Field, temperature, and concentration dependences of the magnetic susceptibility of bismuth–antimony alloys

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In the framework of the McClure model, which describes the electronic energy spectrum of bismuth and its alloys in the neighborhood of the L point of the Brillouin zone, an expression is obtained for the electron energy levels in a magnetic field. This expression is used to calculate the magnetic susceptibility of bismuth alloys at arbitrary magnetic fields. It is shown that the theoretical results are in good agreement with the entire set of published experimental data on the field, temperature, and concentration dependences of the magnetic susceptibility of bismuth–antimony alloys. © *2000 American Institute of Physics.* [S1063-777X(00)00501-6]

INTRODUCTION

The electronic band structure of bismuth and its alloys with antimony has been the subject of many papers (see, e.g., Refs. 1 and 2 and the references cited therein). It has been established that the Fermi surface of bismuth and its alloys (at low concentrations of antimony) consists of one hole ellipsoid, located at the T point, and three closed electron surfaces of nearly ellipsoidal shape, centered at the L points of the Brillouin zone. Another circumstance that is extremely important for understanding many of the properties of bismuth is that in the neighborhood of the L point the conduction band is separated by only a small energy gap from another, filled band. The detailed study of the energy spectra of the charge carriers near the L and T points is done mainly by methods based on oscillation and resonance effects. By now the values of the main parameters characterizing the band structure of bismuth and its alloys with antimony have been determined by these methods.[2]

The smooth (nonoscillatory with respect to the magnetic field H) part of the magnetic susceptibility of the solid solutions $Bi_{1-x}Sb_x$ exhibits noticeable (and often nonmonotonic) changes upon variations of H, the temperature T, the antimony concentration x, and the admixture of dopants that shift the level of the chemical potential ζ of the alloy.[3–7] These changes in the susceptibility are due to electronic states located near the L points and belonging to two bands separated by a small energy gap.[8–10] The rest of the electronic states all give a contribution to the magnetic susceptibility that is practically independent of T, ζ, H, and x and represents a constant background. The study of the ''variable'' contribution to the magnetic susceptibility (i.e., its dependences on T, ζ, H, and x) will make it possible to check and refine the data on the electronic band structure in the neighborhood of the L point as obtained from investigations of oscillation and resonance effects.

Calculations of the special (or ''variable'') contribution to the magnetic susceptibility of bismuth and its alloys in the limit $H \to 0$ were done in Ref. 8–10. The models of the electronic band structure[11,12] used in Refs. 8 and 9 would later be found to give a poor description of the spectrum of bismuth alloys in the neighborhood of the L point. In Ref. 10 the magnetic susceptibility was calculated using a spectrum which is intermediate in accuracy between those proposed in Ref. 13 and in Refs. 14 and 15; both of these last provide a good description of the entire set of experimental data on oscillation and resonance effects in bismuth alloys. However, in Ref. 10 the theoretical and experimental results were compared only for the dependences of the magnetic susceptibility χ on ζ and x, and the comparison was done using values[16] of the spectrum parameters that were later revised considerably.[2] In Ref. 17 the same model of the spectrum as in Ref. 10 was used to calculate the field dependence of the magnetic susceptibility, but only in low magnetic fields. For high magnetic fields a calculation of χ was done in Refs. 6 and 9, but with the use of unrealistic, oversimplified models of the spectrum.[11,12] Thus, at the present time there is no complete quantitative description of the experimental curves of the magnetic susceptibility of bismuth alloys as a function of H, T, ζ, and x.

It was shown in Ref. 18 that under conditions of degeneracy of the electronic energy bands of the crystal in a weak magnetic field ($H \to 0$) there can be giant anomalies of the magnetic susceptibility, and the types of degeneracy of the bands which can lead to such anomalies were listed. In Ref. 19 the problem of the electron energy levels in a magnetic field was solved exactly for two of these types (those most often encountered in crystals), and the special contribution to the magnetic susceptibility was calculated for arbitrary values of H. As expected, this contribution depends strongly on H, ζ, and T. The spectrum of bismuth–antimony alloys in the neighborhood of the L point of the Brillouin zone is close to degenerate and is characterized by the circumstance that for a nonzero gap in the spectrum, the type of degeneracy is intermediate between those considered in Ref. 18. This is what accounts for the strong field, temperature, and concen-

tration dependences of χ in these alloys. However, a detailed comparison of the theoretical and experimental results must be done with allowance for the aforementioned feature of the spectrum of bismuth alloys. Therefore, generalizing the results of Ref. 19, in Sec. 1 of the present paper we give a solution to the problem of the energy levels of an electron in a magnetic field for the McClure spectrum,[13] and in Sec. 2 we obtain the corresponding expressions for the magnetic susceptibility, valid for arbitrary H. In Sec. 3 we use these expressions to compare the theoretical and published experimental results for the field, temperature, and concentration dependences of χ in $Bi_{1-x}Sb_x$ alloys. We conclude with a summary of our findings.

1. SPECTRUM

As we said in the Introduction, the dependences of the magnetic susceptibility on the field and on temperature, impurity concentration, and other external parameters are governed mainly by the electronic states located in the neighborhoods of the L points of the Brillouin zone and belonging to two bands which lie close to each other and to the level of the chemical potential. These electronic states are described using several models of the energy spectrum which have different degrees of accuracy in terms of the parameter

$$\delta = \frac{\varepsilon_0}{E_0} \ll 1,$$

where ε_0 is the characteristic energy scale for the two nearby bands, and E_0 is the energy distance from these bands to the nearest of the remaining bands. The most complete models[10,14,15] have an accuracy of order δ. However, at present the values of the parameters of the spectrum have all been determined for the simpler McClure model,[13] which describes the spectrum with an accuracy of order $\delta^{1/2}$. We will use the McClure model here. In it the Hamiltonian of the electrons in the neighborhood of an L point has the form

$$\mathcal{H} = \begin{pmatrix} \Delta + K_c & 0 & t & u \\ 0 & \Delta + K_c & -u^* & t^* \\ t^* & -u & -\Delta - K_v & 0 \\ u^* & t & 0 & -\Delta - K_v \end{pmatrix}. \qquad (1)$$

