-pressure chamber at room temperature and were then cooled to the temperature of liquid helium. Pressure was transmitted by means of 50% solution of oil in dehydrated kerosene. The magnitude of the pressure retained at the temperature of liquid helium was deduced from the shift of the superconducting transition temperature of a tin wire included in the sample circuit. The measurements were carried out during continuous application of the magnetic field and the potential difference across the sample was automatically recorded as a function of H or 1/H using a double-coordinate automatically-recording potentiometer type ÉP-2K. The maximum magnetic field intensity was 15 kOe. The measurements were made on cylindrical single-crystal samples (about 3 mm in diameter and 10–17 mm long) of "Hilger" brand bismuth which was further purified by 50 recrystallizations in vacuum. On cooling a sample from 300 to 4.2°K, the initial electrical resistance changed by a factor of 300–500. To obtain samples with the required orientation of crystallographic axes, we used the Kapitza method.[15] The orientation of sample was determined optically. During the measurements, the samples were always fixed in such a way that their longitudinal axes were at right angles to the plane of rotation of the magnetic field.

RESULTS OF MEASUREMENTS

A. The deHaas-van Alphen effect was investigated at pressures of 1300–1600 kg/cm^2 for three main orientations of the crystallographic axes: I) the trigonal axis horizontal and the binary axis vertical; II) the trigonal and binary axes horizontal; III) the trigonal axis vertical. (We shall use ψ to denote the angle between the direction of the magnetic field and thr trigonal axis in orientations I and II or the binary axis in orientation III.)

Since the change in the oscillation frequency was small at these pressures, special attention was paid to the elimination of the influence of the possible change of the sample orientation during compression. First, we recorded the rotation diagrams (the dependence of the torque M acting on the sample in a constant magnetic field) before the application of pressure, during compression and after removal of pressure. Examples of such diagrams are shown in Fig. 1. Second, measurements were carried out mainly over such intervals of angles ψ in which the observed oscillations were associated with one "ellipsoid" of the electron constant-energy surface and were, therefore, of the simplest type.

The diagrams shown in Fig. 1 illustrate the nature of the changes in the oscillation amplitude under uniform compression in magnetic fields oriented in different ways. The oscillation amplitude at pressures of about 1500 kg/cm^2 dropped slightly even in relatively weak fields but was re-established almost completely on the removal of pressure. The relative change in the oscillation frequency, proportional to the extremal cross

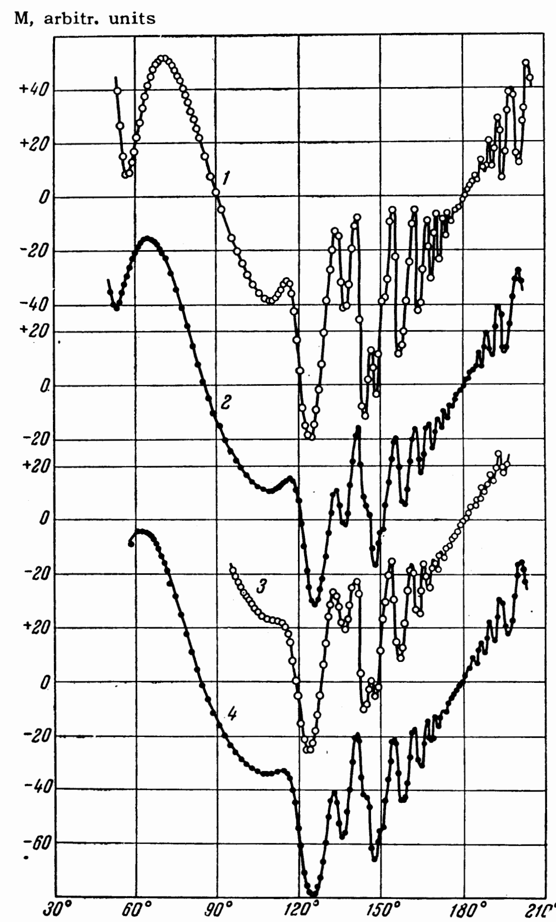

FIG. 1. Dependence of the torque M acting on a bismuth sample (orientation II) on the direction (angle ψ) of the magnetic field H = 6500 Oe during successive application and removal of pressure: 1) pressure (1500 kg/cm^2) removed, T = 1.6°K; 2) p = 1600 kg/cm^2, T = 1.6°K; 3) pressure removed, T = 4.2°K; 4) p = 1400 kg/cm^2, T = 1.6°K.

