PHYSICAL REVIEW B

SOLID STATE

THIRD SERIES, VOL. 1, NO. 6 15 MARCH 1970

Shubnikov–de Haas Effect in Dilute Bismuth-Antimony Alloys. I. Quantum Oscillations in Low Magnetic Fields

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(Received 7 July 1969)

The Shubnikov–de Haas oscillations in the transverse magnetoresistance of Bi-Sb systems were observed at temperatures 1.65, 2.2, and 4.2°K for the concentration of Sb ranging 0–1 at.% with a magnetic field (0–10 kG) in the trigonal plane. No apparent spin splitting was observed in this range of magnetic field at these temperatures. The two-band model was found in good agreement with all our results. The change of the extremal cross section S of the Fermi surface was found to be independent of the orientation. To a good approximation, both S and the Fermi energy were found to vary linearly with the Sb concentration in these dilute alloys. Comparisons between other experimental results and our data indicate that certain band parameters should be nonlinear functions of the Sb concentration before the band overlap vanishes.

I. INTRODUCTION

THE energy-band structure in the semimetal Bi-Sb alloys has been the subject of many recent experimental and theoretical investigations. Although it was generally known that the alloy becomes semiconducting at some Sb concentration around 6–8%, the variations of Fermi surface, spin splitting, and energy gap, etc., in these alloys still remain somewhat unclear.

The Bi-Sb alloy system is particularly suitable for the studies of quantum effects associated with a magnetic field. Owing to the unusually small effective masses of the conduction electrons and the low chemical potentials in these alloys, it has become possible to reach the extreme quantum limit with Landau level spacings comparable to the Fermi energy in a moderately high magnetic field. Furthermore, in the neighborhood of the semimetal-semiconductor transition region, this phase transition[1] can be controlled by applying a magnetic field H. All these interesting phenomena cannot be fully understood until a more quantitative model of the band structure in these alloys is established.

For a systematic investigation of the whole alloy system, it is very useful to carry out some detailed studies of the band structure in the dilute Sb concentration regions. By a small variation of the band structure from that in pure Bi, it is possible to track down the detailed changes taking place in the alloys. In particular, when quantum oscillation methods, such as the Shubnikov–de Haas (SdH) effect, are used to investigate the changes in Fermi surfaces, it then becomes necessary to vary the band structure gradually so as to follow the changes in the oscillation structure, in much the same way as we rotate H gradually in order to study the angular dependence in any oscillatory phenomena [e.g., de Haas–van Alphen (dHvA) effect or cyclotron resonance, etc.]. Moreover, the small changes of band parameters in dilute alloys allow us to make series expansions about the same quantities in more dilute alloys or in pure Bi, greatly simplifying the interpretations.

Previous experimental studies of the band structure in dilute Bi-Sb alloys have been made by Brandt and Shchekochikhina[2] and by Kao *et al.*[3] In these works, no explicit statement has been made on the g factor of electrons and holes in these alloys, and, in particular, there seems to be not enough data for H in the trigonal plane. The validity of the two-band model, which was successfully applied to pure Bi, has not been examined in the alloy system.

In the present work, we concern ourselves with a detailed experimental study of the band structure in order to investigate the validity of the two-band model in the dilute alloys. The SdH oscillations are studied

[1] N. B. Brandt, E. A. Svistova, and R. G. Valeyev, Zh. Eksperim. i Teor. Fiz. **55**, 469 (1968) [English transl.: Soviet Phys.—JETP **28**, 245 (1969)].

[2] N. B. Brandt and V. V. Shchekochikhina, Zh. Eksperim. i Teor. Fiz. **41**, 1412 (1961) [English transl.: Soviet Phys.—JETP **14**, 1008 (1962)].

[3] Y. H. Kao, R. D. Brown, III, and R. L. Hartman, Phys. Rev. **136**, A858 (1964).

with H in the trigonal plane. Special emphasis is placed on the possible occurrence of any effect due to spin splittings. These data, in conjunction with those reported in the previous work, can thus be used to establish a more complete model for the band structure in the dilute Bi-Sb alloys.

II. TWO-BAND MODEL FOR DILUTE Bi-Sb ALLOYS

The energy-band structure in Bi has been investigated by numerous research groups.[4-6] It can now be regarded as established that the conduction bands are nonparabolic; the electron Fermi surface consists of a set of three highly elongated ellipsoids. The hole band is parabolic and the hole Fermi surface is a spheroid. A recent detailed dHvA study[5] has shown that the two-band (ellipsoidal-nonparabolic) model holds in pure Bi to a high degree of accuracy. In this model,[7,8] the energy-momentum relationship for electrons can be written as

$$\epsilon(1+\epsilon/\epsilon_g)=\tfrac{1}{2}\mathbf{p}\cdot\boldsymbol{\alpha}\cdot\mathbf{p}, \tag{1}$$

and that for holes is represented by

$$E=\frac{p_1^2}{2M_1}+\frac{p_2^2}{2M_1}+\frac{p_3^2}{2M_3}, \tag{2}$$

where

$$\boldsymbol{\alpha}=\begin{pmatrix}\alpha_{11} & 0 & 0\\ 0 & \alpha_{22} & \alpha_{23}\\ 0 & \alpha_{23} & \alpha_{33}\end{pmatrix} \tag{3}$$

is the inverse effective-mass tensor for the electrons, ϵ and E are the energies measured from the bottom of the conduction (electrons) band and from the top of the valence (holes) band, respectively, ϵ_g is the energy gap in the two-band model, the p's are the quasimomenta, and M_1, M_3 are the effective masses for the holes. The crystallographic (binary, bisectrix, and trigonal) axes are used for the coordinate axes 1, 2, and 3. There are three ellipsoids for electrons, the other two can be generated from (1) by rotating through $\pm 120°$ around the trigonal axis.

