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Size Effects for Conduction in Thin Bismuth Crystals

Abstract: The size dependence of the electrical conductivity, and preliminary results for galvanomagnetic effects, in thin, single crystals of high-purity bismuth at 4.2°K are reported for a range of thicknesses comparable to the electron mean free path. The results, when interpreted according to the theory of Ham and Mattis and of Price (in the accompanying papers), show that the scattering of electrons by the surface is specular, and confirm the novel predictions of the theory for the case of specular reflection and anisotropic surfaces of constant energy.

Introduction

At 4.2°K, the mean free path of the conduction electrons in high-purity bismuth crystals is of the order of one millimeter.[1] Studies of "thin film" effects—the influence of surface scattering of the carriers on the electrical conductivity—then become possible for specimens of which the thin dimension is of the order of one millimeter. This enables measurements to be made on single crystals; i.e., thin, uniform, strain-free, reproducible samples, the interior of which may be assumed to behave like normal bulk material.

The theory of the electrical conductivity of thin metallic films has been extensively investigated for spherical surfaces of constant energy, isotropic scattering in the bulk and diffuse scattering of the carriers by the surface.[2] Ham and Mattis[3] have investigated, in detail, the situation with nonspherical energy surfaces.

It has been pointed out by Price[4] as well as by Ham and Mattis[5] that there is a size dependence for the electrical conductivity for specular scattering, if the energy surfaces are not spherical. In particular, the conductivity of progressively thinner single crystals should reach a limiting value which is explicitly dependent on the shape of the constant-energy surfaces, and their orientation with respect to the experimental geometry. The conductivity may become anisotropic, even for a crystal of cubic symmetry. This saturation is in contrast to the situation for diffuse reflection, for which the conductivity decreases monotonically (in the thin limit) with decreasing sample thickness, both for spherical and nonspherical energy surfaces.

Bismuth, because of its long carrier mean free path, its highly anisotropic conduction band, and the indications that the surface scattering is specular,[6] is an ideal material from which to obtain experimental data that may reliably be compared with the theory. The results for the conductivity presented below, while incomplete, confirm the theory as applied to bismuth. In addition, preliminary Hall and transverse magnetoresistance data also show a saturation for the thinner samples which, though not yet compared numerically with theory,[4] behave qualitatively as expected.

Properties of bismuth

Bismuth is a slightly distorted face-centered-cubic semimetal with one conduction electron per approximately 10^5 atoms at 4°K.[7] The symmetry is trigonal with three twofold rotation axes normal to the trigonal direction. The conduction band is thought to have three groups of two energy minima each, the two related to each other by inversion through the origin of the Brillouin zone, and each group related by a rotation of 120° about the trigonal axis to one of the other two groups.[6] The Fermi surface (of energy of about 0.018 ev)[7] is describable (Eq. 1) in terms of a highly anisotropic reciprocal effective mass tensor γ for each pair of minima:

$$\begin{bmatrix} \gamma_1 & 0 & 0 \\ 0 & \gamma_2 & \gamma_{23} \\ 0 & \gamma_{23} & \gamma_3 \end{bmatrix};$$

$$\frac{1}{4}\begin{bmatrix} \gamma_1+3\gamma_2 & \pm\sqrt{3}(\gamma_1-\gamma_2) & \pm 2\sqrt{3}\gamma_{23} \\ \pm\sqrt{3}(\gamma_1-\gamma_2) & 3\gamma_1+\gamma_2 & -2\gamma_{23} \\ \pm 2\sqrt{3}\gamma_{23} & -2\gamma_{23} & \gamma_3 \end{bmatrix}. \tag{1}$$

The representation chosen is such that the 1-direction

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is a particular binary direction, the 3-direction is the trigonal axis, and the 2-direction, the so-called bisectrix direction, is perpendicular to the other two. The experimental justification for this band structure, along with a current best estimate of the mass parameters, is reviewed in a recent paper by Smith.[6] The ratios $\gamma_1:\gamma_2:\gamma_3:\gamma_{23}$ may most reasonably be taken as 110:1:50:5. In addition, Smith states that specular reflection at the surface is necessary for an interpretation of his anomalous skin-effect data that is consistent with existing de Haas - van Alphen and cyclotron resonance results.

