ON THE EFFECT OF IMPURITIES ON THE ENERGY SPECTRUM OF ELECTRONS IN BISMUTH

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The effect of small additions of Pb on the quantum oscillations of the magnetic susceptibility in Bi was studied at temperatures between 1.7 and 4.2° K and various orientations of the magnetic field relative to the crystallographic axes of the specimens. It was established that the form of the Fermi surface and the electron effective-mass tensor are practically unchanged when the concentration of lead is increased to 0.037 wt%, while the limiting Fermi energy and the concentration of electrons diminish with increasing lead concentration. It was shown that the change in the anisotropy of the magnetic susceptibility of Bi when the content of Pb is increased cannot be explained by a change in the parameters of the electrons and holes; the experimentally observed variations of susceptibility and its anisotropy with the Pb concentration can be fully explained using an idea (due to Adams[3]) that strong diamagnetism exists in the valence band of bismuth.

INTRODUCTION

TO explain the marked growth of the magnetic-susceptibility anisotropy $\Delta\chi$ in Bi at helium temperatures, due to lead impurities (see reference 1), Heine[2] used an idea, due to Adams,[3] concerning the possible existence of strong diamagnetism in the valence band of Bi. Heine started from the supposition that on increasing C — the concentration of Pb — the form of the Fermi surface for electrons does not change, and only a decrease in the electron concentration occurs. It will be remembered that the Fermi surface for electrons in bismuth consists of three ellipsoids situated in crystal momentum space in such a way that their smallest axes coincide with the two-fold axes, while the largest axes are inclined 5.5° to the plane perpendicular to the three-fold axis; the ellipsoids go into one another by rotations of 120° around the trigonal axis.[4]

At present, however, there are no experimental data to support Heine's supposition. It is not possible to draw any conclusion on how an increase in the lead concentration deforms the Fermi surface in Bi from the work of Shoenberg and Zakki Uddin,[1] since they only studied the change of frequency E_0/β_i (E_0 is the limiting Fermi energy, β_i is a function of the effective masses and the angle ψ between the direction of the magnetic field **H** and the three-fold axis of the specimen) of the quantum oscillations (and, consequently, also the change of the areas S_m, the external sections of the Fermi surface by planes perpendicular to **H**) for two orientations of **H** in the plane perpendicular to the trigonal axis, which corresponds to the change of the smallest value of S_m and that closest to it.

Since the value of $\Delta\chi$ for pure bismuth is mainly determined by the anisotropies of the three ellipsoids of the electronic part of the Fermi surface,[5] and the contribution to the susceptibility of the hole part of the surface obtained in references 6 and 7 is very small, then it would also be supposed that the increase of $\Delta\chi$ for bismuth is associated with the change of form of the ellipsoids.

We have made a study of the oscillations of the magnetic susceptibility in specimens of Bi with various Pb contents and with various crystallographic orientations of the specimens in the magnetic field, in order to determine the nature of the change in the shape of the Fermi surface and the parameters determining it when the concentration of Pb impurity is changed.

MEASUREMENT METHODS, SPECIMENS

The measurements were made on a torsion balance in a homogeneous magnetic field of strength up to 12 koe at liquid-helium temperatures, with the specimen at a fixed position in the

field.[8] The torque N acting on the specimen, was balanced by the torque developed by a compensating device which consisted of a coil mounted on a cylindrical copper damper fixed on the suspension system of the balance. The damper was in the field of a permanent magnet. The coil consisted of 100 turns of PÉ wire of 0.05 mm diameter.

A bronze ribbon suspension with an elastic constant K = 19.4 dyne cm/rad served as one of the current leads to the coil. The fine spiral spring of a type M-25 galvanometer was used for the other lead. The current through the coil was controlled by a KL-48 potentiometer. The position of the suspended system was determined with a mirror system, with accuracy 10–15".

The alloys of Pb and Bi were made up in Pyrex ampoules, using successive dilution to avoid weighing small quantities of substance. "Hilger" Bi (purity 99.998%) was used, purified by 30-fold recrystallization in vacuum. In the original Bi the electrical resistance fell by a factor of approximately 150 on lowering the temperature from 290 to 4.2° K.