Previous experimental works on dilute Bi-Sb systems revealed that alloying Bi with Sb results in a decrease in the overlap energy between the valence and conduction bands while both bands bear strong resemblance in shape to those in pure Bi. It is therefore natural to assume that the two-band model should also hold in dilute Bi-Sb alloys.

If a magnetic field H is applied along the direction $\mathbf{z}$, the energy will then be quantized into Landau levels and each level splits into two owing to the spin. Then, instead of (1) and (2), we have

electrons:

$$\epsilon\left(1+\frac{\epsilon}{\epsilon_g}\right)=(n+\tfrac{1}{2})\hbar\omega_c+\frac{p_z^2}{2m_z}\pm\frac{1}{2}\frac{e\hbar}{m_sc}H, \tag{4}$$

$$\omega_c=eH/m_cc, \quad n=0, 1, 2, \ldots;$$

holes:

$$E=(N+\tfrac{1}{2})\hbar W_c+\frac{p_z^2}{2M_z}\pm\frac{1}{2}\frac{e\hbar}{M_sc}H, \tag{5}$$

$$W_c=eH/M_cc, \quad N=0, 1, 2, \ldots,$$

where m_c, M_c are the orbital cyclotron masses at the edges of the bands; m_s, M_s are the spin effective masses; and m_z, M_z are the longitudinal masses. Usually the spin terms are represented by introducing the g factors

$$\tfrac{1}{2}(e\hbar/m_sc)H\equiv\tfrac{1}{2}g\beta_0H \quad\text{and}\quad \tfrac{1}{2}(e\hbar/M_sc)H\equiv\tfrac{1}{2}G\beta_0H,$$

where $\beta_0=e\hbar/2m_0c$ is the Bohr magneton and m_0 is the free-electron mass. The orbital cyclotron masses and the longitudinal masses are related to the masses in (1) and (2) by

$$m_z=\mathbf{h}\cdot\mathbf{m}^*\cdot\mathbf{h}, \quad m_c=(\det\mathbf{m}^*/m_z)^{1/2},$$
$$M_z=\mathbf{h}\cdot\mathbf{M}^*\cdot\mathbf{h}, \quad M_c=(\det\mathbf{M}^*/M_z)^{1/2},$$

where $\mathbf{m}^*$, $\mathbf{M}^*$ are the effective-mass tensors, and $\mathbf{h}$ is a unit vector in the direction of the magnetic field. By definition

$$\mathbf{m}^*\boldsymbol{\alpha}=I \text{ (unit tensor)}$$

and

$$\mathbf{M}^*=\begin{pmatrix}M_1 & 0 & 0\\ 0 & M_1 & 0\\ 0 & 0 & M_3\end{pmatrix}.$$

It is easy to count the total number of states per unit volume with energy less than the Fermi energy (ϵ_F or E_F), and its derivative with respect to the Fermi energy gives the density of states at ϵ_F or E_F. The results for the density of states at ϵ_F and E_F, the electron and hole Fermi energies, respectively, are given as follows.

Electrons (for one of the three ellipsoids):

$$n(\epsilon_F)=(2^{3/2}eH/h^2c)(m_z)^{1/2}\sum_{n,S}\tfrac{1}{2}(1+2\epsilon_F/\epsilon_g)$$
$$\times[\epsilon_F(1+\epsilon_F/\epsilon_g)-(n+\tfrac{1}{2})\hbar\omega_c+\tfrac{1}{2}S(e\hbar/m_sc)H]^{-1/2}; \tag{6}$$

holes:

$$N(E_F)=(2^{3/2}eH/h^2c)(M_z)^{1/2}$$
$$\times\sum_{N,S}\frac{1}{2}\left(E_F-(N+\tfrac{1}{2})\hbar w_c+\tfrac{1}{2}S\frac{e\hbar}{M_sc}H\right)^{-1/2}, \tag{7}$$

where the sums are over those values of n and N, and of $S=\pm 1$ such that the radicands are non-negative.

[4] L. A. Falkovski, Usp. Fiz. Nauk **94**, 3 (1968) [English transl.: Soviet Phys.—Usp. **11**, 1 (1968)].
[5] R. N. Bhargava, Phys. Rev. **156**, 785 (1967).
[6] W. S. Boyle and G. E. Smith, Progr. Semicond. **7**, 1 (1963).
[7] B. Lax and J. G. Mavroides, *Advances in Solid State Physics* (Academic Press Inc., New York, 1960), Vol. 11.
[8] M. H. Cohen and E. I. Blount, Phil. Mag. **5**, 115 (1960); P. A. Wolff, J. Phys. Chem. Solids **25**, 1057 (1964).

A maximum in the density of states at the Fermi energy corresponds to a minimum in the magnetoresistance. Therefore, the condition for having a minimum in the magnetoresistance is the following.

