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# Electrical Transport Properties of Thin Bismuth Films*

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The resistivity, Hall coefficient, and magnetoresistance coefficient of well ordered but twinned bismuth films were measured between 1.15 and 300 K. It was found that the surface scattering in these films is not specular, contrary to the findings of some other workers. At 300 K the thickness dependence of the resistivity can be roughly fitted by the Fuchs-Sondheimer boundary-scattering theory with a surface reflection coefficient of 0.6, indicating partially diffuse scattering. It was also observed that the apparent surface scattering becomes more diffuse with decreasing temperature until at low temperatures the data can no longer be explained by the Fuchs-Sondheimer theory. This indicates that an additional size-dependent temperature-dependent scattering mechanism exists in thin-film transport. It was observed that at low temperatures the temperature dependence of the conductivity could be explained on the basis of a constant mean free path for the thicker samples. For thinner samples, the temperature dependence of the conductivity again indicates that there is an additional scattering mechanism that becomes stronger with decreasing temperature and decreasing sample thickness. Values of the mobility and mean free path, calculated from the data, were also observed to vary consistently with the sample thickness. The conclusions, drawn from the thickness dependence of the resistivity, concerning the diffuseness of the surface scattering of the charge carriers were confirmed by the dependence of the mean free path upon the sample thickness. Finally, quantum size-effect oscillations were observed in all of the transport properties of the thin bismuth films at low temperatures. The period (about 400 Å) and phase of the oscillations are in reasonable agreement with the theory and in good agreement with other values reported in the literature.

## I. INTRODUCTION

There are two types of size effects observable in thin metal samples. The "ordinary size effect," which is seen when the charge-carrier mean free path is comparable with or greater than the sample thickness, results in a resistivity which is higher than the bulk value, due to the additional scattering of the charge carriers at the sample surface. The "quantum size effect," which manifests itself when the carrier wavelength is comparable with or greater than the sample thickness, consists of oscillations in the transport properties as a function of the sample thickness with a period approximately equal to one-half of the carrier wavelength.

An approximate expression for the ordinary size effect in thin films was derived by Thomson[1] in 1901, and a more rigorous expression was obtained by Fuchs[2] in 1938. In 1952 Sondheimer[3] wrote a review article on the size effect in which he expanded and improved some of the earlier calculations. The Fuchs-Sondheimer theory contains two independent parameters: $k$, which is the ratio of the sample thickness to the bulk-carrier mean free path, and $P$, the surface reflection coefficient. $P$ is defined as the fraction of the carriers that are reflected specularly at the surface of the sample. At the time of Sondheimer's article there appeared to be good agreement between experiments on thin metal foils[4] and the theory with $P = 0$, indicating completely diffuse surface scattering.

One feature of the theory is that for perfectly specular scattering ($P = 1$) there is no size effect, and for $P < 1$ the conductivity tends toward zero as the thickness becomes much less than the mean free path. Price[5] derived a theory for specular surface scattering to include the case where the constant-energy surfaces are ellipsoidal, predicting a size effect in which the conductivity would approach a finite limit, not zero, for very thin samples. Friedman and Koenig[6] apparently verified this theory, finding specular scattering in thin bismuth crystals with electropolished surfaces. One disturbing result of their experiment, however, was that roughening the surface of the sample did not change the specularity of the scattering. Friedman[7] extended Price's theory for nonspherical energy surfaces to include partially diffuse surface scattering and made more extensive size-effect measurements on thin single crystals of bismuth. He concluded that the surface scattering was partially diffuse, but that it was impossible to fit the data to any theory that used the mean free path as a parameter. Finally, Parrott[8] proposed a theory where the reflection coefficient changes from 1 to 0 when the change in electron wave vector upon reflection exceeds a certain value. One consequence of this theory is that the conductivity should approach a finite limit for very thin samples as in the case of specular reflection for nonspherical energy surfaces. Measurements[9] on wedge-shaped samples of bismuth were in only qualitative agreement with this theory.

Andrew[4] and Olsen[10] performed experiments on the temperature dependence of the resistivity of thin wires and found that not only the residual resistivity but also the temperature-dependent part of the resistivity was size dependent. An explanation of this violation of Matthiessen's rule[11] was given by Olsen who proposed that small angle electron-phonon scattering, which is not very important in bulk material, could in thin samples easily deflect the carriers to the surface where they might be scattered diffusely. Blatt and Satz[12] made a calculation of the effect of Olsen's scattering mechanism in thin wires and obtained fair agreement with experiment. An expression for this scattering mechanism in thin films was derived by Azbel' and Gurzhi,[13] but it is very difficult to compare with experiment. Van Zytveld and Bass[14] extended the calculation by Blatt and Satz to include thin films. They also conducted size-effect experiments on thin films and wires of aluminum and concluded that their data were in qualitative agreement with the various theories, but that it was impossible to make a positive statement of agreement.