Theory for specular reflection

A particularly convenient set of orientations to use that demonstrates the contribution of surface reflection to the conductivity is for the trigonal axis to be in the surface of the "film" but normal to the longitudinal (current) direction, and for a binary direction to be rotated out of the surface by an angle ϕ. This is best seen with the aid of Price's Eq. (21), which gives explicitly the size dependence of the conductivity (averaged over the width of the crystal) of a single conduction-band ellipsoid.[4]

$$\sigma_{xx}=\gamma_{xx}\,\xi\left(1-G\left(\frac{a}{2l_z}\right)\frac{(\gamma_{xz})^2}{\gamma_{xx}\gamma_{zz}}\right), \tag{2}$$

where

$l_z=\tau(2\gamma_{zz}\mathcal{E})^{1/2}$.

Here the x direction is the current direction, z the direction normal to the surface, a the sample thickness, τ the scattering time (assumed isotropic), $\mathcal{E}$ the Fermi energy, and ξ a constant such that $\sigma_{xx}=\xi\gamma_{xx}$ in the limit $a/l_z\rightarrow\infty$. (σ_{xx} is the diagonal component of the averaged conductivity tensor for the current direction.) The function $G(y)$ (cf. Eq. 22 of Price[4]) describes the size effect for the conductivity and approaches unity as $a/l_z\rightarrow 0$. for large y, $G(y)\rightarrow 3/(4y)$. As may be seen from Fig. 1, which is the result of a machine computation of $G(y)$, 25% of the size effect still exists for $(a/l_z)=6$.

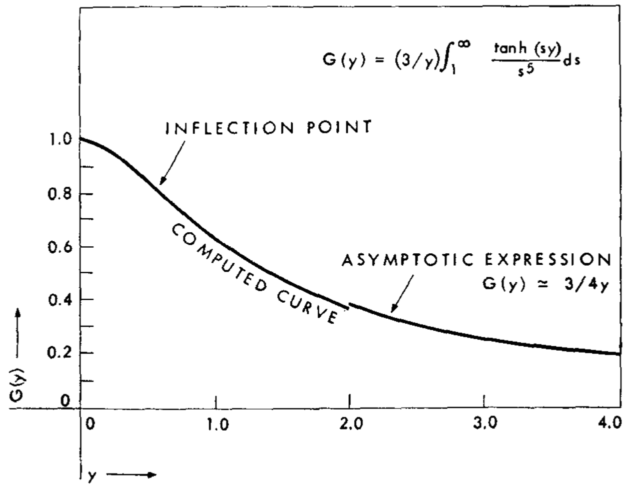


Figure 1 **The variation of the size effect for conductivity, G(y), with y.**

By rotating the matrices of Eq. (1) about the trigonal axis through an angle ϕ, one obtains the inverse mass tensors in a representation appropriate to Eq. (2). The result is given in Eq. (3).

Values of σ_{xx} for the bulk and thin-film limits for each pair of ellipsoids, and also summed over all three pairs for direct comparison with the experimental results to follow, are listed in Table 1 for several values of ϕ. When appropriate, γ_2 has been neglected compared to γ_1. The bulk conductivity is seen to be independent of ϕ; for any uniaxial crystal, the bulk conductivity is, of course, isotropic in a plane normal to the unique axis.