Due to electron:

$$\epsilon_F(1+\epsilon_F/\epsilon_g)=(n+\tfrac{1}{2})\hbar\omega_c\pm\tfrac{1}{2}(e\hbar/m_sc)H; \quad (8)$$

due to hole:

$$E_F=(N+\tfrac{1}{2})\hbar W_c\pm\tfrac{1}{2}(e\hbar/M_sc)H. \quad (9)$$

In this experiment, the oscillations due to holes and those due to heavy-mass electrons when the orientation of the magnetic field is close to a binary axis were not observed, possibly because of their small amplitudes and the limited resolving power of the experimental setup. Thus let us now consider (8) only. If the two-band model is valid, we have in (8), except for those electrons of heavy mass mentioned above,

$$m_c=m_s. \quad (10)$$

Therefore, (8) becomes

$$\epsilon_F(1+\epsilon_F/\epsilon_g)=n(e\hbar/m_cc)H=n\hbar\omega_c, \quad n=0, 1, 2, \ldots. \quad (11)$$

This result, arising from the outstanding feature [Eq. (10)] of the two-band model applied to the Bi-Sb systems, implies that the spin level spacing is equal to the Landau level spacing and there should be no observable "apparent splittings" of the resistance minima due to spin effects. If we denote $(H_n)_{\mathrm{Bi}}$ for the field value at which the nth level in pure Bi reaches the Fermi energy and gives rise to a minimum in the magnetoresistance when the field is in some specified direction, and $(H_n)_{\mathrm{alloy}}$ for the field value at which the same nth level in a Bi-Sb alloy reaches its own Fermi energy with the field H oriented in the same crystallographic direction, we have, according to (11),

$$\frac{(H_n)_{\mathrm{Bi}}}{(H_n)_{\mathrm{alloy}}}=\frac{[m_c\epsilon_F(1+\epsilon_F/\epsilon_g)]_{\mathrm{Bi}}}{[m_c\epsilon_F(1+\epsilon_F/\epsilon_g)]_{\mathrm{alloy}}}. \quad (12)$$

Insofar as the Fermi energies remain unchanged in a low magnetic field region, we see from (12) that the left-hand side should not depend on n. On the other hand, we know from elementary theories that the period in $1/H$ between two successive minima is given by

$$\Delta(1/H)=(e\hbar/m_cc)[\epsilon_F(1+\epsilon_F/\epsilon_g)]^{-1}=(2\pi e\hbar/c)S^{-1}, \quad (13)$$

where S is the extremal cross-sectional area of the Fermi surface perpendicular to the direction of the magnetic field. Therefore, we have

$$\frac{(H)_{\mathrm{Bi}}}{(H)_{\mathrm{alloy}}}=\frac{[\Delta(1/H)]_{\mathrm{alloy}}}{[\Delta(1/H)]_{\mathrm{Bi}}}=\frac{(S)_{\mathrm{Bi}}}{(S)_{\mathrm{alloy}}}, \quad (14)$$

where $(H)_{\mathrm{Bi}}/(H)_{\mathrm{alloy}}$ is the ratio of the field values at the corresponding minima (the same n, which are not difficult to identify).

III. EXPERIMENTAL

A. Preparation of Samples

Bismuth of 99.9999% purity and antimony of 99.999% purity were purchased from the Consolidated Mining and Smelting Company of Canada, Ltd. To grow single crystals of pure Bi, Bi pieces of 200-g total weight were placed in a quartz boat (7 in. long with a trapezoidal cross section about $\frac{1}{2}\times\frac{1}{2}$ in.) of a zone-leveling apparatus. During the zone-leveling process, a $\frac{1}{2}$-in. molten zone was moved at a speed of about 1 in./h to and fro through the 7-in. ingot. Four or five passes were enough for Bi single crystals. A 2.5-kW, 5-Mc/sec Lepel induction heater was used to melt the zone. For growing a single crystal of dilute Bi-Sb alloy of Sb concentration less than 1 at.%, we first grew an ingot of pure Bi using the above procedure. But the Bi ingot was not required to be good single crystal, so that two or three passes were enough. An appropriate amount of Sb, crushed into small pieces, was sprinkled on the bottom of the quartz boat, and the prepared Bi ingot was then put into the boat on the Sb. The same zone-leveling process was then carried out. For growing alloys, no less than 20 passes were required for homogeneity of Sb in Bi. For reducing impurities, both Bi, Sb, and the boat were cleaned carefully. After growing, the ingots were etched in 30% HNO_3 to reveal whether they were good single crystals. An electric discharge machine was used for cutting the ingots to the desired shape. The samples we used were rectangular parallelepipeds of about $\frac{1}{2}\times\frac{1}{8}\times\frac{1}{8}$ in. The trigonal axis was along the longer edge, while the binary and bisectrix axes were along the other edges. To determine these crystallographic axes, we cleaved the crystals in liquid nitrogen and checked the crystal orientations by x-ray studies with an accuracy of 1°. The concentration of Sb in the alloys was determined both by measuring the densities of the specimens and by chemical analyses done at the Schwarzkopf Microanalytical Lab.[9] The results are a little bit less than the calculated concentrations, e.g., 0.48±0.01 at.% for the desired 0.5 at.%, 0.95±0.03 at.% for the desired 1 at.%, etc.

B. Shubnikov-de Haas Effect

During the experiment, the sample was taped to an insulated metal plate, which was the end part of a sample holder. The sample holder was inserted into a liquid-helium Dewar such that the trigonal axis of the sample was vertical, and the binary and bisectrix axes were in the horizontal plane. The accuracy in sample orientation was estimated to be $\lesssim 1°$. A 12-in. Harvey-

[9] The Schwarzkopf Microanalylical Laboratory, 59-19 37th Ave., Woodside, N. Y.

