PRESSURE-INDUCED ELECTRON TRANSITIONS IN BISMUTH-TIN, BISMUTH-LEAD, BISMUTH-ANTIMONY, AND BISMUTH-ANTIMONY-LEAD ALLOYS

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A study was made of the effect of hydrostatic pressure, up to 20 katm, on the galvanomagnetic properties of Bi-Pb, Bi-Sn, Bi-Sb-Pb alloys (in weak magnetic fields) at temperatures of $4.2-295°$K, using various orientations of the current and the field with respect to the crystallographic axes. Pressure-induced electron transitions, predicted by I. M. Lifshitz,[1] were observed and investigated. These transitions were due to basic changes in the energy spectrum: the disappearance of electron surfaces and the appearance of new hole surfaces, as predicted by Golin.[5] It was found that the energy spectrum of electrons in these alloys remained the same as in pure bismuth (the maximum broadening of the bottom of the conduction band of the alloys did not exceed 2×10^{-3} eV) and the main effect of the acceptor impurity was to shift the Fermi level. An alloy with a single-ellipsoid (hole) Fermi surface was obtained for the first time by the combined effect of an impurity and pressure on bismuth, and it was found that the relaxation time of holes was isotropic. It was demonstrated that the main carrier scattering mechanism in bismuth alloys at low temperatures was the scattering by ionized impurities.

INTRODUCTION

I. M. LIFSHITZ has shown[1] that the application of pressure to metals may produce electron transitions involving basic changes in the spectrum: the disappearance and appearance of new parts of the Fermi surface, as well as the transformation of open surfaces into closed ones, and conversely. In Bi and in Bi-Sb alloys, only one such transition may be observed, due to the disappearance of electron and hole constant-energy surfaces and the transition of these substances from the metal to the semiconductor phase.[2,3] The addition of donor (Te, Se) and acceptor (Sn, Pb) impurities to bismuth extends considerably the possibilities of observing electron transitions.

Before we consider electron transitions in Bi alloys, we must discuss some features of the energy spectrum of Bi. According to the results of many investigations (cf. a review given in[4]), the dispersion law of electrons at the L points of the reduced Brillouin zone (the notation is the same as in Golin's work[5]) is described satisfactorily by an ellipsoidal nonparabolic (ENP) nonquadratic model, proposed by Lax. Departures from the ellipsoidal shape at the electron extrema, discussed by M. H. Cohen, as well as by Abrikosov and Fal'kovskiĭ, are evidently very small.[6] The dispersion law for holes can be described, in the first approximation, by an ellipsoidal parabolic (EP) quadratic model, but there are indications of some departure from the quadratic nature of the law.[7]

A detailed calculation of the energy spectrum, carried out by Golin,[5] has shown that Bi has, in addition to the main overlapping extrema (at the points L and T), several completely filled extrema in the valence band and empty extrema in the conduction band. We may expect a study of the influence of the combined effect of impurities and pressure on the energy spectrum of Bi to yield information not only on the existence of addi-
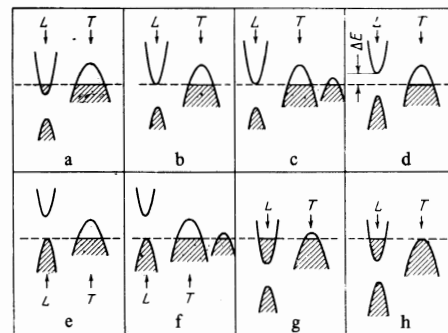

FIG. 1. Possible types of pressure-induced transition in Bi alloys. Spectra of alloys of Bi with acceptor impurities at: a) $p = 1$ atm; b) $p = p_{c1}$; c) $p = p_{c1}$ (in the presence of additional extrema); d) $p > p_{c1}$; e) $p = p_{c2}$; f) $p = p_{c2}$ (in the presence of additional extrema). Spectra of alloys of Bi with donor impurities at: g) $p = 1$ atm; h) $p = p_{c3}$.

tional extrema but also on their positions in the Brillouin zone.

The possible electron transitions under pressure in Bi alloyed with acceptor impurities (Sn, Pb) are shown in Fig. 1. A reduction in the band overlap under the influence of pressure results in the disappearance of electrons at the point L at some pressure p_{c1} at $T = 0°$K (Fig. 1b), i.e., it results in the transition $3_e + 1_h \to 1_h$ (e is an electron and h is a hole ellipsoid). The galvanomagnetic properties of such alloys should change appreciably at this transition since at pressures higher than p_{c1} only one group of carriers with an ellipsoidal Fermi surface remains in such an alloy. A study of this transition makes it possible to determine the pressure dependence of the electron density in an alloy and, if the pressure dependence of the rate of change of the band overlap ϵ_0 is known, we can determine also the dependence of the electron density on the Fermi energy.

When additional (3 or 6) hole extrema exist in the

vicinity of the point T, as predicted by Golin, an alloy of Bi with an acceptor impurity should exhibit pressure-induced transitions of the type $3_e + 3(6)_h + 1_h \rightarrow 3(6)_h + 1_h$ (Fig. 1c). At a pressure p_{c2}, when the Fermi level reaches the ceiling of the valence band, three new hole surfaces appear at L. The transitions $1_h \rightarrow 1_h + 3_h$ (Fig. 1e) or $3(6)_h + 1_h \rightarrow 3(6)_h + 1_h + 3_h$ (Fig. 1f) take place. Measurements at $p > p_{c2}$ should yield information on the hole extrema at L.

The possible pressure-induced changes in the energy spectra of Bi alloys with donor impurities (Te, Se) are shown in Figs. 1g and 1h. At some pressure p_{c3} (at $T = 0°K$), holes disappear at the point T (Fig. 1h) and the Fermi surface changes from the four-ellipsoid to the three-ellipsoid type, i.e., the transition $3_e + 1_h \rightarrow 3_e$ takes place. A study of this transition should, in principle, give information on the nature of the dispersion law of holes (right up to the ceiling of the valence band) in the investigated alloy.

It is known that Te and Se impurities behave as donors in Bi[8] while Sn and Pb impurities behave as acceptors.[6,7] It is very likely that the energy bands in bismuth alloyed with impurities in the usual range of concentrations assume the form typical of heavily doped semiconductors, whose theory has been developed recently.[9] In such semiconductors, the impurities remain ionized right down to the lowest temperatures, the Fermi level shifts considerably, and the dominant scattering mechanism at low temperatures is the scattering by ionized impurities.[10-12] It must be mentioned that the addition of up to 0.22 at.% Te, up to 0.125 at.% Sn or up to 0.39 at.% Pb to Bi does not alter appreciably the parameters of the crystal lattice of bismuth.[13] The Sb impurity which, like Bi, has five valence electrons, exerts a considerable influence on the energy spectrum of the carriers in Bi. When the concentration of Sb is increased, the band overlap in the alloy decreases. At the same time, the dispersion law of carriers remains, in the first approximation, the same as in pure Bi.[14] Pressure (like the addition of Sb) reduces the band overlap in Bi and compresses the Fermi surface which still retains, in the first approximation, its original shape.[15,16]

The present investigation deals with the pressure-induced electron transitions $3_e + 1_h \rightarrow 1_h$ and $3_e + 3(6)_h + 1_h \rightarrow 3(6)_h + 1_h$ in Bi and Bi-Sb alloys with acceptor impurities (Sn, Pb). We investigated the galvanomagnetic properties of single crystals of $Bi_{99.98}Sn_{0.02}$, $Bi_{99.96}Pb_{0.04}$, $Bi_{99.95}Pb_{0.05}$, and $Bi_{97.58}Sb_{2.4}Pb_{0.02}$[1] alloys in weak magnetic fields at pressures up to 20 katm in a wide range of temperatures $(4.2-295°K)$. In spite of the fact that the hole density P in these alloys was much higher (owing to the presence of acceptor impurities) than the electron density N, electrons still made a considerable contribution to almost all the galvanomagnetic coefficients and their presence was perceptible right down to densities of $(2-5) \times 10^{15}$ cm^{-3}. This was because the hole mobility decreased much more than the electron mobility in the case of the scattering of carriers by ionized acceptor impurities, and therefore a
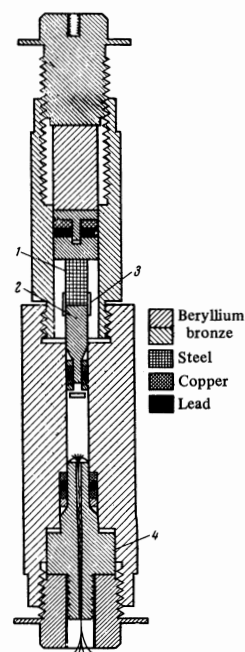
FIG. 2. General view of the pressure booster: 1) steel part of the plunger; 2) 2) bronze part of the plunger; 3) vinyl chloride centring tube; 4) stopper with leads connected to samples.