Here and below the energy and chemical potential ζ are reckoned from the center of the energy gap 2Δ (here $\varepsilon_0 \sim 2\Delta, |\zeta|$) which separates the two bands, denoted c and v, which are nearly twofold degenerate at this point. The quantities t, u, K_c, and K_v are given by the formulas

$$t = q_1 k_1, \quad u = q_2 k_2 + q_3 k_3, \quad K_{c,v} = \frac{\alpha_{22}^{c,v}}{2} k_2^2, \qquad (2)$$

in which q_1, q_3, and $\alpha_{22}^{c,v}$ are real parameters of the model, and q_2 is a complex number. The origin of coordinates for the wave vector $\mathbf{k}$ is at the L point. The axis 1 is along the binary axis, and axis 2 is along the length of the Fermi surface of pure bismuth at the L point, i.e., at an angle $\varphi \approx 6°$ to the bisector direction. For pure bismuth $\mathrm{Re}(q_2) = 0$. In $Bi_{1-x}Sb_x$ alloys the dependences of the parameters q_i, $\alpha_{22}^{c,v}$, and Δ on the antimony concentration x are well described by the linear functions[2]

$$q_1 = 0.457 - 0.188x; \quad \alpha_{22}^c = 0.615 + 0.4x;$$
$$\mathrm{Im}(q_2) = 0.03 - 0.04x; \quad \alpha_{22}^v = 1.1 + 0.7x; \qquad (3)$$
$$q_3 = 0.344; \quad 2\Delta = (10 - 242x)\ \mathrm{meV}$$

(q_i and $\alpha_{22}^{c,v}$ are given in atomic units, a.u.). In addition, as x increases, the parameter $q_2(x)$ generally acquires a real part.[10] A nonzero $\mathrm{Re}(q_2)$ causes the long direction of the electronic isoenergy surfaces to deviate from the axis 2 by an angle $\delta\varphi \sim (\mathrm{Re}(q_2)/q_3)$. Such a deviation was actually observed in Ref. 16, and it follows from the data of that study that

$$\mathrm{Re}(q_2) \sim 0.05x.$$

The band energies $\varepsilon_c(\mathbf{k})$ and $\varepsilon_v(\mathbf{k})$ are found from the equations

$$\left[\varepsilon - \frac{1}{4}(\alpha_{22}^c - \alpha_{22}^v)k_2^2\right]^2 = E^2, \qquad (4)$$

where

$$E^2 = \left[\Delta + \frac{1}{4}(\alpha_{22}^c + \alpha_{22}^v)k_2^2\right]^2 + q_1^2 k_1^2 + |q_2|^2 k_2^2 + q_3^2 k_3^2 + 2q_3\,\mathrm{Re}(q_2)k_2 k_3. \qquad (5)$$

The relative position of these bands as a function of the antimony concentration x is shown in Fig. 1.

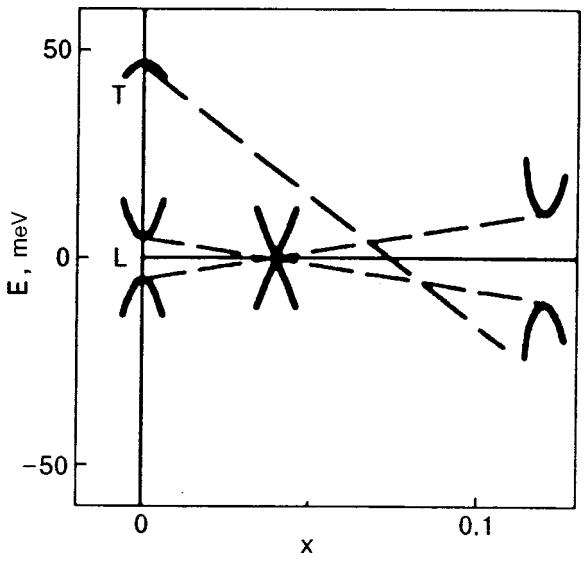

FIG. 1. Diagram of the changes in the electronic energy spectrum of $Bi_{1-x}Sb_x$ alloys at the L and T points of the Brillouin zone. The dashed lines indicate the path of the band edges $\varepsilon_c(0)$ and $\varepsilon_v(0)$ at the L points and $\varepsilon_T(0)$ at the T point as x is changed. The lines were constructed using formulas (3) and (10). At $x \approx 0.04$ the gap in the spectrum at the L point goes to zero, and for $x > 0.07$ the alloy undergoes a transition to a semiconducting state. The solid curves show a schematic illustration of $\varepsilon_c(\mathbf{k})$, $\varepsilon_v(\mathbf{k})$, and $\varepsilon_T(\mathbf{k})$ at the respective points.

The spectrum of electrons in a magnetic field **H** directed along the k_2 axis can be obtained from the general expression[19]

$$S(\varepsilon_n,k_2)=\frac{2\pi eH}{c\hbar}n, \tag{6}$$

where e is the absolute value of the electron charge, $S(\varepsilon_n,k_2)$ is the cross-sectional area of the isoenergy surface on a plane $k_2=\text{const}$, and n is a nonnegative integer. Here it should be kept in mind that the energy levels ε_n with $n>0$ are twofold degenerate. In the derivation of (6) we neglected the direct interaction of the electron spin with the magnetic field, since the purely spin contribution to the magnetic susceptibility is of order δ (but the spin–orbit interaction is taken into account in all the formulas given above). We note that, although the quantization condition (6) has the quasiclassical form, in this case it gives the exact eigenvalues for the energy of an electron with the Hamiltonian (1), (2). From Eqs. (4)–(6) we obtain

$$\varepsilon_n^{c,v}(k_2,H)=\left(\frac{\alpha_{22}^2-\alpha_{22}^v}{4}\right)k_2^2\pm\left[\alpha Hn+\left(\Delta+\frac{\alpha_{22}^c+\alpha_{22}^v}{4}k_2^2\right)^2+(\mathrm{Im}(q_2))^2k_2^2\right]^{1/2}, \tag{7}$$

where $\alpha=2e|q_1q_3|/c\hbar$. If the magnetic field is directed at an angle θ to the k_2 axis, then, as was shown in Ref. 19, to an accuracy of $\delta\tan^2\theta$ the eigenvalues $\varepsilon_n^{c,v}(k_2,H)$ are described, as before, by formula (7) but with $H\cos\theta$ substituted for H.