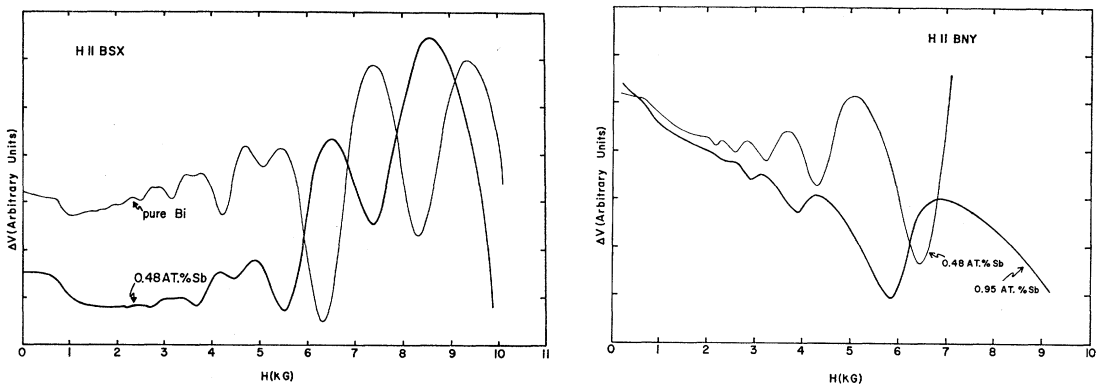

FIG. 1. (a) Bucked potential difference (showing SdH oscillations in the magnetoresistance) versus magnetic field for a pure Bi sample and a Bi-Sb alloy sample of 0.48-at.% Sb concentration. The magnetic field is parallel to the bisectrix axis. (b) Bucked potential difference versus magnetic field for a Bi-Sb alloy of 0.48-at.% Sb and a Bi-Sb alloy of 0.95-at.% Sb. The magnetic field is parallel to the binary axis.

Wells electromagnet was used to produce magnetic fields from 0 to 10 kG. The sample together with the helium Dewar were fixed in space while the magnetic field could be oriented in the horizontal plane by rotating the magnet.

A constant dc current was passed along the trigonal axis, perpendicular to the field. The resistance was proportional to the potential across the two potential leads on the sample. In order to get SdH oscillations with appreciably larger amplitudes, we used a magnetic probe to buck out approximately the monotonic part of the magnetoresistance. The bucked potential was then amplified through a Keithley millimicrovoltmeter whose output was connected to the Y terminal of an XY recorder. The magnetic field was read by a Bell 240 gaussmeter, which gave the X readings.

SdH oscillations versus magnetic field were measured for different orientations of the field in the trigonal plane. To specify orientations of the magnetic field, the first step was to find out the direction for which the field was along the bisectrix axis; this could be done with an accuracy $\lesssim 0.5°$. Then by rotating the magnet we could set the field at any desired angle between the bisectrix axis and the binary axis.

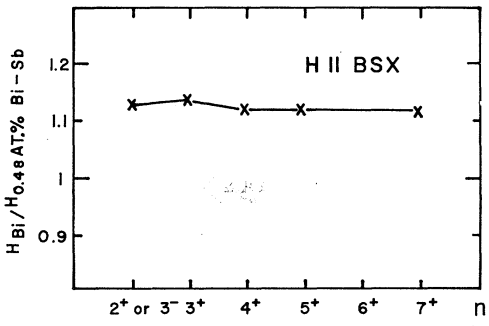

FIG. 2. Ratio of the field values at minima in the magnetoresistance versus the quantum number n. The magnetic field is parallel to the bisectrix axis. The alloy has 0.48-at.% Sb concentration.

Typical curves demonstrating the SdH effect in our alloys are shown in Fig. 1.

IV. RESULTS AND DISCUSSION

The magnetic field values at which the minima in the magnetoresistance occurred were measured for both pure Bi and Bi-Sb alloys of Sb concentrations 0.23, 0.48, 0.72, and 0.95 at.% at temperatures 1.65–4.2°K. The readings of these field values were the same at different temperatures; in other words, we did not find any observable temperature dependence of the field values at the minima. Some results are presented in Table I. To identify the quantum number n for each minimum in the magnetoresistance, we first applied formula (11) to pure Bi, making use of the known data[10] for the Fermi energy ϵ_F, energy gap ϵ_g, and the effective masses. It was not difficult to identify the quantum numbers for the alloys after we had assigned those for the minima in pure Bi. This is due to the fact that the field values at the minimum corresponding to a given quantum number will change continuously when the

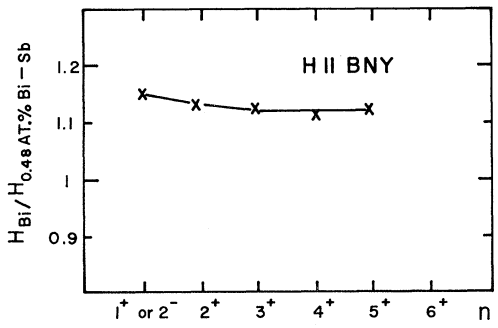

FIG. 3. Ratio of the field values at minima in the magnetoresistance versus the quantum number n. The magnetic field is parallel to the binary axis. The alloy has 0.48-at.% Sb concentration.

[10] G. E. Smith, G. A. Baraff, and J. M. Rowell, Phys. Rev. 135, A1118 (1964).

TABLE I. Field values of the minima of the magnetoresistance. Field values in kG.