▨ Beryllium bronze
▨ Steel
▨ Copper
■ Lead

small number of fast electrons competed successfully with a large number of slow holes.

I. MEASUREMENT METHOD. SAMPLES

Pressures up to 10 000 atm were produced by means of the pressure booster described in[2]. A 50% mixture of dehydrated kerosene and transformer oil was used as the pressure-transmitting medium.[17] The pressure was applied at room temperature and then the booster was frozen. To obtain pressures higher than 10 000 atm, a modified method was used.

In the modified booster (Fig. 2), we used a composite plunger (the lower part was made of heat-treated beryllium bronze and the upper part of steel), we modified the plunger and stopper seals, and we employed a new pressure-transmitting medium (a mixture of 80% pentane and 20% transformer oil). This modification enabled us to extend the applied pressures to 20 000 atm with a maximum pressure inhomogeneity in the working space not exceeding ± 50 atm. Special tests established that the steel part of the plunger, which was demagnetized before use, did not distort appreciably the magnetic field in the region where samples were placed and did not influence the accuracy of the determination of the pressure, which was deduced from the shift of the superconducting transition temperature of tin[18] by a radio method.[19]2) The components of the galvanomagnetic tensor were measured in weak magnetic fields by a compensation method using a PMS-48 potentiometer and a photomultiplier.[20] The accuracy of the electrical measurements, limited by the fluctuations of the thermoelectric power in the measuring circuit, was 5×10^{-9} V. The temperature dependences of the galvanomagnetic coefficients were determined in the $10-100°K$ range using an automatic temperature controller.[21]

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[1]These formulas give the concentrations (in at.%) of Sb, Pb, and Sn determined from the amount of the impurity introduced into the melt during the preparation of these alloys.

[2]This method will be described in detail in a future issue of Pribory i Tekhnika Eksperimenta.

The method used in the preparation of single crystals of the alloys investigated in the present work was similar to that described in[14]. The samples, in the form of rectangular parallelepipeds 3−3.5 mm long and of ∼ 0.7 × 0.8 mm cross section, were cut from the central portions of single crystals by electric-spark machining. The single crystals were first oriented on a goniometer to within ± 0.5° using reflections from etch pits. Before being mounted the samples were etched in a mixture consisting of 50% C_2H_5OH and 50% HNO_3. The whole mounting operation was carried out under an MBS-1 microscope, which was also used to determine the dimensions of the samples and the distances between the electrodes. The current electrodes were soldered with a miniature soldering iron and the potential electrodes (40 μ in diameter) were attached by electric-spark welding.[22] In the majority of cases, the departure of the sample shape from the ideal did not exceed 5% so that the maximum error in the calculation of the electrical resistivity never exceeded 15%.

The samples used in this investigation could be divided into two types (in accordance with the orientation of their crystallographic axes with respect to their faces): samples of type A with their trigonal axis directed along the length of the sample and the binary and bisector axes directed along the lateral faces; in samples of type B with their binary axis along the sample and the trigonal and bisector axes directed along the lateral faces. The accuracy in the determination of the orientation of the crystallographic axes with respect to the faces of the samples was ± 2° (in type B samples, two faces were cleavages along the basal plane).

We placed two samples (one of type A and the other of type B) into the working space of the pressure booster; this enabled us to determine, at one pressure, six independent quantities representing the galvanomagnetic properties of a crystal in a weak magnetic field: for a type A sample, we measured the electrical resistivity ρ_{33}, the transverse magnetoresistance coefficient $(\Delta\rho/\rho H^2)_3 = \rho_{33,11}/\rho_{33}$ and the Hall component of the resistivity ρ_{231}; for a B type sample, we determined the resistivity ρ_{11}, the transverse magnetoresistance coefficient $(\Delta\rho/\rho H^2)_1 = \rho_{11,33}/\rho_{11}$, and the Hall component $\rho_{123} = -\rho_{213}$ (the notation used is generally accepted and it is given in Zitter's paper[23]).[3] The subscript 1 was used to represent the direction of the binary axis; the subscript 2, the direction of the bisector axis; and the subscript 3, the direction of the trigonal axis. The Hall component ρ_{ijk} was equal to the Hall coefficient R_{ijk} with the opposite sign. The magnetic field orientation with respect to the faces of the samples was determined to within ± 2°.

Okada[24] has demonstrated that the galvanomagnetic properties of Bi-type crystals in weak magnetic fields are fully described by 12 independent components of the galvanomagnetic tensor. A calculation was carried out by Abeles and Meiboom[25] and Zitter[23] for pure Bi has related the components of the galvanomagnetic tensor to the carrier densities and mobilities. The equations obtained by Zitter[23] were used in the present investigation to calculate the carrier densities and

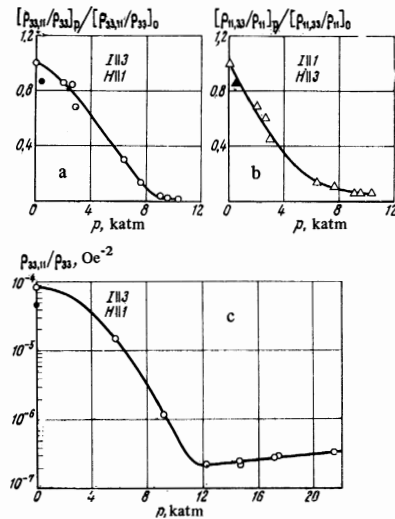FIG. 3. Pressure dependences of the magnetoresistance coefficients $\rho_{33,11}/\rho_{33}$ and $\rho_{11,33}/\rho_{11}$ at T = 4.2°K. a), b) $Bi_{99.95}Pb_{0.05}$ alloy, O, ● − sample B1, △, ▲ − sample B2; c) sample E1 of $Bi_{99.98}Sn_{0.02}$-II alloy (a black dot or triangle represents the state after removal of pressure).

mobilities in the alloys (the influence of the scattering by ionized impurities on the relaxation time anisotropy will be discussed later). To make sure that the interpretation of the results was reliable, the impurity concentrations should be equal for each pair of samples tested at the same time. One of the criteria, indicating that this condition was satisfied in the case of binary alloys, was the equality of the critical pressures at which the electron transitions took place. Usually, pairs of samples (of type A and B) were taken from neighboring regions of a single crystal and this guaranteed, in the majority of cases, that the impurity concentrations in such pairs were equal. The influence of the size effects[26] on the results of measurements could be neglected since the maximum mean free path (for electrons) in alloys of bismuth with Sn and Pb was 7×10^{-3} mm, and in the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy, this path was 1×10^{-2} mm.

II. RESULTS OF MEASUREMENTS

In the measurements of the components of the galvanomagnetic tensor we ensured that the magnetic fields H were weak: $\mu H \ll 1$. The required value of the working field was determined in preliminary measurements from the field dependences of the magnetoresistance and the Hall emf. The measurements showed that the electron transitions were qualitatively similar in all the investigated alloys. This enabled us to present jointly the results obtained for all the alloys (the greater part of the data for the $Bi_{99.96}Pb_{0.04}$ and $Bi_{99.95}Pb_{0.05}$ alloys was presented in[12]).

1. Magnetoresistance

It is evident from Fig. 3 that the transverse magnetoresistance coefficients $\rho_{33,11}/\rho_{33}$ and $\rho_{11,33}/\rho_{11}$ at liquid helium temperatures decrease reversibly with increasing pressure for all the alloys. The effect is particularly strong for the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy, with the lowest concentration of acceptor impurities. At a certain criti-

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[3] For the $Bi_{99.96}Pb_{0.04}$ alloy, we also measured the longitudinal magnetoresistance coefficient $\rho_{11,11}/\rho_{11}$ at p = 0.

Table 1

Alloy	p_{c1}, katm	$P + P_n$ (cf. Table 2), cm^{-3}	ρ_{33}/ρ_{11} at T = 4.2°K	
			p = 1 atm	p = p_{c1}
$Bi_{97.58}Sb_{2.4}Pb_{0.02}$	8±0.5	$(0.7\pm0.1)\cdot10^{18}$	1.17	9.9
$Bi_{99.96}Pb_{0.04}$	12±1	—	1.08	7
$Bi_{99.95}Pb_{0.05}$	9.5±0.5	—	1.62	4.6
$Bi_{99.98}Sn_{0.02}$-I	9±0.5	$1.39\cdot10^{18}$	1.39	4.55
$Bi_{99.98}Sn_{0.02}$-III	5±0.5	$1.77\cdot10^{18}$	2.1	3.1

cal pressure p_{c1}, which depends on the impurity concentration in an alloy (cf. Table 1), the rate of decrease of the magnetoresistance with the pressure slows down very appreciably. Near the critical pressures, the temperature dependences of the magnetoresistance coefficient $\rho_{33,11}/\rho_{33}$ (Fig. 4) exhibit a region of anomalous rise of the magnetoresistance with temperature, which shifts in the direction of higher temperatures when the pressure is increased.