$$\begin{bmatrix} (\gamma_1\cos^2\phi+\gamma_2\sin^2\phi) & (\gamma_2-\gamma_1)\cos\phi\sin\phi & \gamma_{23}\sin\phi \\ (\gamma_2-\gamma_1)\cos\phi\sin\phi & (\gamma_1\sin^2\phi+\gamma_2\cos^2\phi) & \gamma_{23}\cos\phi \\ \gamma_{23}\sin\phi & \gamma_{23}\cos\phi & \gamma_3 \end{bmatrix};$$

$$\begin{bmatrix} \left[\gamma_1\cos^2\left(\phi\pm\frac{2\pi}{3}\right)+\gamma_2\sin^2\left(\phi\pm\frac{2\pi}{3}\right)\right] & (\gamma_2-\gamma_1)\cos\left(\phi\pm\frac{2\pi}{3}\right)\sin\left(\phi\pm\frac{2\pi}{3}\right) & \gamma_{23}\sin\left(\phi\pm\frac{2\pi}{3}\right) \\ (\gamma_2-\gamma_1)\cos\left(\phi\pm\frac{2\pi}{3}\right)\sin\left(\phi\pm\frac{2\pi}{3}\right) & \left[\gamma_1\sin^2\left(\phi\pm\frac{2\pi}{3}\right)+\gamma_2\cos^2\left(\phi\pm\frac{2\pi}{3}\right)\right] & \gamma_{23}\cos\left(\phi\pm\frac{2\pi}{3}\right) \\ \gamma_{23}\sin\left(\phi\pm\frac{2\pi}{3}\right) & \gamma_{23}\cos\left(\phi\pm\frac{2\pi}{3}\right) & \gamma_3 \end{bmatrix}. \tag{3}$$

Table 1 **The theoretically determined relative values of the diagonal contribution to the conductivity by each ellipsoid of the conduction band in the bulk limit (B) and the "thin film" saturation limit (S) is shown for different values of ϕ.**

	σ_{xx}^A/ξ		σ_{xx}^B/ξ		σ_{xx}^C/ξ		σ_{xx}/ξ		
ϕ	B	S	B	S	B	S	B	S	S/B
0°	γ_1	γ_1	$\gamma_1/4$	~ 0	$\gamma_1/4$	~ 0	$3\gamma_1/2$	γ_1	2/3
12°	$0.96\gamma_1$	$0.16\gamma_1$	$0.45\gamma_1$	~ 0	$0.09\gamma_1+0.9\gamma_2$	~ 0	$3\gamma_1/2$	$0.16\gamma_1$	0.11
15°	$0.94\gamma_1$	$0.11\gamma_1$	$\gamma_1/2$	~ 0	$0.06\gamma_1+\gamma_2$	$0.007\gamma_1+0.12\gamma_2$	$3\gamma_1/2$	$0.12\gamma_1$	0.08
30°	$0.75\gamma_1$	~ 0	$0.75\gamma_1$	~ 0	γ_2	γ_2	$3\gamma_1/2$	γ_2	$2\gamma_2/3\gamma_1=0.006$

Note: The longitudinal (current) direction of the sample is normal to the trigonal axis and makes an angle ϕ with a binary axis. The broad surface contains the trigonal axis. The last columns give the sum of the relative contributions of all valleys, and the ratio of the total conductivity in the two limits.

Procedures and results

Measurements were made on several single-crystal samples at 4.2°K as a function of thickness. The thickness of the samples, which typically were 2 to 4 cm long, 7 mm wide and initially 3 mm thick, was destructively varied by successively electropolishing the samples after each measurement. It is possible to reduce the thickness uniformly by more than an order of magnitude in this manner. The bismuth crystals, which consistently have a residual resistance ratio ($R_{300°}/R_{4.2°}$) greater than 400 (somewhat better than anything so far reported), are grown between glass microscope slides on a hotplate, utilizing the temperature gradient near the edge. The material was obtained, already zone refined, from Consolidated Mining and Smelting Company of Canada Ltd. The desired crystallographic orientation is obtained by seeding.

