

## PRESSURE DEPENDENCE OF THE CONCENTRATION OF CURRENT CARRIERS IN SEMIMETALS OF THE BISMUTH TYPE

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The effect of hydrostatic compression on the electrical resistance characteristics in a magnetic field which are independent of the quality of the sample is investigated in bismuth, antimony, and arsenic. The pressure dependences of the current carrier concentration in bismuth, and arsenic are determined on the assumption that with the variation of the pressure  $p$  the variation of the anisotropy of the Fermi surface is not anomalously strong. With increasing pressure the concentration of current carriers in bismuth and arsenic decreases (in bismuth for  $p \approx 15$  kbar it decreases by a factor of five and in arsenic for  $p \approx 30$  kbar by a factor of 1.7). The concentration increases in antimony with increasing pressure (at  $p \approx 40$  kbar by a factor of 1.8). The measurements up to 17 kbar were carried out with single crystals, and above 17 kbar with polycrystalline samples. The results for bismuth are in very good agreement with oscillatory data,<sup>[1]</sup> and those for antimony cast doubt on the considerations of Falicov.<sup>[11]</sup>

### 1. INTRODUCTION

THE energy spectrum of the current carriers of a large number of metals has by now been rather thoroughly investigated and the effect of external factors, in particular of the pressure, upon it is of undoubted interest. By changing the distance between the atoms in the lattice, the pressure can yield valuable information about the genesis of the electronic structure of metals. Of special interest is a study of the effect of pressure on the electronic properties of semimetals. This is mainly due to the fact that in semimetals the concentration of current carriers is low and therefore small changes in the Fermi energy under the action of pressure should give rise to relatively large changes of the electron concentration.

The pressure dependence of the electron spectrum of a crystal is obtained directly from an investigation of various oscillatory effects under pressure. This method was used to determine the pressure dependence of the areas of the extremal cross sections of the Fermi surface in bismuth<sup>[1]</sup> and graphite.<sup>[2]</sup> These investigations were carried out on single-crystal samples up to pressures of the order of 15 kbar. It is extremely difficult to increase the pressure in such experiments because increasing pressure is accompanied by a rise in its nonhydrostatic nature which leads to damage of the crystal and the complete disappearance of the oscillations.

Certain information about the effect of pressure on the electronic structure can also be obtained from the simple dependence of the electrical resistance  $\rho$  of the sample on the applied pressure  $p$ . Such curves determine uniquely the pressure of the phase transition at which the principal rearrangement of the electronic structure occurs. On the other hand, it is often impossible to obtain from the  $\rho(p)$  curves information about changes of an evolutionary nature in the electron spectrum; this is basically due to the uncontrollable

influence of the quasihydrostatic pressure on the mobilities of the current carriers. Thus, in Bridgman's work<sup>[3]</sup> the  $\rho(p)$  dependences for polycrystalline antimony and arsenic samples ( $T = 300^\circ\text{K}$ , pressures up to 100 kbar) are qualitatively different for different samples. For some, for example, antimony samples  $\rho(p)$  increases initially and then decreases after  $\sim 20$  kbar; for others  $\rho$  decreases monotonically with pressure. The arsenic samples also varied in their behavior.

We have previously proposed<sup>[4]</sup> a new method of determining the effect of pressure on the concentration of current carriers in semimetals; this method does not require that the sample remain a single crystal and yields results which do not depend on the quality of the sample and which are determined solely by the magnitude of the applied pressure.

### 2. THEORY

As has already been shown by Pospelov,<sup>[5]</sup> for metals of the bismuth type with a Fermi surface close to a system of ellipsoids, in the relaxation-time approximation<sup>1)</sup> the following relation is valid:

$$\frac{2}{\pi e c} \int_0^\infty \sigma_{xx}(H) dH = \sum_i N_i q_i; \quad (1)$$

here the sum is taken over all types of current carriers,  $H$  is the magnetic field directed along the trigonal axis of the crystal,  $\sigma_{xx} = \rho_{xx}(\rho_{xx}^2 + \rho_{xy}^2)^{-1}$  is the conductivity in the basal plane (perpendicular to the trigonal axis),  $\rho_{xx}$  and  $\rho_{xy}$  are the electrical resistance tensor components measured experimentally,  $N_i$  is the concentration of current carriers of the  $i$ -th kind, and  $q_i$  are dimensionless parameters. In the two-band model

<sup>1)</sup>For bismuth and antimony ( $T = 4.2^\circ\text{K}$ ) such an approximation is according to the experimental data<sup>[6]</sup> close to reality. No corresponding experimental data are available for arsenic.

for a compensated metal ( $N_+ = N_- \equiv N$ ) relation (1) takes on the form

$$\frac{2}{\pi ec} \int_0^{\infty} \sigma_{xx}(H) dH = N(q_+ + q_-). \quad (1a)$$

For the following it is essential that the parameters  $q_i$  depend only on the degree of anisotropy of the mobility tensor, being rather stable against changes of the anisotropy. As a measure of the anisotropy it is convenient to choose the quantity

$$z = \mu_1(a^2\mu_3 + b^2\mu_2)^{-1}, \quad (2)$$

where  $\mu_k$  are the components of the mobility tensor along the axes of the ellipsoid,  $a = \sin \theta$  and  $b = \cos \theta$ ,  $\theta$  is the angle of emergence of the ellipsoid from the basal plane. Then

$$q = (z^{1/2} + z^{-1/2}) / 2. \quad (2a)$$

When the quantity  $z$  changes for example from 1 (isotropic case) to 100, the interval within which  $q$  changes will in all amount to  $1 \leq q \leq 5$ . Thus expression (1a) makes it possible to exclude the role of the mobilities and the ratio of the areas under the  $\sigma_{xx}(H)$  curves measured under various pressures will give directly the pressure dependence of the concentration of current carriers:

$$\int_0^{\infty} \sigma_{xx}^{(p)}(H) dH \Big/ \int_0^{\infty} \sigma_{xx}^0(H) dH = f_1(p) = \frac{N(p)}{N(0)}. \quad (3)$$

