Tilt of the Electron Fermi Surface in Bi

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Many experiments show that the long axes of the three extremely prolate ellipsoids which represent the electron Fermi surface in bismuth are tilted ~6° from the trigonal plane of the Brillouin zone; however, the sign of this tilt angle cannot be unambiguously obtained from the literature. We report results obtained from measurements of the de Haas–van Alphen and de Haas–Shubnikov effects and quadratic magnetoresistance which show that the sign of the tilt angle is positive in terms of the usual conventions, which are carefully defined. More explicitly, the long axis of each ellipsoid lies within the ~18° angle made by a bisectrix direction and a ΓL direction in the Brillouin zone. Our results are shown to agree with the most recent band calculations for Bi. Comparison of de Haas-van Alphen results on Bi and Sb samples, each with the same orientation as determined by x rays, shows that, independently of any convention, the tilt angles of Bi and Sb have opposite signs. We also clarify the procedures for properly orienting a crystal of bismuth by observing either twinning planes or etch pits in the trigonal plane.

INTRODUCTION

THE electron Fermi surface of bismuth is now known[1,2] to be a set of three, geometrically equivalent, highly eccentric ellipsoids. A minor axis of each ellipsoid is along a (different) binary direction (axes of twofold rotational symmetry), the other two axes are in the binary plane, tilted ~6° from the trigonal (threefold) and bisectrix axes as shown in Fig. 1(a). What cannot be uniquely determined from the literature, however, is the sign of the tilt angle, i.e., whether the orientation of the ellipse in the binary plane is as the solid or dotted ellipse in Fig. 1(a). The major confusion is associated with the fact that, though the binary and trigonal axes may be easily located by cursory inspection of a bismuth crystal, the unique assignment of a right-handed triad with respect to the atomic structure requires much more care. The problem may be appreciated by considering Fig. 1(a). By rotating the binary plane about the binary axis, the sense of rotation may be such as to tip the trigonal axis $T\Gamma T$ towards either the L points or the X points. Knowledge of the binary and trigonal axes is not enough to describe the sense of rotation. Rather, a convention must be adopted for the positive (+) bisectrix direction relative to an arbitrarily chosen + trigonal direction, and then the + binary chosen to complete a right-handed triad. The convention must be described with reference to the geometry of the basis vectors of the primitive rhombohedral unit cell of the Bravais lattice (which is uniquely related to the geometry of the Brillouin zone). The orientation of the Bravais lattice must finally be determined by x rays.

The geometry of the electron Fermi surface for Sb and As is very similar to that of Bi. The tilt angles for Sb and As have now been firmly established[3,4] from de Haas–van Alphen measurements, and in terms of the convention described below, are negative. This sign is opposite to that assumed for Bi by Hall and Koenig,[5] but the same as that claimed for Bi by Reneker[6] and Smith.[7] Shoenberg[8] has reported the signs of the tilts for Sb, As, and Bi to be the same, but a comparison of his results with those of Windmiller[3] and Priestley *et al.*[4] shows that he was not comparing analogous bands.

We report here the results of several experiments which show that (1) the sign of the tilt angle for Bi is positive, in terms of the generally accepted conventions, described below, and (2) the signs of the tilts for the analogous electron bands in Bi and Sb are opposite, independent of convention. Additionally, we clarify the procedures for determining the + bisectrix direction from inspection of either twinning planes, or of etch pits in a trigonal plane.

CONVENTIONS

Crystallographic

Though Bi crystallizes with $\bar{3}m$ symmetry (having one trigonal axis of threefold symmetry, three twofold or binary axes each normal to the trigonal direction and to a mirror plane, and a center of inversion), the crystal lattice deviates but a few percent from a simple cubic lattice. The deviation is such that the primitive cell is a slight distortion of that for a face-centered cubic lattice; it is rhombohedral with two atoms per unit cell. The Brillouin zone for Bi, shown in Fig. 1(b), is then very much like that for a face-centered cubic lattice, only somewhat compressed along the $T\Gamma T$ or trigonal direction. The hexagonal faces containing T are regular hexagons. The remaining faces of the zone, which would be regular polygons for the face-centered cubic zone, will be referred to as pseudosquare and