Besides the electronic states in the neighborhoods of the L points of the Brillouin zone, bismuth also has hole states in the neighborhood of the T point. These states have the energy spectrum[1]

$$\varepsilon_T(\mathbf{k})=E_T-\frac{\hbar^2}{2m_1^h}(k_1^2+k_2^2)-\frac{\hbar^2}{2m_3^h}k_3^2. \tag{8}$$

Here the values of the effective masses m_1^h and m_3^h are

$$m_1^h=0.212\ \text{a.u.},\quad m_3^h=0.0639\ \text{a.u.}, \tag{9}$$

k is reckoned from the T point, the axes 1 and 2 coincide with the binary and bisector axes, respectively, and E_T is the energy of the band edge, which in $Bi_{1-x}Sb_x$ alloys falls off linearly with increasing x (see Fig. 1):

$$E_T=(46.9-601.26x)\ \text{meV}. \tag{10}$$

The contribution to χ from the hole states at the T point is small compared to the contribution from the electronic states near the L points and is of order δ. This is because of the relatively large masses $m_{1,3}^h$ and, accordingly, the small distances between energy levels ε_n^T in a magnetic field:

$$\varepsilon_n^T(k_2)=E_T-\frac{\hbar eH}{c\sqrt{m_1^hm_3^h}}\left(n+\frac{1}{2}\right)-\frac{\hbar^2k_2^2}{2m_1^h}. \tag{11}$$

However, while neglecting the contribution of these states to the susceptibility, one must take into account their influence on the position of the chemical potential of the electrons in bismuth–antimony alloys.

2. CALCULATION OF THE MAGNETIC SUSCEPTIBILITY

The magnetic susceptibility of bismuth and its alloys can be written as the sum of a special contribution due to the electronic states near the three L points and a background term due to all the remaining states. The background term is practically independent of the magnetic field and temperature and even remains constant upon variations of the chemical potential $|\delta\zeta|\sim|\Delta|$. The special contribution to the magnetic susceptibility consists of a sum of three terms due to the states near the respective L points. Each of this terms can be obtained from the following expression for the Ω potential (per unit volume):

$$\Omega(H_\theta)=-\frac{eH_\theta T}{4\pi^2c\hbar}\sum_{c,v}{\sum_{n=0}}'\int_{-\infty}^{+\infty}dk_2\times\ln\left\{1+\exp\left(\frac{\zeta-\varepsilon_n^{c,v}(k_2,H_\theta)}{T}\right)\right\}, \tag{12}$$

where the prime on the summation sign means that in taking the sum over n the terms with $n>0$ must be doubled; H_θ is the projection of the magnetic field on the k_2 axis at the given L point. In an experiment one measures the quantity

$$\chi=h_ih_j\chi^{ij},$$

where $\mathbf{h}=\mathbf{H}/H$ is a unit vector in the magnetic field direction, and the differential magnetic susceptibility χ^{ij} is given by the expression

$$\chi^{ij}=-\frac{\partial^2\Omega}{\partial H_i\partial H_j}.$$

Since the Ω potential (12) depends on H only through H_θ, in our approximation (to accuracy $\delta^{1/2}$) we have

$$\chi=\sum_{i=1}^{3}\cos^2\theta_l\chi^{22}(H\cos\theta_l),$$

where θ_l are the angles between the magnetic field **H** and the k_2 axis for the three L points.

In the case of weak magnetic fields, for which the characteristic distance between energy levels in the magnetic field obeys $\delta\varepsilon_H\ll T$, we integrate (12) by parts, use the Euler–Maclaurin summation formula, and differentiate with respect to the magnetic field to obtain for the susceptibility an expression of the form $\chi=\chi_0+\chi_1H^2$, where the expressions for the H-independent terms χ_0 and χ_1 are the same as those obtained previously in Refs. 10 and 17.

Let us now analyze χ^{22} in the case of high magnetic fields, $\delta\varepsilon_H\gg T$. The contribution of the electrons in the conduction band to the magnetic susceptibility can be calculated directly using formula (12), since the number of filled levels ε_n^c is finite. To calculate the contribution of the filled band v to χ^{22}, we once again integrate (12) by parts as many times as necessary, use the Poisson summation formula, and set $T=0$ ($\delta\varepsilon_H\gg T$). The resulting formula includes one summation and integrations over n and k_2. If the quantity $(d\varepsilon_n^v/dn)$ in this formula [where ε_n^v is defined in Eq. (7)] is written as

$$\left|\frac{d\varepsilon_n^{\nu}}{dn}\right| = \frac{2}{\sqrt{\pi}}\int_0^{\infty} dt \exp\left\{-\left(\frac{d\varepsilon_n^{\nu}}{dn}\right)^{-2} t^2\right\},$$

then the summation and integration over n and k_2 can be done in explicit form. As a result, we obtain for $|\zeta|<|\Delta|$

$$\chi^{22}(H) = -\frac{1}{4\pi^2}\left(\frac{e}{c\hbar}\right)\alpha\left(\frac{|Q|}{\pi|\Delta(\alpha_{22}^{c}+\alpha_{22}^{\nu})|}\right)^{1/2} \times \int_0^{\infty} dt\, f\left(\frac{H}{H_{\Delta}}t^2\right) e^{(Q^2-2)t^2} K_{1/4}(Q^2t^2), \qquad (13)$$

where Q is the following dimensionless combination of parameters:

$$Q = \mathrm{sgn}[\Delta(\alpha_{22}^{c}+\alpha_{22}^{\nu})]\left(1+\frac{2(\mathrm{Im}(q_2))^2}{\Delta(\alpha_{22}^{c}+\alpha_{22}^{\nu})}\right); \qquad (14)$$

H_{Δ} is the characteristic magnetic field, at which $\delta\varepsilon_H \sim |\Delta|$, i.e., $H_{\Delta}=\Delta^2/\alpha$; $K_{1/4}(x)$ is a modified Bessel function, and

$$f(x) = 2\left(\frac{x\coth x - 1}{\sinh^2 x}\right).$$

In the derivation of expression (13) we have assumed that the parameter

$$\gamma = \left|\frac{\alpha_{22}^{c}+\alpha_{22}^{\nu}}{\alpha_{22}^{c}-\alpha_{22}^{\nu}}\right| \geqslant 1. \qquad (15)$$

We note that this condition is satisfied for $Bi_{1-x}Sb_x$ alloys for any antimony concentrations x.