At the same time we exclude from consideration such cases as for example that in which the shape of the Fermi surface changes under the action of pressure without its volume changing.<sup>2)</sup>

According to Pospelov,<sup>[5]</sup> in the two-band model of a compensated metal the expression for  $\sigma_{xx}(H)H$  ( $H$  along the trigonal axis) can be given the form

$$\sigma_{xx}(H)H = ecN \sum_{i=1}^2 \frac{q_i H_{si}}{H^2 + H_{si}^2} H, \quad (4)$$

where  $H_{si}$  are certain characteristic fields, "saturation fields," for holes and electrons respectively determined by the relation

$$H_s = \frac{c}{[\mu_1(a^2\mu_3 + b^2\mu_2)]^{1/2}}. \quad (5)$$

There will be either one or two maxima on the  $\sigma(H)H$  curve. The equation for the extremal values  $H_{extr}$ , if one goes over to the dimensionless quantities

$$u = \frac{H_{extr}^2}{H_{s2}^2}, \quad t = \frac{H_{s1}}{H_{s2}}, \quad y = \frac{q_1}{q_2},$$

will take on the form

$$(yt + 1)u^3 + [yt(2 - t^2) + (2t^2 - 1)]u^2 + [yt(1 - 2t^2) + t^2(t^2 - 2)]u - t^3(y + t) = 0. \quad (6)$$

The solutions of Eq. (6) are in the general case very cumbersome but their characteristic features are readily seen from the special case  $y = 1$  (i.e.,  $q_1 = q_2$ ). In this case one can readily obtain all three roots:

$$u_1 = t; \\ u_{2,3} = 1/2[t^2 - 4t + 1 \pm |t - 1|(t^2 - 6t + 1)^{1/2}] \\ = 1/4(t - 1 \pm \sqrt{t^2 - 6t + 1})^2.$$

If  $t^2 - 6t + 1 < 0$ , i.e.

$$3 - 2\sqrt{2} < H_{s1}/H_{s2} < 3 + 2\sqrt{2}, \quad (7)$$

then there is only one maximum  $u = t$  on the  $\sigma(H)H$  curve, i.e.

$$H_{extr} = \sqrt{H_{s1}H_{s2}}. \quad (8)$$

If  $t^2 - 6t + 1 > 0$ , then there are two maxima ( $u_2$  and  $u_3$ ) and one minimum. The values of the function  $\sigma(H)H$  at the extremal points are:

$$(\sigma H)_1 = ecNq \frac{2\sqrt{t}}{1+t} = ecNq \frac{2\sqrt{H_{s1}H_{s2}}}{H_{s1} + H_{s2}} \equiv ecN\alpha_1, \quad (9) \\ (\sigma H)_{2,3} = ecNq \frac{t+1}{2|t-1|} = ecNq \frac{H_{s1} + H_{s2}}{2|H_{s1} - H_{s2}|} \equiv ecN\alpha_2.$$

The parameters  $\alpha$  in (9) do not only depend on the extent of the anisotropy of the mobility tensor  $z$  but through  $t$  they also depend on the ratio of the mobilities of holes and electrons  $\mu_+/\mu_-$ . The general case ( $y \neq 1$ ) leads to analogous formulas:

$$\{\sigma(H)H\}_{H=H_{extr}} = N\alpha, \quad (9a)$$

where  $\alpha$  differs from  $\alpha_1$  and  $\alpha_2$  by being multiplied by some cumbersome function  $F(\mu_+/\mu_-)$ .

The proportionality coefficient  $\alpha$  is less stable, compared with  $q$ , against possible changes of the anisotropy of the mobility tensors under pressure, since it includes mixed terms  $\mu_+/\mu_-$ . Therefore, if the electron and hole mobilities vary differently, then the relation

$$\frac{\{\sigma(H)H\}_{H=H_{extr}}^{(p)}}{\{\sigma(H)H\}_{H=H_{extr}}^{(0)}} = f_2(p) = \frac{N(p)}{N(0)} \quad (10)$$

is fulfilled less rigorously than (3). On the other hand, if (3) and (10) give close values for the functions  $f_1(p)$  and  $f_2(p)$  then the situation in which not the change in the concentration of current carriers but a change in the tensor components of the mobilities (especially such that the various  $q$  and  $\alpha$  parameters vary similarly with pressure) is decisive in the pressure variation of  $f_1$  and  $f_2$  becomes rather unlikely physically.

We note in conclusion that it is clear from considerations of dimensionality that relations of the type of (1a) and (9a) with certain dimensionless parameters of the form  $q$  and  $\alpha$  will also be correct for polycrystalline samples (with the condition  $N_+ = N_-$ ). The validity of this statement for the case of bismuth has been confirmed experimentally in<sup>[4]</sup>.

