Galvanomagnetic Studies of Sn-Doped Bi. I. Positive Fermi Energies

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Oscillatory magnetoresistance and Hall effect have been studied in single crystals of Bi doped with Sn to decrease the Fermi energy to less than 5 meV. (The energy is measured from the bottom of the conduction band at the L point of the Brillouin zone.) The dependence of particular electron and hole surface cross sections on the net carrier concentration p-n (determined from the strong-field Hall coefficient) and the temperature dependence of hole oscillation amplitudes were examined. The data suggest that the hole band and the electron band are nonparabolic; the minimal direct gap at the center of the hexagonal zone face is estimated to be 66±25 meV. Evidence is given for the absence of any "new" bands having a large density of states within 15 meV below the Fermi energy of pure bismuth.

INTRODUCTION

ALTHOUGH bismuth is a semimetal, the band overlap is sufficiently slight that the carrier concentration at low temperatures is relatively small—only about 3×10^{17} electrons and holes per cubic centimeter.[1] Thus small additions of elements from neighboring columns of the periodic table can produce large relative changes in carrier concentration.[2] The portion of the band structure relevant to the present experiments is shown in Fig. 1. The higher lying valence band is thought to be located at the points H (or T), at the centers of the hexagonal faces of the Brillouin zone. The surfaces of constant energy for energies near the band edge form two half-ellipsoids of revolution extending along the trigonal axis.

The conduction-band edges are located at L, the centers of the pseudohexagonal faces, and are characterized by constant-energy surfaces which are highly elongated and may[3,4] or may not[5–7] be ellipsoidal. These bands are known to be highly nonparabolic at the Fermi energy, however. Interband magnetoreflection experiments[8] yield an energy gap of 15 meV at the L point and a Fermi energy of about 25 meV for pure bismuth at 4°K. (The convention followed throughout this paper, unless otherwise specified, is to assign the zero of energy to the bottom of the conduction band at L.) Tin doping up to about 0.02 at. % was used to lower the Fermi energy to less than 5 meV in the samples prepared for studies of the monotonic and oscillatory galvanomagnetic effects in single crystals of these alloys at temperatures below 4°K.

[1] A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962).
[2] K. Tanaka, J. Phys. Soc. Japan **20**, 1374 (1965).
[3] E. P. Vol'skiĭ, Zh. Eksperim. i Teor. Fiz. **49**, 107 (1965) [English transl.: Soviet Phys.—JETP **22**, 77 (1966)].
[4] R. N. Bhargava, Bull. Am. Phys. Soc. **11**, 330 (1966).
[5] M. H. Cohen, Phys. Rev. **121**, 387 (1961).
[6] A. A. Abrikosov and L. A. Falkovskiĭ, Zh. Eksperim. i Teor. Fiz. **43**, 1089 (1962) [English transl.: Soviet Phys.—JETP **16**, 769 (1963)].
[7] V. S. Edel'man and M. S. Khaikin, Zh. Eksperim. i Teor. Fiz. **49**, 107 (1965) [English transl.: Soviet Phys.—JETP **22**, 77 (1966)].
[8] R. N. Brown, J. G. Mavroides, and B. Lax, Phys. Rev. **129**, 2055 (1963).

MEASUREMENTS

The observation of quantum oscillations for electrons in these alloys is facilitated by the band structure. Since the electron cyclotron mass at the band edge is only about one-fourth that at the Fermi energy in pure bismuth, the decrease in cyclotron mass as the Fermi energy is lowered partially compensates for the increased scattering due to impurities.

An indication of the change in carrier concentration produced by doping can be obtained by measurement of the strong-field Hall coefficient. If the field is sufficiently strong for the condition $\omega_c\tau\gg1$ to hold for all carriers, and if the Fermi surfaces are all closed, the Hall coefficient becomes independent of magnetic field and is given by

$$R_\infty^{-1}=(p-n)ec\,,\quad (p\neq n)\,. \tag{1}$$

This result is valid in the quantum as well as the classical regime.[9]

As has been noted by earlier workers,[10] the Hall coefficient oscillates at fields greater than 20 kOe. In practice, the Hall coefficient is observed to reach a high field plateau at fields well below the onset of oscillations. At higher doping levels, the magnitude of the oscillations in Hall voltage becomes negligible compared to the monotonic part below 30 kOe.

The high field region is most easily attained with the field along the trigonal axis, since the hole cyclotron frequency is maximal for that direction. This is also the orientation for which the hole oscillation period is

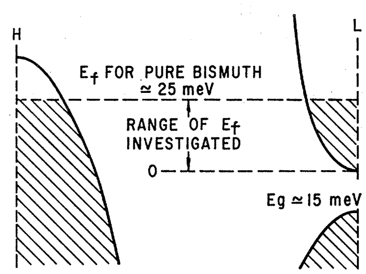

FIG. 1. Bismuth band structure indicating range of Fermi energy investigated.