If the magnetic fields are such that $H \ll H_{\Delta}$, then the magnetic susceptibility (13) is independent of the field, and it is described by the same expression as that given in Ref. 10 for $T\to 0$. On the other hand, if $H \gg Q^2 H_{\Delta}$ (for bismuth–antimony alloys $Q \gg 1$ for $x\sim 0.04$, while for other antimony concentrations $Q \geqslant 1$ in the region $x<0.2$), then

$$\chi^{22}(H) \approx -A\frac{e}{c\hbar}\frac{\alpha^{3/4}}{|\alpha_{22}^{c}+\alpha_{22}^{\nu}|^{1/2}} H^{-1/4}, \qquad (16)$$

where

$$A = \frac{21}{32}\frac{\zeta(7/4)\cos(\pi/8)\Gamma(1/4)}{2^{3/4}\pi^{13/4}} \approx 6.21\times 10^{-2}; \qquad (17)$$

$\zeta(x)$ is the Riemann zeta function, and $\Gamma(x)$ is the gamma function. Formulas (16) and (17) agree with those obtained in Ref. 9.

In Ref. 19 the field dependence of the magnetic susceptibility of electrons was investigated for two of the three types of degeneracy of the energy bands of crystals leading to strong field dependence. According to Eqs. (3)–(5), in $Bi_{0.96}Sb_{0.04}$ alloys there is band degeneracy of the first type according to the classification of Ref. 18, i.e., a band splitting that is linear in the wave vector $\mathbf{k}$ in the neighborhood of the degeneracy point L. However, bismuth alloys are characterized by relatively small values of the matrix element q_2 responsible for this linear splitting along the k_2 axis. That is why we took terms quadratic in k_2 into account in the Hamiltonian (1)–(3). According to Eqs. (3)–(5), as the point $\mathbf{k}$ moves away from the L point along the k_2 axis, the splitting of the bands rapidly deviates from linearity and approaches a quadratic law. This leads to a more complicated dependence of $\chi(H)$ than in Ref. 19 [see Eq. (13)]. The limiting expression (16) corresponds to the case when the initial (linear in k_2) part of the band splitting can be neglected, and one can assume that $|\varepsilon_c(k_2)-\varepsilon_v(k_2)| \propto k_2^2$ (we note that this approximation is justified even for $\Delta\neq 0$). Thus formula (16) actually describes the behavior of $\chi(H)$ for the third type of band degeneracy,[18] for which a giant anomaly of the magnetic susceptibility can occur and which was not considered in Ref. 19. Here Eq. (15) corresponds to the condition when $\varepsilon_c(k_2)$ and $\varepsilon_v(k_2)$ have different signs. If $\varepsilon_c(k_2)$ and $\varepsilon_v(k_2)$ had the same sign, i.e., if $\gamma<1$, then, as one can show, for $H \gg H_{\Delta}Q^2\gamma^2/(1-\gamma^2)$ the magnetic susceptibility is described as before by formula (16) but with a different constant A:

$$A = \frac{21}{16}\frac{\zeta(7/4)\cos(\pi/8)}{2^{1/4}\pi^{11/4}\Gamma(1/4)}\gamma^{1/2}F\left(\frac{1}{4},-\frac{1}{4},\frac{5}{4},\gamma^2\right), \qquad (18)$$

where F is the hypergeometric function. In the limiting case $\gamma=0$ (and $|q_2|=0$) we would arrive at a line of degeneracy of the bands, i.e., at the second case according to the classification of Ref. 18. Then expression (16) with the factor A from (18) agrees with the expression obtained in Ref. 19. Finally, we note that in the case of band degeneracy at an L point or for small Δ the parameter $Q \gg 1$, and there is a region of magnetic fields $H_{\Delta} \ll H \ll Q^2 H_{\Delta}$ in which the part of the band splitting that is linear in k_2 plays the governing role in $\chi(H)$. Then it follows from Eq. (13) that

$$\chi^{22}(H) = -\frac{1}{6\pi^2}\frac{e}{c\hbar}\frac{\alpha}{2|\mathrm{Im}(q_2)|}\ln\left(\frac{H_{\Delta}}{H}\right)^{1/2}.$$

With an accuracy up to the background constant, this result agrees with that obtained in Ref. 19 for the first type of band degeneracy. Thus the strong field dependence of the magnetic susceptibility of bismuth alloys is a manifestation of the fact that the spectrum of these alloys is close to those cases of band degeneracy which lead to a giant anomaly of the magnetic susceptibility.[18]

The chemical potential ζ of the electrons in the crystal, generally speaking, itself depends on the magnetic field. This dependence is determined from the condition that the total electron density is constant:

$$\nu \equiv -\frac{\partial\Omega}{\partial\zeta} = \mathrm{const}. \qquad (19)$$

To evaluate the magnetic susceptibility at constant ν, it is necessary to go over from the Ω potential to the free energy. As a result, for $\chi^{ij}(H,\nu)$ we have[19]

$$\chi^{ij}(H,\nu) = \left[\chi^{ij}(H,\zeta) - \frac{\partial\nu}{\partial H_i}\frac{\partial\nu}{\partial H_j}\left(\frac{\partial\nu}{\partial\zeta}\right)^{-1}\right]_{\zeta=\zeta(H,\nu)}. \qquad (20)$$