### 3. METHOD OF MEASUREMENT AND SAMPLES

Two types of bombs were used to obtain high pressures at liquid helium temperatures. Hydrostatic pressures up to 17 kbar were produced by slow compression at room temperature of a fifty-percent solution of oil in dehydrated kerosene in the working chan-

<sup>2)</sup>In the case of an isotropic relaxation time  $z$  is directly related to the shape of the ellipsoid:  $z^{1/2}$  is the ratio of the semiaxes of the ellipse in the intersection of the ellipsoid and of the basal plane. For bismuth theory<sup>[7]</sup> and experiment<sup>[1]</sup> show that under the action of pressure the change in the shape of the Fermi surface is not appreciable compared with the change of its volume.

nel of the bomb with subsequent cooling down to 4.2°K.<sup>[8]</sup> Slow compression is very important to prevent damage of the sample, since the kerosene-oil mixture thickens at pressures larger than 10 kbar even at room temperature. In this type of bomb the samples were freely mounted directly on the measuring electrodes introduced into the bomb through an Araldite resin seal. This made it possible to avoid additional stresses due to various forms of holders.

In producing pressures above 10 kbar use was made of a composite piston of beryllium bronze and weakly magnetic steel. Quasihydrostatic pressures up to 20–40 kbar were produced with the aid of a pressure booster<sup>[9]</sup> whose broad channel was filled with a solution of alcohol in water and whose narrow channel contained a pellet of AgCl with the samples pressed into it. A single-crystal sample was mounted in measurements in such a bomb but as a result of the nonhydrostatic nature of the compression it was strongly damaged and turned into a polycrystal in which the crystallites obviously had a preferred orientation close to the orientation of the initial single crystal. The measurements were conducted after “pressing” the sample under the maximum pressure in order to exclude strong changes in the mobility of the current carriers due to sample damage in different experiments.

The pressure in the bomb was measured by means of a superconducting manometer placed directly in the channel of the bomb. The superconducting transitions were recorded electronically at 22 cps. The accuracy of the pressure determination was determined by the width of the superconducting transition and amounted to ±0.2 kbar in the case of hydrostatic and to ±0.5 kbar for quasihydrostatic pressures.

Bismuth crystals of purity better than 99.9998 percent grown by the Kapitza method and characterized by a change of resistance of  $R_{300}^{\circ}\text{K}/R_{4.2}^{\circ}\text{K} \approx 100$  were used in the measurements. Single crystals of antimony ( $R_{300}/R_{4.2} \approx 1500$ ) were grown by the Bridgman method from 99.9999 percent pure material. The arsenic single crystal with  $R_{300}/R_{4.2} \approx 500$  grown by the Czochralski method was kindly provided by A. A.

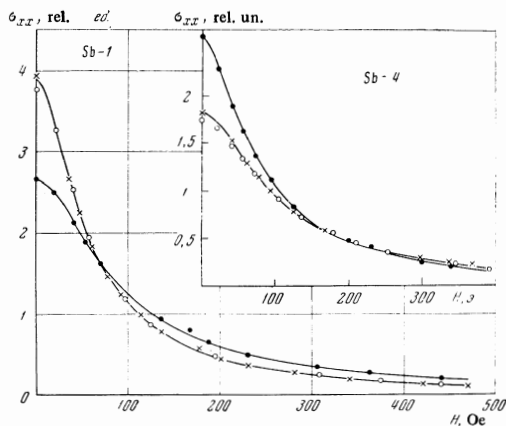


FIG. 1. Dependences  $\sigma_{xx}(H)$  for two single crystal samples of antimony: ● –  $p = 7.6$  kbar, X –  $p = 0$  (before applying pressure), ○ –  $p = 0$  (after taking off the pressure).

Kuliev (Physics Institute of the Azerbaijan S.S.R., Baku). For the polycrystalline samples the ratio  $R_{300}/R_{4.2}$  decreased to values  $\approx 3$  for bismuth,  $\approx 20$  for antimony, and 10–20 for arsenic which attests to the finely dispersed nature of their structure. The dimensions of the samples cut out by electroerosion from bulk single-crystal blocks were limited by the working channel of the bomb and amounted to  $2.5 \times 0.5 \times 0.5$  mm. The orientation of the crystals in mounting was determined from the direction of the cleavage planes, and in a magnetic field— according to the rotation rosettes.

Measurements of the magnetic resistance and the Hall emf in bismuth, antimony, and arsenic were carried out at  $T = 4.2^{\circ}\text{K}$  in magnetic fields (predominantly with  $H$  directed along the trigonal  $C_3$  axis of the crystal) up to 2 kOe for single-crystal samples and up to 19 kOe for polycrystalline samples. The electrical resistance was measured potentiometrically with the use of a M17/1 galvanometer or a photocompensated F-18 microvoltampere meter with a sensitivity of  $\sim 10^{-8}$  V/mm.

The range of fields for which measurements were carried out was determined by the rate of increase of the resistance as a function of the field  $H$  for the given sample. The magnitude of the field  $H_5$  of (5) was estimated from the abscissa of the maximum (8) on the  $\sigma(H)H$  curve. In practice, for calculating the area