2. Hall Effect

At atmospheric pressure and T = 4.2°K, the Hall effect of the investigated alloys is strongly anisotropic (both independent Hall coefficients R_{231} and R_{123} are negative). Under the influence of pressure, the anisotropy of the Hall effect of each of the alloys increases at first (Fig. 5) and then decreases rapidly and disappears at a pressure p_{c1} (cf. Table 1); at this pressure, both Hall coefficients become positive. At pressures $p > p_{c1}$, the Hall coefficients are independent of the magnetic field intensity (Fig. 6).

The nature of the temperature dependences of the Hall coefficients is strongly affected by the pressure (Fig. 7). It should be mentioned that at pressures exceeding the critical values, the Hall coefficients, whose signs have been reversed, begin to depend strongly on the magnetic field when the temperature is increased.
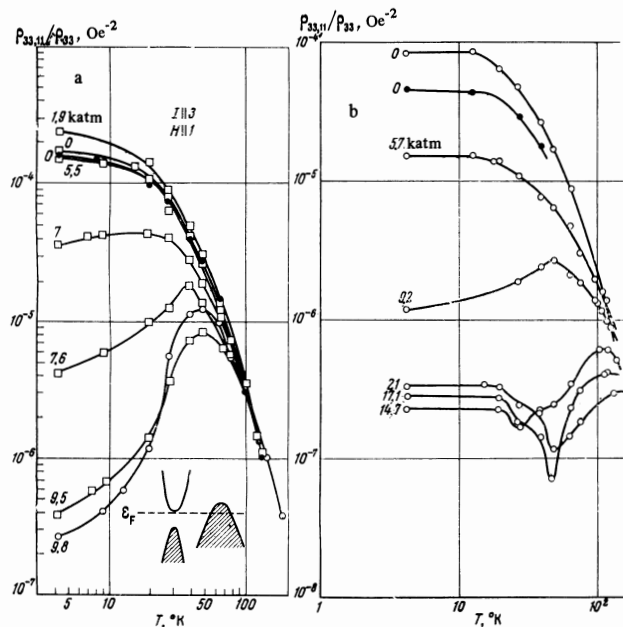

FIG. 5. Pressure dependences of the Hall coefficients R_{231} and R_{123} at T = 4.2°K: a) $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy, samples C1 (O), C2 (□) C3 (△); b) $Bi_{99.98}Sn_{0.02}$-I alloy, samples D1 (O, ●), D2 (+), D3 (□, ■), D4 (△) (a black dot or square represents the state after the removal of the pressure).

3. Resistivity

The anisotropy of the resistivity ρ_{33}/ρ_{11} of the investigated alloys is presented in Table 1 for atmospheric pressure and T = 4.2°K. Under the action of pressure, ρ_{33}/ρ_{11} increases (Fig. 8) and, in the case of some alloys, reaches a considerable value at the critical pressure p_{c1}. At $p > p_{c1}$ (and low temperatures), the resistivities ρ_{33} and ρ_{11} of the $Bi_{99.98}Sn_{0.02}$ alloy decrease when the pressure is increased.

Under the influence of pressure, the temperature dependence of ρ_{33} of all the alloys assumes the "semiconductor" form in a certain range of temperatures (Fig. 9).

III. DISCUSSION OF RESULTS

1. Pressure-Induced Electron Transitions

When the temperature is lowered to T = 0°K, the electron transitions of the type $3_e + 1_h \rightarrow 1_h$ should be

FIG. 4. Temperature dependences of the magnetoresistance coefficient $\rho_{33,11}/\rho_{33}$ at various pressures: a) $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy, samples C1 (□) and C2 (O, ●); b) sample E1 of $Bi_{99.98}Sn_{0.02}$-II alloy (a black dot represents the state after the removal of the pressure).
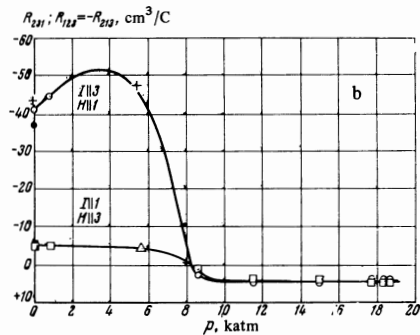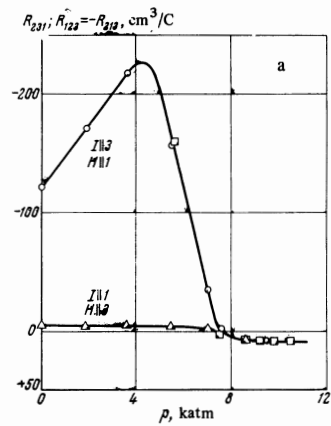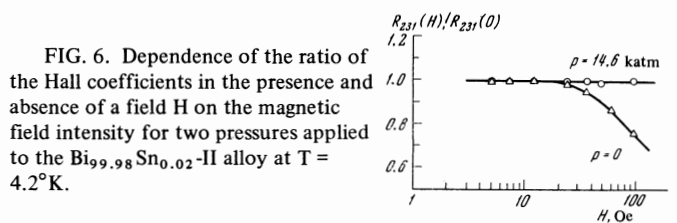
FIG. 6. Dependence of the ratio of the Hall coefficients in the presence and absence of a field H on the magnetic field intensity for two pressures applied to the $Bi_{99.98}Sn_{0.02}$-II alloy at T = 4.2°K.
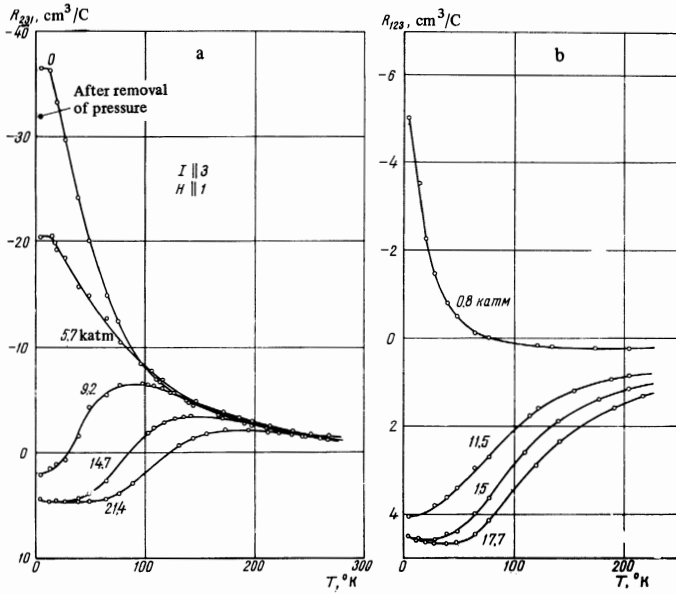
FIG. 7. Temperature dependences of the Hall coefficients R_{231} and R_{123} at various pressures: a) sample E1 of the $Bi_{99.98}Sn_{0.02}$-II alloy; b) sample D3 of the $Bi_{99.98}Sn_{0.02}$-I alloy.

accompanied by large changes in the galvanomagnetic properties of the investigated material:

a) the transverse and longitudinal magnetoresistance coefficients, which are quite large for a complex Fermi surface and a two-band carrier spectrum, should vanish in the transition to a single-ellipsoid Fermi surface if the carrier gas is degenerate, the relaxation time is isotropic, and $T = 0°K$[27].[4)]

b) The Hall effect should become isotropic at $p \geq p_{c1}$; at the same pressure, the dependence of the Hall coefficient on the magnetic field should disappear and the Hall coefficient should change from negative to positive.

c) The electrical conductivity anisotropy should become equal to the anisotropy of the hole mobilities at $p = p_{c1}$.

Obviously, the clearest transition of the $3_e + 1_h \rightarrow 1_h$ type is observed for the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy, which satisfies all the conditions which we have just listed (Figs. 4, 5, and 8). The concentration of ionized Pb impurities, determined at $p > p_{c1}$ is lowest in this alloy, compared with the other investigated alloys (Table 1), and the critical transition pressure p_{c1} is fairly low due to the presence of Sb impurities, which do not change the carrier dispersion law but reduce considerably the energy band overlap. On the other hand, the electron transitions in the $Bi_{99.95}Pb_{0.05}$ and $Bi_{99.98}Sn_{0.02}$ alloys exhibit some features which indicate that these transitions are more complex [one of the possible, more complex transitions, $3_e + 3(6)_h + 1_h \rightarrow 3(6)_h + 1_h$, has been discussed in the Introduction].