If the sample thickness becomes of the order of the carrier wavelength, the resulting discreteness of the energy spectrum appreciably modifies the density of states. This influences the relaxation time and hence the mobility. All the transport properties which depend upon the mobility will oscillate as a function of sample thickness with a period of approximately one-half of the wavelength of the carriers at the Fermi surface. These quantum oscillations were first observed in bismuth by Ogrin, Lutskii, and Elinson[15]; and a theory was worked out by Sandomirskii.[16] In a semimetal, if the sample thickness is less than one-half of the carrier wavelength, this quantization of the energy bands may even cause the overlapping valence and conduction bands to uncross, and the semimetal becomes a semiconductor.

The intent of this study was to first prepare thin bismuth films which are as pure and as structurally perfect as possible and then to observe the various size effects in the electrical transport properties of these bismuth films.

## II. EXPERIMENTAL DETAILS

The bismuth films used in these experiments were grown by slow vacuum deposition onto heated mica substrates in an ion-pumped ultra-high vacuum system. The growth parameters were: substrate temperature 155–165 °C, exaporation rate 10–100 Å/min, pressure typically $3\times10^{-9}$ Torr prior to and $1\times10^{-8}$ Torr during evaporation. This was followed by an anneal at the same substrate temperature for $\frac{1}{2}$ h.

The films grown in this manner have a well ordered but twinned crystal structure whose x-ray diffraction pattern is shown in Fig. 1. The bismuth spots are indicated by arrows and are seen to form a pattern with sixfold rotational symmetry. This is really two interlaced bismuth trigonal patterns,

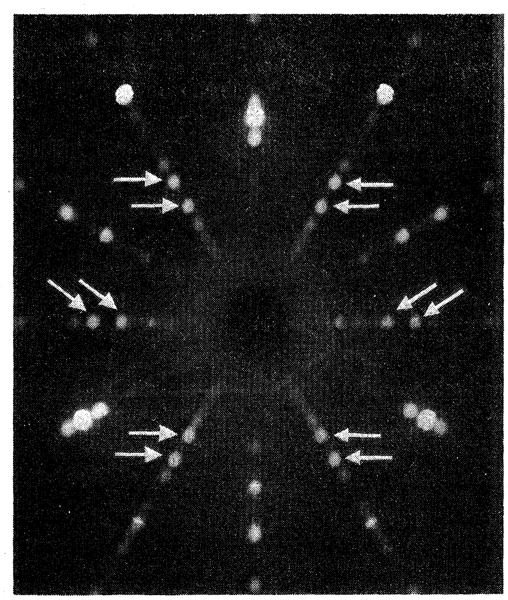

FIG. 1. Laue back-reflection x-ray diffraction pattern of a twinned bismuth film on a mica substrate. The bismuth spots are indicated by arrows.

one rotated from the other by 60°. Examination of etched sample surfaces confirms that there are two orientations present along with grain boundaries. Thus the sample is composed of crystallites all having their trigonal axis perpendicular to the plane of the film, but having two orientations differing by a rotation of 60° (or 180°) about the trigonal axis. Other workers[17,18] have reported growth of single-crystal bismuth films by the above method, but we believe the "twinned" structure is inevitable due to the symmetry of the mica substrate. The crystallite size in these films is 5–10 $\mu$ and is practically independent of sample thickness for thicknesses greater than 2000 Å. Below 2000 Å the crystallite size decreases with decreasing sample thickness. This is in agreement with the findings of others.[19] Electron micrographs of the samples show that they are continuous with no cracks or voids, and electron diffraction confirms the twinned structure.

The mica substrate, muscovite, was cleaved in deionized water prior to mounting in the evaporation system. A mask was used to delimit the sample shape which had provision for two current leads and four voltage probes. The bismuth, 99.9999% pure shot from Semi-Elements, Inc.,[20] was evaporated from a tungsten boat which was covered with a radiation shield and shutter to prevent overheating of the substrate. Sample thicknesses ranged from 710 to 36 800 Å and were determined by the Tolansky multiple-beam interference method.[21]

Measurements of the transport properties were made over the temperature range from 1.15 to 300 K. The sample resistivity and Hall coefficient were measured as the sample temperature drifted slowly, whereas the magnetoresistance coefficient and the magnetic field dependence of the Hall coefficient were determined only at the fixed temperature points 1.15, 4.2, 77, and 300 K. All of the electrical measurements were of the dc potentiometric type. The sample current 1 mA was supplied by a constant-current source and was reversed during each measurement to eliminate errors due to thermal emf's. The magnetic field used in the Hall coefficient and magnetoresistance coefficient measurements was applied perpendicular to the plane of the film. The magnetic field direction was reversed and the results appropriately averaged to eliminate any unwanted probe misalignment voltage when measuring the Hall effect and to eliminate the unwanted Hall voltage, again due to probe misalignment, when measuring the magnetoresistance. The value of the magnetic field was typically 100 G when making Hall effect measurements.