$$\Sigma = \int_0^{\infty} \sigma(H) dH$$

it turned out that it is sufficient to cover a range of

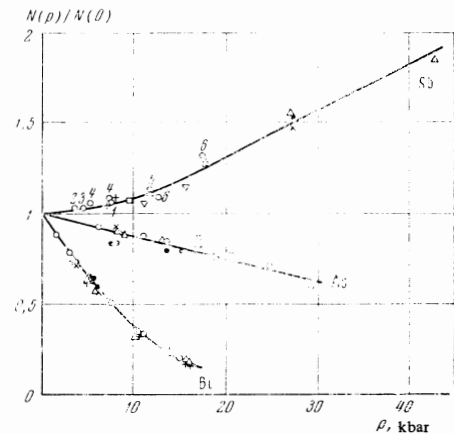


FIG. 2. The relative change of the concentration of current carriers in bismuth, antimony, and arsenic with pressure. Antimony: ○ – single-crystal sample, calculation according to formula (3) (the numbers denote the different samples); + – single-crystal sample, calculation according to formula (10); □, Δ, ▽, ● – polycrystalline samples, calculation according to formula (10); X – calculation according to formula (3) carried out by extrapolation to the region of large fields of the data of the polycrystalline sample (●). Arsenic: Δ – single-crystal sample, calculation according to formula (3), X – calculation according to formula (10); ●, ○ – polycrystalline samples, calculation according to formula (10). Bismuth: ● – single-crystal sample,  $H||C_3$ , calculation according to formula (3); X – single-crystal sample,  $H||C_2$ , calculation according to formula (3); Δ – two polycrystalline samples, calculation according to (3); + – calculation for the same samples according to formula (10); ○ – results of measurements by oscillatory methods.

fields  $\sim(10-20)H_S$  which corresponded to a change in the resistance  $R'(H)/R(0) \sim 250-300$ . The error in determining  $\Sigma$  resulting from the circumstance that the areas under the  $\sigma(H)$  curves were determined within finite limits did not exceed 5-7 percent. Because the sign of the discarded area is always known, the error in determining the ratios of these areas is appreciably lower. The area was determined by means of a planimeter with an accuracy of 1-2 percent.

For single-crystal samples we employed, along with a determination of the change of concentration in accordance with (3), also relation (10). For polycrystalline samples having a large residual resistance magnetic fields up to 19 kOe turned out often to be insufficient for a determination of  $\Sigma$ , and we used only relation (10).

#### 4. MEASUREMENT RESULTS

**A. General remarks.** The first important result is comprised in the fact that the functions  $f_1(p)$  and  $f_2(p)$  determined do not depend on the quality of the sample. This is most clearly illustrated by Fig. 1 which shows  $\sigma(H)$  curves of two single crystal samples of antimony. Under pressure the conductivity in zero field  $\sigma_0$  increases in sample Sb-4 and decreases in sample Sb-1. Nevertheless, the area under the  $\sigma(H)$  curve of sample Sb-1 increases as in the case of Sb-4 with pressure, and the values of  $f_1(p)$  of these samples fall on a single curve (Fig. 2). The decrease of  $\sigma_0$  with pressure in Sb-1 is apparently connected with an appreciable decrease of the mobilities which masks the effect of the increase of the current carriers. This is confirmed by the increase of the saturation fields  $H_S$  for this sample under the action of pressure (Fig. 3). It is seen that the coordinate  $H_{extr}$  for Sb-1 shifts strongly to the right. According to (5) and (8) the field  $H_{extr} \propto \mu^{-1}$ . Thus, relations (3) exclude in fact the role of the mobilities. An analogous conclusion is also valid for relation (10) (Figs. 2 and 3).

A second important result is comprised in the experimental confirmation of the correctness of relations (3) and (10) also for polycrystalline samples. It is seen from Fig. 2 that for all the investigated semimetals the dependences  $f_1(p)$  and  $f_2(p)$  obtained with polycrystal-

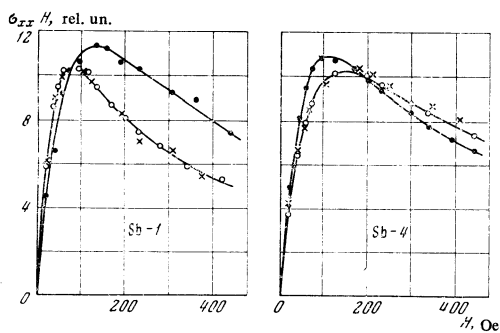


FIG. 3. The dependence of  $\sigma_{xx}H_s$  on  $H$  for two single-crystal samples of antimony:  $\bullet$  -  $p = 7.6$  kbar,  $\times$  -  $p = 0$  (before applying pressure),  $\circ$  -  $p = 0$  (after taking off the pressure).

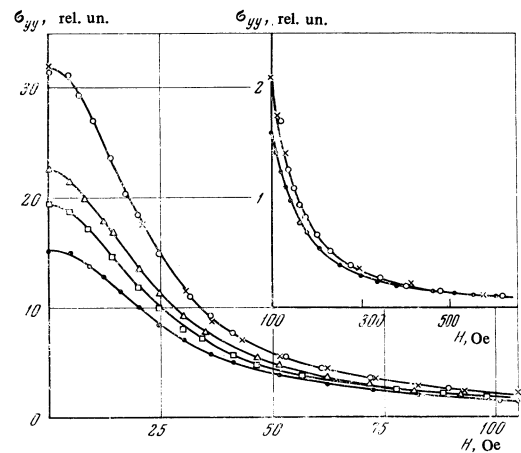


FIG. 4. The  $\sigma_{yy}(H)$  dependences for a single crystal sample of bismuth for  $H||C_2$ :  $\bullet$  -  $p = 6.1$  kbar,  $\square$  -  $p = 5.2$  kbar;  $\Delta$  -  $p = 3.7$  kbar,  $\circ$  -  $p = 0$  (before applying pressure),  $\times$  -  $p = 0$  (after taking off a pressure of 6.1 kbar). The "tails" of the  $\sigma_{yy}(H)$  dependences are shown on the upper right.

line samples are in good agreement with the appropriate dependences for single crystals.