Let us consider first some characteristic properties of the electron transitions associated with the disappearance of three electron ellipsoids, which are common to all the alloys. A strong pressure-induced reduction of the transverse magnetoresistance at $T = 4.2°K$ (for the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy the magnetoresistance coefficient $\rho_{33,11}/\rho_{33}$ decreases reversibly by a factor of ~ 580, while that of the $Bi_{99.98}Sn_{0.02}$ alloy decreases by a factor of ~ 180) stops after the completion of the elec-

tron transition when the electron density becomes $N = 0$. At $p > p_{c1}$, the magnetoresistance of the alloys does not depend strongly on the pressure and a definite kink in the curves indicates that the bottom of the conduction band is quite well defined (Fig. 3). The electron contribution to the Hall coefficients R_{231} and R_{123} at low pressures and $T = 4.2°K$ is greater than the hole contribution, in spite of the fact that $P > N$ even at atmospheric pressure. The Hall coefficient R_{231} is strongly sensitive to the presence of electrons and therefore it even increases initially with increasing pressure (N decreases with pressure) (Fig. 5). The energy band spectra of the alloys are not basically affected by the electron transitions, as indicated by the absence of an appreciable pressure dependence of the Hall coefficients at $p > p_{c1}$. When the electrons (which make an isotropic contribution to the electrical conductivity) disappear, the anisotropy of the resistivity ratio ρ_{33}/ρ_{11} of the alloys increases (Fig. 8) due to a considerable anisotropy of the hole mobilities.
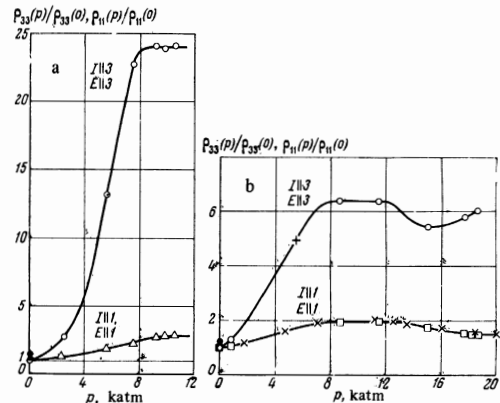

FIG. 8. Relative change in the resistivities ρ_{33} and ρ_{11} due to the application of pressure at $T = 4.2°K$: a) $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy, samples C2 (O, ●), C4 (△, ▲); b) $Bi_{99.98}Sn_{0.02}$-I alloy, samples D1 (O, ●), D2 (+), D3 (□, ■), D4 (X) (a black dot, triangle, or square denotes the state after the removal of the pressure).

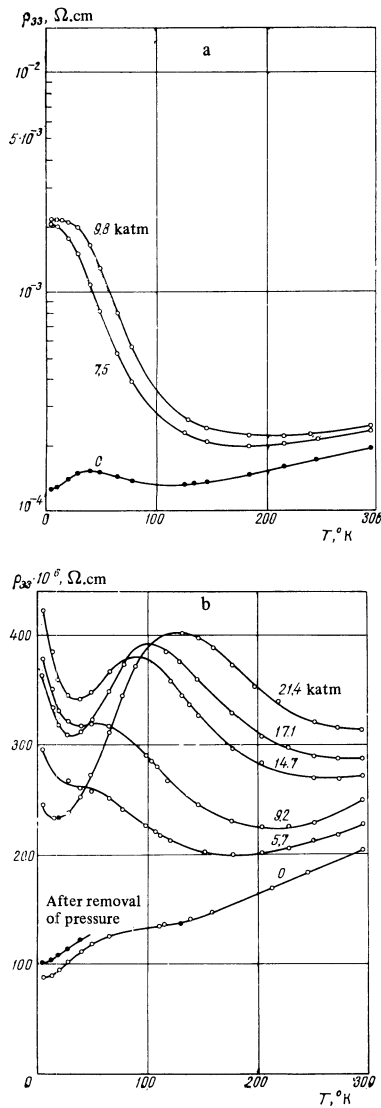[4)]This result follows also from Zitter's formulas [23] for $N = 0$.

FIG. 10. Anisotropy of the hole contribution to the electrical conductivity, $A_h = (\rho_{33}/\rho_{11})_{p_{C_1}}$, for Bi and its alloys as a function of the hole density (Table 2) at $T = 4.2°$K: Bi (O), $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ (□), $Bi_{99.98}Sn_{0.02}$-I (Δ), $Bi_{99.98}Sn_{0.02}$-III (+).

FIG. 9. Temperature dependences of the resistivity ρ_{33} at various pressures: a) sample C2 of the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy (the curve corresponding to zero pressure was obtained after tests at higher pressures p); b) sample E1 of the $Bi_{99.98}Sn_{0.02}$-II alloy.

We must mention also that, at sufficiently high temperatures, the electron transitions in the alloys are "smeared out" because of the thermal generation of carriers in the bands. The thermal generation of fast electrons in the conduction band produces anomalies in the temperature dependences of all the galvanomagnetic coefficients at $p > p_{C_1}$: the temperature dependences of the magnetoresistance show regions of the rise of $\rho_{33,11}/\rho_{33}$ and $\rho_{11,33}/\rho_{11}$ with increasing temperature (Fig. 4), the sign of the Hall coefficient R_{231} is reversed when the temperature is increased (Fig. 7), and the temperature dependences of the resistivity ρ_{33} exhibit regions of the "semiconductor" type (Fig. 9).

The most important feature of the electron transition in samples of the $Bi_{99.98}Sn_{0.02}$ alloy, with a concentration of $(1.37 - 1.77) \times 10^{18}$ cm^{-3} of ionized Sn impurity atoms at $p > p_{C_1}$ (Table 1), is the presence of two regions with the "semiconductor" type of temperature dependence of the resistivity ρ_{33} at $p > p_{C_1}$ (Fig. 9b). The fall of the
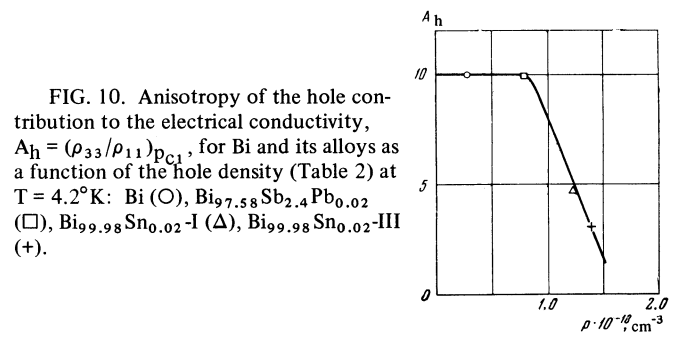
resistivity in the second (high-temperature) region is due to the thermal generation of electrons across a gap ΔE (Fig. 1d), which increases with pressure. The fall of the resistivity (with increasing temperature) in the low-temperature region is, in our opinion, due to the thermal generation of holes at the valence band extrema, which are in the immediate vicinity of the Fermi level of this alloy. The fact that, in this case, we observe the thermal generation of holes and not electrons follows from the constancy of the Hall coefficients in that range of temperatures where the first fall of ρ_{33} is observed (Fig. 7a). The temperature dependence of the magnetoresistance coefficient $\rho_{33,11}/\rho_{33}$ has the usual "metallic" nature and the anomalous rise of the magnetoresistance, caused by the thermal generation of electrons, is observed at higher temperatures (Fig. 4b, curves for $p > 14.7$ katm).

Comparison of the results obtained for the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ and $Bi_{99.98}Sn_{0.02}$ alloys at $p = p_{C_1}$ and $T = 4.2°$K shows that the appearance of new holes in the $Bi_{99.98}Sn_{0.02}$ alloy, associated with a stronger downward shift of the Fermi level under the action of the acceptor impurity, is accompanied by a reduction in the anisotropy of the hole contribution to the electrical conductivity $A_h = (\rho_{33}/\rho_{11})_{p_{C_1}}$ (Fig. 10). Obviously, these new holes partly screen the strongly anisotropic contribution of holes in the ellipsoid at the point T in the Brillouin zone so that this contribution can be observed in its pure form only at ionized acceptor concentrations lower than 0.7×10^{18} cm^{-3}.

The reduction of the resistivity with increasing pressure and the rise of the magnetoresistance coefficient $\rho_{33,11}/\rho_{33}$, observed for samples of the $Bi_{99.98}Sn_{0.02}$ alloy at $p > p_{C_1}$ (Figs. 8b and 3c), can be explained by a pressure-induced redistribution of holes between the ellipsoid at the point T and other extrema of the valence band of Bi in which holes have a higher average mobility.

