Singularities of the magnetic susceptibility of Bi-Sb alloys in strong magnetic fields

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A strong nonmonotonic dependence of the transverse ($H \perp C_3$) differential magnetic susceptibility $\chi_\perp$ was observed in the semiconducting Bi-Sb alloys on the magnetic field at helium temperatures. In the ultraquantum limit of magnetic fields, the susceptibility $\chi_\perp$ of the semimetallic alloys agrees with the value of $\chi_\perp$ of the semiconducting alloys. It is shown that the parallel ($H \parallel C_3$) component $\chi_\parallel$ of the magnetic susceptibility is not altered by the semiconductor-semimetal transition in a magnetic field. The results of the present study are compared with the theory of Beneslavskiĭ and Fal'kovskiĭ (in this issue).

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Our purpose is a detailed investigation of the field dependences of the magnetic susceptibility in semimetallic and semiconducting $Bi_{1-x}Sb_x$ alloys ($0 \le x < 22$ at.%) at low temperatures. For bismuth in semimetallic Bi-Sb alloys there was previously observed an abrupt increase of the transverse component of the differential magnetic susceptibility $\chi_\perp$ on going to the ultraquantum region of magnetic fields.[2,3] It was therefore of interest to study in greater detail the dependence of χ on H in semimetallic and also in pure and doped semiconducting Bi-Sb alloys, to check on the presence of susceptibility singularities in the semiconductor—metal transition in a magnetic field, and to assess the character of the dependence of χ on the temperature T in a strong magnetic field.

1. MEASUREMENT PROCEDURE AND SAMPLES

The procedure described in[2] for measuring the differential magnetic susceptibility was improved somewhat. A magnetic field up to 60 kOe was produced with a superconducting solenoid. The magnetic-field modulation frequency was chosen minimal (~20 Hz) to eliminate the influence of the skin effect. We used coaxial concentric measurement coils rigidly mounted inside the solenoid to reduce the noise. In our system, the sample area was only a small fraction of the coil area, so that the absolute values of the differential magnetic susceptibility χ were calculated with allowance for the coefficient of the flux linkage of the sample with the measuring coil, which was determined with the aid of a standard Bi sample, and amounted to ~0.75 in our case. The χ(H) curves were plotted point by point: at fixed magnetic fields we measured (at the output of a synchronous detector) the unbalance voltage produced across the measuring coils when the sample was placed in them. This increased substantially the measurement accuracy; to approximately 1.5% for the relative changes of χ in the magnetic fields, the absolute values being accurate to ~3%. In order not to miss sharp singularities, the χ(H) curves were continuously plotted with an automatic recorder as a control. To perform the galvanomagnetic measurements at temperatures above 4.2°K, as well as to plot the χ(T) curves, we used a device similar to that described in[4,5] to obtain intermediate temperatures. The heater was made of PÉV-0.05 copper wire wound on a copper thin-wall open cylinder, since constantan could not be used because of its large paramagnetic susceptibility. The procedure for measuring χ(H, T) is described in detail in[6].

We investigated single-crystal samples of Bi-Sb alloys measuring 2.5 × 2.5 × 14 mm, cut along the corresponding crystallographic directions. Most samples were grown at the Baĭkov Metallurgy Institute by drawing from the melt, with allowance for the component distribution coefficients in the liquid and solid phases (with antimony added to the melt as the crystal was grown), a procedure that yielded large single-crystal ingots with high composition homogeneity. The antimony concentration in the ingots was monitored by chemical analysis as well as by a point-by-point x-ray structure analysis with "Cameca" apparatus. The analysis data agreed within ~0.5 at.%. Some of the investigated samples were grown by zone melting in G. A. Ivanov's laboratory (Leningrad State Pedagogical Institute). In these samples, the antimony concentration was determined by x-ray analysis from the values of the crystal-lattice parameter, at the same ~0.5 at.% accuracy. The table lists the data for those samples for which the experimental results are given in the figures.

2. MEASUREMENT RESULTS

Figure 1 shows the field dependence of the transverse (H ∥ C_1 and H ∥ C_2) component of the differential magnetic-susceptibility $\chi_\perp$ of the semiconducting alloy $Bi_{0.924}Sb_{0.076}$ (sample No. 12) at 4.2°K. The behavior of $\chi_\perp$ remains the same for the entire semiconducting range of $Bi_{1-x}Sb_x$ alloys ($7 \lesssim x \lesssim 22$ at.%): in weak fields (0.5–2 kOe) all samples show a more or less pronounced growth of the diamagnetism, followed by a maximum and a gradually slowing decrease.