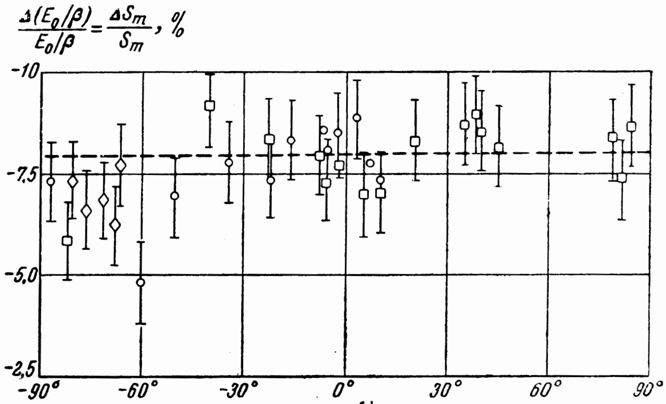

FIG. 2. Relative change of the frequency of the $\Delta(E_0/\beta)/(E_0/\beta)$ oscillations and of the external cross sections $\Delta S_m/S_m = [S_m(p) - S_m(O)]/S_m(O)$ of the electron constant-energy surface for various orientations and values of the angle ψ, reduced to a pressure p = 1600 kg/cm². □ – orientation I; ○ – orientation II; ◇ – orientation III.

sections S_m of the Fermi surface E_0/β, is shown in Fig. 2 for different sample orientations (reduced to a pressure of 1600 kg/cm²). The accuracy of each reading is represented in an arbitrary way because it was difficult to allow for its dependence on the angle ψ. Naturally, the accuracy was higher for small cross sections in the angular region where the cross sections depended weakly on the angle ψ and the observed curves M(1/H) were associated with a single constant-energy surface. It is evident from Fig. 1 that the constant part of the magnetic susceptibility anisotropy $\Delta\chi_0$ varies very weakly on compression, which is in good agreement with the results of previous work.[5]

B. The influence of pressure on the Shubnikov-deHaas effect was investigated only for samples of orientation III. The measurements were made at pressures up to 7500 kg/cm². To check the correct orientation of the sample and determine the direction of the binary axis, we recorded in each test the dependence of the electrical resistance ρ in a constant magnetic field on the direction of this field (the angle ψ). The field intensity was selected to be sufficiently small so that the oscillation effects did not distort this dependence. An example of such a diagram is shown in Fig. 3a. The dependence of the electrical resistance on the magnetic field intensity was measured for two field directions corresponding to the maximum and minimum of ρ in the rotation diagram. At these two extrema, the magnetic field coincided, respectively, with the directions of the bisectrix and the binary axis. The oscillation effects were in the first case due to the minimum principal cross section S_1 of the electron "ellipsoid" and also two coincident cross sections $S^* \approx 2S_1$ of the two other ellipsoids; in the second case, they were due to two coincident cross sections of two "ellipsoids" equal to $S^{**} = 2S_1/\sqrt{3}$. As an example, some curves of the dependence of ρ on H, recorded at various pressures, are shown in Figs. 3b and 3c. It is worth noting that the oscillation amplitude after the removal of pressure rose compared with the amplitude in the original sample (cf. curves 1 and 4). Such a change in the amplitude does not agree with the change in the residual resistance after the removal of pressure. The data on the magnitude of the residual resistance of the test samples are listed in the table.

The dependence of the areas of the cross sections S_1 and S^{**} on the pressure is shown in Fig. 4. This dependence is nearly linear. A linear extrapolation of the curve $S_m(p)$ to the