Figure 2a shows the data obtained from a sample for which $\phi=12\pm2°$, and Fig. 2b from a sample for which $\phi=0\pm3°$. In Table 2, the experimental ratio of the averaged conductivity (in the thin limit) to the bulk conductivity for these samples is compared with the theoretical values taken from Table 1. The agreement is well within experimental uncertainties, among which are the angular error, not only in ϕ but also in the orientation of the trigonal direction, and the fact that the samples initially were not sufficiently thick for the conductivity to represent the bulk limit. This last fact is the reason for the $<$ sign.

Figure 3 shows data for another sample for which $\phi\simeq0$. Attempts were made to treat the surface of this sample so that diffuse scattering might be induced, but were unsuccessful. A preferential chemical etch that changed the mirror-finish, electropolished surface to a dull matte produced no effect. Mechanical abrasion with coarse and/or fine grit, which thoroughly scratched the surface, did not make the surface scattering nonspecular. The handling of the sample during this procedure did distort the sample and lower the bulk conductivity, as is readily seen from Fig. 3.

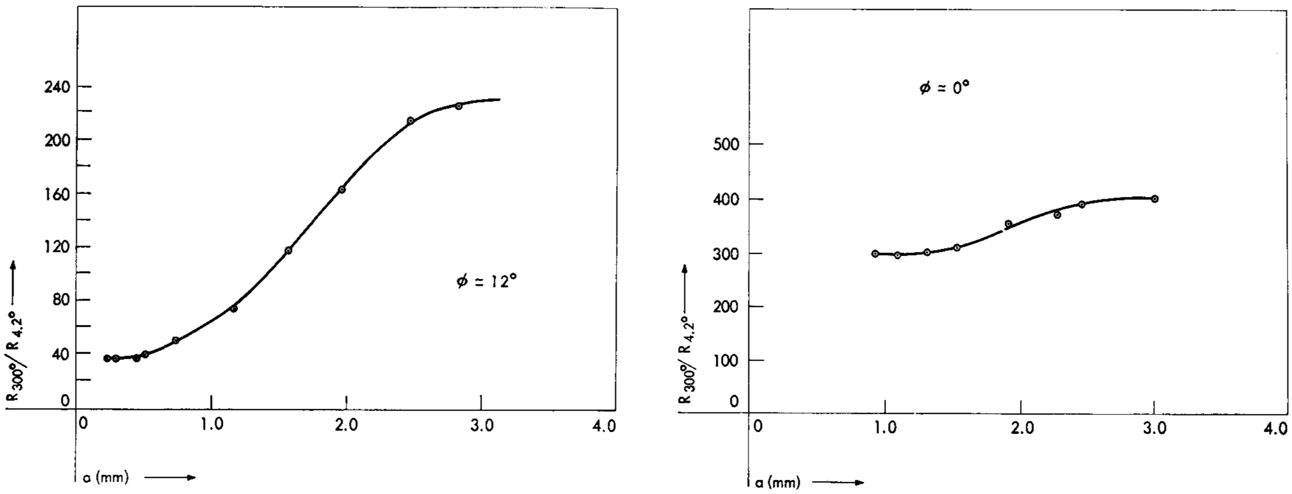
Galvanomagnetic properties of this sample were also studied, as shown in Fig. 3. Preliminary Hall data, taken with a field of 1.4 oersteds normal to the surface (corresponding to a Hall voltage of about 0.3μv) would appear to confirm the expected saturation in the thin limit.[4,5] The effects of the earth's field and of the self field due to current flow in the sample were small enough to be neglected within the experimental uncertainty. The variation of the Hall constant with thickness shown in Fig. 3, however, in general will not be the same as the variation of the longitudinal conductivity.

