PHYSICAL REVIEW VOLUME 115, NUMBER 5 SEPTEMBER 1, 1959

Magnetic Susceptibility of InSb

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(Received March 26, 1959)

The magnetic susceptibility of *n*-InSb has been measured for a range of extrinsic carrier densities extending from 10^{16} to 6×10^{18} cm^{-3}. Measurements were made in the temperature range 300°K to 1.3°K. The degenerate conduction electron susceptibility was determined from the data. The deviation of the conduction band from parabolic form is clearly exhibited in the susceptibility. A theoretical analysis has been made using Kane's band-structure calculation. The mixing of the conduction and valence bands resulting from the magnetic field has been treated exactly. Consideration of these two bands alone will not explain the dependence on concentration of the observed susceptibility; at the higher carrier densities, higher bands are important and a perturbation-theoretical treatment of these indicates that the observed susceptibility is consistent with Kane's model.

INTRODUCTION

THIS paper describes a study of the contribution of extrinsic electrons to the static magnetic susceptibility of InSb.[1] The purpose was to compare the observed susceptibility with theoretical expectations and by this means obtain information concerning the band structure. InSb was chosen because its conduction band departs from the simple parabolic form[2,3] in the experimentally attainable range of carrier concentrations; this seemed a logical extension of the work of one of the authors on the susceptibility of Ge, where the band remains parabolic under similar conditions.[4] The reader is referred to reference 4 for the details of the analysis of experimental data.

The only previous detailed study of the susceptibility of InSb is due to Stevens and Crawford.[5] Most of their measurements concern intrinsic carriers above 77°K. The extrinsic conduction electron contribution was determined at only one carrier density, 1.6×10^{16} cm^{-3}. Recently Matyas[6] has published a study of intrinsic carrier susceptibility, obtaining results very similar to those of Stevens and Crawford.

Our measurements cover a temperature range from 300°K to 1.3°K and a range of carrier densities from 10^{16} to 6×10^{18} cm^{-3}. The Fermi level at absolute zero for the highest density was calculated to be 0.35 ev,[2] so that this work provides information concerning the form of the conduction band to levels of 0.35 ev.

The conduction electron susceptibility is mainly orbital in character because of the smallness of the effective mass. However, spin-orbit effects cannot be neglected.

Our measurements show that the dependence of the conduction electron susceptibility on carrier density does indeed depart strongly from that expected for a parabolic band. A theoretical analysis will be given which is based on the band structure proposed by Kane and exhibits the following features. In the parabolic region, consideration of the conduction and valence bands alone is sufficient to determine χ. Beyond the parabolic range, the influence of other bands cannot be neglected. In particular certain higher bands have a large effect on the susceptibility, much larger than their effect on the energy $E_c(\mathbf{k})$ in the absence of a field. These higher bands are those which determine the value of the effective mass of the heavy holes. The resulting calculated susceptibility is in good agreement with the experimental results.

EXPERIMENTAL METHODS

The methods of susceptibility measurements were identical to those used in the Ge work.[4] The specimen dimensions were $0.2\times0.2\times5$ cm.

The specimen of highest purity was cut from a zone-refined ingot. The doped material was prepared by the Bridgman method, selenium being used as the doping agent; the resulting ingots were polycrystalline with an average grain dimension of several mm. The uniformity of doping of the final susceptibility specimens has been examined by measuring the Hall coefficient of 4 or 5 plates which were cut along the length of the specimen from a slice of the ingot adjacent to that from which the specimens were cut.

The number of carriers has been derived from measurements of the Hall coefficient in the extrinsic temperature range (77°K for specimens with carrier densities less than 10^{17} cm^{-3} and 300°K for the more highly doped specimens). The donor density n has been calculated from the Hall coefficient using the relation $R_H=\alpha/ne$, taking α to be unity[7] for the following reasons: (1) At the temperature of the Hall measurement, the electron gas is degenerate in a band with a single minimum. (2) It can be shown that the general formula[8] for the degenerate Hall coefficient reduces to $R_H=1/ne$ for nonparabolic bands provided they have

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[1] R. Bowers, Bull. Am. Phys. Soc. **3**, 120 (1958).
[2] E. O. Kane, J. Phys. Chem. Solids **1**, 249 (1957).
[3] W. G. Spitzer and H. Y. Fan, Phys. Rev. **106**, 882 (1957).
[4] R. Bowers, Phys. Rev. **108**, 683 (1957).
[5] D. K. Stevens and J. H. Crawford, Jr., Phys. Rev. **99**, 487 (1955).
[6] M. Matyas, Czechoslov. J. Phys. **8**, 544 (1958).
[7] Compare with reference 4, p. 685.
[8] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, Oxford, 1936), p. 282.

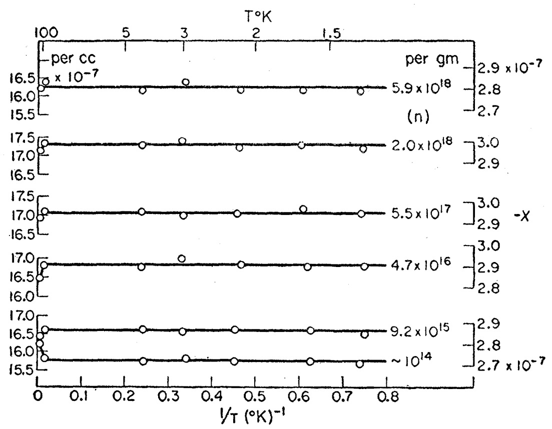

FIG. 1. The total magnetic susceptibility of various specimens of n-InSb plotted against $1/T$. The numbers listed under (n) are the carrier densities as determined from the Hall coefficients. Note that the left-hand ordinate gives the susceptibility per cc, while the right-hand ordinate gives the susceptibility per gram.

spherical symmetry. While the admixture of higher bands will cause a departure from spherical symmetry, the effect of this is small.

Allowing for any lack of uniformity, the carrier densities of specimens are estimated to be known to an accuracy of 20%. The cube root of the carrier density is the important parameter for interpreting our data and this is estimated to be known to 7%.