[1] A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962).
[2] R. N. Bhargava, Phys. Rev. **156**, 785 (1967).
[3] L. R. Windmiller, Phys. Rev. **149**, 472 (1967).
[4] M. G. Priestley, L. R. Windmiller, J. B. Ketterson, and Y. Eckstein, Phys. Rev. **154**, 671 (1967).
[5] J. J. Hall and S. H. Koenig, IBM J. Res. Develop. **8**, 241 (1964).
[6] D. H. Reneker, Phys. Rev. **115**, 303 (1959).
[7] G. E. Smith, Phys. Rev. **115**, 1561 (1959).
[8] D. Shoenberg, in *Progress in Low Temperature Physics* (North-Holland Publishing Co., Amsterdam, 1957), Vol. II.

pseudohexagonal faces in what follows. Similarly, we will use the prefix "pseudo" for directions and planes that would be equivalent in the cubic limit to the true binary, bisectrix, and trigonal directions and planes in Bi.

If we choose to call the + trigonal direction the upward direction, as shown in Fig. 1(a), then our convention, the usual one,[9] is to have the + bisectrix as shown. The + binary is then defined so that the binary (x), bisectrix (y), and trigonal (z) axes form a right-handed triad. A positive tilt angle is then defined, again as is usual though not universal,[10] by a rotation about the binary axis so as to rotate $+y$ through the first quadrant toward $+z$. Thus the solid ellipse in Fig. 1(a) has its major axis tilted by a small positive angle from the bisectrix direction.

Figure 1(c) shows the primitive rhombohedral cell of Bi drawn in a somewhat distorted cube, the orientation of which is identical to the distorted cube from which the Brillouin zone of Fig. 1(b) is derived. The lines OA, OB, OC are the basis vectors in real space of the crystal lattice, and their orientation may be determined by x rays. The convention for obtaining the + bisectrix direction from this information in real space is as follows: after choosing the direction to be used as + trigonal, project one of the basis vectors whose projection is along the + trigonal [e.g., OB rather than $O'B'$ in Fig. 1(c)] onto the trigonal plane. The direction of the projection, outward from the trigonal axis, is the + bisectrix direction. This again is the usual convention.

The trigonal plane is the primary cleavage plane of Bi. Examination of an etched cleaved surface usually shows lines which are parallel to the three binary directions. However, a knowledge of only the binary directions is not adequate to orient Bi uniquely. One must know the sense of rotation about a binary direction that corresponds to the positive rotation defined above. Bi has three twinning planes, which are pseudobinary planes.[11] These planes intersect the trigonal plane along binary directions. If these planes can be observed, then the crystallographic orientation can be uniquely determined by defining a + bisectrix direction according to the following rule (cf. Fig. 2): Find a twinning plane that intersects a trigonal plane. Choose the + trigonal direction as the outward normal to the plane, and locate a trigonal axis so that the intercept of the twinning plane with the trigonal axis lies below the surface; the origin is defined by the intersection of the trigonal axis and the surface. Draw a line from the origin perpendicular to the binary line defined by the