When obtaining the function $\zeta(H,\nu)$ using formula (19) it is necessary to take into account the contributions to the Ω potential not only from the electronic states near the L points but also the states near the T point, and also the influence of donor and acceptor impurities. The states at the T point give

a term in the Ω potential which is determined by formula (12) with the energy levels from (11). Impurities, first, cause scattering of the charge carriers and, second, give an additional impurity contribution to the Ω potential in semiconducting alloys. The scattering of charge carriers can be taken into account in a simple way by the introduction of a Dingle temperature T_D, i.e., by replacing T by $T+T_D$ in all the formulas. In semiconducting alloys of $Bi_{1-x}Sb_x$ ($x>0.07$) we consider the impurity contribution to the Ω potential, $\Omega_{\rm imp}$, in the limiting case of lightly and heavily doped n-type semiconductors. The case of light doping is characterized by the presence of carrier–impurity bound states, the energies of which form a narrow impurity band lying in the gap of the spectrum. In bismuth–antimony alloys these energies ε_i practically coincide with the band edge, i.e., $\varepsilon_i \approx |\Delta|$. We then have

$$\Omega_{\rm imp} = -T\nu_{\rm imp}\ln\left(1+\exp\left(\frac{\zeta-\varepsilon_i}{T}\right)\right), \quad \nu=\nu_{\rm imp}, \qquad (21)$$

where $\nu_{\rm imp}$ is the density of doping impurities. As we know,[20] the main condition for the existence of impurity levels is that the average size d of the carrier–impurity bound state be small compared to the distance between impurities, i.e., the condition $d\nu_{\rm imp}^{1/3} \ll 1$. The dimension d is of the order of the ''Bohr'' radius $d \sim a_B^* = \kappa\hbar^2/e^2m^*$, where κ is the dielectric constant of the crystal and m^* is the effective mass of a charge carrier. For a heavily doped semiconductor $d\nu_{\rm imp}^{1/3} \geqslant 1$, and carrier–impurity bound states do not arise. In this case we have

$$\Omega_{\rm imp}=0, \quad \nu=\nu_{\rm imp}, \qquad (22)$$

i.e., the semiconductor is transformed into a ''poor'' metal with an intrinsic electron density $\nu_{\rm imp}$. If the semiconductor is in a magnetic field H, then we must take into account the dependence on H of the average size d of a localized state. In a weak magnetic field we have $d \sim a_B^*$, as before. However, when the magnetic length $\lambda \cong (\hbar c/eH)^{1/2}$ becomes smaller than a_B^*, the size of the localized state in the directions perpendicular to **H** is determined by the value of λ, and the average size $d \sim (\lambda^2 a_B^*)^{1/3}$ falls off with increasing H. Therefore, in sufficiently high fields $H \geqslant H_{\rm cr} \sim (\hbar c/e)\nu_{\rm imp}a_B^*$ there occurs a magnetic ''freeze-out'' of the electrons,[21] and the heavily doped semiconductor is transformed into a lightly doped one.

3. COMPARISON OF THE RESULTS OF THE CALCULATION OF χ WITH EXPERIMENTAL DATA

In Refs. 3–7 significant changes in χ were observed in bismuth–antimony alloys upon variations in the magnetic field, temperature, antimony concentration, or chemical potential, the level of the last being regulated by the introduction of doping impurities in the alloy. Our theoretical analysis of the dependence of the susceptibility on H, T, x, and ζ will be done on the basis of the formulas obtained in Sec. 2, using the values in (3), (9), and (10) for the parameters of the spectrum.

Let us first consider the dependence of $\chi(H\to 0)$ on the antimony concentration x in $Bi_{1-x}Sb_x$ alloys (Fig. 2). Expressions for the magnetic susceptibility in low fields were obtained previously.[10] In the present paper, however, the calculations using these expressions were done with the new values of the parameters (3), (9), (10). In comparing the theoretical and experimental results we chose the constant background in the susceptibility so as to obtain coincidence with the corresponding values for pure bismuth. In the calculation it is necessary to find the dependence of the chemical potential ζ on x for the semimetallic alloys $Bi_{1-x}Sb_x$ ($x<0.07$) from the condition that there be equal numbers of electrons and holes at the L and T points, respectively. In the region of semiconducting alloys ($x>0.07$) the chemical potential is assumed to lie in the gap of the spectrum between the valence band and conduction band, and the impurity concentration $\nu_{\rm imp}$ is taken equal to zero. From the results presented in Fig. 2 it follows that the use of the parameter set (3), (9), (10) provides a better description of the experimental data for the semiconducting alloys than does the set from Ref. 16. In addition, we have calculated the dependence of χ in a weak field H on the level of the chemical potential ζ for the alloys $Bi_{0.92}Sb_{0.08}$ and $Bi_{0.97}Sb_{0.03}$. The results of the calculation with the new parameter values agreed with the results of Ref. 10 to within the limits of experimental error.

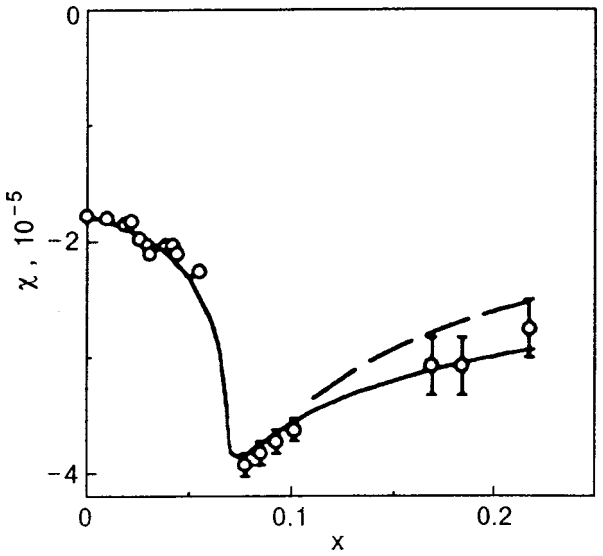

FIG. 2. Low-field magnetic susceptibility χ as a function of the antimony concentration x in $Bi_{1-x}Sb_x$ alloys. The magnetic field is applied in the basal plane of the crystal. $T=4.2$ K. χ is normalized to a unit volume; ○—experimental data of Ref. 7; solid curve—calculation according to the formulas of Ref. 10 with the use of the parameter values given in Eqs. (3), (9), (10); dashed curve—calculation done in Ref. 10 using the spectrum parameters given in Ref. 16.