## III. EXPERIMENTAL RESULTS

### A. Comparison with Bulk Bismuth

We first compare the values of the resistivity, Hall coefficient, and magnetoresistance coefficient for the thickest sample (36 840 Å) with the bulk bismuth values at room temperature. The electron mean free path in the latter is about 1 $\mu$ (10 000 Å), so for this sample the effect of boundary scattering should be small. The values are given in Table I. It is seen that there is reasonable agreement between the values of the transport coefficients of the thick bismuth film and the standard bulk values. This suggests that the quality of the film is good, and gives some reason to believe that the thinner films are also reasonably good and that the alterations of properties are due mainly to the size.

### B. Resistivity and Hall Coefficient

A typical set of data for the temperature dependence of the resistivity and Hall coefficient for a fairly thick bismuth film (15 700 Å) is shown in Fig. 2. The points are the experimental data and the lines represent bulk bismuth in the same orientation as the film.[22] It is seen that the bulk resistivity decreases monotonically as the temperature is lowered. In the film, the resistivity first also decreases as the temperature is lowered until the mean free path of the charge carriers becomes comparable with the sample thickness. At this point boundary scattering becomes increasingly important in limiting the mean free path. Since in bismuth the number of carriers decreases as the temperature is lowered, limiting of the mean free path will cause the resistivity to increase with decreasing temperature. This is seen in Fig. 2 at temperatures below 150 K. Indeed, some effect of boundary scattering is noticeable for this sample even at 300 K. Below about 20 K the carrier concentration and mean free path and hence the resistivity become practically independent of temperature.

It has been suggested[19] that this semiconductor-like behavior observed in thin bismuth films, i.e., the negative temperature coefficient of the resistivity, is due to the uncrossing of the conduction and valence bands predicted by the quantum size-effect theory.[16] However, we believe it is a consequence of the limiting of the carrier mean free path

TABLE I. Comparison of measured transport coefficients of a thick bismuth film with bulk values. $\rho_{11}$ denotes the resistivity in the trigonal plane, $R_{21}(3)$ the Hall coefficient with the magnetic field along the trigonal axis, and $M_{11}(3)$ the magnetoresistance coefficient measured in the trigonal plane with the magnetic field along the trigonal axis.

| | Bulk[a] | 36 840-Å film |
|---|---|---|
| $\rho_{11}$ ($\Omega$ cm) | $1.20\times10^{-4}$ | $1.15\times10^{-4}$ |
| $R_{21}(3)$ ($\Omega$ cm/G) | $+4.5\times10^{-10}$ | $+5.0\times10^{-10}$ |
| $M_{11}(3)$ ($G^{-2}$) | $27\times10^{-10}$ | $23\times10^{-10}$ |

[a]Reference 22.

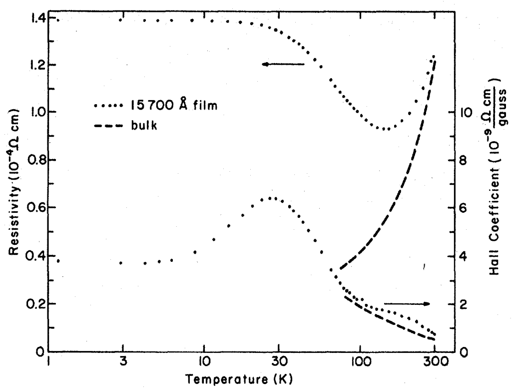


FIG. 2. Temperature dependence of the resistivity and Hall coefficient for a film with thickness 15 700 Å.

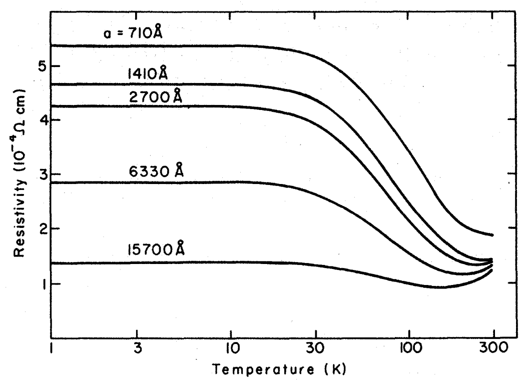


FIG. 3. Temperature dependence of the resistivity for films of various thicknesses.

and the decrease in the number of carriers with decreasing temperature. This will be discussed in detail in Sec. IV A 2 on the temperature dependence of the conductivity.