EXPERIMENTAL RESULTS

In Fig. 1 are shown measurements of the total susceptibility of various specimens of n-InSb plotted against $1/T$. The susceptibility was found to be independent of magnetic field (maximum field 4500 gauss for low temperature measurements and 8300 gauss for the room temperature points). It should be noted that the ordinate in Fig. 1 is not continuous; this has been done in order to separate the various sets of data. The lowest curve $n \sim 10^{14}$ cm^{-3} represents, at low temperatures, the pure InSb (lattice) susceptibility since the coduction electron susceptibility in this specimen is smaller than our estimated error.

Figure 2 is a plot of the degenerate conduction electron susceptibility plotted against $n^{\frac{1}{3}}$. The experimental points on this curve were obtained by subtracting the low-temperature lattice susceptibility from the susceptibility of doped material. The results designated by closed circles have been obtained from measurements of the susceptibility of doped specimens which extended down to 1.3°K and are illustrated in Fig. 1. The open circles were obtained from room temperature measurements on other specimens, a small correction (less than 2%) being made for any expected change in the total susceptibility of the sample between room temperature and liquid helium temperatures. The corrections were interpolated from the data in Fig. 1. This expedient was used in order to avoid measurements of all specimens to 1.3°K; its justification results from the fact that Fig. 1 shows the susceptibility to be almost independent of temperature for densities larger than 10^{17} cm^{-3}. The straight line in Fig. 2 shows the sum of (a) the Landau-Peierls expression for a constant effective mass[9] $m^* = 0.013 m_0$ and (b) the Pauli spin paramagnetism for a magnetic moment $\boldsymbol{\mu} = g\beta\mathbf{S}$ associated with the spin $\mathbf{S}$ and due to spin-orbit interaction. Here β is the Bohr magneton and $g = -53$.[10] By a comparison with the case of free electrons, we see that the ratio of the paramagnetism to the diamagnetism in the present case is $(-3)(g/g_s)^2(m^*/m)^2 = -0.35$.

THEORETICAL INTERPRETATION

The difficulty of interpreting these results arises from the fact that there is no general formula giving the susceptibility in terms of the band shape except for the simplest case of parabolic bands. The χ_3 term of Peierls[11] which relates the susceptibility to the curvature of the Fermi surface in k-space is only part of a more complete expression; its use would not be justified here.[12] In particular, it does not include spin-orbit interaction. In view of this, we have made a calculation specifically for InSb using the band-structure parameters of Kane. A somewhat similar calculation for the case of graphite has been made by McClure[13]; however, the band struc-

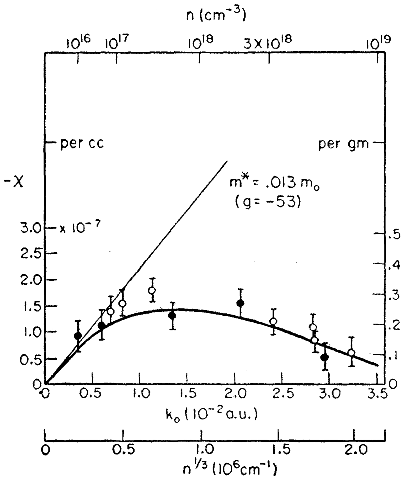

FIG. 2. The magnetic susceptibility of conduction electrons in InSb plotted against $n^{\frac{1}{3}}$. An abscissa scale for k_0 is also given. The solid curve is the result of the calculation in this paper.

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[9] Dresselhaus, Kip, Kittel, and Wagoner, Phys. Rev. **98**, 556 (1955).

[10] This is the g factor at the bottom of the conduction and was first given by L. M. Roth *et al.*, Bull. Am. Phys. Soc. **3**, 128 (1958).

[11] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 594.

[12] The inadequacy of the χ_3 term alone has been stressed by E. N. Adams, Phys. Rev. **89**, 633 (1953); E. N. Adams and R. Zitter, Phys. Rev. **96**, 1705 (1954). Only at the bottom of the band and without spin-orbit coupling is the susceptibility given by χ_3, as shown by T. Kjeldaas and W. Kohn, Phys. Rev. **105**, 806 (1957).

[13] J. W. McClure, Phys. Rev. **104**, 666 (1956).

ture of graphite and InSb are so dissimilar that different problems arise.

We shall calculate the susceptibility using the Luttinger and Kohn representation[14] (hereafter abbreviated as L.K.). This representation was the one employed in the band structure calculation and our use of it will enable us to compare the effect of the various matrix elements on the energy $E_c(\mathbf{k})$ with their effect on the susceptibility. According to Kane, the small value of the effective mass is due to a strong interaction[15] between conduction and valence bands which are separated by a small energy gap. A subdivision of the susceptibility calculation is suggested by the band structure calculation, i.e., (a) to treat exactly the part of the Hamiltonian[16] connecting the conduction and valence bands, and (b) to include the effects of other bands by perturbation theory.

In the next three sections we calculate (I) the energy levels in a magnetic field resulting from the conduction band interaction, (II) the resulting susceptibility, and (III) the effect of higher bands.

I. Energy Levels

A method has been found[17] for determining the magnetic energy levels in a spherical band which will be applied to the conduction band of InSb. In the approximation where only the interaction between the conduction and valence bands is included, the conduction band is not quite spherical because of the nonvanishing constants K_2, K_3 arising[2] from interband matrix elements of the spin-orbit interaction. The magnitude of these is, however, so small that we shall neglect them and follow Kane in choosing for the orbital part of our L.K. states the complete set $u_{n0}(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ where the u_{n0} are the solutions at $\mathbf{k}=0$ of the periodic Hamiltonian without the spin-orbit interaction. Let $|S\rangle$; $|X\rangle$, $|Y\rangle$, $|Z\rangle$ denote the normalized orbitals $u_{n0}(\mathbf{r})$ for the conduction band and valence bands respectively; under the symmetry operations of the crystal, the last three of these transform as the coordinates along the cubic axes. Because of cubic symmetry, the susceptibility is isotropic and the magnetic field $\mathcal{H}$ has been taken for convenience to be along the [100] direction.