Figure 3 shows the field dependence of the magnetization M of pure bismuth in magnetic fields so high that the only the lowest Landau level in the conduction band remains occupied, and there are no de Haas–van Alphen oscillations. In accordance with Eqs. (13) and (16), this curve is nonlinear in H. Here for a detailed comparison of the results of the calculation with the experimental data of Ref. 6, we took into consideration that $\zeta > \Delta$ in bismuth, and we added to Eq. (13) the contribution due to the conduction electrons. The expression for this contribution was obtained directly from

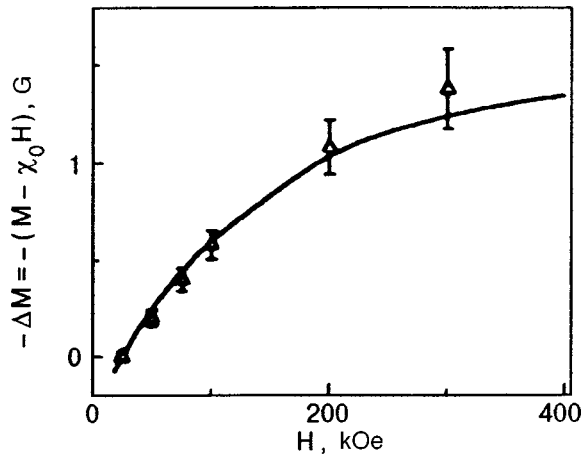

FIG. 3. Magnetization M of pure bismuth as a function of the magnetic field H, directed along the binary axis, for $T=20$ K and $H \geqslant 20$ kOe; △—the experimental data of Ref. 6; solid curve—the calculation of the present paper.

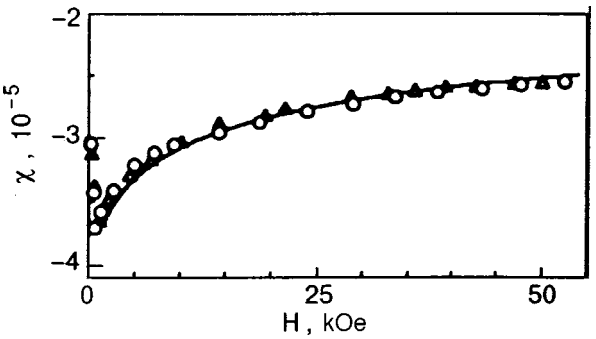

FIG. 5. Magnetic susceptibility χ as a function of magnetic field H for fields greater than 3 kOe, for the same alloy as in Fig. 4. The calculation was done using formula (13) for two orientations of the magnetic field—along the binary axis and along the bisector direction. The results of the calculation for the two cases practically coincide (solid curve); △,○—the experimental data of Ref. 7 for the first and second of the indicated directions of **H**, respectively. The values of x, ν_{imp}, T, and T_D are the same as in Fig. 4.

Eq. (12). We see that the agreement of the theoretical and experimental results is quite good, and it is achieved without the use of any adjustable parameters.

The results of the calculations of the field dependence of the magnetic susceptibility of the semiconducting alloys $Bi_{0.92}Sb_{0.08}$ with a concentration of donor impurities $\nu_{\text{imp}} = 10^{15}\,\text{cm}^{-3}$ are presented in Fig. 4. The two $\chi(H)$ curves shown differ in that they correspond to the dependence of ζ on H obtained for heavily and lightly doped semiconductors. For the given value of ν_{imp} an estimate of the field H_{cr} gives $H_{\text{cr}} \sim 1$ kOe. In accordance with the arguments set forth in Sec. 2, at fields much smaller than H_{cr} the theoretical curve corresponding to the case of heavy doping gives a good description of the experiment. For magnetic fields that are so weak ($H < 50$ Oe) that the characteristic distance between electronic energy levels at the L points is much less than the temperature ($T=4.2$ K), the aforementioned curve is approximated by the expression $\chi(H)=\chi_0+\chi_1 H^2$, and the values of χ_0 and χ_1 agree with those calculated using the formulas in Refs. 10 and 17. As the magnetic field is increased a transition to the case of light doping occurs on account of the magnetic freeze-out of the electrons, and, accordingly, in the region $H > H_{\text{cr}}$ the agreement with experiment is better for the other curve. As the magnetic field is increased further, the chemical potential of the electrons comes to lie in the gap of the spectrum, and the field dependence of $\zeta(H)$ ceases to influence the magnetic susceptibility; then the theoretical curves in Fig. 4 practically coincide. Here one can find $\chi(H)$ directly using formula (13). The results of this calculation are shown in Fig. 5. We see that, in complete agreement with experiment, the magnetic susceptibility is practically independent of the direction of the magnetic field **H** in the basal plane.

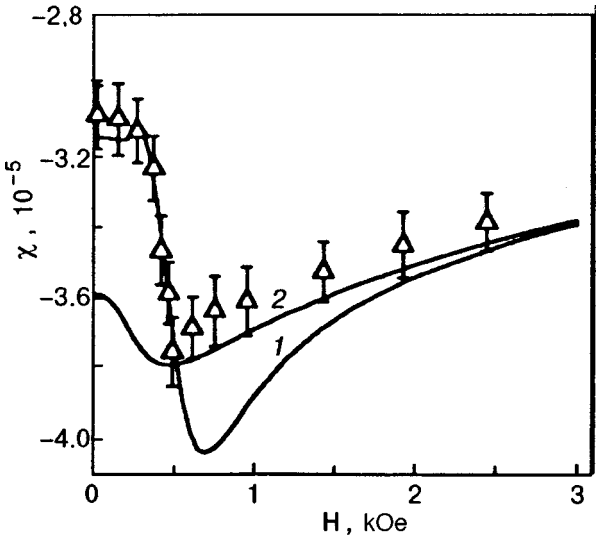

FIG. 4. Magnetic susceptibility χ as a function of the magnetic field H for the semiconducting alloy $Bi_{0.92}Sb_{0.08}$ with a concentration of donor impurities $\nu_{\text{imp}} = 10^{15}\,\text{cm}^{-3}$. The magnetic field is directed along the binary axis; $T=4.2$ K, $T_D=3.5$ K; χ is the susceptibility per unit volume. The curves *1* and *2* correspond to the cases of heavily doped [Eq. (22)] and lightly doped [Eq. (21)] semiconductors, respectively; △—the experimental data[7] for an alloy $Bi_{1-x}Sb_x$ with $x = 0.076 \pm 0.005$.