The Hall coefficient that was measured is labeled $R_{21}(3)$ in the notation of Abeles and Meiboom[22] designating the magnetic field along the trigonal direction, the measured electric field along the bisectrix, and the current along the binary axis. The bulk data available for the Hall coefficient of bismuth in this orientation are not very reliable, particularly below 77 K. This is because the coefficient is small and positive while in other directions it is large and negative, so that it is virtually impossible to position the voltage probes so as not to mix in the large negative components. Figure 2 shows that the Hall coefficient of the film increases with decreasing temperature as in the bulk, although the functional dependence is not the same. The flattening in the temperature dependence of the Hall coefficient, at about 150 K in this figure, regularly occurs at the same temperature as the resistivity minimum. As the temperature is lowered further, the Hall coefficient goes through a maximum, then decreases and becomes temperature independent at low temperatures.

A composite plot of the temperature dependence of the resistivity for samples of various thicknesses is shown in Fig. 3 where the bottom curve is the one shown previously in Fig. 2. Several features to be noted are: (i) The resistivity varies consistently with sample thickness, (ii) the resistivity minimum shifts towards higher temperatures with decreasing sample thickness, and (iii) the temperature at which the resistivity becomes temperature independent is independent of thickness. The thickness dependence of the resistivity at constant temperature and the behavior of the resistivity at low temperatures will be discussed in Sec. IV. A plot of the temperature at which the resistivity reaches a minimum vs sample thickness shows that the data lie on a smooth curve, supporting the idea that the resistivity minimum occurs because of a limiting of the carrier mean free path by boundary scattering. The mean free path becomes comparable with the sample thickness at higher temperatures for thinner films causing the resistivity minima to occur at higher temperatures.

Figure 4 is a plot of the temperature dependence of the Hall coefficient showing data for several samples of different thicknesses. Again the bottom curve is the one shown in Fig. 2. The flat portion of the Hall coefficient vs temperature curve shifts to higher temperatures for thinner films as did the resistivity minimum. It is seen that the value of the Hall coefficient, and in particular its low-temperature behavior, is very dependent upon the sample thickness. The expression for the Hall coefficient of an isotropic material with two types of carriers is[23]

$$R=(p\mu_p^2-n\mu_n^2)/e(p\mu_p+n\mu_n)^2\ . \qquad (1)$$

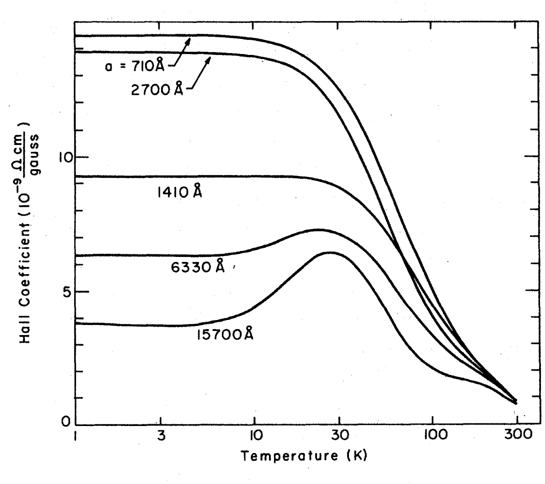


FIG. 4. Temperature dependence of the Hall coefficient for films of various thicknesses.

Although this formula does not apply to bismuth, which is highly anisotropic, it illustrates that the Hall coefficient may be very sensitive to small differences in the number of electrons and holes and to differences in the electron and hole mobilities, making it difficult to account in detail for the observed behavior.

### C. Magnetoresistance and Field Dependence of Hall Coefficient

The expression for the magnetoresistance coefficient for the case of two types of carriers in an isotropic crystal is[24]

$$M = \mu_n \mu_p \, . \tag{2}$$

The magnetoresistance data are qualitatively consistent with this expression; i.e., the magnetoresistance coefficient is larger for conditions of higher mobility, namely, the thicker samples and the lower temperatures. The magnetoresistance coefficient is moderately dependent upon the magnetic field intensity for cases of high mobility, for example, about 30% reduction at 3.5 kG for a thick film at 4.2 K. Conversely, it is practically independent of field for cases of low mobility.

The Hall coefficient, as well as the magnetoresistance, was found to be strongly field dependent for cases of higher mobility. It even changed sign, from positive to negative, for high fields in the thicker samples at low temperatures. Again the field dependence was small for cases of low mobility.