We choose for the periodic part of our L.K. functions the following states which diagonalize the Hamiltonian, including spin-orbit interaction to first order, at $\mathbf{k}=0$:

$$\begin{gathered} |iS-\rangle, \quad |iS+\rangle; \\ (\tfrac{1}{2})^{\frac{1}{2}}|(X-iY)-\rangle, \quad (\tfrac{2}{3})^{\frac{1}{2}}|Z-\rangle+(\tfrac{1}{6})^{\frac{1}{2}}|(X-iY)+\rangle, \\ (\tfrac{2}{3})^{\frac{1}{2}}|Z+\rangle-(\tfrac{1}{6})^{\frac{1}{2}}|(X+iY)-\rangle, \quad (\tfrac{1}{2})^{\frac{1}{2}}|(X+iY)+\rangle, \qquad (1) \\ (\tfrac{1}{3})^{\frac{1}{2}}|Z-\rangle-(\tfrac{1}{3})^{\frac{1}{2}}|(X-iY)+\rangle, \\ (\tfrac{1}{3})^{\frac{1}{2}}|Z+\rangle+(\tfrac{1}{3})^{\frac{1}{2}}|(X+iY)-\rangle. \end{gathered}$$

The spin quantum numbers $-$, $+$ refer to a direction of quantization along $\mathcal{H}$. The Zeeman energy $\beta\mathcal{H}\sigma_z$, where β is the Bohr magneton and σ_z a Pauli spin matrix, will be neglected because of its smallness.

The eigenvalue equation, in the L.K. representation, consists of a set of coupled differential equations. This set is simply the Schrödinger equation in $\mathbf{k}$ space. The wave function is given by a set of 8 functions $F_i(\mathbf{k})$ where the index i refers to the order of the states in (1). These states transform under the symmetry operations like states of definite total angular momentum $J(i)=\frac{1}{2}$ and $\frac{3}{2}$ and definite Z component of angular momentum $m_J(i)$. Because of the cubic symmetry of InSb, the interaction matrix between the s like and p like levels is formally the same as if the states $|S\rangle$, $|X\rangle$, $\cdots$ were the product of a radial function and a spherical harmonic; according to reference 17 the eigenvalue problem can be solved exactly in terms of harmonic oscillator functions of k_x.

In atomic units, and using Kane's notation in which E_G is the band gap at $\mathbf{k}=0$, Δ is the spin-orbit splitting of the valence band and P is the interband momentum matrix element, the eigenvalue equations in matrix form are given by

$$\begin{bmatrix} E_G-\lambda' & 0 & (\frac{1}{2})^{\frac{1}{2}}P\bar{k}_- & (\frac{2}{3})^{\frac{1}{2}}Pk_z & -(\frac{1}{6})^{\frac{1}{2}}P\bar{k}_+ & 0 & (\frac{1}{3})^{\frac{1}{2}}Pk_z & (\frac{1}{3})^{\frac{1}{2}}P\bar{k}_+ \\ 0 & E_G-\lambda' & 0 & (\frac{1}{6})^{\frac{1}{2}}P\bar{k}_- & (\frac{2}{3})^{\frac{1}{2}}Pk_z & (\frac{1}{2})^{\frac{1}{2}}P\bar{k}_+ & -(\frac{1}{3})^{\frac{1}{2}}P\bar{k}_- & (\frac{1}{3})^{\frac{1}{2}}Pk_z \\ (\frac{1}{2})^{\frac{1}{2}}P\bar{k}_+ & 0 & -\lambda' & 0 & 0 & 0 & 0 & 0 \\ (\frac{2}{3})^{\frac{1}{2}}Pk_z & (\frac{1}{6})^{\frac{1}{2}}P\bar{k}_+ & 0 & -\lambda' & 0 & 0 & 0 & 0 \\ -(\frac{1}{6})^{\frac{1}{2}}P\bar{k}_- & (\frac{2}{3})^{\frac{1}{2}}Pk_z & 0 & 0 & -\lambda' & 0 & 0 & 0 \\ 0 & (\frac{1}{2})^{\frac{1}{2}}P\bar{k}_- & 0 & 0 & 0 & -\lambda' & 0 & 0 \\ (\frac{1}{3})^{\frac{1}{2}}Pk_z & -(\frac{1}{3})^{\frac{1}{2}}P\bar{k}_+ & 0 & 0 & 0 & 0 & -\Delta-\lambda' & 0 \\ (\frac{1}{3})^{\frac{1}{2}}P\bar{k}_- & (\frac{1}{3})^{\frac{1}{2}}Pk_z & 0 & 0 & 0 & 0 & 0 & -\Delta-\lambda' \end{bmatrix} \begin{bmatrix} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \\ F_6 \\ F_7 \\ F_8 \end{bmatrix} \equiv 0. \qquad (2)$$

Here λ' is the operator $\lambda-\bar{k}^2/2$ where $\bar{k}^2=\bar{k}_x^2+\bar{k}_y^2+k_z^2$ and λ is the eigenvalue. The gauge $(0,\mathcal{H}x,0)$ is used and the operators $\bar{k}_\pm=\bar{k}_x\pm i\bar{k}_y$ with $\bar{k}_x=k_x$; $\bar{k}_y=k_y+is\partial/\partial k_x$; $s=e\mathcal{H}/\hbar c$. The eigenvalues of the operators k_y, k_z will be denoted by primes, k_y', k_z'. Because the dependence of the energy on the magnetic field involves only the combination $k_y+is\partial/\partial k_x$, the energy of a state is independent of the value of k_y'. This is seen by transforming $k_y'+is\partial/\partial k_x$ by means of the unitary transformation $\exp(-ik_y'k_x/s)$. For ease of computation k_y' is put equal to zero. In (2) the small contribution

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[14] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[15] For the sake of brevity, the expression "interaction between two bands" will be used to refer to the interband coupling in the Hamiltonian resulting from the interband matrix elements of the velocity between the L.K. states of the two bands.

[16] The one-electron picture is used and the Hamiltonian in the absence of the magnetic field is the familiar periodic Hamiltonian with spin orbit interaction.