[9] I. M. Lifshitz, J. Phys. Chem. Solids **4**, 11 (1958).
[10] B. H. Schultz and J. M. Noothoven van Goor, Philips Res. Rept. **19**, 103 (1964).

most insensitive to field orientation. On the other hand, the long electron period is relatively insensitive to field orientation when the field is along a bisectrix axis. For this reason, most of the measurements were made on samples of the type shown in Fig. 2. The Hall coefficient and transverse magnetoresistance were examined with the magnetic field along the trigonal axis, and the hole oscillation period was determined from the magnetoresistance by a technique described in the next section. Experiments with various sample orientations revealed that the electron oscillations were most pronounced when the magnetic field was nearly parallel to the direction of the current, and that they practically disappeared for all but the most lightly doped samples when the magnetic field was perpendicular to the current. The electron oscillations in the longitudinal magnetoresistance (bisectrix direction) were therefore studied as a function of doping.

The angular dependence of the electron oscillation periods was investigated for a few samples. However, this aspect of the work was not pursued in view of the earlier investigation of Bhargava[4] on the de Haas–van Alphen effect in Pb-doped bismuth. The present work differs from his in the sense that considerably lower Fermi energies were obtained by doping, a wider variety of sample compositions were examined, and the angular dependence of the electron periods was not studied in detail.

In the determination of the long electron period for the field along a bisectrix axis, only oscillations occurring at fields less than 2 kOe were considered. At higher fields, short-period oscillations begin to appear and complicate the pattern. Interband transfer of carriers, which disturbs the periodicity of the oscillations, also begins to occur. This quantum interband transfer becomes so pronounced at higher fields that it produces a "giant" negative longitudinal magnetoresistance, that is, the resistance drops to a very small fraction of its zero-field value.

EXPERIMENTAL DETAILS

The single crystals from which the samples were cut were grown from tin-doped melts by the Czochralski technique. After the orientation was determined from x-ray photographs, samples of the type shown in Fig. 2 were cut by spark erosion from the pulled crystals along the bisectrix direction most nearly perpendicular to the growth direction. Typical dimensions of these samples were 1.5 mm×2.5 mm×7 mm. The subsequent liquid-helium-temperature Hall measurements on these samples revealed an increase in $(p-n)$ toward the bottom of the crystal, suggesting an effective distribution coefficient considerably less than unity, as is expected from the phase diagram. Since the crystals were very large compared to a typical sample, it was possible to obtain several relatively homogeneous samples from each pulled crystal. Twisted leads were soldered to each sample in the arrangement shown in Fig. 2 with a Bi-Cd eutectic alloy.

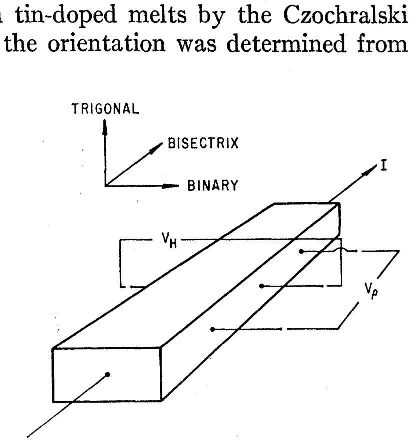

FIG. 2. Sample configuration.

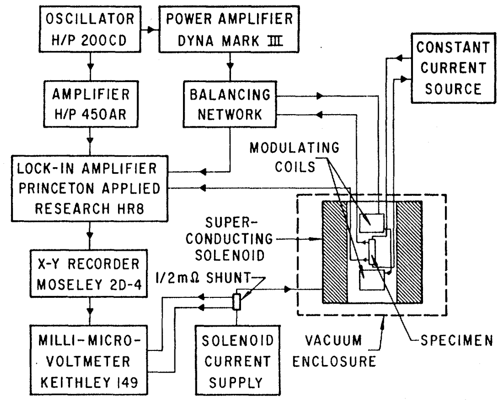

FIG. 3. Apparatus for observation of oscillatory galvanomagnetic effects.

A block diagram of the apparatus employed for observation of magnetoresistance oscillations is shown in Fig. 3. The apparatus is very similar in principle to those described earlier by Lerner[11] and by Ketterson and Eckstein.[12] The balancing network has been added to reduce the voltage induced in the sample leads by the modulation coils. This voltage is independent of the sample current, and although it is approximately 90° out of phase with the signal at low frequencies, it can be so much larger than the signal that it introduces additional fluctuations at the output of the lock-in amplifier.