### D. Imperfect Samples

It was found that when the bismuth films contain imperfections, such as impurities or slight crystallite misalignment, the transport properties are drastically altered: The resistivity is higher particularly at low temperatures, the resistivity minimum occurs at a higher temperature, the magnetoresistance coefficient is smaller, and the Hall coefficient changes sign with decreasing temperature. The resistivity and magnetoresistance behavior are both indicative of lower mobility, while the change in sign of the Hall coefficient may arise in several ways such as crystal misalignment mixing in the negative Hall component, impurity doping changing the concentrations of electrons and holes, or some type of scattering which affects the electron and hole mobilities differently. Values of the Hall coefficient for bismuth films recently reported[25] show a change in sign with decreasing temperature, and in view of the foregoing results, it is felt that the films may have been of somewhat poorer quality than the present ones.

### E. Quantum Size-Effect Regime

In this subsection we present data for samples in the quantum size-effect regime, i.e., samples with thicknesses less than 2000 Å. As an example of the quantum size effect, Fig. 5 shows the thickness dependence of the resistivity ratios $\rho_{4.2}/\rho_{300\text{ K}}$ and $\rho_{77}/\rho_{300\text{ K}}$. The ratios were plotted in order to eliminate the error in the absolute resistivity resulting from the thickness measurement. The horizontal error bars give an estimate of the error in the thickness measurement. Relative errors in the resistivity ratio arising from the intercomparison of different samples can be estimated by comparing thicker samples, where there is no quantum size effect. This error is found to be about 2% (this applies to the resistance *ratio*, not the absolute resistivity). The Hall and magnetoresistance coefficients were also found to exhibit the same type of oscillatory behavior as the resistivity ratio at low temperatures.

The data will be compared with the quantum size-effect theory in Sec. IV.

## IV. DISCUSSION AND CONCLUSIONS

### A. Comparison with Theory: Classical Regime

#### 1. *Size Dependence of Resistivity*

The Fuchs-Sondheimer boundary scattering theory gives values for the resistivity ratio $\rho/\rho_\infty$ for various values of two parameters: $k$, the ratio of the sample thickness to the bulk mean free path, and $P$, the surface scattering reflection coefficient. In order to compare the experimental data with the Fuchs-Sondheimer theory, the bulk resistivity and bulk mean free path must be known. In the present case, the mean free path in the trigonal direction (perpendicular to the film plane) is of interest. Since in this direction $\mu_n \gg \mu_p$, we may estimate the electron mean free path from the one-carrier formula

$$l = v_f \tau = \frac{(3\pi^2)^{1/3} \hbar n^{1/3}}{m^*} \left( \frac{m^* \mu}{e} \right) \, , \tag{3}$$

which, with $\rho_\infty^{-1} \simeq ne\mu_n$, gives

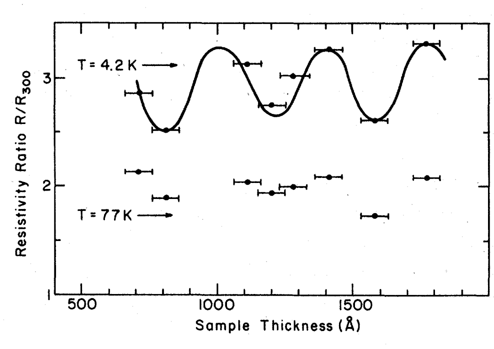


FIG. 5. Thickness dependence of the resistivity ratio at 4.2 and 77 K.

$$l_n = (3\pi^2)^{1/3}\hbar/e^2 n^{2/3}\rho_\infty \ . \tag{4}$$

At 300 K using the standard bulk values of the resistivity and the carrier concentration, Eq. (4) yields $l_n = 0.59\ \mu$. This value of the mean free path was used along with various assumed values of the reflection coefficient for comparison with the experimental data. It was found that there is a fair fit to the Fuchs-Sondheimer theory for $P = 0.6$, that is for partially diffuse surface scattering.

For the data at lower temperatures it is difficult to estimate the bulk resistivity value appropriate for our samples, in which some scattering by grain boundaries and imperfections is inevitably present. However, the Fuchs-Sondheimer theory gives the following expression for the resistivity in the limit of thick films[3]:

$$\rho = \rho_\infty [1 + (3l/8a)(1-P)] \ , \tag{5}$$

where $a$ is the sample thickness. Equation (5) predicts a linear dependence of $\rho$ on $1/a$ for thick films. To demonstrate this, Fig. 6 shows a plot of the sample resistivity vs the reciprocal of the thickness for temperatures of 300, 77, and 4.2 K for thicknesses greater than 2000 Å, i.e., thicker than the quantum size-effect region. It is seen that there is a good straight-line fit to the data for the thicker samples at all temperatures. The bulk sample resistivity is obtained from the intercept at $(1/a) = 0$; and by assuming a value for the carrier concentration, the appropriate bulk mean free path can then be determined using Eq. (4). The slope of the straight line along with the bulk resistivity and mean free path allow a determination of the reflection coefficient $P$. The parameters determined in this manner from Fig. 6 are given in Table II. The value of the apparent bulk resistivity obtained from the intercept on the graph (column 2) agrees with the standard bulk value (column 3) for 300 K, while for the lower temperatures the apparent bulk resistivity is larger than the standard value. At low temperatures where the mean free path for lattice scatter-