Landau levels with ± spin	Pure Bi		0.23 at.% Bi-Sb		0.48 at.% Bi-Sb		0.72 at.% Bi-Sb		0.95 at.% Bi-Sb	
	$H\|\|$Bsx	$H\|\|$Bny	$H\|\|$Bsx	$H\|\|$Bny	$H\|\|$Bsx	$H\|\|$Bny	$H\|\|$Bsx	$H\|\|$Bny	$H\|\|$Bsx	$H\|\|$Bny
0^+ or 1^-										
1^+ or 2^-		7.35±0.05		6.78±0.05		6.40±0.05		5.70±0.05	9.75±0.05	5.90±0.05
2^+ or 3^-	8.38±0.05	4.80±0.05	7.82±0.05	4.57±0.05	7.38±0.05	4.25±0.05	6.65±0.05	3.85±0.05	6.70±0.05	3.94±0.05
3^+ or 4^-	6.30±0.05	3.60±0.05	6.00±0.05	3.43±0.05	5.55±0.05	3.20±0.05	4.95±0.05	2.90±0.05	5.15±0.05	2.95±0.05
4^+ or 5^-	5.00±0.05	2.85±0.05	4.80±0.05	2.74±0.05	4.45±0.05	2.56±0.05	4.00±0.05	2.30±0.05	4.10±0.05	
5^+ or 6^-	4.15±0.05	2.39±0.05	3.98±0.05		3.70±0.05	2.13±0.05	3.30±0.05		3.40±0.05	
6^+ or 7^-	3.55±0.05		3.41±0.05							
7^+ or 8^-	3.10±0.05		2.98±0.05		2.75±0.05		2.45±0.05			

Sb concentration in the dilute alloys is continuously varied.

For pure Bi and any one of the Bi-Sb alloys we used, the ratios of the field values at the minima corresponding to the same quantum numbers n were found to be practically independent of n and the orientation of the magnetic field. Results are shown in Figs. 2–4 for an alloy of 0.48-at.% Sb concentration. We have one constant ratio for each given Sb concentration. These constants depend on the concentration of Sb, and for dilute Bi-Sb alloys this dependence is approximately linear (Fig. 5). The slope is in good agreement with recent work by Brandt *et al.*[11]

The fact that all these ratios are independent of n gives a direct evidence that the band structure of Bi-Sb alloys is similar to that of pure Bi. It follows that

$$(m_c)_{\mathrm{Bi}}/(m_c)_{\mathrm{alloy}}=(m_s)_{\mathrm{Bi}}/(m_s)_{\mathrm{alloy}}. \qquad (15)$$

In addition, this ratio is independent of the orientation. These observations led us to conclude that the orbital effective masses together with the spin effective masses change proportionally (or both are unchanged) when alloying Bi with small amount of Sb.

We have attempted to look for the spin splitting effect due to deviations from the two-band model in the dilute Bi-Sb system. No observable "apparent splittings" were found in this experiment. Every minimum in all the the magnetoresistance curves was identified unambiguously using Eq. (11) and the most recently known parameters of the band structure for pure Bi.[5] In particular, for pure Bi, we have also investigated the oscillation minima with H in the binary and the bisectrix planes. To the lowest temperature (1.65°K) we reached in this experiment, all the minima were clearly identified in close agreement with Bhargava's recent dHvA work. Within our experimental limit, in samples with residual resistance ratio in the neighborhood of 400, we found no "apparent" spin splittings for H up to 10 kG. In the dilute alloys, if ϵ_g becomes smaller for increasing Sb concentration, we would expect the two-band model to be more valid than in pure Bi. This agrees with our results.

Based on our results, $(H)_{\mathrm{Bi}}/(H)_{\mathrm{alloy}}$ being independent of n and the orientation and no observable spin effects in all our alloys, it appears that the two-band model should give an excellent description of the band structure in dilute Bi-Sb alloys. Within the sensitivity and accuracy limits of our experiment, however, we may set a tentative limit for any possible deviation from this model. From our observations, we conclude that the condition $m_c=m_s$ holds in dilute alloys with at most 10% deviations.

Mase *et al.*[12] reported some detailed studies of the spin splitting effects in Bi by magnetoacoustic attenuation. In particular, they attributed the apparent line splittings with H in the neighborhood of the bisectrix direction to the spin effect. We actually also observed the similar splittings in our magnetoresistance minima when H was not exactly aligned with the bisectrix axis. Rotating H for 1° from the exact alignment could produce the doubling analogous to those observed by Mase *et al.* In our case, we identified all these splittings as due to Fermi surfaces giving rise to two nearly equal cyclotron frequencies. Actually, one would expect to see least deviations from the two-band model when H is parallel to the bisectrix direction. It seems conceivable that the splittings due to spin effects are more improbable in this direction than the case when H is along other directions.

Assuming the validity of the two-band model we next deduce from our data the changes in band parame-

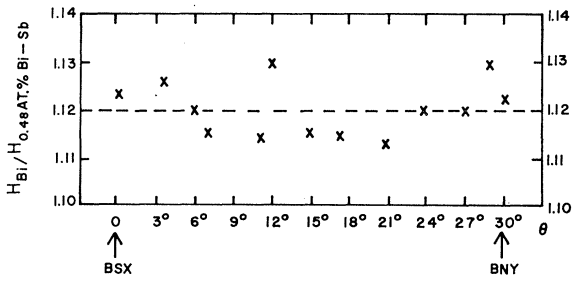

FIG. 4. Angular variation of the ratio of the field values at minima in the magnetoresistance. The alloy has 0.48-at.% Sb concentration.

[11] N. B. Brandt, L. G. Lyubutina, and N. A. Kryukova, Zh. Eksperim. i Teor. Fiz. **53**, 134 (1967) [English transl.: Soviet Phys.—JETP **26**, 93 (1968)].