Thirdly, the dependences  $f_1(p)$  and  $f_2(p)$  determined for bismuth, antimony, and arsenic in accordance with (3) and (10) turn out to be close to one another (Fig. 2). As has been noted above, such internal agreement between the various effects should indicate that relations (3) and (10) yield directly the pressure dependence of the concentration of current carriers. This circumstance also removes the possible suspicion of the effect of the sample dimensions on the results of the measurements in the hydrostatics. For example, for the antimony samples ( $R_{300}/R_{4.2} \sim 1500$ ) the mean free path of the current carriers at  $T = 4.2^\circ K$  is of the order of 0.1 mm which is comparable with the dimensions of the samples used. It is clear, however, that for polycrystalline samples ( $R_{300}/R_{4.2} \sim 20$ ) this effect is absent. The agreement

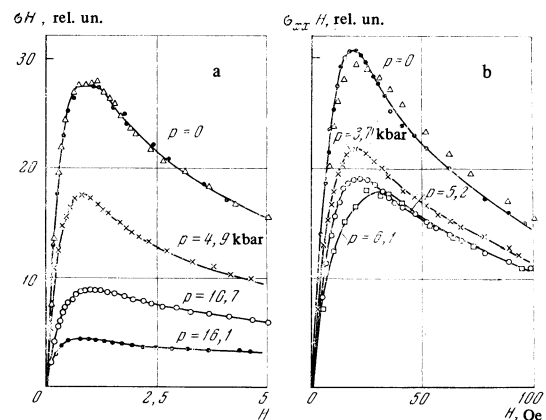


FIG. 5. The dependences of  $\sigma_H$  on  $H$  for polycrystalline (a);  $H$  in kOe) and single-crystal samples (b) of bismuth. The notation for  $p = 0$  in the case of a:  $\bullet$  - after taking off a pressure of 16.1 kbar,  $\Delta$  - after taking off a pressure of 4.9 kbar; in the case of b:  $\circ$  - before applying pressure,  $\Delta$  - after taking off a pressure of 6.1 kbar.

of the results for  $f(p)$  from single-crystal and polycrystalline samples indicates that if indeed there is a size effect (single crystal), then it does not affect the results of the determination of  $f(p)$ .

**B. Bismuth.** The curves of the dependences of  $\sigma$  on  $H$  for single-crystal and polycrystalline samples of bismuth up to pressures of 6 and 16 kbar respectively were presented in<sup>[4]</sup>. Here we present the combined curve of the dependence of  $f$  on  $p$  (Fig. 2), the dependences  $\sigma_{yy}(H)$  measured in a magnetic field directed along the binary  $C_2$  axis of the crystal up to 6 kbar (Fig. 4), as well as the dependence  $\sigma(H)H$  for single-crystal and polycrystalline samples (Fig. 5).

In Fig. 2 we see the good agreement between the results obtained for bismuth according to (3) and (10) and the direct determination of  $N(p)/N(0)$  from the pressure dependence of the oscillatory effects.

The decrease of the areas under the  $\sigma_{yy}(H)$  curves with increasing pressure, clearly exhibited in Fig. 4, is analogous to the case when the field  $H$  is directed along the trigonal  $C_3$  axis of the crystal. The corresponding values of  $f_1(p)$  fall on the general curve of Fig. 2. This fact points to a low sensitivity of the  $f_1(p)$  dependence of (3) on the sample orientation and attests once again to the applicability of relations of the type of (3) to polycrystalline samples.

Figure 5 shows that the  $\sigma H$  dependences on  $H$  for bismuth have one clearly expressed maximum whose ordinate decreases reversibly with pressure. The abscissa of the maximum  $H_{extr} \approx (H_S^{(+)} H_S^{(-)})^{1/2}$  which serves as an estimate of the magnitude of the saturation fields increases from  $\sim 20$  Oe for a single-crystal sample (Fig. 5b) up to  $\sim 1000$  Oe for polycrystalline sample (Fig. 5a). However, the form of the curves (a single maximum) is retained in the entire range of variation of the saturation fields. This confirms the fact<sup>[6]</sup> that the saturation fields  $H_S^{(+)}$  and  $H_S^{(-)}$  can vary strongly from sample to sample but their ratio [see (7)] changes little. According to data in the literature  $H_S^{(-)}/H_S^{(+)} \sim 2$ .<sup>[6]</sup> Values of  $f_2(p)$  calculated from values of  $\{\sigma(H)H\}_{H=H_{extr}}$  are shown in Fig. 2 and differ from the corresponding values of  $f_1(p)$  by no more than 7--10 percent.

**C. Antimony**<sup>3)</sup>. Measurements of the  $\sigma_{xx}(H)$  dependence were carried out at pressures up to 17 kbar using six single crystals and at pressures up to 43 kbar using four polycrystalline samples. We note that whereas in bismuth the Hall component of the resistivity tensor  $\rho_{xy}$  is small and was not taken into account in calculating  $\sigma_{xx}$ , in the case of antimony the ratio  $\rho_{xy}/\rho_{xx}$  reached a value of  $\sim 0.3$  at the maximum and the contribution of  $\rho_{xy}$  to the conductivity turned out to be appreciable.