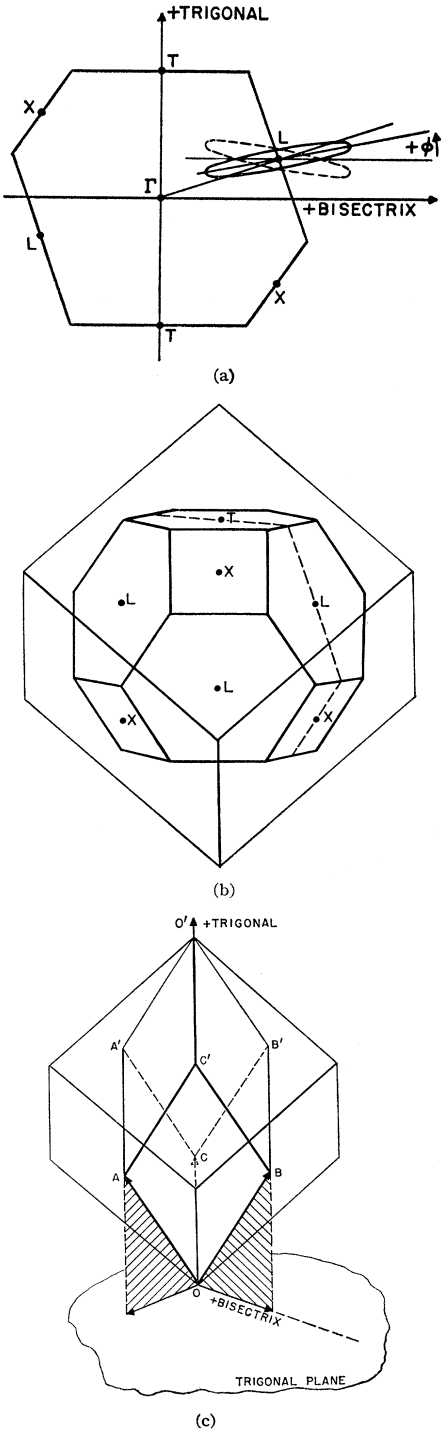


FIG. 1. (a) A binary plane of the bismuth Brillouin zone showing a cross section of two possible orientations of the electron Fermi surface in the neighborhood of one L point. The cross section is drawn solid for a positive tilt angle and dotted for a negative tilt angle. The surfaces within the zone are actually half-ellipsoids centered at L but for clarity are shown as full ellipsoids by continuation into the next zone. (b) The Brillouin zone of the slightly distorted face-centered cubic lattice of bismuth. (c) The primitive rhombohedral cell of bismuth drawn in the same distorted cube as in (b).

[9] See W. G. Cady, *Piezoelectricity* (McGraw-Hill Book Co., New York, 1946), p. 23.

[10] See Ö. Öktü and G. A. Saunders, Proc. Phys. Soc. (London) **91**, 156 (1967).

[11] See E. O. Hall, *Twinning and Diffusionless Transformations in Metals* (Butterworths, London, 1952), p. 81. We have measured the angle between the trigonal plane and the observed plane as defined by etch lines on the crystal facts; its value is as expected for a pseudobinary plane.

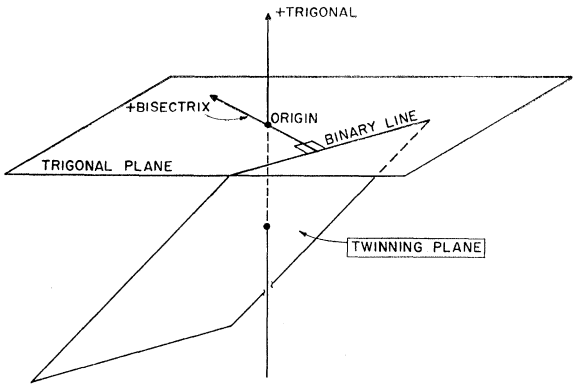


FIG. 2. Directions of the positive trigonal and bisectrix axes shown in relation to the primary cleavage (trigonal) plane and a twinning (pseudobinary) plane in bismuth.

intersection of the trigonal and twinning planes. The direction from the binary line toward the origin along this perpendicular is the + bisectrix. This rule should be correct if the twinning planes are as described in the literature. We have independently verified this by x-ray measurements and include in Fig. 3 an x-ray Laue pattern with the directions marked in accordance with the conventions described here. The orientation of the crystal for this pattern is such that no error can result from a mixup of left and right; the mirror plane is vertical and contains the x-ray beam.

Several authors[12,13] have oriented their crystals using the tetrahedral etch pits revealed by etching a cleaved trigonal surface with 33% HNO_3 in water. The faces exposed by etching, however, are not twinning planes, though the intersections of the etch-pit faces with the trigonal plane are parallel to binary directions. If one assumes that the exposed faces are twinning planes, one obtains the wrong direction for the + bisectrix. (The rule for obtaining the + bisectrix from etch pits is then obvious.) In particular, at least two photographs of etch pits in the literature[12] have arrows, ostensibly indicating a + binary direction, which in fact point along the − binary.