2. Calculation of Carrier Densities and Mobilities

A. Hole density and mobility at $p \geq p_{C_1}$. When electrons disappear and the Fermi surface of an alloy consists of one hole ellipsoid, the expressions for ρ_{33} and ρ_{11} are of the form

$$\rho_{33} = 1/eP\nu_3, \qquad (1)$$

$$\rho_{11} = 1/eP\nu_1, \qquad (2)$$

where e is the electron charge; ν_1 and ν_3 are the hole mobilities along the binary and trigonal axes, respectively. The Hall coefficients R_{231} and R_{123} are given by the relationship

Table 2. Results of calculations of the hole densities and mobilities in the investigated alloys

Alloy	p, katm	$P \times 10^{-18}$, cm^{-3}	$\nu_1 \times 10^{-4}$, cm^2.V^{-1}.sec^{-1}	$\nu_3 \times 10^{-4}$, cm^2.V^{-1}.sec^{-1}	$P_n \times 10^{-17}$, cm^{-3}	$\nu_n \times 10^{-4}$, cm^2.V^{-1}.sec^{-1}	$C_{ion} \times 10^{-18}$ cm^{-3}	$C^* \times 10^{-18}$, cm^{-3}
Bi$_{97.58}$Sb$_{2.4}$Pb$_{0.02}$	7.8	0,7	4,05	0.41	0	—	0,7	5.64
Bi$_{99.98}$Sn$_{0.02}$-I $\left\{\begin{array}{l}\\\\\end{array}\right.$	11,5	1,23	4,0	0.41	1,6	4,8	1.39	5.64
	15	1,22	4,4	0.45	1,73	5,3	1,39	5.64
	17,7	1,17	5,0	0,51	1,8	4.1	1,35	5,64
Bi$_{99.98}$Sn$_{0.02}$-III	4,7	1.4	4,3	0.44	3,7	4,7	1,77	5,64

Note. C_{ion} is the concentration of ionized acceptor impurities, $C_{ion} = P + P_n$; C^* is the concentration of Pb or Sn, determined from the number of impurities introduced into the melt.

$$R_{231} = R_{123} = 1/eP. \qquad (3)$$

The single-ellipsoid model describes quite satisfactorily the galvanomagnetic properties of the alloy Bi$_{97.58}$Sb$_{2.4}$Pb$_{0.02}$ at $p \geq p_{C1}$ and T = 4.2°K. The hole density P and the hole mobilities ν_1 and ν_3, determined for this alloy from Eqs. (1), (2), and (3), are given in Table 2.

A very important point is that $R_{231} = R_{123}$ and that ρ_{33}, as well as ρ_{11} (and consequently P, ν_1, and ν_3), do not vary with pressure at $p > p_{C1}$ (Figs. 5a and 8a). This means that pressure does not affect directly the energy spectrum of the holes. We may expect that when the pressure is increased from the atmospheric value to p_{C1}, the quantities P, ν_1, and ν_3 change only as a result of the lowering of the Fermi energy in the hole ellipsoid due to a leakage of electrons from the conduction to the valence band. However, this change is very slight so that even at atmospheric pressure the hole density in all the investigated alloys is much higher than the electron density (cf. Fig. 11a and Table 2). Therefore, we may assume that at least ν_1/ν_3 is constant throughout the investigated range of pressures.

In the first approximation, the dispersion law of carriers in Bi is not affected by the addition of Sb and Pb impurities,[28] so that we may assume that the ratio of the hole masses in the alloy Bi$_{97.58}$Sb$_{2.4}$Pb$_{0.02}$ is $m_3/m_1 \approx 10$, as in pure Bi.[29] The anisotropy of the hole mobilities in this alloy is $\nu_1/\nu_3 = \rho_{33}/\rho_{11} = 9.9$ at T = 4.2°K and therefore $\nu_1/\nu_3 \approx m_3/m_1$. Hence, it follows that the hole relaxation time in this alloy is isotropic, in spite of the heavy doping with acceptor impurities.

The presence of a small number of new holes on the completion of the electron transition in samples of the Bi$_{99.98}$Sn$_{0.02}$ alloy prevents us from determining whether the isotropy of the hole relaxation time at the point T, found for the alloy Bi$_{97.58}$Sb$_{2.4}$Pb$_{0.02}$, applies also to Bi$_{99.98}$Sn$_{0.02}$. However, it is clear that the anisotropy of the relaxation time cannot be appreciable because at high ionized impurity concentrations the anisotropy can only decrease when the impurity concentration is increased.[30]

We shall carry out an approximate calculation of the density P_n and the average mobility ν_n of new holes as well as of the density and mobility of holes at the point T for $p \geq p_{C1}$ at a temperature of 4.2°K for samples of the Bi$_{99.98}$Sn$_{0.02}$ alloy on the assumption that the mobility of the new holes is isotropic (the limited experimental results prevent us from employing a more complex model). The expressions for ρ_{11}, ρ_{33}, R_{231}, and R_{123} have the following form:

$$\rho_{11} = e^{-1}(P_n\nu_n + P\nu_1)^{-1},$$
$$\rho_{33} = e^{-1}(P_n\nu_n + P\nu_3)^{-1},$$
$$R_{231}/\rho_{11}\rho_{33} = e(P_n\nu_n^2 + P\nu_1\nu_3),$$
$$R_{123}/\rho_{11}^2 = e(P_n\nu_n^2 + P\nu_1^2). \qquad (4)$$

If we assume that holes in the Bi$_{99.98}$Sn$_{0.02}$ alloy at the point T also satisfy the condition $\nu_1/\nu_3 = 9.9$, we can use the expressions in Eq. (4) to determine P, ν_1, ν_3, P_n, and ν_n. The results of such a calculation are given in Table 2. They show that the new holes are somewhat more mobile than the holes at the point T and that the density of the new holes P_n is considerably lower than the density of holes P at the point T. The small downward shift of the Fermi level under the action of Sn impurities, which increases the hole density at the point T from 1.2×10^{18} cm^{-3} to 1.4×10^{18} cm^{-3}, results in a strong increase of P_n. On the other hand, both P and P_n depend weakly on the pressure. This is obviously due to the smallness of the pressure-induced displacement of the hole extremum from the point T, relative to the extrema with the new holes.

The hole density P for the Bi$_{97.58}$Sb$_{2.4}$Pb$_{0.02}$ alloy, determined from Eq. (3), and the sum P + P_n for Bi$_{99.98}$Sn$_{0.02}$ alloy, determined using Eq. (4), are equal to the concentrations of ionized, i.e., dissolved in the host matrix, impurities provided each dissolved atom of Pb or Sn contributes to one hole. Table 2 lists also the impurity concentrations calculated from the amount of impurity introduced into the melt during the preparation of the samples as well as the concentrations calculated from the galvanomagnetic coefficients. It is clear that the number of ionized (dissolved) Sn impurity atoms is, depending on the sample, about $\frac{1}{3}$–$\frac{1}{4}$ of the total number of atoms introduced into the melt. In the case of Pb, the dissolved fraction is approximately $\frac{1}{8}$ of the total amount of the introduced impurity.

It is interesting to note that the low "activity" of acceptor impurities has been found in practically all the investigations of Bi-Sn and Bi-Pb alloys. This effect is obviously related to the low solubility of acceptor impurities in Bi.

As already mentioned, the scatter of the values of the impurity concentration in samples of a given alloy can be estimated from the shift of the critical pressure in these samples. For example, we can easily calculate (cf. Table 1) that a shift of p_{C1} by 1 katm in samples of the Bi$_{99.98}$Sn$_{0.02}$ alloy corresponds to a change in the Sn impurity concentration of about 7%.

B. Carrier density and mobility at $p < p_{c1}$. We shall
calculate the electron densities and mobilities in the
investigated alloys using Zitter's formulas. Zitter's
formulas are valid when the anisotropy of the relaxation
time of electrons and holes is not too strong. The re-
laxation time of holes in the investigated alloys satis-
fies this condition. However, there are indications that
the anisotropy of the electron relaxation time in Bi
alloys is stronger than that in pure Bi due to the rela-
tive increase in the relaxation time along the directions
of the long axes of the ellipsoids.[10] The reliability of
the results of calculations obtained using Zitter's
formulas has been checked by comparing the values
obtained for the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy with the results
of measurements of the de Haas-van Alphen effect in the
same alloy. The agreement between the results obtained
by these two methods is satisfactory (we shall discuss
this later).

We have already pointed out that, when the pressure
is increased, the electron ellipsoids in pure Bi shrink
without a change in shape (in the first approximation)
and their orientation in the k-space does not change
appreciably. When the concentrations of Sb, Sn, and Pb
impurities are increased, the electron ellipsoids also
shrink in a similar manner (in the first approximation).
Hence, we may assume that the following inequality is
satisfied by the investigated alloys:

$$\mu_2, \mu_4, \nu_3 \ll \mu_1, \mu_3, \tag{5}$$

which is valid for pure Bi[23] (μ_i and ν_i are the com-
ponents of the electron and hole mobility tensors in a
system of coordinates related to the crystallographic
axes). Zitter has shown that the inequality (5) makes it
possible to simplify the expressions for the components
of the galvanomagnetic tensor and the error in the solu-
tion, due to this simplification of the initial equations,
does not exceed several percent.