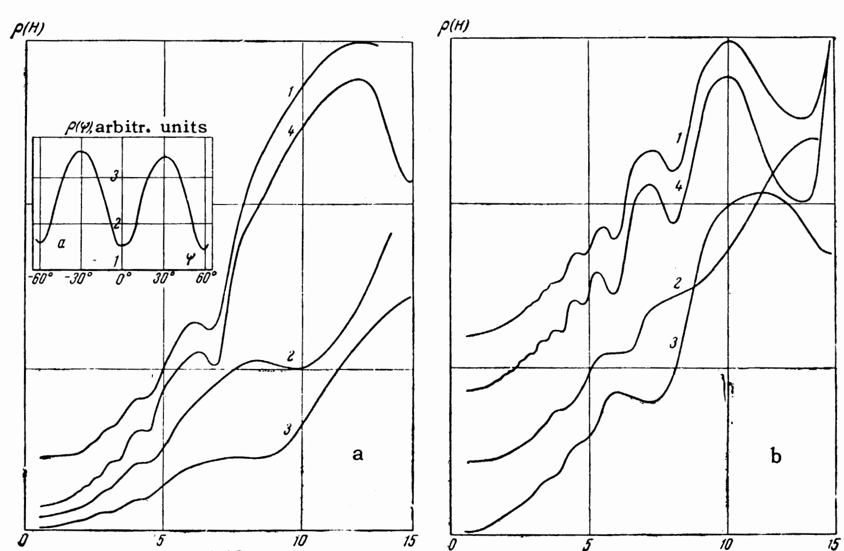

FIG. 3. Dependence of the electrical resistance of bismuth (orientation) III) on the magnetic field for various pressures at T = 1.5°K: a) the resistance anisotropy in a constant magnetic field H = 3 kOe at p = 0; b) the dependence of the resistance on the magnetic field parallel to the binary axis (ψ = 0°); c) the same but with a field along the bisectrix (ψ = 30°). Curves 1) represent p = 0, 2) p = 4600 kg/cm², 3) p = 7500 kg/cm², 4) pressure removed. The measuring current and the circuit sensitivity were the same in all cases. The curves are displaced in an arbitrary fashion with respect to the ordinate axis.

p, kg/cm²	ρ (300 °K)/ρ (4.2° K)		
	sample No. 1	sample No. 2	sample No. 3
0	460	370	190
3000	56		
4600		43	
5600			35
7100	37	32	
7500			29
0	140	156	135

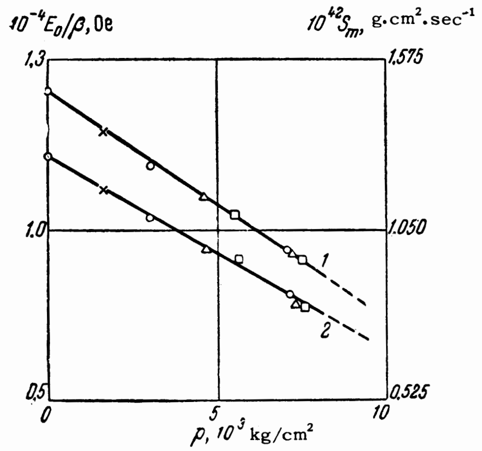

FIG. 4. Pressure dependence of the frequency of the E_0/β oscillations of the electrical resistance and of S_m of bismuth: 1) cross section S**; 2) cross section S_1. Points: o – sample No. 1; Δ – sample No. 2; □ – sample No. 3; × – data obtained from measurements of the de Haas – van Alphen effect.

zero value of S_m makes it possible to estimate the magnitude of the pressure at which the volume of the electron ellipsoids in bismuth should vanish. This pressure is of the order of 20,000 kg/cm².

DISCUSSION OF RESULTS

A. Comparison of data obtained during the investigation of the deHaas-van Alphen and Shubnikov-deHaas effects in bismuth. The results obtained in our investigation of the influence of pressure on these two effects in bismuth are in good mutual agreement (cf. Fig. 4). The disagreement with the data obtained by Dmitrenko, Verkin and Lazarev [2] for zinc is obviously due to the strong departure of the compression used by these authors from hydrostatic conditions. In [2] a spherical sample was mounted in a chamber in such a way that the gap between the sample and the chamber walls was considerably smaller than the distance from the sample to the bottom and to the stopper that sealed the chamber. We can assume that, on cooling the chamber, water froze first in the narrow gap around the sample without establishing strong pressure. Then, because the thermal conductivity of the sample was higher than that of water, the sample became surrounded with a layer of ice and when the water froze completely, the sample was compressed in the same way as by two vertical pistons. Since the principal axis of the crystal was oriented at right angles to the longitudinal axis of the chamber, the sample was subjected to very strong uniaxial compression at right angles to this axis.