Electronic

The expression for the surface of constant energy corresponding to one electron ellipsoid is usually written as

$$2m_0E=\mathbf{p}\cdot\boldsymbol{\alpha}\cdot\mathbf{p}=\alpha_1p_x^2+\alpha_2p_y^2+\alpha_3p_z^2+2\alpha_4p_yp_z. \quad (1)$$

Here, $\mathbf{p}$ is the Fermi momentum, E is the Fermi energy, m_0 is the free electron mass, and $\boldsymbol{\alpha}=\mathbf{m}^{-1}$ is the reciprocal of the effective mass tensor:

$$\boldsymbol{\alpha}\equiv\begin{pmatrix}\alpha_1 & 0 & 0\\ 0 & \alpha_2 & \alpha_4\\ 0 & \alpha_4 & \alpha_3\end{pmatrix},$$

$$\boldsymbol{\alpha}^{-1}\equiv\begin{pmatrix}\alpha_1^{-1} & 0 & 0\\ 0 & \alpha_3/\Delta & -\alpha_4/\Delta\\ 0 & -\alpha_4/\Delta & \alpha_2/\Delta\end{pmatrix}, \quad (2)$$

where $\alpha_2\alpha_3-\alpha_4^2=\Delta>0$, since Eq. (1) describes an ellipsoid. The elements of $\mathbf{m}$ are often, but not always, defined such that

$$m_1=\alpha_1^{-1},\quad m_2=\alpha_3/\Delta,\quad m_3=\alpha_2/\Delta,\quad m_4=-\alpha_4/\Delta. \quad (3)$$

Then the form of the mass tensor is the same as for $\boldsymbol{\alpha}$:

$$\mathbf{m}=\begin{pmatrix}m_1 & 0 & 0\\ 0 & m_2 & m_4\\ 0 & m_4 & m_3\end{pmatrix}. \quad (4)$$

The mass tensor is sometimes written[14] with $m_4=\alpha_4/\Delta$, so that the nonzero off-diagonal elements of the mass tensor must be written as $-m_4$. We will use the convention of Eqs. (3) and (4), in which case m_4 and α_4 are always of opposite sign. The expression for the tilt angle φ may readily be shown to be

$$\tan2\varphi=2\alpha_4/(\alpha_2-\alpha_3)=2m_4/(m_2-m_3) \quad (5)$$

independently of the sign of φ. The reason for our preference for the convention of Eq. (3) is so that in Eq. (5) $\tan2\varphi$ is given in terms of the components of either $\boldsymbol{\alpha}$ or $\mathbf{m}$ by relations of identical form.

It is straightforward to show that if the long direction of the ellipse in Fig. 1(a) is near the bisectrix direction, then $\alpha_3>\alpha_2$, and, for $\varphi>0$,

$$\alpha_4<0 \quad \text{and} \quad m_4>0. \quad (6)$$

It is useful to note, for φ small and positive, the long axis of the ellipse in Fig. 1(a) lies between the + bisectrix direction and the direction ΓL.

Transport Parameters

The fourth-rank tensor $\mathbf{A}$ that describes the quadratic variation of the resistivity tensor with magnetic field may be written as a 6×6 matrix in a manner analogous to the somewhat more symmetric fourth rank elastic stiffness tensor. We adopt Eq. (7) as the defining equation for $\mathbf{A}$:

$$\begin{pmatrix}S_{11}\\ S_{22}\\ S_{33}\\ S_{23}\\ S_{31}\\ S_{12}\end{pmatrix}=\begin{pmatrix}A_{11} & A_{12} & A_{13} & A_{14} & 0 & 0\\ A_{12} & A_{11} & A_{13} & -A_{14} & 0 & 0\\ A_{31} & A_{31} & A_{33} & 0 & 0 & 0\\ A_{41} & -A_{41} & 0 & A_{44} & 0 & 0\\ 0 & 0 & 0 & 0 & A_{44} & A_{41}\\ 0 & 0 & 0 & 0 & A_{14} & A_{66}\end{pmatrix}\begin{pmatrix}B_1^2\\ B_2^2\\ B_3^2\\ 2B_2B_3\\ 2B_3B_1\\ 2B_1B_2\end{pmatrix}. \quad (7)$$

[12] W. S. Boyle and G. E. Smith, in *Progress in Semiconductors* (John Wiley & Sons, Inc., New York, 1963), Vol. 7; L. C. Lovell and J. H. Wernick, J. Appl. Phys. **30**, 234 (1959).
[13] R. A. Connell and J. A. Marcus, Phys. Rev. **107**, 940 (1957).
[14] D. Shoenberg, Phil. Trans. Roy. Soc. London **A425**, 1 (1952).