Since the density of new holes P_n is much lower than
P for the majority of the investigated alloys, we can
describe the galvanomagnetic properties of the alloys
at $0 < P < P_{c1}$ using a single-ellipsoid model for the
hole group of carriers but the anisotropy of such an
"equivalent" ellipsoid differs from the anisotropy of
the mobilities of the ellipsoid at the point T because of
the presence of new holes (P_n). For the sake of conven-
ience, we shall use this model in calculations concerned
with holes in the $Bi_{99.96}Pb_{0.04}$ and $Bi_{99.95}Pb_{0.05}$ alloys, as
well as for the $Bi_{99.98}Sn_{0.02}$ alloy for which P_{c1} = 9 katm;
the values of $(\nu_1/\nu_3)_{eq}$, equal to ρ_{33}/ρ_{11} at p = p_{c1}, are
given in Table 1. We shall now give the necessary
Zitter's formulas, transformed taking into account the
inequality (5) (in those cases when no ambiguity is likely
to arise, we shall use the same notation for the density
and mobility of holes at the point T in the Brillouin zone
and for the density and mobility of holes in the "equiva-
lent" ellipsoid):[5]

$$\sigma_{11} = \frac{e}{2}(N\mu_1 + 2P\nu_1), \tag{6}$$

$$\sigma_{33} = e(N\mu_3 + P\nu_3), \tag{7}$$

$$\frac{\rho_{33,11}}{\rho_{33}} = \frac{e^2}{2}\frac{N\mu_1\mu_3^2 P\nu_1}{\sigma_{11}\sigma_{33}}, \tag{8}$$

$$\frac{\rho_{11,33}}{\rho_{11}} = \frac{e^2N\mu_1}{4}\frac{N\mu_1^2\mu_2 + 2P\nu_1(\mu_1\mu_2 + \nu_1^2 + 4\mu_2\nu_1)}{\sigma_{11}^2}, \tag{9}$$

$$\frac{\rho_{11,11}}{\rho_{11}} = \frac{e}{8}\frac{N\mu_1^2\mu_3}{\sigma_{11}}, \tag{10}$$

$$R_{231} = \frac{e}{2}\frac{N\mu_1\mu_3 - 2P\nu_1\nu_3}{\sigma_{11}\sigma_{33}}. \tag{11}$$

In the preceding section, we have shown that the
anisotropy of ν_1/ν_3 is constant for the $Bi_{97.58}Sb_{2.4}Pb_{0.02}$
alloy at all the investigated pressures. The same con-
dition should apply at $0 < p < p_{c1}$ to the "equivalent"
ellipsoid of the $Bi_{99.95}Pb_{0.05}$ alloy and to samples of the
$Bi_{99.98}Sn_{0.02}$ alloy with p_{c1} = 9 katm, since the pressure
dependences of ρ_{33} and ρ_{11} of these alloys disappear, in
a wide range of pressures, after the completion of the
electron transition. Thus, at $0 < p < p_{c1}$, we have

$$\nu_1/\nu_3 = (\rho_{33}/\rho_{11})_{p_{c1}} = \text{const.} \tag{12}$$

The most convenient expressions from the point of
view of calculations are Eqs. (6)–(8), (10) and (12).
They can be used to obtain the five quantities: N, μ_1,
μ_3, $P\nu_1$, and $P\nu_3$. The application of these formulas to
samples of the $Bi_{99.96}Pb_{0.04}$ alloy at p = 1 atm and
T = 4.2°K shows that μ_1/μ_3 = 1.46 (for pure Bi, we have
μ_1/μ_3 = 1.43[23]), indicating that the ratio of the electron
relaxation times along the binary and trigonal axes
(τ_3^e/τ_1^e) is practically unaffected by the addition of an
acceptor impurity to Bi. If we bear in mind that the
electron ellipsoids are reduced similarly by the pres-
sure, we may assume that, in the first approximation,

$$(\mu_1/\mu_3)_{\text{alloy}} = (\mu_1/\mu_3)_{\text{Bi}} = \text{const} \tag{13}$$

for all the investigated alloys at all pressures. The re-
lationship (13) allows us to ignore the pressure depen-
dence of the longitudinal magnetoresistance $\rho_{11,11}/\rho_{11}$.
All subsequent calculations will be carried out using
Eqs. (6)–(8), (12), and (13). Some of the data needed in
the calculations are listed in Table 3.

The results of calculation of N and μ_1 for several
alloys are presented in Figs. 11 and 12. The value of
$P\nu_1$ for all the alloys does not vary greatly with pres-
sure, which shows that the Fermi energy of holes de-
creases only by a small amount when electrons leak
from the conduction to the valence band under the influ-
ence of pressure.

The electron density N decreases with increasing
pressure, obeying approximately the same law (Fig. 11a)
for all the alloys and the temperature dependence of N
can be represented by a power function at sufficiently
high temperatures: $N \propto T^a$; the value of a is consider-
ably greater than 3/2 even at $p \lesssim p_{c1}$, which indicates
that the electron spectrum is not quadratic (Fig. 12a).
Investigations of the de Haas-van Alphen effect in the
$Bi_{97.58}Sb_{2.4}Pb_{0.02}$ alloy show that the extremal cross
sections S* of the electron ellipsoids of this alloy are
five times smaller than those of Bi.[28] In the case of
the ENP model, we have $N \propto (S^*)^{3/2}$ and N_{alloy}
= $N_{\text{Bi}}/(S_{\text{Bi}}^*/S_{\text{alloy}})^{3/2}$ = 2.5×10^{16} cm^{-3}. We have found
that the electron density in this alloy is 2.44×10^{16} cm^{-3}.
Thus, we may assume that calculations carried out for

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5)The expression for $\rho_{33,11}$ given by Zitter[23] has a misprint.
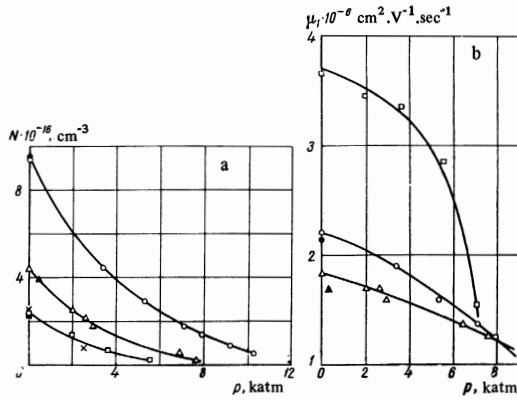
FIG. 11. Pressure dependences at T = 4.2°K of: a) the electron density, and b) the electron mobility along the binary axis for samples of $Bi_{99.96}Pb_{0.04}$ (O, ●), $Bi_{99.95}Pb_{0.05}$ (Δ, ▲), $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ (□, ■, and X) (a black dot, triangle, or square represents the state after the removal of pressure).

these alloys using Zitter's formulas give reliable results.

The electron mobility decreases strongly when the pressure is increased (and, consequently, when the Fermi energy ϵ_F^e is increased), in spite of the fact that the electron masses decrease on approach to the bottom of the energy band[14] (Fig. 11b). This means that the electron relaxation time $\tau_1^e = \mu_1 m_1^*/e$ increases when the Fermi energy is increased, which is typical of the scattering by ionized impurities.[31] We may thus conclude that, in all the investigated alloys, the main scattering mechanism at T = 4.2°K is the scattering by ionized impurities. When the temperature is increased, the scattering by phonons begins to predominate and the dependence of the electron mobility on the pressure (i.e., on ϵ_F^e) becomes very weak (Fig. 12b).

Comparison of the results given in Fig. 11b and in Table 2 shows that, in the investigated alloys $\mu_{av} \gg \nu_{av}$ at liquid helium temperatures. This is because the scattering of holes by ionized acceptor impurities is stronger than that of electrons. The relative decrease in the hole mobility in the alloys (compared with Bi) is so large that the Hall coefficient R_{123}, which is positive at T = 4.2°K for Bi,[23] becomes negative for all the investigated alloys (at low pressures), in spite of the fact that P (or $P + P_n$) > N (Fig. 5). The transition to the scattering by phonons (when the temperature is increased) changes the sign of R_{123} back to positive (Fig. 7b).

The weak pressure dependences of P, ν_1, and ν_3 at $0 < p < p_{c1}$ make it possible to use Eq. (11) as a check and Eq. (9) to calculate the electron mobility μ_2 along the bisector axis. Calculations show that at T = 4.2°K and atmospheric pressure μ_2 of all the alloys obeys the condition (5) but the ratio μ_1/μ_2 is considerably smaller than that for Bi, which is obviously due to an increase in the ratio of the relaxation time along the long axes of the electron ellipsoids to the relaxation time along the binary axes (τ_2^e/τ_1^e).