[17] Y. Yafet, following paper [Phys. Rev. **115**, 1172 (1959)].

from the **k**-dependent spin-orbit interaction[2] has been neglected.

The set of Eqs. (2) is solved by a perturbation method: Because the effective mass $m^*=0.013$ is so much smaller than the free mass m_0, a first approximation to the levels is obtained by neglecting all the terms $\bar{k}^2/2$ (diagonal) that contain the free mass. The effect of the free mass will be included later. With this approximation, the set (2) is reduced by elimination of all F_i but F_1 and F_2 to the two uncoupled equations:

$$\begin{aligned}&\{(E_G-\lambda)\lambda+\tfrac{2}{3}P^2(k_z^2+k_x^2-s^2\partial^2/\partial k_x^2+\tfrac{1}{2}s)\\&\quad+[P^2\lambda/3(\Delta+\lambda)](k_z^2+k_x^2-s^2\partial^2/\partial k_x^2-s)\}F_1=0,\\&\{(E_G-\lambda)\lambda+\tfrac{2}{3}P^2(k_z^2+k_x^2-s^2\partial^2/\partial k_x^2-\tfrac{1}{2}s)\\&\quad+[P^2\lambda/3(\Delta+\lambda)](k_z^2+k_x^2-s^2\partial^2/\partial k_x^2+s)\}F_2=0.\end{aligned}\tag{3}$$

These are immediately solved by harmonic oscillator eigenfunctions $\Phi_n(k_x)$ of the dimensionless variable $k_x/\sqrt{s}$. Further the other F_i are also such eigenfunctions as seen from (2) and the wave functions can be written as

$$\begin{aligned}\psi_{k_z', n, \pm}{}^{(\alpha)}(\mathbf{k})&\equiv\{F_i{}^{(\alpha)}\}\\&=\{C_i{}^{(\alpha)}(k_z', n, \pm)\Phi_{n-m_{J(i)}\pm\frac{1}{2}}(k_x)\},\end{aligned}\tag{4}$$

with the coefficients $C_i{}^{(\alpha)}$ to be determined from (2). The trivial dependence $\delta(k_y)\delta(k_z-k_z')$ on k_y and k_z has been omitted. The band index α stands for one of the letters c, l, h, or d, according to whether the state is in the conduction band, light hole, heavy hole, or split-off bands, respectively.

The spin quantum number is $-$ or $+$ for the state having a nonvanishing component in the L.K. states obtained from $|(X-iY)-\rangle$ or $|(X+iY)+\rangle$, respectively. For the heavy-hole states[18] which are spin-degenerate to this approximation (with $\lambda^{(h)}=0$) this assignment is made by choice of the proper linear combinations. The energy levels are given by the solutions of

$$\begin{aligned}D(\lambda_{n\pm})\equiv\lambda_{n\pm}(\lambda_{n\pm}-E_G)(\lambda_{n\pm}+\Delta)&\\-P^2[k_z^2+s(2n+1)][\lambda_{n\pm}+\tfrac{2}{3}\Delta]&\\\pm\tfrac{1}{3}P^2\Delta s=0,&\end{aligned}\tag{5}$$

where $\lambda_{n\pm}$ stands for $\lambda_{k_z, n, \pm}{}^{(\alpha)}$. For zero magnetic field, (5) reduces to Kane's equation (10). The spin-dependent terms are proportional to s and give the g shift. In the limit $\Delta\rightarrow\infty$, the factor at the bottom of the band becomes equal to the reciprocal of the effective mass, $g=-(m^*)^{-1}=-(4/3)(P^2/E_G)$. For the values of $\Delta=0.9$ ev, $E_G=0.23$ ev, and $P^2=0.44$ a.u. given by Kane, the g factor at $k=0$ is -55; the Zeeman term reduces it to -53.

Equation (5) is cubic in λ and an analytical expression for the energy levels would not be useful. The equation is sufficient however for a numerical calculation of the susceptibility. Before doing this we want to show that the off-diagonal matrix elements of the neglected free-mass terms $\bar{k}^2/2$ between any two states of (4) are small compared to the level separation so that they can be treated by perturbation theory.

It is sufficient to confine attention to the case where the two levels are in conduction band since $k^2/2E_G$ is smaller than 0.1 even at the concentration of 10^{19} cm^{-3}. If the states have the same spin, the matrix element of $\bar{k}^2$ is zero as results from (4) and the fact that each F_i is an eigenfunction of $\bar{k}^2$; if they have opposite spin quantum numbers, there is a nonvanishing matrix element only between $\Psi_{k_z, n, -}{}^{(c)}$ and $\Psi_{k_z, n-1, +}{}^{(c)}$. This is of the order of $P^2k^2s/E_G{}^2$ and therefore small compared to the level separation P^2s/E_G.

The correction to the energy levels due to the free mass is found by keeping the $\bar{k}_i{}^2/2$ terms to first order in the operations leading to Eq. (5). (Second order effects are negligible.) It is given by

$$\delta\lambda_{n\pm}=\frac{\epsilon_n\lambda_{n\pm}+\eta_{n\pm}/\lambda_{n\pm}}{2[1+\frac{1}{2}\lambda_{n\pm}/(\Delta+\lambda_{n\pm})]}\frac{d\lambda_{n\pm}}{dk_z{}^2},\tag{6}$$

where

$$\epsilon_n=(3/2P^2)[k_z^2+s(2n+1)],$$

$$\begin{aligned}\eta_{n,\pm}=&\left[1+\frac{\lambda_{n\pm}{}^2}{2(\Delta+\lambda_{n\pm})^2}\right]\{[k_z^2+s(2n+1)]^2+2s^2\}\\&\mp\left[1-\frac{\lambda_{n\pm}{}^2}{(\Delta+\lambda_{n,\pm})^2}\right](s/2)[k_z^2+s(2n+1)].\end{aligned}$$

II. Susceptibility

The susceptibility per unit volume is

$$\chi=-(1/\mathcal{H})\partial\varphi/\partial\mathcal{H},$$

where the free energy φ is given by

$$\begin{aligned}\varphi=N\zeta-\textstyle\sum_{\text{spin}}\left(\frac{1}{2\pi}\right)^2&\int dk_zskT\\&\times\textstyle\sum_n\ln\{1+\exp[(\zeta-E(k_z, n, \pm))/kT]\}.\end{aligned}\tag{7}$$