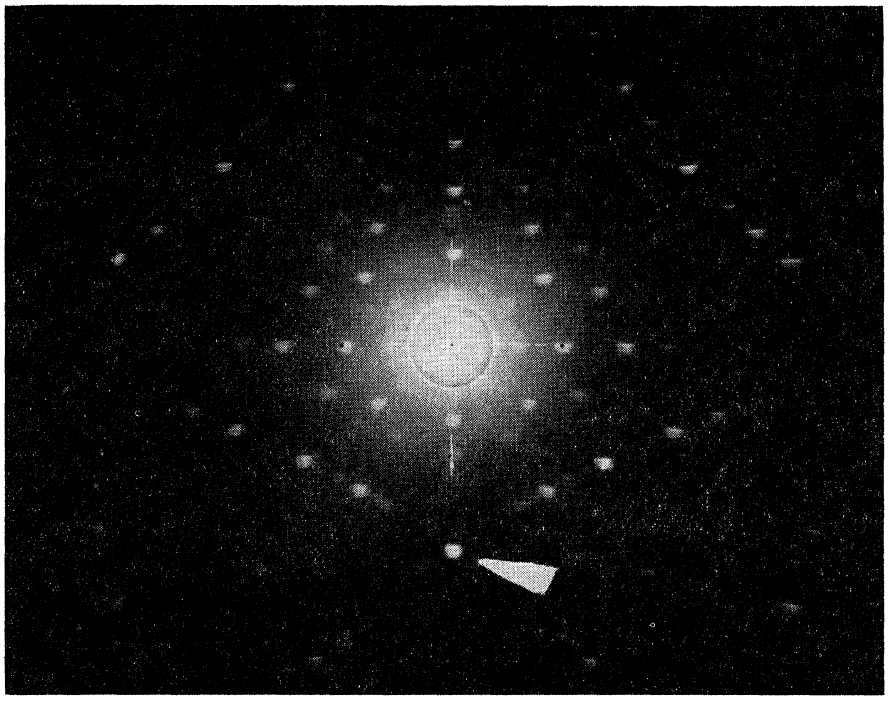


FIG. 3. A Laue back-reflection pattern for bismuth with the x-ray beam along a bisectrix axis and with the trigonal axis vertical. The orientation of the Brillouin zone for this picture is as in Fig. 1(b), with the x-ray beam normal to the paper. The indicated reflection is due to the pseudotrigonal planes represented by the lowest L point in Fig. 1(b). If the + trigonal is taken to point upward, then the + bisectrix points into the figure.

Here $A_{66}=\frac{1}{2}(A_{22}-A_{12})$ and the S_{ij} are the terms in the components of the resistivity tensor (arranged as a six-vector with no factors of 2) which depend quadratically on the components of the magnetic field $\mathbf{B}$.

There are minor variations in the definition of $\mathbf{A}$ used by various authors.[15] We prefer the convention of Eq. (7) because it is analogous to the 6×6 matrix universally used for the elastic stiffness,[9,16] particularly with respect to the location of the minus signs in the second and fourth rows.

It is possible to determine experimentally the coefficients of the tensor $\mathbf{A}$ in terms of the conventions already described for the definition of the + bisectrix direction. (A change in this convention alters the signs of A_{14} and A_{41}.) It is also possible to compute the elements of $\mathbf{A}$ in terms of the components of the conductivity tensors associated with disconnected parts of the Fermi surface. By comparing the two, the sign of the tilt angle for the conductivity tensor can be obtained from the signs of A_{14} and A_{41}. We assume for one electron ellipsoid a mobility tensor $\mathfrak{y}$ similar in form to $\boldsymbol{\alpha}$:

$$\mathfrak{y}=\begin{pmatrix}\mu_1 & 0 & 0\\ 0 & \mu_2 & \mu_4\\ 0 & \mu_4 & \mu_3\end{pmatrix}. \tag{8}$$