3. Dependences of the Carrier Density and Electron Relaxation Time on the Energy

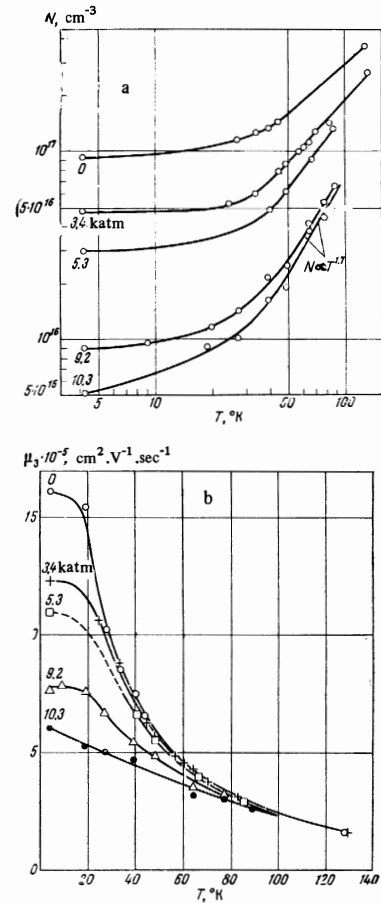If the energy band overlap ϵ_0 in the investigated alloys decreases linearly with increasing pressure p,

FIG. 12. Temperature dependences, at various pressures, of: a) the electron density, and b) the electron mobility in the $Bi_{99.96}Pb_{0.04}$ alloy.

the knowledge of the value of $\partial\epsilon_0/\partial p$ should make it possible to determine the value of the Fermi energy ϵ_F^e for electrons in the alloys at all pressures $p < p_{c1}$. In fact, at $p = p_{c1}$, we have $\epsilon_F^e = 0$ and at $p < p_{c1}$, we have

$$\varepsilon_F^e = (\partial\varepsilon_0/\partial p)(p_{c1} - p) - \Delta_p, \qquad (14)$$

where Δ_p is the amount by which the Fermi energy of holes decreases when electrons leak from the conduction to the valence band under the action of pressure $(\Delta_p \to 0$ as $p \to p_{c1})$.

The value of $\partial\epsilon_0/\partial p$ can be estimated from the temperature dependences of ρ_{33} and ρ_{11} obtained for the $Bi_{99.98}Sn_{0.02}$ alloy at $p > p_{c1}$. From the temperature dependences of ρ_{33} and ρ_{11}, corresponding to a given pressure, we can find the electron contribution to the conductivity, using Eqs. (6), (7), (12), and (13). At $p > p_{c1}$, when a gap ΔE appears (Fig. 1d), the electron contributions $(N\mu_1)_{p_1}$ and $(N\mu_1)_{p_2}$, corresponding to the pressures p_1 and p_2 are given by

$$\frac{(N\mu_1)_{p_1}}{(N\mu_1)_{p_2}} = \frac{e^{-\Delta E_1/kT}(\mu_1)_{p_1}}{e^{-\Delta E_2/kT}(\mu_1)_{p_2}}$$

$$= \exp\left(\frac{\Delta E_2 - \Delta E_1}{kT}\right)\frac{(\mu_1)_{p_1}}{(\mu_1)_{p_2}}$$

$$\approx \exp\left(\frac{\Delta E_2 - \Delta E_1}{kT}\right), \qquad (15)$$

Table 3. Some components of the galvanomagnetic tensor of the investigated alloys at p = 1 atm
and T = 4.2 °K

Alloy; sample		$\rho_{33} \times 10^6$, Ω.cm	$\rho_{11} \times 10^6$, Ω.cm	$\rho_{33,11}/\rho_{33}$, 10^{-5} Oe^{-2}	$\rho_{11,33}/\rho_{11}$, 10^{-5} Oe^{-2}	$\rho_{11,11}/\rho_{11}$, 10^{-5} Oe^{-2}	R_{231}, cm^3/C	R_{123}, cm^3/C
$Bi_{97.58}Sb_{2.4}Pb_{0.02}$;	C1, C3	94.5	85.0	17.3	2.43	—	122.0	5.4
	C2, C4	89.8	76.3	20.0	2.50	—	147.0	6.9
$Bi_{99.96}Pb_{0.04}$;	A1, A4	39.0	36.0	6.6	2.75	4.9	32.5	3.61
$Bi_{99.95}Pb_{0.05}$;	B1, B2	86.0	53.0	6.0	2.7	—	38.5	3.76
$Bi_{99.98}Sn_{0.02}$-I;	D1, D3	77.3	55.7	9.7	2.45	—	40.8	5.2

and the condition $(\mu_1)_{p_1}/(\mu_1)_{p_2} \approx 1$ is satisfied at temperatures $T > 100°K$ (cf. Fig. 12). Equation (15) can be used to determine the change in the gap $\Delta E_2 - \Delta E_1$ when the pressure is increased from p_1 to p_2 (in the method used to produce the pressures, the difference $p_2 - p_1$ is altogether independent of temperature[17]). A calculation carried out for the $Bi_{99.98}Sn_{0.02}$ alloy shows that, up to pressures of 20 katm, the hole extremum at the point T shifts relative to the electron extremum at the point L in the Brillouin zone at a rate of $\partial\epsilon_0/\partial p = \partial(\Delta E)/\partial p = (1.5 \pm 0.2) \times 10^{-6}$ eV/atm. We shall show that, in accordance with[3], in the $Bi_{95.9}Sb_{4.1}$, $Bi_{95}Sb_5$, and $Bi_{93.5}Sb_{6.5}$ alloys the energy gap E_0 increases with increasing pressure at a rate of $\partial E_0/\partial p \approx 1.4 \times 10^{-6}$ eV/atm, which is in good agreement with the value of $\partial\epsilon_0/\partial p$, obtained for the $Bi_{99.98}Sn_{0.02}$ alloy. An estimate of the value of $\partial\epsilon_0/\partial p$ for Bi given in[3] is in error since it has been obtained on the basis of the EP model.

If the ENP model is valid, the ratio of two extremal cross sections of the electron ellipsoid S_1^e and S_2^e, corresponding to the Fermi energies ϵ_1^e and ϵ_2^e, is

$$S_1^e/S_2^e = \epsilon_1^3(1 + \epsilon_1^e/E_{g1})/\epsilon_2^e(1 + \epsilon_2^e/E_{gL}), \qquad (16)$$

where E_{gL} is independent of the pressure (in the first approximation).[32] For the hole ellipsoid at the point T:

$$S_1^h/S_2^h = \epsilon_1^h/\epsilon_2^h. \qquad (17)$$

Using Eqs. (16) and (17), we shall determine the pressure dependences of the Fermi energies of electrons and holes in Bi (Fig. 13) from the pressure dependences of the extremal cross sections of the electron and hole ellipsoids reported for Bi in[15,16]. It follows from these dependences that $\partial\epsilon_0/\partial p = \partial\epsilon_F^e/\partial p + \partial\epsilon_F^h/\partial p = 1.4 \times 10^{-6}$ eV/atm. Comparison of the values of $\partial\epsilon_0/\partial p$ for pure Bi, Bi-Sb alloys, and $Bi_{99.98}Sn_{0.02}$ shows that $\partial\epsilon_0/\partial p$ for alloys of Bi with low impurity concentrations has the same value as for pure Bi.

The dependence of the electron density N in the investigated alloys at T = 4.2°K on the Fermi energy ϵ_F^e,

calculated using Eq. (14), is given in Fig. 14. The continuous line in Fig. 14 represents the ENP model calculation for pure Bi with $E_{gL} = 0.015$ eV,[33] $\epsilon_F^e = 0.027$ eV,[34] and the corresponding electron density $N = 2.8 \times 10^{17}$ cm^{-3};[35] the dashed curve in Fig. 14 represents the EP model. The maximum value of Δ_p for the $Bi_{99.96}Pb_{0.04}$ alloy is 1.3×10^{-3} eV, while for the remaining alloys it is $(0.5-0.6) \times 10^{-3}$ eV.
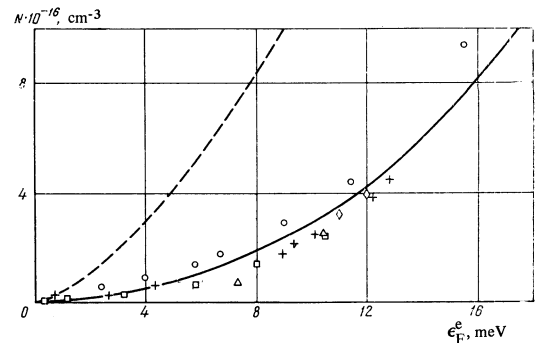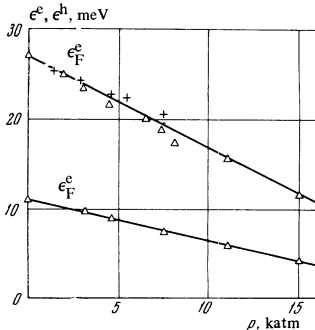

FIG. 14. Dependence of the electron density on the Fermi energy of Bi and its alloys: $Bi_{97.58}Sb_{2.4}Pb_{0.02}$ ($\square$ and $\triangle$), $Bi_{99.96}Pb_{0.04}$ (O), $Bi_{99.95}Pb_{0.05}$ (+), $Bi_{99.98}Sn_{0.02}$-I ($\diamond$); the continuous curve is drawn for Bi on the basis of the ENP model and the dashed curve is based on the EP model.