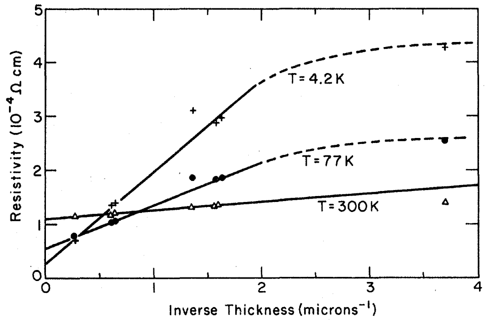


FIG. 6. Dependence of the resistivity on the reciprocal of the thickness at 4.2, 77, and 300 K.

TABLE II. Values of the bulk resistivity ($\rho_\infty$), bulk mean free path ($l$), and reflection coefficient ($P$), determined from Fig. 6.

| $T$(K) | $\rho_\infty$ ($\Omega$ cm) | $\rho_\infty std$($\Omega$ cm)[a] | $n$(cm$^{-3}$) | $l(\mu)$ | $P$ |
|---|---|---|---|---|---|
| 300 | $1.14\times10^{-4}$ | $1.20\times10^{-4}$ | $2.6\times10^{18}$ | 0.59 | 0.56 |
| 77 | $0.58\times10^{-4}$ | $0.35\times10^{-4}$ | $5.0\times10^{17}$ | 3.5 | −0.02 |
| 4.2 | $0.31\times10^{-4}$ | $3\times10^{-7}$ | $3.3\times10^{17}$ | 8.0 | −0.75 |

[a]References 22 and 7.

ing is long, this is probably due, in the main, to scattering at the crystallite boundaries in the film giving rise to a larger "bulk" resistivity than in a large single-crystal sample. However, since the crystallite size does not change appreciably with sample thickness, the size effects can still be attributed solely to surface scattering and not to grain-boundary scattering. It is seen that the apparent surface-reflection coefficient determined in this manner is a function of temperature. At 300 K, $P = 0.56$, in agreement with the previously mentioned findings indicating partially diffuse surface scattering. At 77 K, $P$ is approximately zero, ostensibly indicating completely diffuse scattering. But at 4.2 K, $P = -0.75$. This negative value of the reflection coefficient is completely meaningless within the framework of the Fuchs-Sondheimer theory; however, it does indicate that there is another scattering mechanism operating which is both size and temperature dependent.

A similar result for the resistivity of thin wires was found by Olsen.[10] He attributed the additional size-dependent temperature-dependent scattering mechanism to the increased importance of small-angle electron-phonon scattering in thin wires. In bulk material, small-angle electron-phonon scattering is abundant, but it does not contribute appreciably to the resistivity. However, in thin wires and films small-angle scattering will deflect an electron to the surface where it may be scattered diffusely. Hence small-angle electron-phonon scattering, which is temperature dependent, will result in a size-dependent resistivity in thin wires and films. As noted above, Blatt and Satz[12] found this mechanism to be in qualitative agreement with available experimental data for the resistivity of thin wires. Azbel' and Gurzhi[13] made the calculation for films. Their expression is difficult to compare with experiment, but qualitatively it does *not* give the correct temperature dependence for our data.

The extension of the Fuchs-Sondheimer theory given by Price[5] for nonspherical energy surfaces is only a small correction, about 1%, for bismuth with the thin direction along the trigonal axis, while the modification proposed by Parrott,[8] where the reflection coefficient changes from 1 to 0, can never result in scattering that is more diffuse than that given by $P = 0$ in the Fuchs-Sondheimer theory.

Hence neither of these modifications is able to account for the observed surface scattering.

As noted previously, Friedman[7] performed size-effect measurements on thin single crystals of bismuth and concluded that the surface scattering of the carriers was partially diffuse, but that it was impossible to fit the data to any theory that used the carrier mean free path as a parameter.