Figures 2 and 3 show the field dependences of the differential magnetic susceptibility $\chi_\perp$ at H ∥ C_1 and H ∥ C_2 at 4.2°K for a number of semimetallic $Bi_{1-x}Sb_x$ alloys ($0 \le x \le 7$ at.%). The same figures show for comparison the measured magnetic suscepti-

Sample No.	Sb concentration at. %	Field orientation: H∥	Sample No.	Sb concentration at. %	Field orientation: H∥
1	0	C_1, C_2	7	4.0	C_2
2	1.0	C_1, C_2	8	5.5	C_1
3	1.9	C_1, C_2	9	7.2	C_1
4	2.0	C_1, C_2	10	7.6	C_1, C_2, C_3
5	3.6	C_1, C_2	11	9.2	C_2
6	3.8	C_1, C_2	12	7.6	C_1, C_2

Notes. 1) Samples 1 to 7 and 10 to 12 were grown at the Baĭkov Metallurgy Institute of the USSR Academy of Sciences, samples 8 and 9 were grown at the Leningrad State Pedagogical Institute. 2) C_1, C_2, and C_3 are respectively the bisector, binary, and trigonal axes of the crystal.

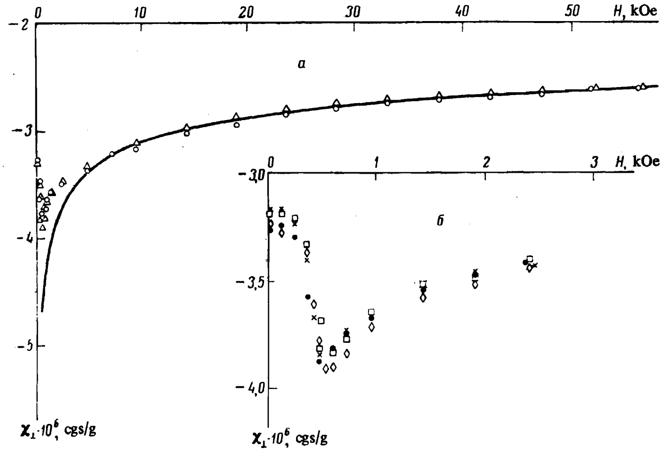

FIG. 1. Plots of the differential magnetic susceptibility $\chi_\perp$ of the alloy $Bi_{0.924}Sb_{0.076}$ (sample No. 12) vs. the magnetic field at T=4.2°K. a) $H\|C_1$ (○) and $H\|C_2$ (△); b) $H\|C_2$ at various modulation frequencies: ●–21.9×–36.4, ◇–61.9, □–94.1 Hz.

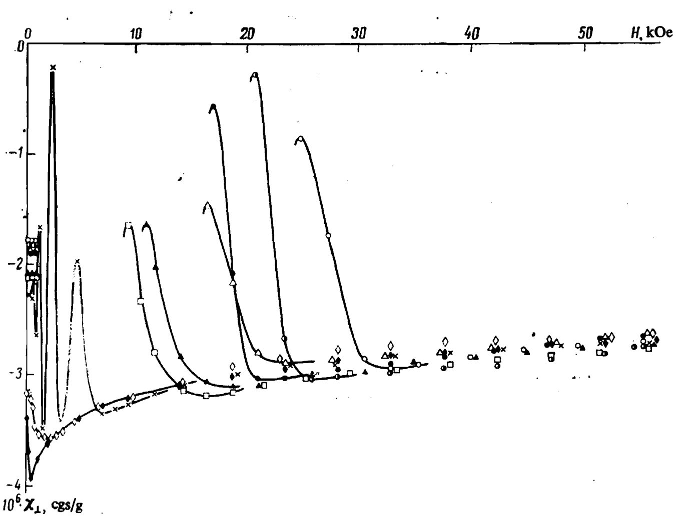

FIG. 2. Plots of the differential magnetic susceptibility $\chi_\perp$ vs. the magnetic field $H\|C_1$ at 4.2°K for the samples: ○–No. 1, ○–2, ●–3, △–4, ▲–5, □–6, ×–8, ◇–9, ◆–10.