The dependences of the hole densities P and P_n on the Fermi energy ϵ_F^e can be plotted from the results obtained for the $Bi_{99.98}Sn_{0.02}$ alloy on the assumption that the band overlap in this alloy at atmospheric pressure is the same as in Bi, i.e., $\epsilon_0 = 0.038$ eV. When $p = p_{c1}$, the Fermi energy of holes belonging to the point T is found from the relationship

$$\epsilon_F^h = \epsilon_0 - (\partial\epsilon_0/\partial p)p_{c1}. \qquad (18)$$

The results of the calculation are presented in Fig. 15. The dashed curve represents Bi in accordance with the EP model. It follows from Table 2 that P_n in an alloy increases slightly under the effect of pressure so that the dependence of P_n on the Fermi energy, shown in

FIG. 13. Pressure dependences of the electron and hole Fermi energies of Bi: ($\triangle$) results reported in [16]; (+) results reported in [15].

FIG. 15. Dependences of the hole density P at the point T in the Brillouin zone and of the density of the new holes P_n on the Fermi energy of the holes at the point T and Bi and its alloys: Bi ($\square$), $Bi_{99.98}Sn_{0.02}$-I ($\triangle$), $Bi_{99.98}Sn_{0.02}$-III (∇), $Bi_{97.58}$ $Sb_{2.4}Pb_{0.02}$ (O); the dash-dot curve represents the EP model for Bi.
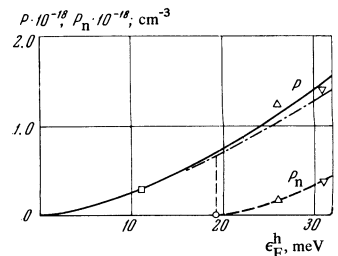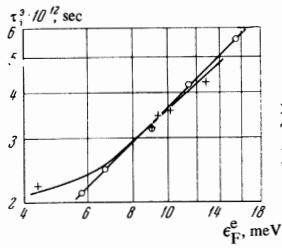
FIG. 16. Dependence of the electron relaxation time τ_1^e on the Fermi energy at $T = 4.2°K$ for: $Bi_{99.96}Pb_{0.04}$ (O), $Bi_{99.95}Pb_{0.05}$ (+).

FIG. 17. Schematic energy spectrum of Bi with additional extrema in the valence band [Σ(TW)?].

Fig. 15, is also valid (in the first approximation) at atmospheric pressure.

The expression for the electron mobility $\mu_1 = e\tau_1^e/m_1$ contains two terms: τ_1^e and m_1, both of which depend on the energy ϵ_F^e.[40] According to the ENP model, $m_1 \propto (1 + 2\epsilon_F^e/E_{gL})$ and then $\mu_1(1 + 2\epsilon_F^e/E_{gL}) = C\tau_1^e$, where C is a constant.[40] It is evident from Fig. 16 that, that, at $T = 4.2°K$, the investigated alloys obey $\tau_1^e \propto \epsilon_F^e$, which is in agreement with the conclusions of a theory developed for the scattering by ionized impurities.[31]

4. Influence of Acceptor Impurities on the Energy Spectrum of Bismuth

It is evident from Fig. 14 that the dependences of the electron density N on the Fermi energy ϵ_F^e for Bi and for the investigated alloys are in good agreement. Similar dependences for holes at the point T in the Brillouin zone of Bi and its alloys are also in agreement (in the first approximation). Hence, we may conclude that the electron spectrum of the investigated alloys remains practically the same as in Bi and the main effect of acceptor impurities is to shift the Fermi level in the alloys. If there is a "tail" of states below the bottom of the conduction band at the point L, due to the perturbing influence of impurities, it must be smaller than 0.002 eV. According to a theory developed for heavily doped semiconductors,[9] this means that in Bi alloys the potential of impurity atoms is well screened so that corrections to the unperturbed parameters of the spectrum are small. A strong screening of the impurity potential in Bi alloys is evidently due to a high permittivity ϵ (~ 100) and the small effective carrier masses.

We may expect the perturbing effect of acceptor impurities on the valence band to be stronger than the effect on the conduction band and this should apply particularly to the ceiling of the valence band at point T because the extremum at T lies higher than the other energy extrema. However, the results reported in the present investigation cannot be used to estimate such a distortion of the valence band.

5. Positions of the Additional Extrema in the Valence Band of Bi

Many new holes in the $Bi_{99.98}Sn_{0.02}$ alloy are observed immediately after the disappearance of electrons. It follows that even at $p \sim 9$ katm the extrema containing new holes overlap the electron extrema at the point L. If we assume that these new holes belong to the hole extrema at L, it follows that the density-of-states "tails" extending from the top of the valence band at L overlap the whole gap E_{gL}, and the density of states in
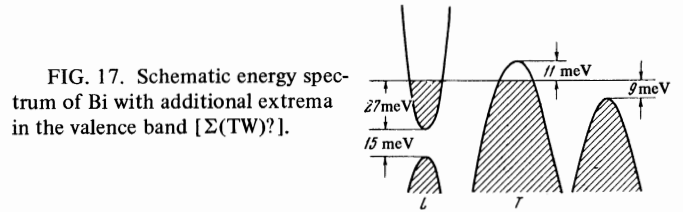
the "tails" is very high ($P_n \sim 10^{17}$ cm^{-3} at $p = p_{c1}$). The gap E_{gL} should disappear but this contradicts the observation that the dispersion law for electrons in the alloys is the same as in pure Bi (Fig. 14). Moreover, we should then observe a strong pressure dependence of P_n since pressure reduces the band overlap at a constant rate. This does not agree with the weak rise of P_n when the pressure is increased (cf. Table 2). Moreover, the saturation of the pressure dependences of ρ_{33} and ρ_{11} at high pressures (Fig. 8b) cannot be explained on the assumption that new holes are located at L.

Evidently, the application of pressure shifts downward the extrema with the new holes, together with the extremum at T, relative to the bottom of the conduction band at L. The rate of shift is approximately the same for these extrema, which is possible when these additional extrema are in or close to the hexagonal plane of the reduced Brillouin zone near the point T. The possibility of the existence of such extrema is suggested by a calculation carried out by Golin.[5] In the simplest case, the number of such extrema is three, they are ellipsoids, and their effective masses are comparable, according to Golin's calculations, with the masses for the ellipsoid at T. The total density of states in the ellipsoids near T and the density of states in the ellipsoid at T should also be similar, which is in agreement with the results of the present investigation (Fig. 15).

Thus, the valence band of Bi can be represented by a scheme shown in Fig. 17. We must draw attention to the considerable overlap of the additional hole extrema with the conduction band (~ 0.018 eV). Because of this overlap, it is in principle impossible to obtain a Fermi surface consisting of one hole ellipsoid by lowering the Fermi level in Bi only by adding acceptor impurities. For this reason, investigations of the galvanomagnetic properties of Bi-Sn and Bi-Pb alloys have failed to give a value higher than 3 for the resistance anisotropy ρ_{33}/ρ_{11} or an isotropic Hall effect at $T = 4.2°K$.

In the present investigation, we have failed to observe the appearance of "light" holes at L under the influence of pressure; this may have been due to some increase of the gap E_{gL} due to compression.

The influence of the hole extrema at L may be considerable in Bi-Sn and Bi-Pb alloy when the Fermi level is lowered by an amount greater than 0.040 eV[36] and in Bi-Sb alloys when the latter are transformed to the semiconductor state.[37] The low-temperature conductivity of semiconducting Bi-Sb alloys is most probably due to the overlap of "tails" formed in the forbidden band as a result of the perturbing effect of impurities (the formation of "tails" in Ge-Si alloys is discussed in[38]). If the density-of-states "tail" of the hole extremum at T shifts below the "tails" of the hole extrema at L (under the influence of Sb impurities or pressure), the contribution of the "tails" of the hole

extrema at L predominates and this lowers the residual resistance of the alloy because of the higher mobility of the L holes. Obviously, this explains the anomalous behavior of the pressure dependence of the resistivity at low temperatures, which has been reported for the $Bi_{87.5}Sb_{12.5}$ alloy.[39] The appearance of a maximum in the temperature dependence of the Hall emf in this alloy[3] can also be explained by an increase in the average hole mobility (due to a "tail" at L) under the influence of pressure.

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