The transverse magnetoresistance is shown in Fig. 4. The effect is proportional to the square of the field strength for changes in conductivity by a factor of about 10^3. The magnetoconductivity varies with thickness exactly as the zero-field conductivity. In the thin limit, for this orientation, two of the three pairs of ellip-

Table 2 **A comparison of the experimental results with the (appropriate) theoretical predictions taken from Table 1.**

ϕ	0°	12°
Experiment	<0.75	<0.15
Theory	0.67	0.11

Note: The $<$ sign arises because the samples initially were not sufficiently thick to give true bulk conductivity.



a) Sample 24: 2.5 cm×3.7 mm×a(mm)

b) Sample 28: 3 cm×7 mm×a(mm)

Figure 2 **The variation with sample thickness of $R_{300°}/R_{4.2°}$ (which is proportional to conductivity at 4.2°K).**

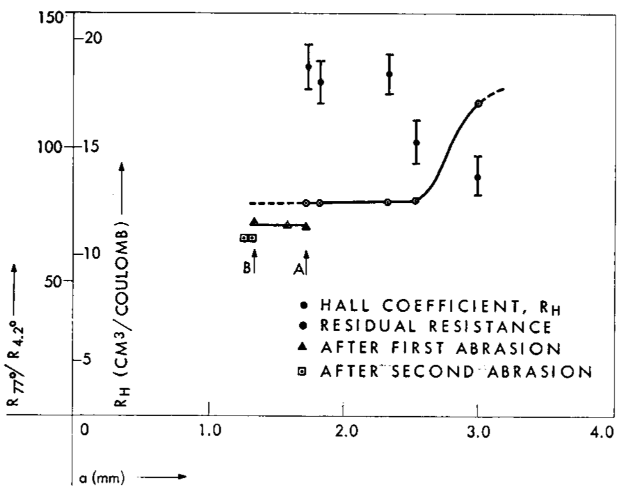
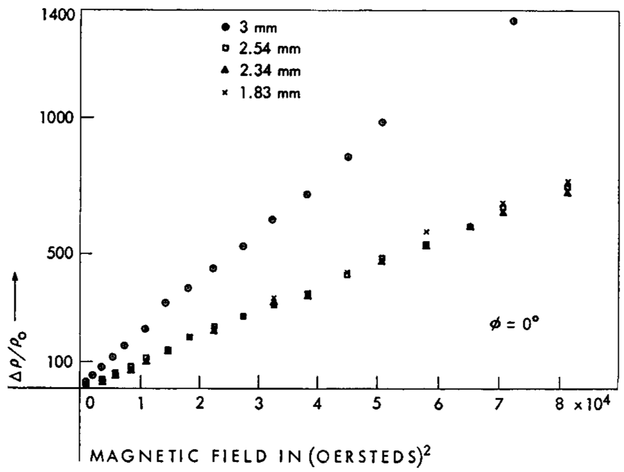
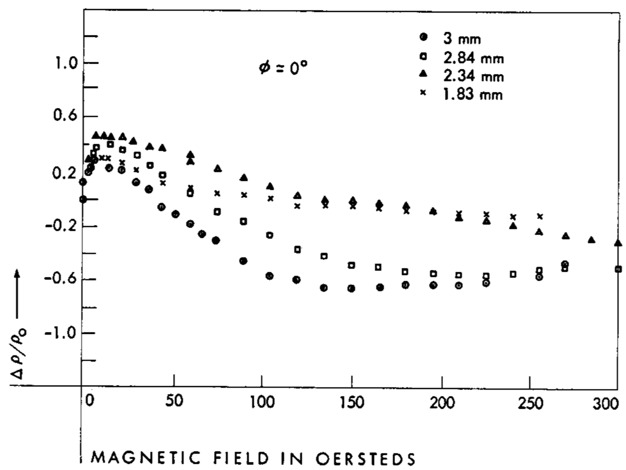


Figure 3 **The variation, at 4.2°K, with sample thickness of $R_{77°}/R_{4.2°}$, and the Hall constant R_H.**
Sample 30: $\phi \simeq 0$, $H \simeq 1.4$ oersteds. Attempts at abrading the surface at thicknesses A and B resulted only in decreasing the bulk conductivity, as the subsequent data to the left of each point indicates.