To guarantee the most complete dissolution of the Pb in the Bi, the alloys were held at a temperature of 450° C for 3–4 hours, after which they were rapidly cooled. Seeds from the polycrystalline ingots served (using the method of Kapitza[9]) as primers to grow single-crystal cylinders of length ≈15 mm and diameter about 3.6 mm. In order to decrease the inhomogeneity in impurity distribution, which arises during the growth of a crystal, the specimens were cut off from the primers, attached to them the other way round, and the growing process was repeated.

Specimens about 8 mm long were cut from the central portion of the cylinders and annealed in an atmosphere of helium at 260° C for 5 to 30 days, depending on the Pb concentration. They were then etched in concentrated nitric acid heated to 70–90° C, and their crystallographic orientation was determined on a goniometer with an accuracy of 0.2 to 0.3°.

RESULTS OF THE MEASUREMENTS

Nine specimens of Bi were studied, with Pb contents of 0, 0.012 (two specimens), 0.02 (two specimens), 0.025, 0.03 (two specimens), and 0.037 wt%. The three-fold axis of the specimens was orientated perpendicular to the suspension axis of the balance, whilst the two-fold axis was parallel to it. Measurements were made for various angles ψ between the direction of the trigonal axis and the magnetic field. No measurements were made for the two other main orientations of the crystallographic axes, since they would give no fresh information.

As an example, several curves are given in Fig. 1 showing the variation of the magnetic susceptibility anisotropy $\Delta\chi' = N/H^2 \sin\psi\cos\psi$ on 1/H for the annealed Bi specimens with various Pb contents at a temperature of 1.67° K, and two values of the angle ψ close to $\psi = 0°$ and $\psi = 90°$.

Curves showing the angular variation of the oscillation frequency $E_0/\beta_i \sim S_m$ are given in Fig. 2 for a specimen of the original Bi and specimens of Bi with impurity concentrations of 0.03%. The continuous curves were constructed using Landau's formulae (cited by Shoenberg[4]) and the tensor effective masses proposed for pure Bi by Shoenberg[4] (the dashed curves correspondingly for Bi + 0.03% Pb). As is seen from Fig. 2, the angle of rotation of the Fermi surface ellipsoids about the two-fold axes is practically unchanged on increasing the Pb concentration to 0.03 wt%.

Analysis of the data on the angular variation of E_0/β_i for various Pb concentrations shows that, for all angles, ψ, the impurity causes the frequency of the oscillation, and consequently S_m

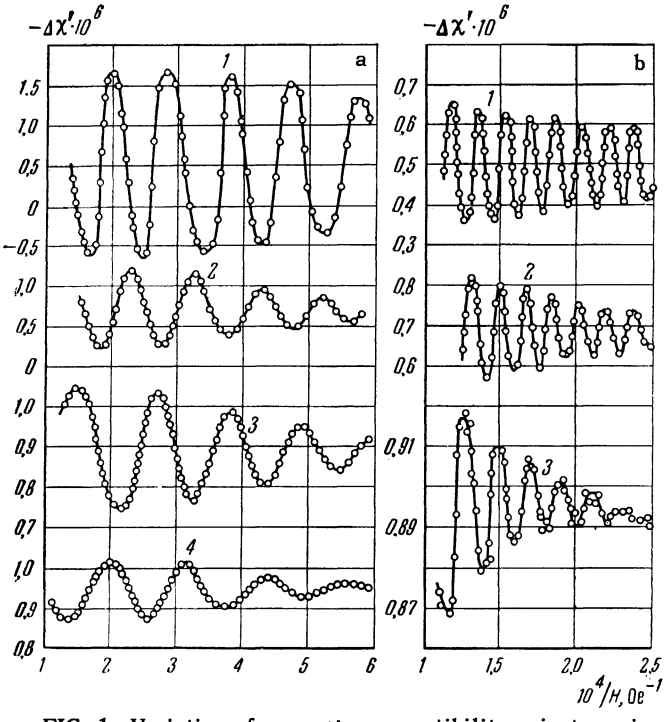

FIG. 1. Variation of magnetic susceptibility anisotropy in Bi-Pb alloys with magnetic field strength for T = 1.65° K: a – for $\psi = +82°$; b – for $\psi = -3°$. Curve 1 – original Bi, Curve 2 – Bi with 0.012% Pb, Curve 3 – Bi with 0.03% Pb, Curve 4 – Bi with 0.037% Pb.