[12] S. Mase, Y. Fujimori, and H. Mori, J. Phys. Soc. Japan **21**, 1744 (1966).

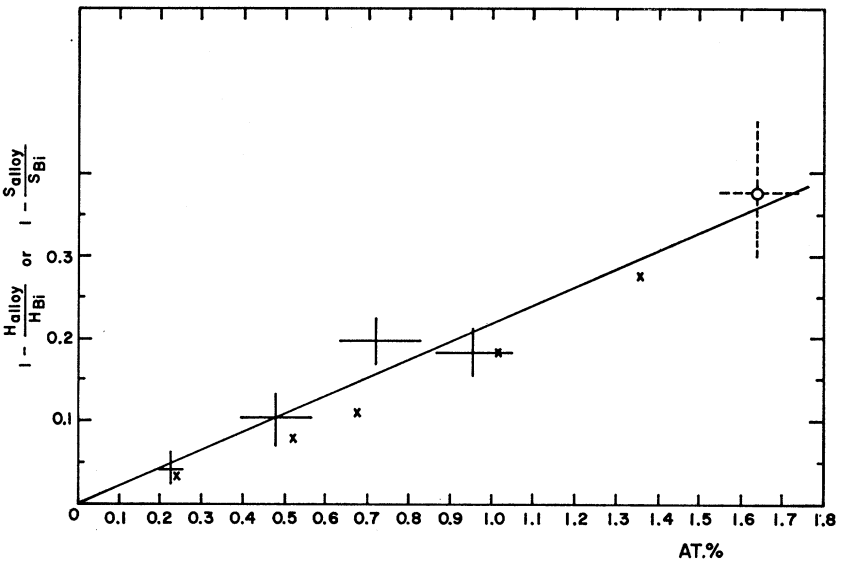

FIG. 5. Dependence of the change of the extremal cross-sectional area of the Fermi surface on the Sb concentration. ×: Brandt *et al.* (Ref. 2); ○: Kao *et al.* (Ref. 3).

ters in these alloys. From Eq. (14) and the slope of the straight line in Fig. 5, we found that

$$\frac{\Delta S}{S_{\mathrm{Bi}}}\equiv\frac{S_{\mathrm{Bi}}-S_{\mathrm{alloy}}}{S_{\mathrm{Bi}}}=1-\frac{(H)_{\mathrm{alloy}}}{(H)_{\mathrm{Bi}}}\cong 0.22x, \quad (x<1) \quad (16)$$

where x is the at.% concentration of Sb in Bi. Our linear variation of S_{alloy} versus x is to be compared with those measured by Brandt *et al.*[11] (The only other experimental curve of S_{alloy} versus x appeared in the literature.) This comparison is shown in Fig. 6. Curve 1 shows our data extrapolated to slightly higher x; curve 2 represents the data reported in Ref. 11 by Brandt *et al.* The initial slopes ($x<1$) determined by both experiments are in very good agreement. If the linear variation of S_{alloy} as determined in (16) is assumed to be also true in higher values of x up to where $S_{\mathrm{alloy}}=0$, then the linear extrapolation of our data (curve 1, Fig. 6) predicts that S_{alloy} vanishes at $x\simeq 4.5$. This intercept of $x=4.5$ seems too low in view of the recent experimental results[13,14] showing that S_{alloy} vanishes at $x\simeq 7$.

In Ref. 11, Brandt and co-workers measured the variation in S_{alloy} for alloys of Sb concentration up to $x=4$. The decrease of S_{alloy} versus x was approximately linear and by linear extrapolation they suggested that S_{alloy} would vanish at $x=5$. In his recent works,[1,15] however, Brandt found that this concentration, at which S_{alloy} vanishes, should be about 7 or 8. Brandt[15] observed that the alloy with $x=6.5$ was still semimetallic. Besides, Tichovolsky and Mavroides[16] estimated that this concentration would be somewhere between $x=5$ and $x=8$.

According to Eq. (13), the electron Fermi energy ϵ_F vanishes when S vanishes unless the effective masses could be zero or infinite (physically impossible). Equation (13) is derived from the two-band model. For the nonellipsoidal-nonparabolic model, a similar relation between S and ϵ_F exists (see, for example, Ref. 3), showing that these two quantities go to zero simultaneously. According to the charge neutrality condition, the hole Fermi energy E_F must go to zero when ϵ_F goes to zero. Therefore, at the concentration at which the semimetallic Bi-Sb alloy becomes semiconducting the quantities S, ϵ_F, E_F, and the energy overlap go to zero simultaneously.

On account of the value of x ($x\simeq 7$) for $S_{\mathrm{alloy}}=0$, we should therefore modify (16) in order to obtain an expression for the x dependence of S_{alloy} in the entire range $0<x\lesssim 7$. Without accurate data in the range $1<x<7$, we first propose a simplest extension of (16) by adding a term px^2 to $0.22x$. Setting $S_{\mathrm{alloy}}=0$ at $x=7$ yields $p=-0.011$. In this simple-minded qualitative approximation, we have the following expression for S_{alloy} versus x:

$$S_{\mathrm{alloy}}/S_{\mathrm{Bi}}=1-0.22x+0.011x^2 \quad (0<x<7). \quad (17)$$

While the accuracy of Eq. (17) may be subject to questions, the point to be stressed here is that the x dependence of S_{alloy} should be *nonlinear*. A plot of Eq. (17) is shown by curve (3) in Fig. 6.