Figure 4 **The variation of transverse magnetoresistance with sample thickness at 4.2°K.** *(Sample 30.)*

Figure 5 **The variation of longitudinal magnetoresistance with sample thickness at 4.2°K.** *(Sample 30.)*





soids give zero contribution to the conductivity (cf. Table 1), while the contribution of the third pair is independent of size. The magnetoresistance in the thin limit is that contributed by the one ellipsoid.

Figure 5 shows the variation of longitudinal magnetoresistance with sample thickness. The initial increase followed by a "negative" magnetoresistance is similar to that observed by MacDonald[8] in fine sodium wires, by Babiskin[9] in bismuth at much higher temperatures and fields and by Steele[10] in antimony. The occurrence of the negative slope is very sensitive to the orientation of the magnetic field direction relative to the current flow, and is observable only over an angular spread of about $\pm 3°$. There is, presumably, nothing fundamental about this; rather, since the transverse magnetoresistance is so large, even a small component of magnetic field in the transverse direction will obscure the effect.

Discussion

It has been demonstrated that the surface scattering is specular in bismuth and that the "thin film" conductivity varies in a manner consistent with the current theories[4,5] and the existing information on the band structure. Moreover, we have not succeeded in producing a surface that gives other than specular reflection. The reasons for this are not clear, though it is reasonable that specular reflection should occur in Bi (unlike the situation for metals), for optically shiny surfaces. The argument, given earlier by Smith,[6] is that the de Broglie wavelength of the carriers at the Fermi surface is extremely long because of the low Fermi level and small effective masses, and therefore extremely small-scale surface irregularities will not be resolved by the carriers.

- *Longitudinal magnetoresistance*

The behavior of the longitudinal magnetoresistance is puzzling. In the thin crystal limit for $\phi=0$, the only pair of ellipsoids that contribute to the conductivity are so oriented as to give zero longitudinal magnetoresistance for the approximation of constant relaxation time. Thus the initial increases of $\Delta\rho/\rho$ at low fields may well be due to the fact that ϕ is not quite zero. The onset of the negative slope has in the past been associated with a magnetic field sufficiently strong to keep the carriers with spherical energy surfaces in spiral orbits away from the surface, thereby reducing the surface contribution to the resistivity.[8-10] As was the case in References 9 and 10, the magnetic field at which the effect sets in corresponds to an orbit radius which is an order of magnitude smaller than the smallest sample dimension.

- *Holes*

No mention has been made so far of the hole contribution to the conductivity. The constant-energy surface for the holes is believed to be two ellipsoids of revolution about the trigonal axis, and the density-of-states effective mass to be of the order of the free electron mass.[7]

Since for pure material the density of holes is the same as that of electrons, and their mean Fermi momentum is the same (except for a factor determined by the relative number of electron-to-hole ellipsoids), the previous argument for specular reflection should hold for holes as well. For any value of the angle ϕ, there should be no size effect for the holes, and if they made any appreciable contribution to the bulk conductivity, the observed size effect would be lower than the theoretical value. The uncertainties of the present data at best allow for only a small hole contribution. In addition, the measured bulk Hall constant which, for this orientation, equals $1/ne$ within ½% (Fig. 3), is about 18 cm^3/coulomb and corresponds to a carrier density $n \simeq (18\times 1.6\times 10^{-19})^{-1} \simeq 3.5\times 10^{17}/\text{cm}^3$ and a mobility μ of about 4×10^7 cm^2/volt sec. The value for n agrees[11] with the range of numbers calculated from the mass tensor and the known Fermi energy. On the other hand, the Hall constant would not be simply related to the carrier density if the holes made an appreciable contribution to the conductivity. It would appear, then, that the holes do not contribute significantly to the conductivity.

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