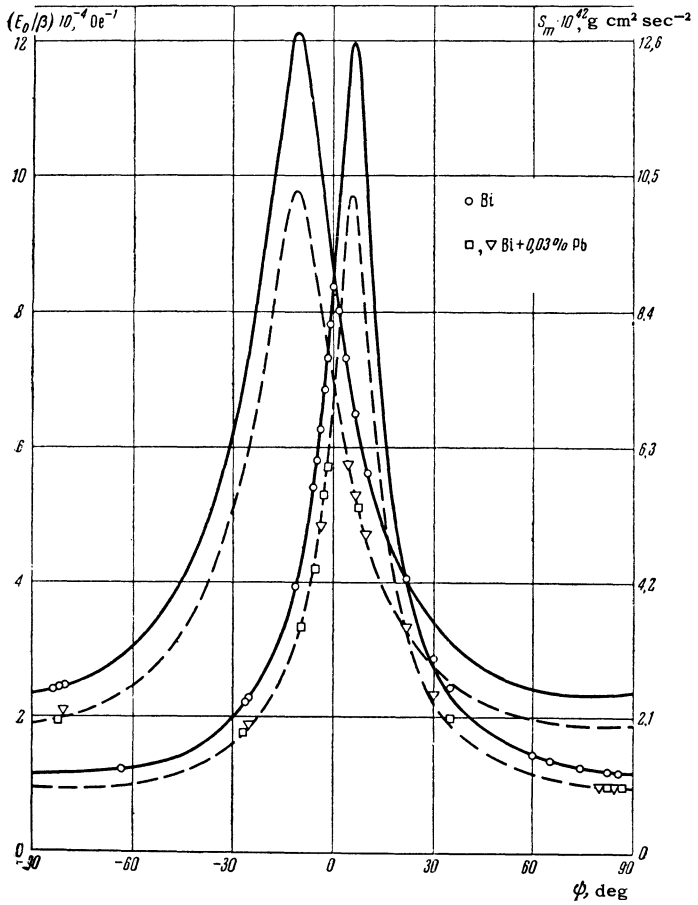

FIG. 2. Variation of oscillation frequency $E_0/\beta_i \approx S_m$ with the angle ψ between the trigonal axis of the specimen and the magnetic field (the two-fold axis was parallel to the suspension axis of the balance).

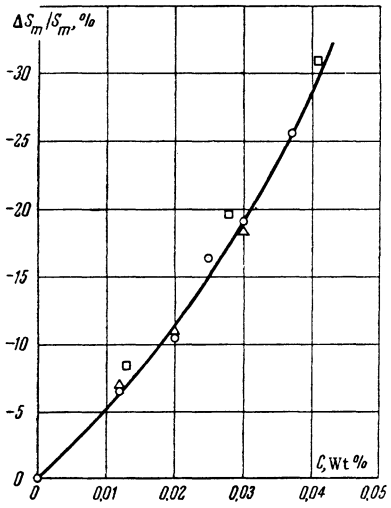

FIG. 3. The change of the extremal sections of the Fermi surface (in %) on increasing the Pb concentration (□ – data of reference 1 for the orientation with **H** perpendicular to the trigonal axis of the specimens).

also, to decrease in the same percentage ratio. The variation of the percentage change of S_m on the concentration of added Pb is given in Fig. 3.

The amplitude of the oscillations decreases strongly with increasing Pb concentration (Fig. 1) – the greatest decrease of amplitude being observed for high-frequency oscillations corresponding to the range of angles close to $\psi = 0°$. This fact greatly hampers the analysis of data obtained for lead concentrations exceeding 0.04 wt%.