In our experiment, we studied the ratios of H at the minima corresponding to the same quantum number. As we can see from Eq. (14), if the two-band model is valid, this method is equivalent to the conventional method of studying the periods of quantum oscillations $\Delta(H^{-1})$. As a matter of fact, these two methods should lead to the same conclusion as long as the Fermi

[13] M. R. Ellett, R. B. Horat, L. R. Williams, and K. F. Cuff, J. Phys. Soc. Japan Suppl. **21**, 666 (1966).
[14] L. S. Lerner, K. F. Cuff, and L. R. Williams, Rev. Mod. Phys. **40**, 770 (1968).
[15] N. B. Brandt, E. A. Svistova, and Yu. G. Kashirskii, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaksiyu **9**, 232 (1969) [English transl.: Soviet Phys.—JETP Letters **9**, 136 (1969)].
[16] E. J. Tichovolsky and J. G. Mavroides (unpublished); for a short report, see Bull. Am. Phys. Soc. **14**, 433 (1969).

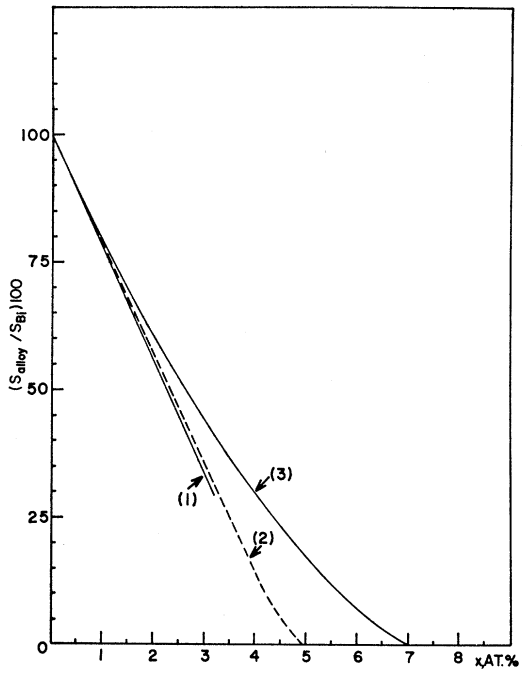

FIG. 6. $S_{\text{alloy}}/S_{\text{Bi}}$ versus Sb concentration ×. (1) Our result (extrapolated); (2) results of Brandt *et al.*; (3) nonlinear variation computed from Eq. (17).

energy ϵ_F is unshifted in low H. When H is higher than a certain value (in our case, about 5 kG), ϵ_F changes with H, and the direct comparison of H rather than $\Delta(H^{-1})$ proves to be more meaningful as the oscillations may eventually become nonperiodic.

From the measurements of S_{alloy}, we may deduce the variations of ϵ_F in our alloys. It should be noted that in the two-band model for electrons, ϵ_F can be derived from S only if ϵ_g is known. In the case of alloys, this is concerned with the problem of how ϵ_g varies with x. Until recently, there has been no direct determination of ϵ_g in Bi-Sb alloys. Experimental results have hitherto been explained on the assumption of a fixed ϵ_g.[2,3,11]. Golin[17] proposed in a recent paper that the conduction- and the valence-band edges may just reverse positions at $x=11.4$ and suggested as a first approximation that ϵ_g varies linearly with x as

$$(\epsilon_g)_{\text{alloy}}=(\epsilon_g)_{\text{Bi}}-\beta x, \quad \beta\simeq 2.7 \text{ meV}. \tag{18}$$

This prediction was qualitatively borne out in a recent magnetoreflection experiment by Tichovolsky and Mavroides.[16] In this experiment, starting with an alloy with $x=2$, the variation of ϵ_g with x was ascertained. We computed the variation of $(\epsilon_F)_{\text{alloy}}$ with x based on both Golin's model and these recent data on ϵ_g; we made a comparison between these deductive results and the experimental data of $(\epsilon_F)_{\text{alloy}}$.[11,13]

Assuming the two-band model and using the $\mathbf{k}\cdot\mathbf{p}$ approximation, we can easily see that the effective

[17] S. Golin, Phys. Rev. **176**, 830 (1968).

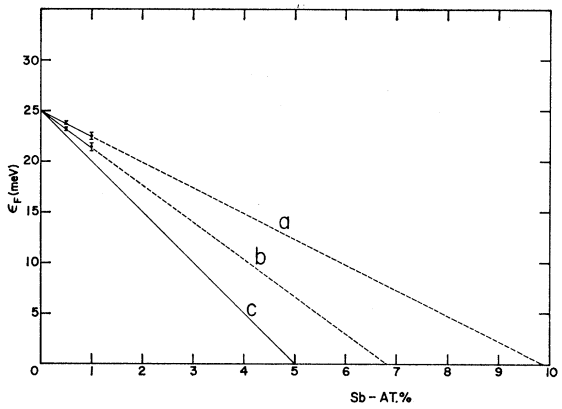

FIG. 7. Electron Fermi energy ϵ_F versus Sb concentration. Solid line of curve a is computed from Eq. (20) and Golin's model. Solid line of curve b is computed from Eq. (20) and a fixed value of $\epsilon_g=15$ meV. Curve c: results of Brandt *et al.*

masses are proportional to ϵ_g. We therefore write

$$\frac{S_{\text{alloy}}}{S_{\text{Bi}}}=\frac{[m_c\epsilon_F(1+\epsilon_F/\epsilon_g)]_{\text{alloy}}}{[m_c\epsilon_F(1+\epsilon_F/\epsilon_g)]_{\text{Bi}}}$$
$$\simeq[\epsilon_F(\epsilon_F+\epsilon_g)]_{\text{alloy}}/[\epsilon_F(\epsilon_F+\epsilon_g)]_{\text{Bi}}. \tag{19}$$