Characteristic  $\sigma_{xx}(H)$  dependences for two single-crystal samples at various pressures are shown in Fig. 1. The increase of the area under the  $\sigma_{xx}(H)$  curves with pressure indicates an increase in the concentration of current carriers. For these samples  $\sigma_{xx}(H)H$  dependences which have a clearly expressed

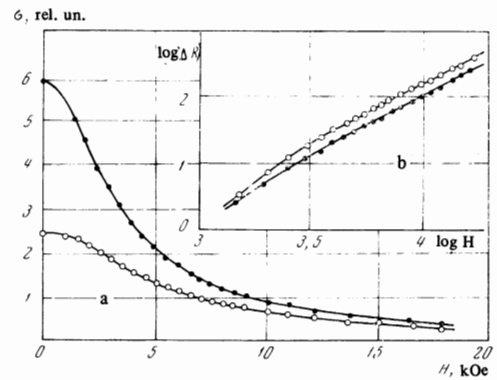


FIG. 6. The dependences  $\sigma(H)$  and  $\log \Delta R = f(\log H)$  for a polycrystalline sample of antimony:  $\circ - p = 0$ ,  $\bullet - p = 27.4$  kbar.

maximum whose height increases with pressure are presented in Fig. 3. According to<sup>[6]</sup>  $H_S^{(-)}/H_S^{(+)} \sim 5$  which is in agreement with the presence of a single maximum. The values of the saturation fields changed a little from sample to sample and were of the order of 100 Oe which is larger by a factor of 4--5 than in bismuth. The values of  $f_2(p)$  calculated from values of  $\{\sigma(H)H\}_{H=H_{extr}}$  agree with the data of the integral method with an accuracy of 4 percent.

In Fig. 6a we show the  $\sigma(H)$  dependence for one of the polycrystalline samples of antimony. The small change of the resistance in a magnetic field [ $R(H)/R(0) \sim 10$  for  $H \approx 19$  kOe] makes it impossible to determine  $\Sigma$  for polycrystalline samples from the experimental points. For this reason a calculation of the change of the concentration of current carriers with pressure was in this case carried out with the aid of (10) from the value of the maximum of the  $\sigma(H)H$  dependence.

Figure 7 shows characteristic  $\sigma(H)H$  curves for

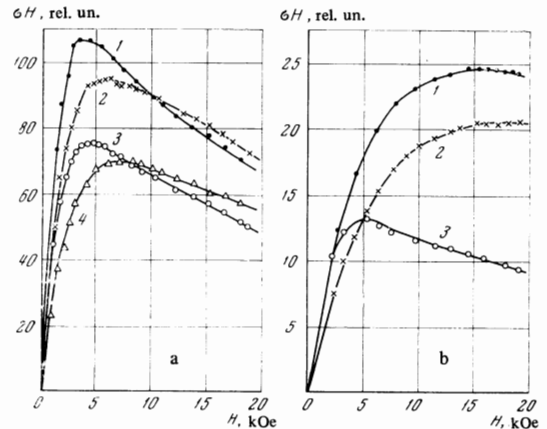


FIG. 7. The dependence of  $\sigma H$  on  $H$  for two polycrystalline samples of antimony. a: curve 1 -  $p = 27.4$  kbar, 2 -  $p = 17.8$  kbar, 3 -  $p = 0$  (after taking off a pressure of 17.8 kbar), 4 -  $p = 0$  (after taking off a pressure of 27.4 kbar); b: 1 -  $p = 43$  kbar, 2 -  $p = 27.2$  kbar, 3 -  $p = 6$  kbar (after taking off a pressure of 43 kbar).

<sup>3)</sup>Preliminary results obtained for antimony and arsenic were published in<sup>[10]</sup>.

two different polycrystalline samples at pressures up to 43 kbar. The increase of the ordinate of the maximum on these curves with pressure attests to a further increase in the concentration of current carriers. The saturation fields for the sample for which the data are presented in Fig. 7b are of the order of 20 kOe; as a result of this the maximum on the corresponding curves is not clearly evident. Generally speaking, we cannot maintain that for this sample there is only one maximum on the  $\sigma(H)H$  curve. However, if only the first maximum appears in Fig. 7b, then according to (9) the ratio of these maxima will also be proportional to the ratio of the concentrations of current carriers in the samples. The only thing of importance is that the shape of the  $\sigma(H)H$  curve should not change qualitatively with pressure. One can readily confirm the weak dependence of the ordinate of the maximum of the  $\sigma(H)H$  curves on the quantity  $t = H_{S1}/H_{S2}$  by means of (9).

It also turned out to be possible to estimate the variation of  $f(p)$  for polycrystalline samples from relation (3). Figure 6 shows the  $\sigma(H)$  dependences for one of the samples for  $p = 0$  and  $p = 27.4$  kbar, as well as  $\log \Delta R$  as a function of  $\log H$  for this sample. It is seen that starting with fields  $H \approx 4$  kOe,  $\Delta R \propto H^{1.8}$  with the law of variation of the resistance in a field not changing with the pressure. This circumstance makes it possible to extrapolate the curves of Fig. 6a into the region of high fields and carry out an estimate of  $f(p)$  by the method of (3). Such estimates at  $p = 17.8$  kbar and  $p = 27.4$  kbar give values of 1.30 and 1.47 which agree with calculations according to (10) with an accuracy of up to 6 percent.

The  $N(p)/N(0) = f(p)$  curve for antimony is shown in Fig. 2.