Field sweeps were made while detecting at the modulation frequency and at twice the modulation frequency. The second-harmonic data were employed in the analysis for electrons, and the first-harmonic data in the analysis for holes. A least-squares fit of successive peak positions to a relation of the form, $H_n^{-1}=P(n+\gamma)$, was made with a digital computer to obtain the periods P. The extremal hole cross sections (in **k**-space) perpendicular to the trigonal axis and the extremal electron cross sections perpendicular to a

[11] L. S. Lerner, Phys. Rev. **127**, 1480 (1962).
[12] J. Ketterson and Y. Eckstein, Phys. Rev. **132**, 1885 (1963).

TABLE I. Parameters employed for fitting various band models.

Conduction band at L	Valence band at H	ϵ_0 meV	ϵ_{f0} meV	E_g meV	E_1 meV	$(\alpha_1\alpha_3)^{1/2}$	α_2	$\beta_\perp(0)$	$\beta_{\parallel}(0)$	n_0 10^{17} cm^{-3}
Parabolic (EP)	Parabolic									
Assumed						110	0.584	14.8	1.32	
Derived		25.5	15							2.9
NENP	Parabolic									
Assumed			25	15		470		14.8	1.32	
Derived		36					1.4			2.9
NENP	Nonparabolic									
Assumed			25	15		470				
Derived		37			66		1.4	20.3	1.81	2.9

bisectrix axis (long period) were calculated from the periods and are plotted as a function of $(p-n)$ in Fig. 4.

ANALYSIS

In the initial attempt to fit these data, the following assumptions were made: (1) The band structure is not altered by doping. (2) The valence band at H is parabolic-ellipsoidal and is characterized by the mass ratio,[13] $\beta_\perp=14.8$, $\beta_{\parallel}=1.32$. (3) The bands at H and L are the only bands which are intersected by the Fermi level. (4) The energy gap at L is 15 meV.[3] (5) $n=p$ for pure bismuth, and the Fermi energy of pure bismuth is 25 meV for the nonparabolic models. Three different models for the conduction band at L were then employed, the ellipsoidal parabolic (EP) model,[14] the ellipsoidal nonparabolic (ENP) model[8] and Cohen's nonellipsoidal nonparabolic (NENP) model[5] with $m_2=m_2'$. The results for the latter two models were very similar and only the nonellipsoidal case is considered here. The inverse mass ratio α_2 was considered to be the most uncertain and was therefore adjusted to fit the data for pure bismuth. The parameters assumed and derived are listed in Table I. Curves indicating the predictions of the EP model and the NENP model are plotted in Fig. 4, where it is observed that both models appear to underestimate the electron cross sections, although the nonparabolic model gives a much better fit.

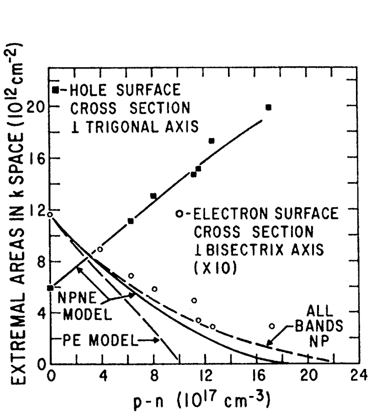

FIG. 4. Dependence of electron (H along bisectrix-long period) and hole (H along trigonal) extremal cross sections on $(p\text{-}n)$.

[13] Y. Kao, Phys. Rev. **129**, 1122 (1963).
[14] D. Shoenberg, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. II.

In this attempt to fit the data, the valence band at H has been assumed parabolic-ellipsoidal. The validity of this assumption is open to question, however, because Esaki and Stiles[15] have found evidence from interband tunneling studies that the direct gap at H might be as small as 15 meV, which is comparable to the Fermi energy for holes ($\sim$12 meV). The nonparabolicity of the valence band was investigated by comparison of hole periods and effective masses as determined from the temperature dependence of the oscillation amplitudes. This was possible for some samples because large amplitude oscillations characterized by a single period were obtained. An example is shown in Fig. 5.

In the case of a nonparabolic band, Abrikosov and Falkovskiĭ[6] have shown that the extremal cross section S and inverse effective mass ratio at the zone edge $\beta_\perp$, for H along the trigonal axis are

$$S=\frac{2\pi m}{\hbar^2\beta_\perp(0)}\epsilon_h\left(1+\frac{\epsilon_h}{E_1}\right), \tag{2}$$

$$\beta_\perp^{-1}=\beta_\perp^{-1}(0)(1+2\epsilon_h/E_1), \tag{3}$$

where ϵ_h is the energy measured downward from the band edge and E_1 is the gap at H.