The good agreement between the results obtained on two specimens (0.012% Pb), cut from different sides of the original single-crystal cylinder, shows that possible inhomogeneity in the distribution of impurities along the specimens is small, and its effect does not influence the limits of accuracy of the measurements. For two specimens (0.03% Pb) with identical annealing treatments, a larger oscillation amplitude was observed in the specimen for which the original alloy was maintained for three hours at a temerature of 450° C. This result appears to show that an "anneal" of the original alloy diminishes the microinhomogeneity in the impurity distribution. A small discrepancy between the data obtained on specimens with 0.02% Pb concentrations (one specimen was not annealed, the other was annealed for four days) shows that the effect of annealing on the frequency of the oscillations is small, although the oscillation amplitude after annealing increased.

A small increase of the oscillation frequency occurred on lowering the temperature. This effect, absent in pure Bi, increases on increasing the Pb concentration. The maximum observed change of the quantity E_0/β_i on lowering the temperature from 3.2 to 1.6° K in specimens with concentrations 0.012 to 0.037% Pb amounted to 0.7 to 3%.

DISCUSSION OF THE RESULTS

1. Change of the Form of the Fermi Surface for Electrons. The data presented in Fig. 2 show that two of the principal sections (the smallest, S_1, and the intermediate, S_2) of the Fermi surface ellipsoids change in the same percentage ratio. Since the anisotropy of the ellipsoids is principally determined by the anisotropy of these two sections, it can be supposed that the third (the largest) principal section, S_3, changes in the same percentage ratio.

Thus, under the influence of small lead concentrations (up to 0.03%), the Fermi surface for electrons is unchanged in shape. This is, apparently, connected with the fact that Pb atoms, having atomic radius close to Bi atoms, do not essentially change the anisotropy of the Bi lattice. It is interesting to note that the variation of $\Delta S_m/S_m$ (see Fig. 3) with Pb concentration is noticeably nonlinear. Thus, the value of the derivative $\partial(\Delta S_m/S_m)/\partial C$ increases by a factor of

approximately 1.5 on increasing C from 0 to 0.035%.

2. Change of the Limiting Fermi Energy for Electrons. To determine E_0^e, the temperature variation of the oscillation amplitude [for angles $\psi = -(15 \text{ to } 27)°$ and $+22°$] was used; knowing this, the value of β_i can be calculated, and then from the known quantity E_0^e/β_i one can also evaluate E_0^e.

From Landau's formulae[4] (on the assumption that the Dingle factor does not depend on temperature), it follows that the ratio of the amplitudes ω_T, at two different temperatures, T_1 and T_2, where $T_2 = 2T_1$ for the same value of the field has the form

$$\omega_{T_1}/\omega_{T_2} = \cosh(2\pi^2 kT_1/\beta_i H) \quad (1)$$

(k is the Boltzmann constant). The variation of E_0^e with Pb concentration calculated in this way is shown in Fig. 4. It is apparent that the variation of E_0^e with C is not linear and that the derivative $\partial E_0^e/\partial C$ increases with increase of C.

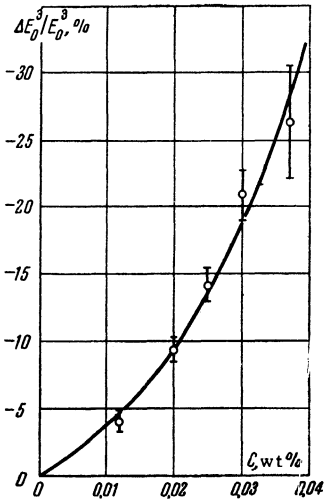

FIG. 4. The change of the limiting Fermi energy for electrons (in %) in Bi as the Pb concentration changes.

It is necessary to bear in mind that the nonlinear variation of E_0^e on C can also be caused by the presence in the original Bi of small concentrations of impurity elements of Group VI (donors), which can compensate part of the added Pb, and by a variation of the Dingle factor[4] x with temperature, which gets greater as C increases. (The Dingle factor x takes into account the change of oscillation amplitude due to scattering of electrons by impurities and irregularities in the lattice.)

A study of the galvanomagnetic properties of the original Bi at helium temperatures and the treatment of the data obtained by the method given in reference 10 shows, however, that elements of Group IV predominate in the original Bi, and the determination of x from the variation of the oscillation amplitude with magnetic field strength for T = const (which, unfortunately, cannot be done sufficiently accurately) appears to exclude also the second possible cause of nonlinearity in the variation of E_0^e with C.