Figure 6 shows the results of calculations of $\chi(H)$ for the alloy $Bi_{0.92}Sb_{0.08}$ with admixtures of the dopant telluride at concentrations $\nu_{\text{imp}} \approx 3\times 10^{16}$ but $4\times 10^{17}\,\text{cm}^{-3}$. For the first of these concentrations $H_{\text{cr}} \sim 30$ kOe, and in fields lower than this, the difference in χ for the heavily and lightly doped semiconductor practically vanishes. For the second of these concentrations $H_{\text{cr}} \sim 400$ kOe, and the alloy remains heavily doped throughout the magnetic field region considered. Thus for an analysis of the $\chi(H)$ curves it suffices to use the formulas corresponding to a heavily doped semiconductor. The introduction of the donor impurity Te raises the level of ζ significantly, and the first few de Haas–van Alphen oscillations appear; these, however, cannot be described by the quasiclassical formulas. We see that, although the magnetic susceptibility is a nonmonotonic function of H, the theoretical curves rather accurately describe both the positions of the extrema of χ and the overall trend of the function $\chi(H)$. We note one final circumstance. In constructing the theoretical curves in Figs. 4–6 the Dingle temperatures T_D were chosen so as to give the best fit of these curves with the experimental data. In agreement with the existing ideas about

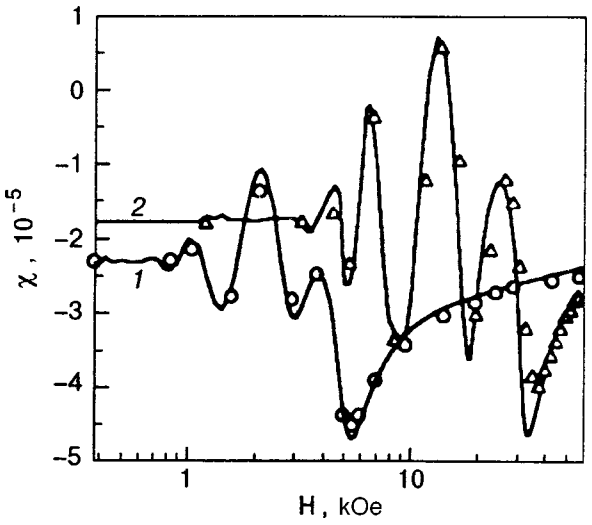

FIG. 6. Magnetic susceptibility χ as a function of magnetic field H for a field directed along the bisector direction, for the alloy $Bi_{0.92}Sb_{0.08}$ with two different concentrations of the donor impurity tellurium: $\nu_{imp}=3\times10^{16}\,cm^{-3}$ (curve *1*) and $\nu_{imp}=4\times10^{17}\,cm^{-3}$ (curve *2*). The calculation was done using formula (22); $T=4.2$ K, $T_D=7$ K and 11 K for curves *1* and *2*, respectively; ○,△—the experimental data of Ref. 7 for $Bi_{1-x}Sb_xTe_{0.000001}$ and $Bi_{1-x}Sb_xTe_{0.00001}$, respectively, where $x=0.076\pm0.005$.

the scattering of charge carriers in heavily doped semiconductors,[20] the values obtained for T_D are of the order of order of the characteristic Bohr energies $E_B=m^*e^4/2\hbar^2\kappa^2$ and depend approximately logarithmically on ν_{imp}.

The temperature dependence of the magnetic susceptibility of bismuth–antimony alloys is shown in Fig. 7 and 8. The nonmonotonic behavior of $\chi(T)$ (Fig. 8b) is easily explained on the basis of qualitative arguments. For the alloy

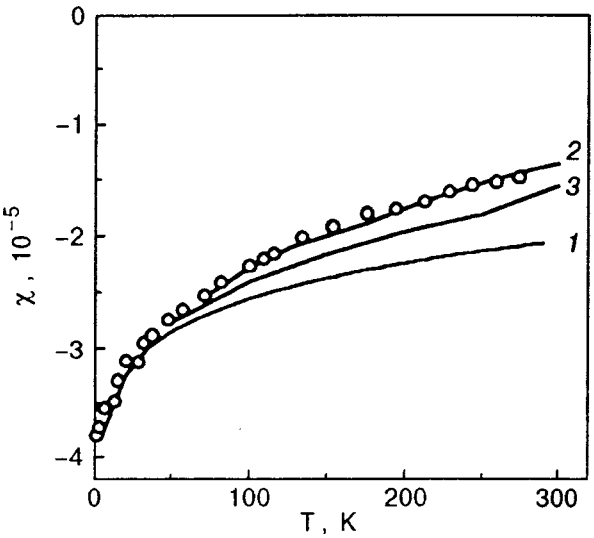

FIG. 7. Magnetic susceptibility χ as a function of temperature T in a constant magnetic field $H=500$ Oe applied along the bisector direction, for the same alloy as in Fig. 4. Curve *1* is for temperature-independent parameters of the spectrum; curve *2* is for parameters having temperature dependences described by formulas (23) and (24); curve *3* is obtained for parameters q_1, q_3, and Δ depending on T according to Eq. (23) but for $q_2(T)=q_2(0)$; ○—experimental data of Ref. 7 for $Bi_{1-x}Sb_x$ with $x=0.076\pm0.005$.