For Bi the scattering time is sufficiently isotropic,[17,18] so that the relative values of the components of $\mathfrak{y}$ are roughly the same as those of $\boldsymbol{\alpha}$. Specifically, we anticipate that[19] $\mathfrak{y}$ should yield the same sign for the tilt angle as does $\boldsymbol{\alpha}$. From $\mathfrak{y}$ one can calculate the electron contribution to $\mathbf{A}$. If $\mu_4=0$, $A_{41}=A_{14}=0$; for $\mu_4\neq0$, one has the relations[18]

$$\begin{aligned}A_{14}&=-\frac{\mu_4[\mu_1(\mu_1-\mu_2)]}{Ne[(\mu_1+\mu_2)+2c\nu_1]^2},\\ A_{41}&=-\frac{\mu_4[\mu_3(\mu_1-\mu_2)+\mu_4^2]}{2Ne(\mu_3+c\nu_3)[(\mu_1+\mu_2)+2c\nu_1]}.\end{aligned} \tag{9}$$

Here the ν_i refer to the hole-mobility components, N is the electron concentration, and $c\simeq1$ is the ratio of hole to electron concentrations. Since the hole surface is not tilted, the holes contribute only to the normalization of A_{14} and A_{41}, and not to their signs. It is clear that if the signs of A_{14} and A_{41} are determined experimentally, the sign of μ_4 and by reference, the signs of α_4 and the tilt angle, can be obtained for the electron Fermi surface in Bi. For Sb, the situation is more complex. Unlike Bi, for which the holes do not influence the signs of A_{14} and A_{41}, Sb has two sets of tilted carriers—one holes, the other electrons; thus for Sb there is no simple relation between the signs of A_{14} and A_{41} and

[15] T. Okada, J. Phys. Soc. Japan **12**, 1327 (1957); H. J. Juretschke, Acta Cryst. **8**, 716 (1955); C. Smith, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 6.

[16] Y. Eckstein, A. W. Lawson, and D. H. Reneker, J. Appl. Phys. **31**, 1534 (1960).

[17] R. N. Zitter, Phys. Rev. **127**, 1471 (1962).

[18] R. L. Hartman (to be published).

[19] This point will be justified in detail in Ref. 18. Suffice it to say that not only are the signs of the tilt angles for $\mathfrak{y}$ and $\boldsymbol{\alpha}$ the same, the magnitudes are similar as well.

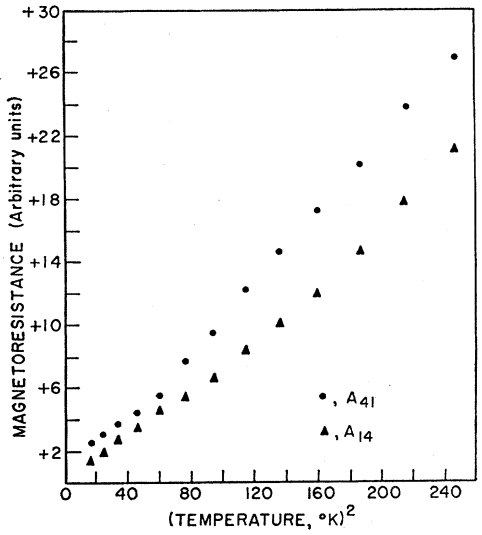


FIG. 4. Magnetoresistance coefficients A_{41} and A_{14} as functions of the temperature squared. No attempt has been made either to normalize one set of magnetoresistance data to the other or to have the same relative scale for both.

the signs of the tilts of the surfaces of constant energy of either carrier.

EXPERIMENTAL RESULTS AND DISCUSSION

Quantum Oscillations

We have measured the de Haas–Shubnikov effect in Bi, using the apparatus described earlier by Brown,[20] on samples whose orientations were subsequently determined by x rays. We have also measured the de Haas–van Alphen effect, using the apparatus described by Bhargava,[2] on a sample cut from the same crystal. From the angular dependence of the periods obtained from both of these measurements, we find the *tilt angle positive* (the magnitude is 6.4°, as previously reported[2]).

We have also measured the de Haas–van Alphen effect in Sb. To avoid any confusion due to conventions, we have oriented the Bi and Sb samples by x rays and mounted the Sb sample in the low-temperature apparatus in the same orientation as the Bi samples. The result is a tilt angle of absolute magnitude $2\pm0.5°$, in a sense opposite of that of Bi, for those carriers called electrons by Windmiller[3] who measures $-2.3°$. (The sense and magnitude of the hole tilt angle also agrees with Windmiller's results.)