Here ζ is the Fermi energy and the $E(k_z, n, \pm)$ are the energy levels in the conduction band. By means of Euler's summation formula,

$$\sum_{n=0}^{\infty}f(n+\tfrac{1}{2})=\int_0^{\infty}f(x)dx-(1/24)[f'(\infty)-f'(0)],\tag{8}$$

we obtain φ to second order in s. We shall first neglect the free mass and take $E(k_z, n, \pm)=\lambda_{n,\pm}{}^{(c)}$. The energy levels are obtained from (5) as a power series in s,

$$E(k_z, n, \pm)=E^{(0)}\mp sE^{(1)}+s^2E^{(2)},\tag{9}$$

where $E^{(0)}$, $E^{(1)}$, and $E^{(2)}$ depend only on the argument $k_z^2+s(2n+1)$. The term $E^{(0)}(k^2)$ is just the energy in

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[18] The heavy-hole states are not given by (3) but are obtained from the set (2) by neglecting the free mass and setting $\lambda=0$, $F_1=F_2=F_7=F_i=0$.

the absence of a magnetic field;

$$E^{(1)}=\tfrac{1}{3}P^2\Delta\Big/\left(\frac{\partial D}{\partial\lambda_n}\right)_{\lambda_n=E^{(0)}}, \tag{10}$$

and

$$E^{(2)}=-\tfrac{1}{2}\left[(E^{(1)})^2\left(\frac{\partial^2 D}{\partial\lambda_n{}^2}\right)\Big/\left(\frac{\partial D}{\partial\lambda_n}\right)\right]_{\lambda_n=E^{(0)}}. \tag{11}$$

The energy levels $E^{(0)}[k_z{}^2+s(2n+1)]$ are just the Onsager levels[19] for the Hamiltonian $E^{(0)}(k^2)$ since at fixed k_z, the energy curve which they define embraces an area equal to $2\pi s(n+\frac{1}{2})$ in k_x, k_y space; the terms in $E^{(1)}$ and $E^{(2)}$ are field-dependent energy shifts of these levels.

We now evaluate the second term in Euler's formula (8). $E^{(1)}$ and $E^{(2)}$ give contributions of order higher than s^2 so that it reduces simply to

$$\varphi_a=\frac{s^2}{6}\int_{-\infty}^{+\infty}\frac{dk_z}{(2\pi)^2}\left[g(E^{(0)},\zeta)\frac{\partial E^{(0)}}{\partial k_z{}^2}\right]_{s=0}, \tag{12}$$

where $g(E,\zeta)$ is the Fermi function. Here the spherical symmetry of $E^{(0)}(k^2)$ has been used. The resulting susceptibility at absolute zero is

$$\chi_a=-\frac{1}{6\pi^2}\frac{e^2}{\hbar^2c^2}\int_0^{k_0}\frac{dE^{(0)}(k_z{}^2)}{dk_z{}^2}dk_z. \tag{13}$$

We consider next the first term of (8). The substitution $2sx=k_x{}^2+k_y{}^2$ transforms the double integral $\int f(k_z{}^2+2sx)sdxdk_z$ into $2\int f(k^2)k^2dk$. The term in $E^{(0)}$, being independent of s, does not contribute to this part of the susceptibility; the term in $E^{(1)}$ contributes a "spin" susceptibility (just as the ordinary spin moment does) given by

$$\chi_b=\left(\frac{e^2}{\hbar^2c^2}\right)(E^{(1)})^2\left[\frac{dn}{dE^{(0)}}\right]_{k_0}, \tag{14}$$

where $[dn/dE^{(0)}]_{k_0}$ is the density of states at the Fermi surface. The $E^{(2)}$ part contributes

$$\chi_c=-\left(\frac{2}{\pi^2}\right)\left(\frac{e^2}{\hbar^2c^2}\right)\int_0^{k_0}E^{(2)}(k^2)k^2dk. \tag{15}$$

The subdivision of the susceptibility into the three contributions χ_a, χ_b, and χ_c is mathematically convenient. In addition, each of the terms has a simple meaning: χ_a results from the semiclassical quantization of the levels, χ_b results from the orbital moment induced by spin-orbit interaction, and χ_c is due to the energy-level shifts of order s^2.

In order to evaluate the susceptibility, the values of $E^{(0)}$ have been obtained from (5) for a number of values of k and the quantities $E^{(1)}$, $E^{(2)}$, and $dn/dE^{(0)}$ have been calculated by substitution in (10) and (11). The sum of χ_a, χ_b, and χ_c has been plotted in curve (1) of Fig. 3.

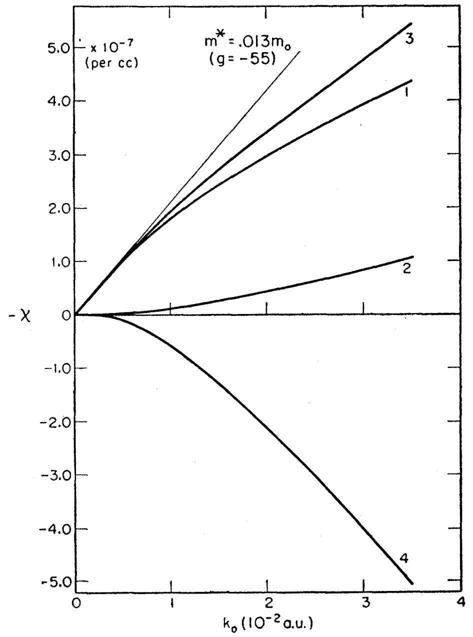

FIG. 3. The various calculated contributions to the susceptibility of n-InSb. Curve 3 represents the effect of the conduction band—valence band interaction and is the sum of Curves 1 and 2 as described in the text. Curve 4 represents the effect of the higher bands. The straight line has been drawn for a value of $g=-55$, consistent with the neglect of the Zeeman term in the calculated curves.