3. Change of Electron Concentration. The electron concentration can be determined from the formulae

$$n^e = \frac{6V}{(2\pi\hbar)^3}, \qquad V = \frac{4}{3\sqrt{\pi}}(S_1S_2S_3)^{1/2}, \quad (2)$$

where V is the volume of one of the Fermi surface ellipsoids. For pure Bi the concentration of electrons n^e, determined from (2), is 0.39×10^{18} cm^{-3}. Using the data of Fig. 2, we obtain the dependence of n^e on C (Fig. 5). The fact that this variation is nearly linear indicates that it is correct to consider Pb impurities at small concentrations as acceptors. However, one must bear in mind here that Pb has an exceptionally low "efficiency" as an acceptor in Bi: to decrease the carrier concentration by one electron requires ~55 atoms of Pb. Therefore, the assumption that one Pb atom changes the electron concentration by unity, which was made by Galt et al,[11] is too crude an approximation.

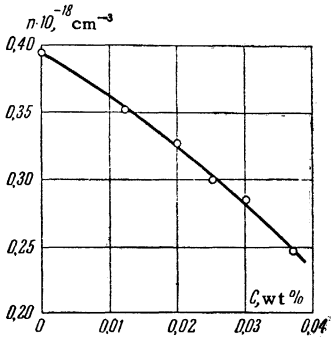

FIG. 5. Variation of electron concentration n in Bi with the concentration of Pb impurity.

4. Change of Effective Masses. The effective masses m_1^e, m_2^e, and m_3^e, in the system of coordinates related to the principal axes of the Fermi surface ellipsoids, are given by the formulae

$$S_1 = 2\pi E_0 \sqrt{m_1^e m_3^e}, \qquad S_2 = 2\pi E_0 \sqrt{m_1^e m_2^e},$$
$$S_3 = 2\pi E_0 \sqrt{m_2^e m_3^e}. \quad (3)$$

Since,

$$\Delta S_1/S_1 = \Delta S_2/S_2 = \Delta S_3/S_3,$$

it follows from (3) that

$$\Delta m_1^e/m_1^e = \Delta m_2^e/m_2^e = \Delta m_3^e/m_3^e = \Delta S/S - \Delta E_0^e/E_0^e.$$

The first quantities $\Delta S/S$ and $\Delta E_0^e/E_0^e$, as can be

seen from Figs. 2 and 3, lie close to one another. Therefore, to a first approximation it can be considered that the effective masses do not change on increasing the Pb concentration from 0 to 0.037%. This result agrees with the data obtained by studying cyclotron resonance in Bi containing impurities.[11]

5. Change of the Constant Part of the Magnetic Susceptibility Anisotropy. The constant part of the magnetic susceptibility anisotropy for electrons has the form

$$\Delta\chi^e = \chi^e_\perp - \chi^e_\parallel = \frac{e^2E_0^{1/2}}{4\sqrt{2}\,\pi^2c^2\hbar\rho}\,\frac{m_1^e + m_2^e - 4m_3^e}{(m_1^e m_2^e m_3^e)^{1/2}}. \qquad (4)$$

As shown in reference 5, the measured value of the anisotropy* for pure Bi, $\Delta\chi' = \chi'_\perp - \chi'_\parallel = -(1.7\times10^{-6} - 1.2\times10^{-6}) = -0.5\times10^{-6}$ cgs emu at helium temperatures agrees well with the value $\Delta\chi^e$ calculated from formula (4), using the effective mass values determined by Shoenberg:

$$m_1^e = 2.4\cdot10^{-3}m_0, \qquad m_2^e = 2.53m_0, \qquad m_3^e = 0.025m_0.$$

In fact, calculation gives

$$\Delta\chi_0^e = \chi_\perp^e - \chi_\parallel^e = -(0.52\cdot10^{-6} - 0.02\cdot10^{-6}) = -0.5\cdot10^{-6}.$$