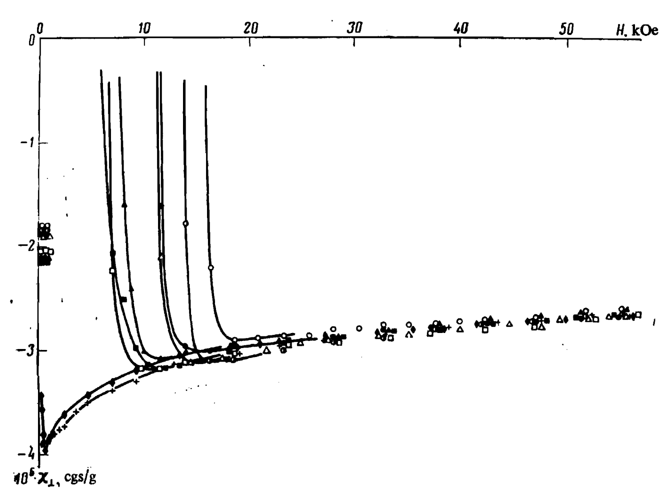

FIG. 3. Plots of the differential magnetic susceptibility $\chi_\perp$ against the magnetic field $H\|C_2$ at 4.2°K for the samples: ○–No. 1, ○–2, ●–3, △–4, ▲–5, □–6, ■–7, ◆–10, +–11.

bility of semiconducting alloys with $7 < x < 10$ at.%. In order not to clutter up the figures, the dependence of $\chi_\perp$ on H, including the de Haas-van Alphen oscillations, is shown only for semimetallic sample No. 8 in the entire range of magnetic fields. The measurement results are not shown for the remaining samples in the magnetic field region where de Haas-van Alphen oscillations are observed. The numerical values of $\chi_\perp(0)$ for the semimetallic alloys agree well with the published data.[7,8]

Figures 2 and 3 show clearly the previously described[3] increase of $\chi_\perp$ in a magnetic field for the semimetallic Bi-Sb alloys after the ultraquantum limit is reached; the value of the latter decreases with increasing Sb concentration, owing to the decrease of the extremal section of the electronic equal-energy surfaces. The values of the small extremal sections, at orientations of the magnetic field along the bisector (C_1) and binary (C_2) axes of the crystal differ somewhat (they are larger for $H \parallel C_1$), so that the transition to the ultraquantum limit (when all the carriers are on the last 0^- Landau level) occurs at $H \parallel C_1$ in stronger fields than at $H \parallel C_2$. In addition, at $H \parallel C_1$ the ultraquantum limit in fields up to 60 kOe is reached for all three electronic equal-energy surfaces at the point L, and at $H \parallel C_2$ for only two of them. It must be noted that all the plots of $\chi_\perp$ against H for semimetallic and semiconducting Bi-Sb alloys seem to coincide in strong magnetic fields, even though the initial susceptibilities of alloys with different Sb concentrations differ strongly (by up to 100%).

For semiconducting samples (Nos. 9–12 in Figs. 1–3), the initial values of the susceptibility $\chi_\perp(0)$ agree with the published data much worse than for the semimetallic samples: they tend mainly to be lower, by up to 10%, in comparison with the results of[8]. The discrepancy can be attributed to the fact that in[8] the author actually measured not the differential susceptibility as $H \to 0$, but the magnetic moments in fields ~6 kOe.

Figure 4 shows data on the temperature dependences of $\chi_\perp$ for semiconducting sample 10 in weak and strong fields.

Figure 5b shows the dependence of the longitudinal component of the differential magnetic susceptibility $\chi_\parallel$ of the alloy $Bi_{0.924}Sb_{0.076}$ (sample No. 10) at 4.2°K on the magnetic field $H \parallel C_3$.

3. DISCUSSION OF RESULTS

The anomalously large diamagnetism of the Bi-Sb alloys is explained by the presence of occupied bands with small negative effective mass[9-11,1]. The paramagnetic contribution of the carriers with positive effective mass in the conduction band decreases the diamagnetism (see formula (16) of the paper of Beneslavskiĭ and Fal'kovskiĭ [1]). This conclusion is confirmed by measurements of χ for semimetallic alloys with large carrier density. In this case $\chi(0)$ is independent of the magnitude of the gap ϵ_g at point L of the Brillouin zone and is determined mainly by the Fermi energy of the electrons (formula (18) of[1]): with decreasing carrier density in the conduction band, the diamagnetism $\chi(0)$ increases. The decrease of the carrier density in Bi-Sb alloys with increasing Sb content as a result of the decrease of the overlap of the balance band (at the point T of the Brillouin zone) and of the conduction band

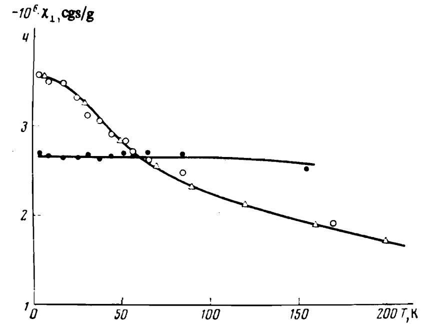

FIG. 4. Temperature dependences of the differential magnetic susceptibility $\chi_\perp$ of sample No. 10 for two values of the magnetic field H||C$_2$: ○—2.4 kOe, ●—47.2 kOe; △—data of [8] for $\chi_\perp(0)$ of the alloy $Bi_{0.92}Sb_{0.08}$.