We now discuss the relative contributions of these terms. At very small k_0, χ_c is negligible, being proportional to $k_0{}^3$; the ratio of χ_a to χ_b is 1 to -0.35. Hence the Pauli susceptibility of the anomalous spin moment is appreciable at small k_0.[20] With increasing k_0 the g factor drops sharply, exhibiting a behavior not unlike that of the reciprocal effective mass. Because of this drop the Pauli paramagnetism becomes unimportant at large concentrations. The g factor at the Fermi surface is plotted as a function of $k_0{}^2$ in Fig. 4. Finally the term χ_c which is also proportional to the spin splitting, increases with k_0 initially, reaches a maximum and then decreases; it is always small compared to χ_a, reaching at its maximum a value of $0.25\chi_a$. Thus, except near $k_0=0$, the susceptibility is due mainly to χ_a.

The effect of the corrections (6) to the energy levels, arising from the free-mass terms, is to modify the three terms of the susceptibility. Let χ_a', χ_b', and χ_c' be the three correction terms. Since (13) and (15) are linear in the energy eigenvalues, χ_a' and χ_c' are found directly

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[19] L. Onsager, Phil. Mag. 43, 1006 (1952).

[20] Values of the effective mass near the band edge were deduced by Stevens and Crawford[5] and also Matyas[6] from their susceptibility measurements. The values obtained were more than twice the cyclotron resonance value of 0.013; this is caused by a combination of (1) change in band curvature and (2) effect of the g factor. In these experiments the latter effect happens to be the more important.

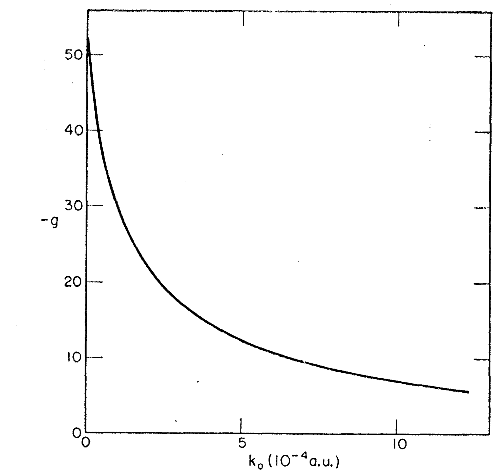

FIG. 4. The g factor for the conduction band of InSb as a function of k_0^2. The free spin g value has been taken positive, $g_s=+2$. Only the interaction between the conduction and valence bands is included.

by using the contribution of the free-mass terms to $E^{(0)}$ and $E^{(2)}$. The contribution to $E^{(0)}$ is simply $k^2/2$, resulting in the free-electron susceptibility for χ_a', while the contribution to $E^{(2)}$ is extracted from (6). The term χ_b' is slightly more complicated to evaluate and it has been neglected; it is of the same order as χ_a' and has the same sign. For the region where the band is no longer parabolic, χ_c' is the dominant term; thus at $n=10^{19}$/cc, we find that $\chi_c'\simeq 6\chi_a'$. The sum of χ_a' and χ_c' is plotted in Curve 2, Fig. 3.

The sum of curves 1 and 2 gives the total susceptibility resulting from the interaction between the conduction and valence bands and it is plotted as Curve 3 in Fig. 3. Curve 3 disagrees with the experimental points shown in Fig. 2. We therefore investigate in the next section whether higher bands, omitted sofar, have an appreciable effect on χ.

III. Effect of Higher Bands

This section is schematic in character and can only serve as a guide to the actual calculation. This has been done because the calculation is lengthy but presents no difficulty. Only the expression for the most important matrix elements will be exhibited.

The fact that the heavy-hole mass is close to $0.2m_0$[21] shows that there is a substantial interaction between the valence band and higher bands. Since these bands are energetically far removed, it is sufficient to treat them to order k^2. Two of these bands will be taken into account first, those transforming like Γ_3 and Γ_4 and giving rise, in Kane's paper, to the constants B and C. This is done by eliminating the interband matrix elements to first order in $\bar{k}_i$ and one obtains an effective Hamiltonian, H', consisting of terms quadratic in $\bar{k}_i$ and connecting any two of the six L.K. functions of the valence band. Neglecting the spin-orbit splitting of the higher states, the matrix elements of H' between the L.K. states with periodic parts $|X\rangle$, $|Y\rangle$, $|Z\rangle$ are given by

$$\begin{aligned} H_{jj}'&=C\bar{k}^2+(B-C)\bar{k}_j^2, \quad j=x,y,z,\\ H_{xy}'&=(C-\tfrac{1}{2}B)\bar{k}_y\bar{k}_x+\tfrac{1}{2}Bis,\\ H_{yx}'&=(H_{xy}')^\dagger=(C-\tfrac{1}{2}B)\bar{k}_x\bar{k}_y-\tfrac{1}{2}Bis,\\ H_{zj}'&=H_{jz}'=(C-\tfrac{1}{2}B)k_z\bar{k}_j, \quad j=x,y. \end{aligned} \tag{16}$$

The states obtained in II are now no longer eigenstates, and the energy levels cannot be obtained by perturbation theory, there being some off-diagonal elements of order $(B+C)ns$, where ns is of order k_0^2, between states belonging to the conduction band and differing in energy by P^2s/E_G. For the purpose of obtaining the non-oscillatory part of the susceptibility, perturbation theory on the free energy, with the complete set of states $\Psi_{n,\pm}^{(\alpha)}$ can still be used[17] provided that $kT\ll\zeta$ and $|H'|\ll\zeta$ which is the case here. Formal expansion of the free energy gives

$$\begin{aligned} \varphi=N\zeta&-\textstyle\sum_i kT\ln\{1+\exp[(\zeta-E_i)/kT]\}\\ &+\textstyle\sum_i g(E_i-\zeta)H_{ii}'+\frac{1}{2}\sum_i(\partial g/\partial E_i)(H_{ii}')^2\\ &+\textstyle\frac{1}{2}\sum_i\sum_{j\neq i}\{[g(E_i)-g(E_j)]/(E_i-E_j)\}|H_{ij}'|^2. \end{aligned} \tag{17}$$