If E_1 is as small as 15 meV, Eq. (3) predicts a strong dependence of effective mass on Fermi energy similar to that for the conduction band at L, which should be easily observable. The best effective mass data were

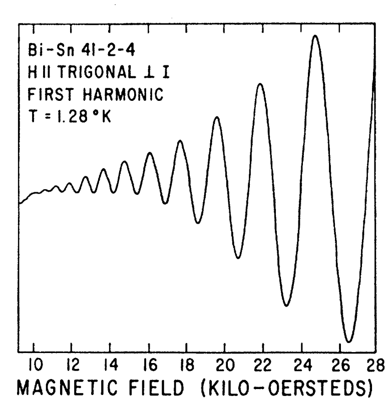

FIG. 5. Hole oscillations in sample with $p\simeq1.5\times10^{18}$ cm^{-3}.

[15] L. Esaki and P. J. Stiles, Phys. Rev. Letters **14**, 902 (1965).

obtained in the temperature range 1.3–2.3°K for the sample of Fig. 5. The minimal hole cross section for this sample was 3.07 times its value in pure bismuth. It can be shown that the error in this cross section due to interband transfer is negligible. The mass ratio $\beta_\perp$ was obtained by fitting the oscillation amplitudes at constant field to the function[16] $A_0(u/\sinh u)$ where

$$u=2\pi^2kTmc/heH\beta_\perp. \quad (4)$$

The value obtained for this sample was $\beta_\perp=10.7\pm0.6$ as compared to the cyclotron resonance value 14.8 for pure bismuth. Other samples gave less precise but consistent values. Substitution of the periods and masses into Eqs. (2) and (3) yields the values: $E_1=66\pm25$ meV, $\beta_\perp(0)=20\pm2$, and ϵ_h (pure Bi)$=12.3\pm0.7$ meV. The large uncertainty in E_1 is a consequence of the well-known insensitivity of this type of analysis to the magnitude of the gap.[8] It is apparent, however, that the gap is considerably larger than 15 meV.

Although the gap we derive is larger than that estimated from interband tunneling studies, it is smaller by more than a factor of 10 than that obtained by Falkovskiĭ and Razina[17] who fitted data on *electrons at L* as well as holes at H to the theory of Abrikosov and Falkovskiĭ. Their method makes use of the alleged interrelation between the minimal energy gaps at H and L. The present method is more direct, however, because it assumes only the validity of the general form of the dispersion relation at points on the zone boundary near H, which results from symmetry considerations, and does *not* depend on the relations between widely separated points in the zone.

Unfortunately, a knowledge of the energy gap E_1 does not uniquely determine the dispersion relation for holes. The theory of Abrikosov and Falkovskiĭ contains two parameters, Δ and γ, which govern the deviations from parabolicity. The gap E_1 is just $2(|\gamma|-|\Delta|)$ and the nonparabolicity on the zone boundary depends only on E_1. The behavior away from the boundary depends on Δ and γ in a different way however. As a first approximation, we have assumed $\epsilon/E_1\ll\gamma/\Delta$. This leads to the simple dispersion relation

$$\epsilon_h(1+\epsilon_h/E_1)=(\hbar^2/2m)[\beta_{\shortparallel}(0)k_z^2+\beta_\perp(0)(k_x^2+k_y^2)], \quad (5)$$

which is an ENP model and depends only on E_1.

The electron extremal cross sections calculated assuming both bands nonparabolic are compared with the data in Fig. 2. The agreement with the electron-surface cross sections is seen to be improved. The predicted hole cross sections are essentially the same as before and are not plotted.

It should be emphasized that the correlation made here between the Hall coefficient and the extremal cross sections would be very sensitive to the presence of other bands. Suppose, for example, that a heavy-mass valence band were to exist just below the Fermi energy in pure bismuth.[18] As the Fermi energy is lowered, this band would cause a rapid increase in hole concentration which would be detectable in the strong field Hall coefficient even if the mobility of the hypothetical carriers were very low. This would cause the experimental hole cross sections to fall well below the theoretical curve in Fig. 2 as $(p-n)$ increases. Assuming a mobility of 1000 cm^2/V sec, for the hypothetical carriers, for example, analysis of our results by means of a three carrier expression for the Hall coefficient valid for arbitrary fields parallel to the trigonal axis indicates that no more than 10^{16} new carriers per cubic centimeter can be present when the Fermi energy is 5 meV. Thus the presence of any band edges having large densities of states within about 15 meV below the Fermi energy of pure bismuth is ruled out.

ACKNOWLEDGMENTS

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[16] D. E. Soule, J. W. McClure, and L. B. Smith, Phys. Rev. **134**, A453 (1964).

[17] L. A. Falkovskiĭ and G. S. Razina, Zh. Eksperim. i Teor. Fiz. **49**, 265 (1965) [English transl.: Soviet Phys.—JETP **22**, 187 (1966).

[18] L. S. Lerner, Phys. Rev. **130**, 605 (1963).