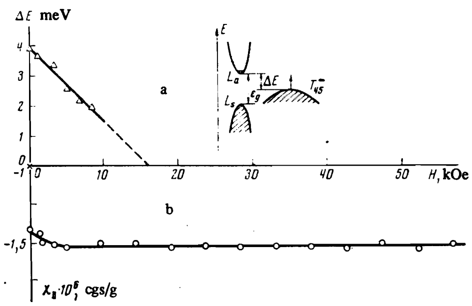

FIG. 5. a) Gap ΔE in the spectrum of the alloy $Bi_{0.924}Sb_{0.076}$ (sample No. 10) vs. the magnetic field H||C$_3$. The arrow in the insert indicates the motion of the edge of the band in a magnetic field at H||C$_3$. b) Differential magnetic susceptibility $\chi_\parallel$ of the same alloy at H||C$_3$, T= 4.2°K.

(at the point L) is in fact the main cause of the growth of $\chi_\perp(0)$ (Figs. 2 and 3).

The growth of the diamagnetism in weak fields for semiconducting alloys (Fig. 1 and Figs. 2 and 3—samples 9 and 10) cannot be due to the presence of magnetic impurities, for these would make an isotropic contribution to the susceptibility, and no analogous growth of the diamagnetism is observed for the component $\chi_\parallel$ (see Fig. 5b, sample No. 10). Nor can the growth of the diamagnetism be due to the influence of the skin effect: Fig. 1b shows in enlarged scale the initial part of the curve for sample No. 12 (H || C$_2$), plotted at various modulation frequencies (from 20 to 90 Hz). We see that these curves coincide within the limits of measurement accuracy.

The cause of the growth of the diamagnetism of semiconducting samples in weak fields is the vanishing of the contribution made to the susceptibility by the impurity carriers in the ultraquantum limits. As seen from formula (27) of[1], if all the carriers are on the last Landau level and their density is constant, then the Fermi level tends to the bottom of the conduction band $\mu - \epsilon_g/2 \sim 1/H^2$. The differential paramagnetic susceptibility of these carriers is then $\chi \sim H^{-4}$, i.e., it vanishes very rapidly with increasing field. A transition to the ultraquantum limit takes place in the investigated samples 10 and 12, with light-electron density $\sim 5 \times 10^{15}$ cm^{-3} at the point L of the Brillouin zone in a field ~1 kOe, which coincides precisely with the position of the diamagnetism maximum in weak fields.

The growth of the diamagnetism on going to the ultraquantum limit in bismuth and in semimetallic Bi-Sb alloys, shown in Figs. 2 and 3, is also due to the vanishing of the paramagnetic contribution of light electrons, but here these are majority carriers and not impurity electrons. The concentration of the light electrons in the ultraquantum limit is determined by the electroneutrality condition (the number of electrons must equal the number of holes). This leads to the same dependence of the chemical potential on the field, but the paramagnetic contribution of the light electrons vanishes in stronger fields, in view of their larger density. Thus, after the ultraquantum limit is reached, the diamagnetism of semimetallic alloys should increase and reach the value of the susceptibility of semiconducting alloys, as is indeed observed in experiment (Figs. 2 and 3).

In the ultraquantum region, the susceptibility $|\chi_\perp(H)|$ decreases monotonically with increasing field. The reason is that in a magnetic field the main contribution to the susceptibility is determined both by the gap ϵ_g, which depends weakly on the field, but by the energy distance $\lambda = v\sqrt{e\hbar H/c}$ (see[1] between the Landau levels, which increases with increasing field. Thus, in a 60-kOe field λ of pure Bi exceeds ϵ_g by almost an order of magnitude.[12] The restructuring of the "bare" spectrum (i.e., the spectrum in a weak field) following addition of Sb to Bi, which leads to relatively small shifts of the extrema in L (on the order of 10—20 meV) at Sb concentrations lower than 22 at.%, has little effect on $\chi_\perp$ in a strong field (several dozen kOe), where the decisive role is played by the magnetic energy $\lambda \sim 100$ meV.