The susceptibility resulting from (17) is still a sum of three terms of the type χ_a, χ_b, χ_c although when the band is not spherical the expression for χ_a will be different from (13). We consider first the correction terms χ_a'', χ_b'', χ_c'' that are of the first order in H'; they are due to the diagonal matrix elements of H' over the states of the conduction band, given by:

$$\begin{aligned} H_{ii}'=\frac{P^2}{N_{n\pm}^2(\lambda_{n\pm}^{(c)})^2}\bigg\{&\frac{B+2C}{3}\bigg[\frac{11}{15}k^4\mp\frac{s}{30}(35k^2-16q^2)\\ &+\frac{26}{15}s^2+\frac{\lambda_{n\pm}}{\Delta+\lambda_{n\pm}}\left(\frac{2}{15}k^4\pm\frac{s}{30}(10k^2+4q^2)+\frac{2}{15}s^2\right)\\ &+\frac{(\lambda_{n\pm})^2}{(\Delta+\lambda_{n\pm})^2}\left(\frac{5}{15}k^4\pm\frac{s}{30}(25k^2-20q^2)+\frac{25}{30}s^2\right)\bigg]\\ &+(4C-3B)\bigg[\frac{1}{270}(7k^4+10k^2q^2-35q^4)\mp\frac{s}{5}q^2-\frac{1}{40}s^2\\ &+\frac{\lambda_{n\pm}}{(\Delta+\lambda_{n\pm})}\bigg(\frac{1}{135}(7k^4+10k^2q^2+q^4)\\ &\pm\frac{s}{5}q^2-\frac{1}{20}s^2\bigg)\bigg]\bigg\}, \end{aligned} \tag{18}$$

where $k^2=k_z^2+s(2n+1)$, $q^2=k_z^2-s(n+\frac{1}{2})$ and $N_{n,\pm}$ is the normalization factor for the state $\Psi_{n,\pm}^{(c)}$.

The term χ_a'' resulting from (18) is positive and the magnitude of its ratio to χ_a, of order $|H'|/\zeta$, is found to be less than 0.2. The term χ_b'' is negative and of order

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[21] Experimental evidence is summarized in reference 2.

$0.1\chi_a$. These two terms have been neglected. The most important contribution is due to the level shifts of order s^2 in (18). These level shifts are given not only by the terms which are explicitly of order s^2 in (18), but also by the terms of order s and s^2 in the expressions for $N_{n\pm}$ and $\lambda_{n\pm}$ occurring in (18). By a detailed consideration of the various s^2 terms, it can be seen that they are approximately equal to

$$(P^2/N_n^2\lambda_n^2)[(B+2C)/3](26/15)s^2, \tag{19}$$

the other s^2 terms nearly cancelling each other. In particular, the departure of the band from sphericity which is measured by the value of the coefficient $(4C-3B)$ has only a negligible effect on the susceptibility for reasonable values of B and C. (It may be noticed that there is no first order effect, proportional to $(4C-3B)$ on the free energy in the absence of a field, while there is a small effect on the susceptibility). The contribution χ_c'' is calculated by simply integrating the energy term (19) over the spherical distribution of the electrons in $\mathbf{k}$ space, and it is found that the resulting susceptibility it not small, being comparable to χ_a of (13), so that it is necessary to include second order terms. We just enumerate the matrix elements of interest:

(a) Within the conduction band, $|n,\mp\rangle$ is connected to $|(n+4),\mp\rangle$ and $|n,-\rangle$ to $|(n-1),+\rangle$. The first of these matrix elements vanishes if $4C-3B=0$; in this case the bands are spherical and the energy levels can be obtained exactly. Both of these matrix elements give negligible contributions.

(b) The most important matrix elements are those connecting $\psi_{n,\pm}^{(c)}$ to $\Psi_{n,\pm}^{(l)}$, $\psi_{n,\pm}^{(c)}$ to $\psi_{n,\pm}^{(h)}$ and $\psi_{n,\pm}^{(c)}$ to $\Psi_{(n\pm1),\mp}^{(h)}$. These have been evaluated; at $n=10^{19}$ they amount to 25% of the first order contribution.

The susceptibility due to the higher bands, calculated to order $(H')^2$, is plotted in curve (4), Fig. 3. The constants B and C for which there is no direct experimental evidence have been chosen somewhat arbitrarily to be in the ratio 1 to 1.6, i.e., that taken by Stern,[22] and their magnitude has been adjusted to fit the measured susceptibility data at $n=10^{19}$. The required values are $C\simeq-8/3$ and $B\simeq-5/3$ a.u. The spherical average of the heavy hole mass for these values is $1/m^*=1+3/5(2C+B)=3.2$ or $m^*=0.31$. The total theoretical susceptibility of the electrons in the conduction band is given by the sum of curves 3 and 4, Fig. 3 and is plotted on Fig. 2; the fit to the experimental points is seen to be reasonably good. We now ask about the possible effect of the interactions responsible for the other constants in Kane's theory:

The constant A which involves the interaction between a p-like and an s-like band does not contribute to χ_c in the absence of spin-orbit interaction[17]; so its actual contribution will be small; the constant F has a small effect for the same reason; the constant D is believed to be small[2]; the only constant that may have an appreciable effect is G. The second order in $\bar{k}_i$ Hamiltonian H'' resulting from this interaction has matrix elements:

$$H_{is,x}''=-2iGk_z\bar{k}_y;\quad H_{is,y}''=-2iGk_z\bar{k}_x;$$
$$H_{is,z}''=-iG(\bar{k}_x\bar{k}_y+\bar{k}_y\bar{k}_x)=-\tfrac{1}{2}G(\bar{k}_+^2-\bar{k}_-^2).$$