B. Influence of uniform compression on the Fermi surface shape. The data shown in Figs. 2 and 4 indicate that under uniform compression all the observed cross sections of the electron constant-energy surface decrease. It is evident from Fig. 2 that, within the experimental error, at pressures up to 2000 kg/cm² the sections of the electron surface formed by planes passing through the binary axis p_1 (up to sections making an angle of 6° with the direction p_2 along the longest dimension of the "ellipsoids") change in the same percentage ratio. This is true also of the cross sections S_1, S* and S** right up to pressures of 7500 kg/cm². The average value of the change in the extremal cross sections under uniform compression amounted to $-(8 \pm 1.5)\%$ at 1600 kg/cm² and $-(37 \pm 3)\%$ at 7500 kg/cm².

It follows from Fig. 2 and from an analysis of the dependence of the extremal cross sections of bismuth on the angle ψ for orientation I, that the angle of rotation in the "ellipsoids" about the axis p_1 is not altered greatly by uniform compression.

Thus, the shape of the electron constant-energy surface is, in the first approximation, not affected by uniform compression up to 2000 kg/cm². Each surface is compressed in the direction of its center but it remains self-similar. If we assume that this is correct, then a reduction of the extremal cross sections by 37% should correspond to a reduction of the electron density by 50%. Since, under elastic deformations of the bismuth lattice, the condition of equality of the electron and hole densities cannot change, the density of holes similarly decreases.

C. Change of the effective masses and the Fermi energy E_{0e} on compression. The effective mass of electrons, $(\partial S_m/\partial E)/2\pi$, for free and compressed samples of bismuth was determined from the temperature dependence of the oscillation amplitude A using the formula*

$$\frac{A(T_1)}{A(T_2)} = \frac{T_1}{T_2}\,\frac{\operatorname{sh}(2\pi^2 k T_2/\beta H)}{\operatorname{sh}(2\pi^2 k T_1/\beta H)},$$

*sh = sinh.

where $\beta = eh/c\,(\partial S_m/E)$ and k is Boltzmann's constant. Calculations showed that the effective mass for various angles ψ in samples compressed by a pressure of about 1500 kg/cm^2 exhibited a tendency to decrease by about 2%. Although this change is too small to be regarded as reliable, qualitatively it agrees with Cohen's theory [7], according to which the effective mass in bismuth should decrease when the electron density is reduced.

To determine the relative change of the Fermi energy, we can use the formula

$$\Delta E_e / E_{0e} = \Delta S_m / S_m + \Delta\beta / \beta,$$

which is valid both for the quadratic dispersion law and, in the first approximation, for the ellipsoidal model of Cohen with a nonquadratic dispersion law. At p = 1600 kg/cm^2, this change is $\Delta E_e/E_{0e} \approx -6\%$.

D. Influence of uniform compression on the phase of oscillations in the Shubnikov-deHaas effect. The phase δ of the magnetic susceptibility oscillations was not greatly altered by a pressure of 1600 kg/cm^2, i.e., $\partial\delta/\partial p$ is in any case less than 0.01 deg/(kg/cm^2). However, Overton and Berlincourt [16] observed a considerable change in the phase of the Hall emf oscillations in bismuth even at a pressure of 130 kg/cm^2. To determine the influence of pressure on the phase of the electrical resistance oscillations, we plotted in Fig. 5 the number (n) of maxima and minima of the $\rho(1/H)$ curve as a function of 1/H for different pressures and $\psi = 30°$. It is evident that, within the accuracy of the plot, the phase of the oscillations, represented by the segment on the ordinate axis from its origin to the intersection with the straight lines n(1/H), is not affected by compression up to 7500 kg/cm^2. It is not very likely that the phase of the Hall emf oscillations is more sensitive to pressure than the phase of the electrical resistance oscillations. Therefore, the data of Overton and Berlincourt are obviously wrong.