The anisotropy of the hole susceptibility is negligibly small. Using the hole parameters previously determined:[6,7]

$$m_1^h = m_2^h = 0.05m_0, \qquad m_3^h = 0.7m_0,$$
$$E_0^h = 2.5\cdot10^{-14}\ \text{erg} \qquad (n^h = 0.34\cdot10^{18}\ \text{cm}^{-3}),$$

we find

$$\chi_\perp^h = -0.002\cdot10^{-6}, \qquad \chi_\parallel^h = -0.026\cdot10^{-6},$$
$$\Delta\chi_0^h = -0.024\cdot10^{-6}.$$

It is, therefore, of interest to determine, using (4), the change of $\Delta\chi^e$ on increasing the Pb concentration, and to compare the result obtained with the experimentally observed variation of $\Delta\chi'$ with C. The results of this comparison are given in Fig. 6. As is seen from Fig. 6, not only a quantitative, but also a marked qualitative, difference is observed between the curves. Thus, if the value of $\Delta\chi'$ in pure Bi is determined principally by the anisotropy of the electronic part of the Fermi surface, then on increasing the Pb concentration there appears an additional susceptibility anisotropy, which cannot be explained by changes in either the electronic or the hole parts of the Fermi surface.

*Primes are used, in what follows, to indicate experimental values of the corresponding quantities.

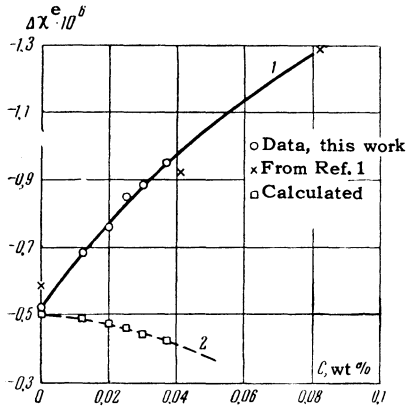

FIG. 6. The variation of the constant part of the magnetic susceptibility anisotropy $\Delta\chi^e$ for Bi with the Pb concentration. Curve 1 – experimental data, Curve 2 – calculated from formula (4).

It is very possible that the results obtained indicate the correctness of a deduction made by Adams[3] about the existence of a large diamagnetism, χ^A, caused by the presence of filled states close to the zone boundaries and unfilled states outside it with small effective masses.

As Adams showed, the value of this additional diamagnetism for a given orientation **H** is given by the formula

$$\chi^A \approx (m_0/\overline{m})\,\chi_0, \qquad (5)$$

where $\overline{m}$ is the mean value of the electron effective mass at the boundary of the zone in the plane perpendicular to **H**, and χ_0 is the susceptibility corresponding to the valence band of Bi. The presence of electrons outside the zone and holes inside it causes χ^A to decrease. Since at helium temperatures the experimental values of the diamagnetic susceptibility of Bi in directions perpendicular and parallel to the trigonal axis are $\chi'_\perp = -1.7\times10^{-6}$ and $\chi'_\parallel = -1.2\times10^{-6}$, but the calculated values are $\chi_\perp = \chi_\perp^e + \chi_\perp^h = -0.522\times10^{-6}$ and $\chi_\parallel = \chi_\parallel^e + \chi_\parallel^h = -0.046\times10^{-6}$, then the value of χ^A, decreased due to the presence of 0.39×10^{18} cm^{-3} electrons and 0.34×10^{18} cm^{-3} holes, should be isotropic and equal to $\sim1.2\times10^{-6}$ (the paramagnetism of electrons and holes in Bi can apparently be neglected, owing to their effective mass).

It follows from the experimental data of Shoenberg and Zakki Uddin[1] that on increasing the Pb concentration the value of $\chi'_\perp$ increases to $\sim2.5\times10^{-6}$, goes through a maximu at C ≈ 0.15%, and then decreases. The value of $\chi'_\parallel$ decreases monotonically on increasing C; however, this change is a slower one than for $\chi'_\perp$ (see Fig. 7).