The diagonal element of H'' over the $\psi_{n,\pm}^{(c)}$ is found to vanish, just as is the case in the absence of a magnetic field.[2] The contribution of H'' is thus of second order and appreciably smaller than that of H'. The matrix elements of H'' that are important are found to be those connecting $\psi_{n-}^{(c)}$ to $\psi_{(n-3),+}^{(h)}$ and $\psi_{n-}^{(c)}$ to $\psi_{(n+1),+}^{(h)}$. A crude estimate of their contribution to the susceptibility shows that it is negative and for a value of G equal to C, which is reasonable, the values of C and B required for a fit of the susceptibility at $n=10^{19}$ become $C=-3.4$ a.u. and $B=-2.1$ a.u. which result in a heavy-hole mass of $m^*=0.23$. The shape of the χ *versus* $n^{\frac{1}{3}}$ curve would be little changed by this new correction, the curve becoming slightly flatter with the height at the maximum decreasing by about 5%. In view of the approximate nature of our numerical work, it appears that the agreement with Kane's theory is satisfactory. If (a) the experimental measurements could be significantly improved in accuracy and (b) the effects of the impurities on the band structure were better understood, then it might be worthwhile to do the present calculation more carefully. Curve fitting of χ *versus* $n^{\frac{1}{3}}$ would then restrict the possible choices of values for the band parameters.

Finally, it is worth considering how higher bands can produce such a large effect on the susceptibility: The term χ_a, which is the dominant part of curve 3 of Fig. 3, results solely from the difference between a sum and an integral; the factor (1/24) in the second term of Euler's formula makes this a small effect. It is only because of the s and p characters of the bands involved that the χ_c contribution is smaller than χ_a: Equation (5) shows that in the absence of spin-orbit coupling there are no level shifts and χ_c is rigorously zero. The presence of spin-orbit effect results in a small value for χ_c. In contrast to this situation, the higher bands make their contributions mainly through the level shifts in the absence of spin-orbit interaction. They contribute via the first Euler term and the absence of a small numerical coefficient in this term makes their contribution comparable to that of the valence band. We had another example of the importance of the level shifts in computing the effect of the free mass terms when we found that $\chi_c'\simeq6\chi_a'$ at $n=10^{19}$ cm^{-3}. Loosely speaking and neglecting the orbital moment, the higher bands give the effect of an additional effective-mass term with $m^*\sim-(1+1/0.2)^{-1}=-(1/6)m_0$ and contribute a susceptibility of the order of -6 times that of the free mass.

In view of the similarity of the band structure of

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[22] F. Stern, Bull. Am. Phys. Soc. **2**, 347 (1957).

InAs to that of InSb, the theory presented may also be applied to Geist's susceptibility data on InAs.[23] As expected, there is a qualitative similarity between the data on these two substances.

CONCLUSION

The results of measurements on the carrier susceptibility in n-InSb show that the susceptibility departs appreciably from that of a parabolic band. The essential feature of the observed susceptibility is that it increases with increasing carrier density at low carrier densities and decreases at high carrier densities. A theoretical analysis based on current ideas about the band structure of InSb shows that at low carrier densities the interaction between the valence band and the conduction band is the principal contributor to the susceptibility. This interaction alone cannot explain the observed behavior of χ at the higher densities. The effect of higher bands is estimated to be of sufficient magnitude to account for the decrease of the susceptibility at the higher densities. Within the limitation resulting from the approximate computation of the higher band interactions, the observed susceptibility appears consistent with Kane's band-structure calculation.

ACKNOWLEDGMENTS

We wish to thank E. N. Adams, E. I. Blount, T. Holstein, T. Kjeldaas, and W. Kohn for helpful comments on this work. We also wish to acknowledge the assistance of D. Watt in carrying out the experiments.

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PHYSICAL REVIEW VOLUME 115, NUMBER 5 SEPTEMBER 1, 1959

Energy Levels of Conduction Electrons in a Magnetic Field

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(Received March 26, 1959)

The energy levels of an electron in a periodic potential and a constant magnetic field are found as the solutions to a secular determinant when the following approximations are made: (a) the energy band of interest is spherically symmetric and (b) lattice broadening of the levels is neglected. Inclusion of spin-orbit coupling gives the g factor as function of position in the band. Perturbation theory is used to treat the effect on the free energy of small departures of the band from spherical symmetry.

INTRODUCTION

THIS paper is concerned with the determination of the energy levels of an electron in a periodic potential and an applied constant magnetic field. The problem is formulated in the Luttinger-Kohn[1] representation and since this representation has been used in several papers dealing with the magnetic properties of conduction electrons, we first review briefly this previous work.

The treatments of Luttinger and Kohn[1] and Kjeldaas and Kohn[2] for nondegenerate bands are based on an expansion in powers of k_0, the wave-vector at the Fermi surface and thus are useful only if this expansion converges fast enough. Considering the magnetic levels of the valence band of germanium, Luttinger[3] included the interactions[4] between the valence band and other bands to order k^2. When the band structure coefficients were such that the valence band was spherically symmetric, the magnetic levels could be obtained exactly. On the other hand, in the case of two-dimensional graphite the energy is not an analytic function of $\mathbf{k}$ at $k=0$ so that an expansion in powers of k is impossible. For this case, McClure[5] obtained the magnetic levels for any k exactly as far as the magnetic interactions are concerned; however other approximations were made in the calculation.

It is the purpose of this paper to extend these results by pointing out that in the approximation of spherical bands the existence of a selection rule in the interband matrix elements of the velocity makes it possible to obtain the energy levels exactly[6] for arbitrary k. Since energy bands are not in general spherical, the levels thus obtained are strictly speaking, not those of an electron in a lattice, except in the case of cubic symmetry with only s and p bands interacting. Rather they are the levels of a model which is an approximation to substances with nearly spherically symmetric energy bands, such as the alkali metals or semiconductors such as InSb.[7] The corrections to the energy

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[1] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[2] T. Kjeldaas and W. Kohn, Phys. Rev. **105**, 806 (1957).

[3] J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).

[4] The expression "interaction between bands" refers to the off-diagonal elements in the hamiltonian matrix, resulting from the interband matrix elements of the velocity between the L. K. states.

[5] J. W. McClure, Phys. Rev. **104**, 666 (1956).

[6] Except for the lattice broadening which is neglected; see below.

[7] Treated in R. Bowers and Y. Yafet, preceding paper [Phys. Rev. **115**, 1165 (1959)].