### 2. *Temperature Dependence of Resistivity*

It was noted in connection with Fig. 3 that the temperature at which the resistivity became temperature independent did not depend upon the sample thickness. This can be explained by the fact that when the mean free path is truly limited by a combination of surface and grain-boundary scattering and is thus temperature independent, the temperature dependence of the resistivity is determined only by the carrier concentration, which should be the same for all samples. Rewriting Eq. (4) we find

$$\sigma \propto n^{2/3} l \; . \qquad (6)$$

Thus, for a constant mean free path, the conductivity should be proportional to the $\frac{2}{3}$ power of the carrier concentration, i.e.,

$$\sigma_T / \sigma_0 = (n_T / n_0)^{2/3} \; , \qquad (7)$$

where $\sigma_0$ and $\sigma_T$ denote the conductivity at absolute zero and at temperature $T$, respectively, and $n_0$ and $n_T$ similarly denote the carrier concentration.

Figure 7 is a logarithmic plot of the conductivity vs the carrier concentration ratio $(n_T/n_0)$ for several samples of different thicknesses. A temperature scale is included at the top of the graph for reference. Values of the conductivity as function of temperature were obtained from the experimental data, and the temperature dependence of the carrier concentration was calculated using Cohen's[26] non-ellipsoidal nonparabolic-band model of bismuth with band parameters given by Bate and Einspruch.[27] If the foregoing assumption of constant mean free path is true, the data points should lie on a straight line with slope $\frac{2}{3}$. This is the case for the thickest sample and is reasonable since the crystallite size of about 5 to 10 $\mu$ and the thickness of 1.6 $\mu$ are both much less than the phonon-scattering mean free path at low temperatures. However, for a thinner sample (6330 Å), the slope of the line is greater than $\frac{2}{3}$. It can be seen from Eq. (6) that a steeper slope indicates that the mean free path increases with increasing temperature. This confirms what was inferred from the results of Fig. 6, i.e., that there is an additional scattering which becomes stronger with decreasing temperature and decreasing sample thickness. Whereas previously this

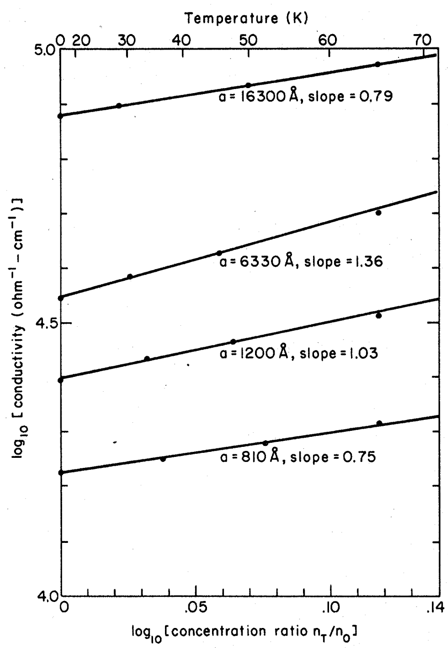


FIG. 7. Logarithmic plot of the conductivity vs the carrier concentration ratio for films of various thicknesses.

conclusion was reached by measuring the resistivity of samples of various thicknesses at a fixed temperature, we are here considering the temperature dependence of the resistivity of a single sample. Thus, any possible effects due to different growth conditions or variations of the crystallite size with sample thickness are eliminated.

Finally, it is seen that the slopes of the curves for the thinnest samples (in the quantum size-effect region) again become smaller. However, the temperature dependence of the carrier concentration in this region is not well known, and there is some indication that the carrier concentration ratio is smaller for these thinner samples. If the conductivity of the thin samples had been compared with the smaller carrier concentration ratio, then the slope of the line would be greater, in at least qualitative agreement with the samples of intermediate thicknesses.

### 3. *Mobility and Mean Free Path*

The Hall coefficient and the magnetoresistance coefficient vary smoothly with the sample thickness, but there are no theories with which to compare the data. Therefore, in order to have a means of intercomparing all of the various measurements, we have calculated values for the electron and hole mobilities, the electron and hole mean free paths, and the carrier concentrations at 4.2, 77, and 300 K using the expressions for the transport coefficients for two types of carriers in an isotropic medium. The expressions used are Eqs. (1) and (2) and also

$$\sigma = ne\mu_n + pe\mu_p . \qquad (8)$$

It was found that the calculated values of the mobility and mean free path vary in a consistent manner with the sample thickness and temperature. However, even for the thickest sample at 300 K, for which the values of the transport properties agree with the bulk values, the isotropic expressions underestimate the value of the mobility and mean free path. For the thicker samples, the calculated carrier concentration is practically independent of thickness as it should be, while for thinner samples it increases with decreasing thickness. This cannot be explained at present, other than to say that the isotropic expressions are not strictly correct; they do, however, give some approximation to the actual situation.