#### D. Arsenic. Measurements of the $\sigma(H)$ dependence

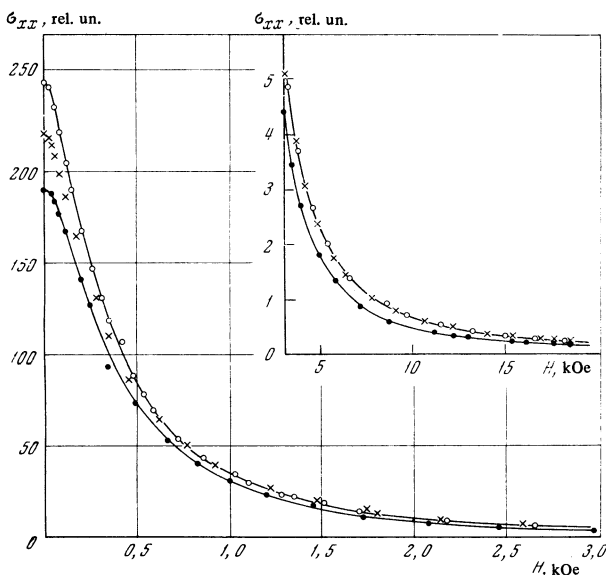


FIG. 8. The  $\sigma_{xx}(H)$  dependences for a single-crystal sample of arsenic:  $\bullet$  -  $p = 17.1$  kbar,  $\circ$  -  $p = 0$  (before applying pressure),  $\times$  -  $p = 0$  (after taking off the pressure). The "tails" of the  $\sigma_{xx}(H)$  dependences are shown on the upper right.

were carried out on one single-crystal sample of arsenic up to a pressure of 17 kbar and on two polycrystalline samples up to pressures of 30 kbar. Figure 8 shows the  $\sigma_{xx}(H)$  dependences for the single-crystal sample. The area under the  $\sigma_{xx}(H)$  curve decreases with increasing pressure. The height of the maximum on the corresponding curves of the  $\sigma_{xx}(H)$  dependence on  $H$  also decreases with pressure. This indicates that, unlike in the case of antimony, in arsenic the functions  $f_1(p)$  and  $f_2(p)$  decrease with pressure. The values of the functions  $f_1(p)$  and  $f_2(p)$  differ by no more than 7 percent.

Figure 9 shows the  $\sigma(H)H$  dependences for one of the polycrystalline samples. It is seen that the ordinate of the maximum also decreases with pressure.

The good agreement between all these data makes it possible to assume that the functions  $f_1(p)$  and  $f_2(p)$  give directly the change of the concentration of current carriers in arsenic with pressure. The  $f(p)$  dependence for arsenic is shown in Fig. 2.

## 5. DISCUSSION OF RESULTS

In Fig. 2 we present the variation of the concentration of current carriers (in relative units) in semimetals of the bismuth type with pressure obtained by the above method. The results for bismuth, are, as has already been indicated, in excellent agreement with the results of a direct determination of the volume of the Fermi surface under pressure by oscillatory methods. By the same token these results which are not new in essence are important as an experimental check and as an illustration of the proposed new method.

The data on the dependence  $N(p)/N(0) = f(p)$  for antimony and arsenic have been obtained for the first time. Of these the most interesting and to some extent unexpected is the result indicating an increase of current carriers in antimony with pressure. All the three metals, bismuth, antimony, and arsenic, have as is well known a similar crystallographic structure ( $D_{3d}^5$ ) and energy spectrum. It seemed natural to expect<sup>[11]</sup> that they change in a similar way under pressure. But the experimental facts presented in this article indicate

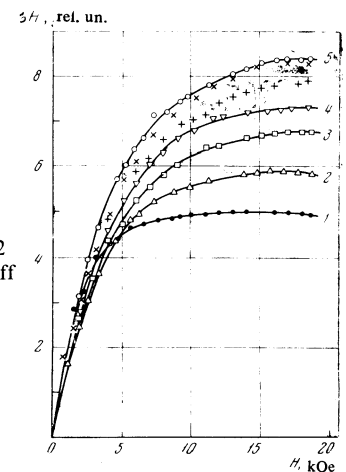


FIG. 9. The dependences of  $\sigma H$  on  $H$  for a polycrystalline sample of arsenic: 1 -  $p = 29.3$  kbar, 2 -  $p = 24.8$  kbar, 3 -  $p = 13.5$  kbar, 4 -  $p = 6.2$  kbar, 5 -  $p = 0$  (after taking off the pressure):  $\circ$  - 29.3 kbar,  $\times$  - 24.8 kbar, and  $+$  - 6.2 kbar.



otherwise. Even if one does not connect the functions  $f_1(p)$  and  $f_2(p)$  directly with the change of the concentration of current carriers under pressure, even then [since  $f_1(p)$  and  $f_2(p)$  are altogether not determined by the quality of the sample] the experimental data are uncontested evidence of various changes in the electron structure of these semimetals under pressure. However, as has been noted previously, taking into account the aggregate of experimental data the in itself anomalous fact of a change of the shape of the Fermi surface only under hydrostatic compression without a change of its volume appears unlikely. The increase of  $N(p)$  in antimony contradicts calculated estimates of the  $N(p)$  dependence carried out by Falicov<sup>[11]</sup> on the basis of a pseudopotential and experimental data<sup>[12]</sup> on the pressure dependence of the lattice parameter  $a$  and the rhombohedral angle  $\alpha$  of antimony. If the pseudopotential and the magnitude of the spin-orbit splitting in<sup>[11]</sup> were chosen correctly, then the reason for the discrepancy between Falicov's theoretical calculations and the data of this paper is probably the decisive influence of the change of the parameter  $u$  characterizing the displacement of the sublattices in antimony under pressure on the electron spectrum. No information is available on the change of the parameter under pressure; for this reason no account was taken in<sup>[11]</sup> of the possible change of  $u$  with pressure and the effect of such a change on the electron spectrum. In his prediction of the decrease of  $N$  with pressure in antimony Falicov also started out from the analogy of the structures appearing in the phase transitions BiI-BiII and SbI-SbII.<sup>[12,13]</sup> However, in accordance with the latest data,<sup>[14]</sup> the BiII modification is not cubic (like SbII) but monoclinic.