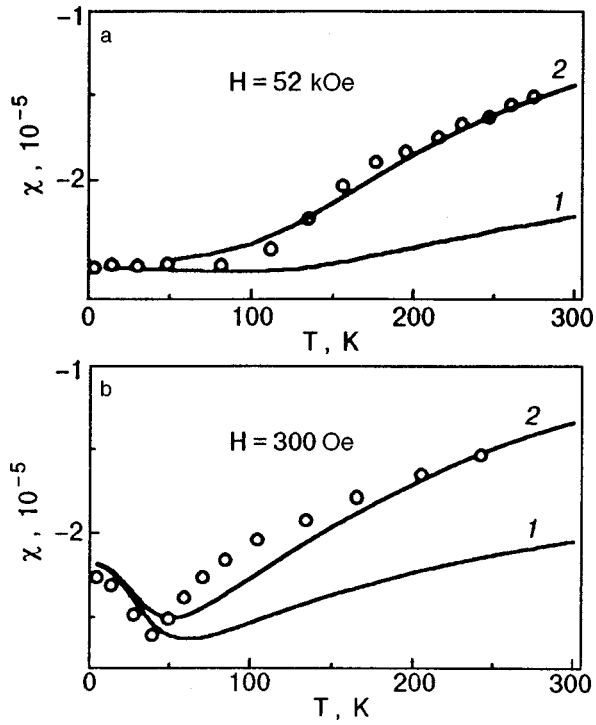

FIG. 8. Temperature dependence of χ in constant magnetic fields applied along the bisector direction, with a value of 52 kOe for the alloy $Bi_{0.92}Sb_{0.08}$ (a) and a value of 300 Oe for the alloy $Bi_{0.92}Sb_{0.08}$ with a concentration of the the donor impurity tellurium $\nu_{imp}=3\times10^{16}\,cm^{-3}$ (b); curves *1* are for temperature-independent spectrum parameters; curves *2* are for spectrum parameters with temperature dependences described by formulas (23) and (24); ○—experimental data of Ref. 7 for $Bi_{1-x}Sb_x$ (a) and $Bi_{1-x}Sb_xTe_{0.000001}$ (b) with $x=0.076\pm0.005$.

$Bi_{0.92}Sb_{0.08}$ at $H\leqslant500$ Oe the characteristic distance between electron energy levels in the magnetic field $\delta\varepsilon_H$ is less than or of the order of 10 K, and the $\chi(T)$ curves in Fig. 7 and 8b actually correspond to the low-field case, when $\delta\varepsilon_H<T$. Here, as follows from the results of Ref. 18, $|\chi|$ falls off monotonically with increasing temperature if ζ lies in the gap of the spectrum or if $\zeta-|\Delta|\lesssim T$. It is just such a situation that is observed in the case with $\nu_{imp}=10^{15}\,cm^{-3}$ (Fig. 7), since $\zeta-|\Delta|\lesssim20$ K in that case. For the alloy with $\nu_{imp}=3\times10^{16}\,cm^{-3}$ (Fig. 8b) one has $\zeta-|\Delta|\approx120$ K at $T=0$.

As the temperature is raised, the chemical potential of the degenerate electron gas decreases, $\zeta(0)-\zeta(T)\sim T^2/(\zeta(0)-|\Delta|)$, approaching the bottom of the conduction band. As long as $\zeta(T)-|\Delta|>T$, the behavior of χ can be explained by using the results of Ref. 18 for the function $\chi(\zeta,T=0)$. According to those results, $|\chi|$ increases with decreasing ζ. Finally, when T becomes greater than $\zeta(T)-|\Delta|$ (i.e., for $T\gtrsim70$ K), $|\chi|$, as we have said, begins to fall off with increasing T. This explains the appearance of an extremum of $\chi(T)$ in Fig. 8b. As to the data presented in Fig. 8a, they correspond to $\delta\varepsilon_H\sim600$ K. As long as $T\ll\delta\varepsilon_H$ one can assume $T=0$ in all the formulas presented in this paper, and χ is practically independent of temperature. It is only for $T\gtrsim\delta\varepsilon_H$, when a transition to the low-field case occurs, that one should expect to see an appreciable decrease of $|\chi|$ with increasing T. If it is assumed that the parameters of the spectrum do not change as the temperature increases, then the

calculated functions $\chi(T)$ give a good quantitative description of all the experimental data only for $T<50$ K. In Ref. 22 the temperature dependences of some of the parameters of the spectrum for pure bismuth were determined from magnetooptical measurements:

$$q_1(T)q_3(T)=q_1(0)q_3(0)-1.35\times10^{-4}\,T-3.8\times10^{-7}\,T^2\,[\text{a.u.}],\tag{23}$$

$$\Delta(T)=\Delta(0)+2.1\times10^{-3}\,T+2.5\times10^{-4}\,T^2\,[\text{meV}].$$

These parameters indeed vary hardly at all for $T\leqslant50$ K. The results of a calculation of the magnetic susceptibility with allowance for formulas (23) are presented in Fig. 7. It is seen that taking the temperature dependences (23) into account noticeably improves the agreement with the experimental data. Moreover, from the function $\chi(H)$ one can determine the temperature dependence of those parameters of the spectrum which cannot be found from magnetooptical measurements. In particular, by fitting the theoretical curve to the experimental data presented in Fig. 7, we obtain the temperature dependence $q_2(T)$:

$$q_2(T)=q_2(0)+8.9\times10^{-7}\,T^2\,[\text{meV}].\tag{24}$$

Interestingly, the use of this temperature dependence together with (23) for calculating $\chi(T)$ at another value of the magnetic field (Fig. 8a) or impurity concentration (Fig. 8b) yields a satisfactory description of the other experimental results as well.

CONCLUSION

The strong field, temperature, and concentration dependences of the magnetic susceptibility of bismuth–antimony alloys is explained by the fact that the electronic energy spectrum of these alloys is nearly degenerate. The magnetic susceptibility χ calculated in this paper for $Bi_{1-x}Sb_x$ solid solutions with the use of the McClure model gives a good quantitative description of all the aforementioned dependences, provided that one uses for the parameters of the spectrum the values reported in Ref. 2, which were obtained from oscillation and resonance effects. Here, in analyzing the field dependence of χ for the semiconducting Bi–Sb alloys, one must take into account that these alloys are heavily doped even at relatively low concentrations of donor or acceptor impurities. In particular, a comparison of the theoretical and experimental results for the alloy $Bi_{0.92}Sb_{0.08}$ shows that the Dingle temperature is a nonlinear function of the dopant concentration ν_{imp}, and for $\nu_{\text{imp}}\sim10^{15}\,\text{cm}^{-3}$ a magnetic freeze-out of the electrons occurs. The temperature dependence of χ appears to give evidence of an appreciable influence of the electron–phonon interaction on the magnetic susceptibility of semiconducting alloys of bismuth at $T>50$ K. The existing experimental data can be described in the framework of an extremely simple approach in which this interaction affects only the temperature dependence of the parameters of the spectrum.

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