[20] R. D. Brown III, IBM J. Res. Develop. **10**, 462 (1966).

Magnetoresistance

Samples of Bi cut from one of the crystals used for the above measurements were used for a complete study of the low-temperature galvanomagnetic properties of Bi.[18] The results of interest are plotted in Fig. 4 as a function of temperature. Both A_{14} and A_{41} are positive, from which, using Eqs. (5) and (9) and knowing[17,18] $\mu_1 \gg \mu_2$, we have

$$\mu_4 < 0. \tag{10}$$

This corresponds to a positive tilt angle for the electron-conductivity tensor ellipsoid, and by inference, to a positive tilt angle for the electron surfaces of constant energy.

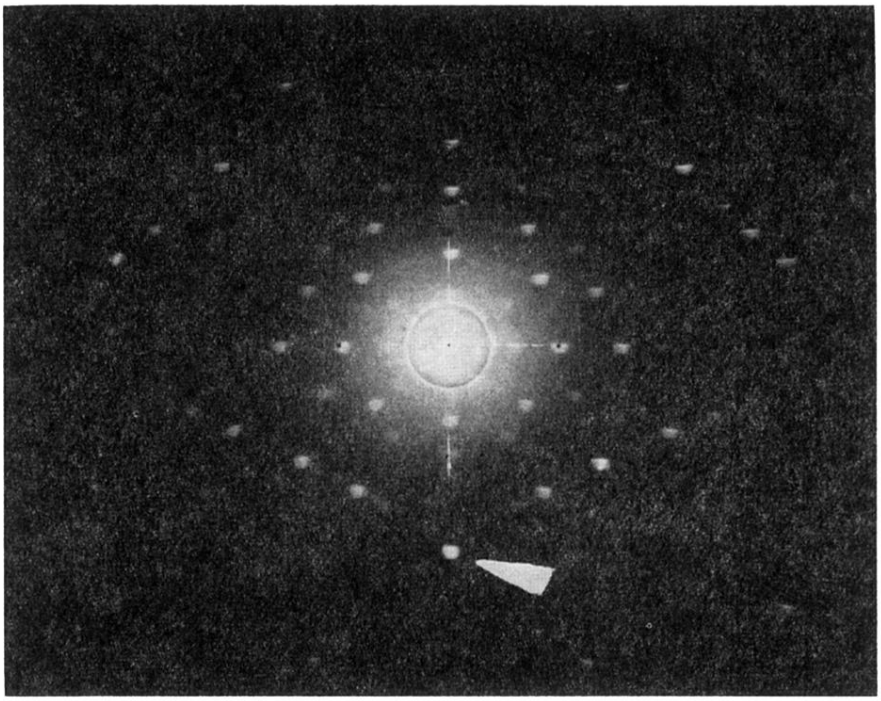
Comparison with Theory

There are two recent band calculations for Bi, one by Golin[21] and one by Ferreira.[22] Golin pays particular attention to the sign of the tilt angle (his sign conventions are the same as ours), which he calculates to be $+10°$, in reasonable agreement with the experimental value of $+6.4°$. In his second paper, Ferreira uses existing data to obtain empirically the best values for the important matrix elements that determine the detailed shape of the conduction-band energy surfaces near L. He then computes the tilt angle and finds[23] $\varphi=+3.5°$.

ACKNOWLEDGMENTS

The thinking which eventually led to the work reported here was started by a chance inquiry from Professor S. Golin regarding the experimental basis for the sign of the tilt angle. Further impetus was added by discussions one of the authors (R. L. H.) had with Dr. Alberto Lopez concerning discrepancies in the galvanomagnetic formula in the literature. We thank Professor S. Golin for sending a preprint of his work, Professor G. Pratt for sending copies of the work of Dr. L. Ferreira, and Dr. L. Ferreira for a discussion clarifying his sign conventions. J. Angilello and Dr. A. Segmuller gave us considerable aid in obtaining and interpreting the x-ray patterns.

[21] S. Golin, Phys. Rev. **166**, 643 (1968).
[22] L. G. Ferreira, J. Phys. Chem. Solids **28**, 1891 (1967); **29**, 357 (1968).
[23] L. G. Ferreira (private communication) clarified for us the sign conventions that he was using.



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