It is useful to point out a definite correlation of the data obtained by us and data on the Bi-Sb alloys. According to Barrett,<sup>[15]</sup> on adding antimony to bismuth the lattice parameter  $a$  decreases (compression analog) and on adding bismuth to antimony  $a$  increases (dilation analog). As is well known, the concentration of current carriers decreases in both instances<sup>[16]</sup> bringing the alloy with 8.5 percent antimony<sup>[17]</sup> from the bismuth side and with ~60 percent bismuth<sup>[18]</sup> from the antimony side into the semiconducting state.

It should also be noted that data on the  $R(p)$  dependence in antimony<sup>[3,19]</sup> indicate that prior to the phase transition at  $p \approx 70$  kbar in antimony the resistance decreases rather rapidly with increasing pressure, a fact which is difficult to reconcile with Falicov's assumption<sup>[11]</sup> that at pressures close to  $p \approx 70$  kbar antimony goes over into the semiconducting state.

If after the phase transition at  $p \approx 70$  kbar the antimony lattice becomes simple cubic, then according to Luttinger's rule<sup>[20]</sup> antimony should become a good metal. According to our data (Fig. 2) the concentration of current carriers in antimony increases continuously up to 40 kbar. We note that the symmetry of the Fermi surface in rhombohedral antimony does not correspond to cubic symmetry and cannot go over into the latter in a continuous manner; one cannot, therefore, represent the electron structure of cubic antimony as the result of a continuous increase in the volume of the Fermi surface of rhombohedral antimony. It is not clear what happens to the electron structure

at the transition itself, and it would therefore be extremely interesting to obtain any experimental data on the electronic structure of antimony directly near the phase transition at  $p \approx 70$  kbar.

Some remarks about the data obtained for arsenic follow. According to Priestley et al.<sup>[21]</sup> the hole part of the Fermi surface differs considerably from a simple ellipsoidal model and is on account of the presence of connecting necks a complex multiply-connected surface. However, in the case in which we are interested ( $H \parallel C_3$ ) the cross sections of the connecting necks making small angles with the trigonal axis are in accordance with<sup>[21]</sup> weakly prolate ellipsoids, i.e. their parameter  $q \approx 1$ . Since the volume of these connecting necks is also small compared with the "ellipsoidal" portion of the surface, the contribution of the corresponding quantity  $N_i q_i$  to the right-hand side of equality (1) can be neglected. Therefore even such a considerable change in the topology of the Fermi surface of arsenic as the disappearance of these connecting necks which can occur under the action of pressure apparently should not be appreciably reflected in the calculation of  $f_1(p)$  according to (3).

These considerations are generally inapplicable for polycrystalline samples of arsenic. Nevertheless, it was of definite interest to obtain the function  $f_2(p)$  according to (10) for pressures above 20 kbar and to compare it with the data of a calculation of  $f_1(p)$  by the integral method of (3) for single crystals at lower pressures. The reasonable agreement in the behavior of the functions  $f_1(p)$  and  $f_2(p)$  allows one to hope that in the case of arsenic the obtained information yields directly the change of the concentration of current carriers of arsenic with pressure.

Let us also note that the absolute change of the concentrations of current carriers in arsenic and antimony (Fig. 2) is much larger than in bismuth, since  $N(0)_{As}/N(0)_{Bi} \sim 700$  and  $N(0)_{As}/N(0)_{Bi} \sim 200$ . In this sense there is interest in the investigation of the effect of pressure on the Fermi surfaces of good metals, in a considerable number of which the change of the volume of large equal-energy surfaces is unexpectedly large. Thus, in lead all the observed frequencies of de Haas-van Alphen oscillations, proportional to the extremal cross sections of the Fermi surface, increase with pressure by 0.3 percent/kbar.<sup>[22]</sup>

We conclude with several remarks about the proposed method of obtaining information about the variation of carrier concentration with pressure. It is clear that from the galvanomagnetic characteristics one can also form other quantities which will also be of zeroth power in the mobilities and proportional to  $N(p)$ . The simplest is the quantity inversely proportional to the Hall coefficient,  $R^{-1} \propto N$ . However, this quantity turns out often to be less convenient than  $\Sigma$  and the ordinate of the maximum of the  $\sigma(H)/H$  curve. First, it is of first power in the charge, i.e. a difference characteristic which always leads to a large error. Secondly, as one can readily verify, it depends more strongly on a possible change of the anisotropy of the mobility tensor. The characteristics proposed in this paper are easily measured; in addition, they augment one another and a comparison of  $f_1(p)$  and  $f_2(p)$  allows one to form a reliable judgement of the dependence  $N(p)/N(0)$

$= f(p)$ .

From dimensionality considerations it is clear that relations of the type (3) and (10) will be valid for arbitrary compensated metals with two types of carriers. If the Fermi surface cannot be approximated by a system of ellipsoids, then the resulting mathematical difficulties do not make it possible to give an explicit expression for  $q$  even in the isotropic relaxation-time approximation. One can only state that certain dimensionless parameters which will depend on the shape of the Fermi surface will enter in relations of the type of (3) and (10).

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