Since for C ≈ 0.1% Pb the concentration of electrons should tend to zero (Fig. 5), extrapolation of the falling parts of the curves $\chi'_\perp(C)$ and $\chi'_\parallel(C)$ back to C = 0 (the broken curves in Fig. 7) allows the values of $(\chi_\perp^A)'$ and $(\chi_\parallel^A)'$ to be eval-

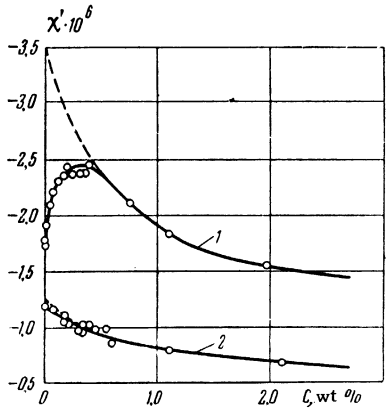

FIG. 7. Variation of $\chi'_{\perp}$ (curve 1) and $\chi'_{\parallel}$ (curve 2) with Pb concentration according to the data of reference 1.

uated for the valence zone of Bi in the absence of electrons and holes: $(\chi^A_{\perp})' \approx 3.5 \times 10^{-6}$, $(\chi^A_{\parallel})' \approx -1.3 \times 10^{-6}$.

It is interesting to note that the values of $(\chi^A_{\perp})'$ and $(\chi^A_{\parallel})'$ found in this way agree well with the values of $\chi^A_{\perp}$ and $\chi^A_{\parallel}$ calculated from formula (5). Writing formula (5) in the form

$$\chi^A_{\perp} = \chi_0 m_0 / \sqrt{m^e_1 m^e_3} + \chi_0 m_0 / \sqrt{m^h_0 m^h_3},$$

$$\chi^A_{\parallel} = \chi_0 m_0 / \sqrt{m^e_1 m^{e*}_2} + \chi_0 m_0 / m^h_1 \qquad (6)$$

and substituting in it the values of the effective masses $m^e_1 = 0.0024m_0$, $m^{*e}_2 = \frac{1}{2}m^e_2 = 1.26m_0$, $m^e_3 = 0.025m_0$, $m^h_1 = m^h_2 = 0.05\ m_0$, $m^h_3 = 0.7m_0$ and the value $\chi_0 = -0.034 \times 10^{-6}$, calculated* for electrons in the valence band of Bi with effective mass $\sim m_0$ and end-point energy ~ 7.5 ev, we obtain

$$\chi^A_{\perp} = -4.3 \cdot 10^{-6} - 0.18 \cdot 10^{-6} = -4.5 \cdot 10^{-6},$$

$$\chi^A_{\parallel} = -0.62 \cdot 10^{-6} - 0.68 \cdot 10^{-6} = -1.3 \cdot 10^{-6}.$$

We remark that Eqs. (6) also describe well the variation of $\chi'_{\perp}$ and $\chi'_{\parallel}$ on Pb concentration.

The first term of formula (6) provides the main contribution to $\chi^A_{\perp}$, and therefore the decrease of electron concentration on increasing the Pb concentration causes a pronounced increase of $\chi^A_{\perp}$, and, consequently also of $\chi'_{\perp}$. For $C \approx 0.1\%$ the electron zone is completely emptied and the further slower decrease of $\chi'_{\perp}$ is associated with the increasing concentration of holes in the valence band of Bi.

The electronic contribution to $\chi^A_{\parallel}$ does not have a decisive role, and therefore when the concentration of holes is increased by increasing the Pb concentration the value of $\chi'_{\parallel}$ diminishes.

Thus, if it is assumed that in bismuth, apart from the two groups of electrons and holes mentioned, there are no other carriers possessing large (of the order 1×10^{-6}) diamagnetic susceptibility, the magnetic properties of Bi at helium temperatures and their variation on impurity content can be completely explained on the basis of the work of Heine[2] and Adams.[3]

In conclusion we take the opportunity of thanking A. I. Shal'nikov for his interest in the work, M. I. Kaganov for discussion of the results, and G. A. Kytin for help with the measurements.

*It should be borne in mind that the calculation of χ_0 for the valence band of Bi by Landau's formula, as done in reference 3, is not rigorous, nor is the assumption that χ_0 is isotropic. However, since the values of the effective masses for electrons are not sufficiently accurate, there does not exist at the present time the basis from which to calculate the anisotropy of χ_0 by formula (6).

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