In the range of Sb concentrations studied in our work ($x<1$), Eq. (16) represents a fairly good expression for $S_{\text{alloy}}/S_{\text{Bi}}$. Combining (16) and (19) and using $\epsilon_F=25$ meV, $\epsilon_g=15$ meV for pure Bi,[18] we arrived at

$$[\epsilon_F(\epsilon_F+\epsilon_g)]_{\text{alloy}}\simeq 1000(1-0.22x) \quad (x<1). \tag{20}$$

The x dependence of $(\epsilon_F)_{\text{alloy}}$ was then solved for by using different models for the variation of ϵ_g.

The solid-line portion of curve a in Fig. 7 shows the computed ϵ_F variations using Eq. (20) and Golin's model. A linear extrapolation of this line will lead to a

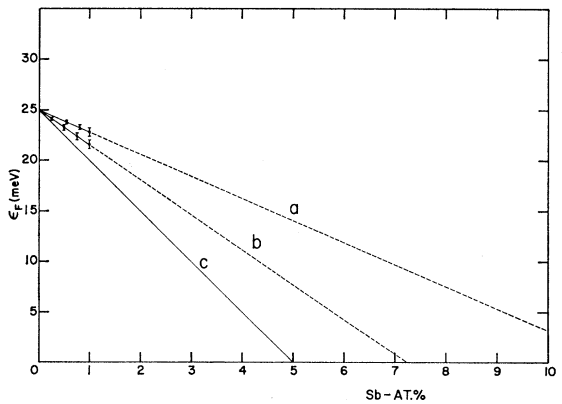

FIG. 8. Electron Fermi energy ϵ_F versus Sb concentration. Solid line of curve a is computed from Eq. (20) and the results of Tichovolsky and Mavroides. Curve b is computed from Eq. (20) and a fixed value of $\epsilon_g=12$ meV as used by Tichovolsky and Mavroides. Curve c: results of Brandt *et al.*

[18] R. N. Brown, J. G. Mavroides, and B. Lax, Phys. Rev. **129**, 2055 (1963).

value of x at which ϵ_F vanishes too much higher than 7%. Presented also in Fig. 7 are the computed values of ϵ_F assuming that ϵ_g is independent of x for $x<1$ (solid-line portion, curve b). Note that this line extends to a value of $x=6.8\%$ at $\epsilon_F=0$ (dashed line, curve b). This straight line agrees quite well with the data obtained by Ellett *et al.* The data due to Brandt *et al.* are included for comparison (curve c).

Likewise, we computed the values of ϵ_F using the nearly constant slope of the ϵ_g-versus-x curve (for small x) obtained by Tichovolsky and Mavroides.[16] The results are shown in Fig. 8. Once again, linear extrapolation of curve a leads to a value of x too high for $\epsilon_F=0$, and curve b shows fairly good agreement with the data of Ellett *et al.* Results obtained by Brandt *et al.* (curve c) always lie below the two computed curves.

In both Figs. 7 and 8, curves labeled "a" all lie above the experimental values. In view of the above observations, neither the Golin model nor the linear variation of ϵ_g in low x obtained by Tichovolsky and Mavroides in their present form can be brought into consistency with our measurements together with the results of Refs. 11 and 13. We believe that the next step to improve the present situation is to investigate the nonlinear properties of the band-structure variation. Our results seemingly suggest that for $x<1\%$, the energy gap ϵ_g is essentially unchanged (curve b, Figs. 7 and 8). However, this prediction cannot be justified without direct measurements of ϵ_g in the dilute Sb region. Since the lowest Sb concentration studied by Tichovolsky and Mavroides is 2%, measurements of ϵ_g in the region $0<x<2$ would be highly desirable.

Nevertheless, the agreement between our curve b in Figs. 7 and 8 and the experimental results by Ellett *et al.* might prove to be fortuitous. This agreement, as well as the disagreement with the data of Brandt *et al.*, could all arise from a difficult technical problem of preparing alloys with a high degree of homogeneity. As we noticed that even our samples were all prepared by using more than 20 zone-leveling passes, the Sb concentration near the ends of a sample may still differ by as much as 10% from that in the middle.

V. CONCLUSION

The close resemblance in the band structure of dilute Bi-Sb alloys to that of pure Bi has been further ascertained experimentally. The orbital and spin effective masses were found to change proportionally when alloying Bi with Sb. The contraction of the Fermi surface is independent of the crystallographic orientations. No "apparent" spin splittings in the Bi-Sb system have been observed in this experiment. Within our experimental limits, the two-band model can be considered as in excellent agreement with the results for both pure Bi and Bi-Sb alloys.

Combining our results in the low Sb concentration region and the previous work showing that the semimetallic Bi-Sb becomes semiconducting at an Sb concentration about 7 at.%, we conclude that the contraction of the Fermi surface, which is approximately linear in low Sb concentrations ($x<1$), should, in general, be nonlinear in x for $0<x\lesssim 7$. Though the energy gap ϵ_g as well as the effective masses at the conduction-band edge vary with the Sb concentration as reported by others, our results suggest strongly that these quantities do not change appreciably in dilute Bi-Sb alloys (Sb$\lesssim$1 at.%).

ACKNOWLEDGMENTS

We wish to thank E. Marston, J. Kirschenbaum, and R. Graham for their technical assistance.