It is also clear that for the same reason, a transition to a gapless state in a magnetic field,[10] i.e., inversion of the 0^- levels at one and the same point of the Brillouin zone with increasing magnetic field, will not influence the susceptibility noticeably.

It is of interest to compare the obtained experimental data with the law deduced by Beneslavskiĭ and Fal'kovskiĭ [1] for the variation of $\chi_\perp$ in a strong field (their formula (26)). The character of the change of $\chi_\perp$ of semiconducting alloys (Figs. 1—3) in strong fields can be described by the expression

$$\chi_\perp(H) = \chi_0 + AH^{-\alpha}. \quad (1)$$

The exponent α and the coefficient A can be determined from the experimental relation

$$\lg|d\chi_\perp/dH| = -(\alpha+1)\lg H + \lg|\alpha A|$$

by least squares. The calculations were made for six different semiconducting Bi-Sb samples at H > 5 kOe. $\chi_\perp(H)$ was taken to be the mean value at H || C$_1$ and H || C$_2$. The obtained averaged values $\tilde{\alpha} = 0.26 \pm 0.06$ and $\tilde{A} = -(2.1 \pm 0.8) \times 10^5$ (we are citing here the rms errors averaged over a number of samples) are in good agreement with the theoretically obtained[1] $\alpha = 1/4$ and $A = -2.0 \times 10^{-5}$. The value of A was calculated using the following band parameters of bismuth: $v_x = 0.97 \times 10^8$ cm/sec, $v_y = 0.67 \times 10^8$ cm/sec, $M_1 = 0.82m_0$, and $M_2 = 1.3m_0$. For sample 12 the values are $\alpha = 0.27$, $\chi_0 = -1.82 \times 10^{-6}$ [cgs/g], $A = -1.40 \times 10^{-5}$ H [Oe], and the solid curve of Fig. 1 is the result of calculation by formula (1) with the presented values of α, A, and χ_0.

We note that according to our data χ is practically independent of the magnetic-field orientation in a strong field if H is in the basal plane, in agreement with formula (26) of[1]. The presence of holes at the T extremum does not change the susceptibility $\chi_\perp$ of semimetallic alloys.[1,10]

The results of temperature measurements (Fig. 4) agree qualitatively with the conclusions of Beneslavskiĭ and Fal'kovskiĭ: in weak fields the diamagnetism increases with decreasing temperature, and in strong fields, when λ is large in comparison with T, the temperature dependence of the susceptibility vanishes. However, the scarcity of experimental material does not permit as yet a quantitative comparison with theory.

It is seen from Fig. 5b that within the limits of errors, in the entire range of fields (except for the very weakest), $\chi_{\parallel}$ remains constant at a value that agrees with the known value of $\chi_{\parallel}(0)$ in a weak field[8] (the small change of $\chi_{\parallel}$ in weak fields is due to the paramagnetic contribution of the impurity carriers in L), although the energy spectrum of this alloy is significantly restructured in a magnetic field $H \parallel C_3$. Figure 5a shows the dependence of the thermal gap ΔE in the spectrum on a magnetic field $H \parallel C_3$, obtained from measurements of the temperature dependences of the longitudinal magnetoresistance in various magnetic fields. The method used to reduce the galvanomagnetic-measurement data is discussed in detail in[14]. The gap ΔE connected with the size of the gap between the extrema L_a and T_{45}^-, decreases in a magnetic field and the transition from the semiconducting to the semimetallic state, previously observed in a number of studies, (see, e.g.,[15]), takes place at $H \sim 16$ kOe. The rate at which the edges of the bands in L and T approach each other (i.e., the levels 0^-), $\partial(\Delta E)/\partial H \approx -0.25$ meV/kOe, is close to the calculated estimate (~ -0.2 meV/kOe) obtained by using the spin and orbital masses of only holes in the T_{45}^- extremum of pure bismuth (the edge of the band in L is hardly shifted in a magnetic field).

This behavior of the magnetic susceptibility $\chi_{\parallel}$ in a magnetic field agrees with the conclusions of Beneslavskiĭ and Fal'kovskiĭ, that $\chi_{\parallel}$ depends little on the magnetic field, on the parameters of the band structure, and on the temperature. The groups of majority carriers that appear when the sample goes from the semiconducting to the semimetallic state are in the ultraquantum limit and make no noticeable contribution to the susceptibility; this seems to explain the absence of the χ singularities predicted by Azbel' and Rakhmanov[17] in semiconductor—metal transitions in a magnetic field.

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