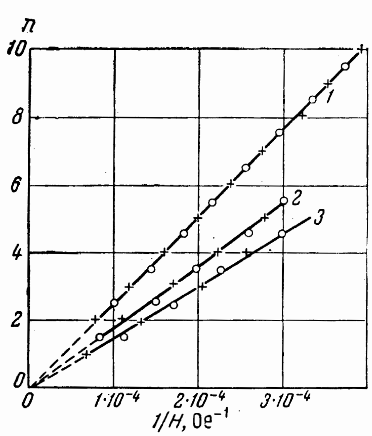

FIG. 5. Dependence of the number of minima (+) and maxima (o) in the ρ(H) curves on the reciprocal of the magnetic field: 1) p = 0; 2) p = 5600 kg/cm^2; 3) p = 7500 kg/cm^2.

E. Form of the electrical resistance oscillations. Figure 6 shows, by way of example, the dependence of the oscillating part of the electrical resistance on the magnetic field for samples at various pressures. It is evident that in an uncompressed sample the shapes of the maxima are considerably different from those of the minima. On increase of the magnetic field, the minima become sharper. Such a shape of these curves is the consequence of the spin splitting of the Landau levels.[17] On the other hand, this shape may be related to a mechanism discussed by Skobov.[18]

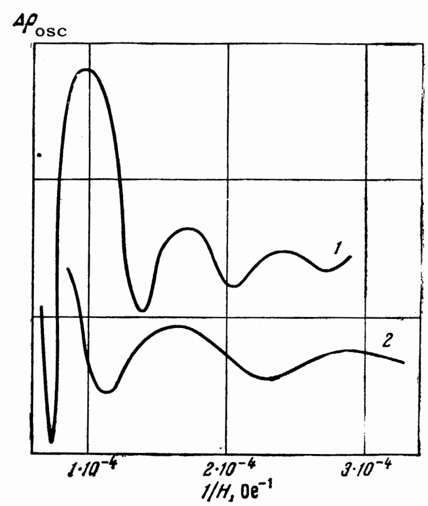

FIG. 6. Dependence of the oscillating part of the ρ(H) curve on the reciprocal of the magnetic field at T = 1.5°K. Curve 1 represents p = 0, curve 2 represents p = 7500 kg/cm^2. The curves are shifted along the ordinate axis by arbitrary amounts.

Under pressure, the ρ(H) curves become more symmetrical. If we adopt the first assumption, then under uniform compression the value of the spin splitting should increase, which may be due to a reduction of the effective mass.

F. Influence of pressure on the amplitude of oscillations and the residual resistance. We have mentioned that after the removal of pressure the amplitude of the electrical resistance oscillations become greater than before the application of pressure, although the residual resistance ρ_0 rose irreversibly (cf. the table). The increase of the amplitude after compression indicated that the quality of the single crystals had improved. This is because elastic deformation may, under certain conditions, reduce the number of defects in the lattice; this has been found, for example, for cadmium.[1] The increase of the residual resistance may be due to the formation of microcracks (which do not affect the oscillation amplitude) on compression and on the removal of pressure.

G. Some remarks on the relationship between the volume enclosed by the Fermi surface and the lattice parameters of bismuth. We showed above that in bismuth the appearance of groups containing small numbers of carriers is associated with nonzero values of the parameters **u** and γ of the bismuth lattice. There are as yet no data on the change in these parameters at low temperatures under pressure. Therefore, we cannot yet say definitely which of the parameters—**u** or γ—determines the amount of band overlap and, therefore, the carrier density in bismuth. However, the available data indicate that any change in the parameters a and c of the bismuth lattice, leading to a change of the c/a anisotropy, should reduce the electron and hole densities. The greater the change in the ratio c/a due to elastic deformation the greater the effect on the carrier density. This conclusion is in good agreement with the anomalously strong influence of uniaxial compression of bismuth along its trigonal axis on the electron density.[19]

At liquid helium temperatures, the phase transition to the metallic modification Bi III occurs at about 45,000 kg/cm^2.[20] We may also expect (Fig. 4) that the electron and hole densities in bismuth will vanish at a much lower pressure. Thus, at helium temperatures, bismuth should become a dielectric in the pressure range 20,000—45,000 kg/cm^2, if the Fermi surface model consisting of three electron ellipsoids and one hole ellipsoid is valid.[9,10]

In conclusion, we take this opportunity to express our gratitude to L. F. Vereshchagin and A. I. Shal'nikov for their interest in this work and to V. A. Sukhoparov for his help in carrying out the experiments.

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Translated by A. Tybulewicz
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