Figure 8 shows the thickness dependence of the ratio of the sample mean free path to that in an infinitely thick sample at 300 K. The points are taken from the calculated values of the mean free path, and the curve is the prediction of the Fuchs-Sondheimer theory assuming $l = 0.6\ \mu$ and $P = 0.6$, which are the values found from the plot of the thickness dependence of the resistivity at 300 K. It is seen that there is a good fit between the data and the form of the Fuchs-Sondheimer curve, indicating that the surface scattering is partially diffuse; however, the extrapolated calculated value of the mean free path for a film of infinite thickness, $(l_{\text{cal}})_\infty = 0.185\ \mu$, does not agree with the value of the bulk mean free path used in the Fuchs-Sondheimer theory, $l = 0.6\ \mu$. This is again an indication that the isotropic calculation underestimates the value of the mean free path.

At low temperatures the calculated values of the mean free path vary smoothly with the sample thickness, but the data do not fit the Fuchs-Sondheimer theory. The observed surface scattering appears to be more diffuse than allowed for by the theory, which once again points out the existence of an additional size- and temperature-dependent scattering mechanism.

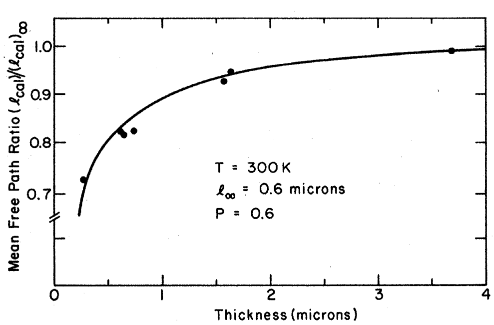


FIG. 8. Thickness dependence of the carrier mean free path at 300 K. The curve is the prediction of the Fuchs-Sondheimer theory for $l = 0.6\ \mu$ and $P = 0.6$.

### B. Comparison with Theory: Quantum Regime

Hitherto, we have mainly been concerned with the thicker films, i.e., those with thicknesses greater than 2000 Å. For samples thinner than this, the carrier wavelength becomes comparable with the sample thickness and the quantum size effect becomes observable.

The quantum size-effect theory of Sandomirskii[16] predicts that the mobility, resistivity, and magnetoresistance coefficient should oscillate as functions of sample thickness with a period $\bar{a}$ in thickness given by

$$\bar{a} = \pi\hbar/(2m'\Delta)^{1/2} , \qquad (9)$$

where

$$m' = m_p m_n/(m_p + m_n) ,$$

the $m$'s being the effective masses in a direction perpendicular to the plane of the film, and $\Delta$ being the energy overlap of the conduction and valence bands. The Hall coefficient should not oscillate but should have a regular change in slope with period $\bar{a}$. When the sample thickness becomes less than $\bar{a}$, the overlap of the conduction and valence bands is eliminated and the semimetal should become a semiconductor causing the resistivity and Hall coefficient to become very large.

Now, for bismuth in this orientation, $m_n \simeq 0.01 m_0$, $m_p \simeq m_0$, and $\Delta = 30$ meV. Using these values in Eq. (9) we obtain a value of $\bar{a} = 350$ Å for the period of the oscillations.

Examination of Fig. 5 shows that the resistivity ratio does oscillate as a function of sample thickness with a period of about 400 Å, in qualitative agreement with the prediction of the theory. The values of the effective masses and energy-band overlap used in the calculation of the period are not known well enough to expect better agreement. It is seen that the oscillations damp out at higher temperatures, being barely detectable at 300 K, as the relaxation time is shortened and the uncertainity in the energy levels becomes comparable with the spacing between them. The thinnest sample measured was 710 Å, and hence it was not possible to observe the transition from a semimetal to a semiconductor expected at a thickness of about 400 Å.

The Hall and magnetoresistance coefficients were also observed to oscillate with a period of about 400 Å even though the oscillations in the Hall coefficient were not predicted by the present theory.

In order to tie all of the measurements together,

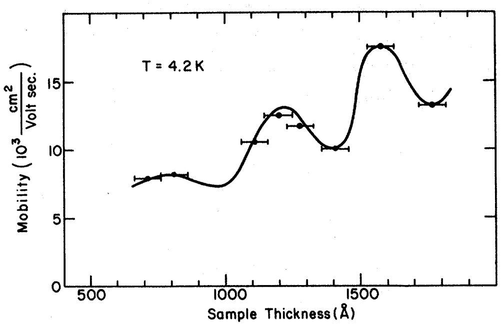


FIG. 9. Thickness dependence of the carrier mobility at 4.2 K.

Fig. 9 is a plot of the thickness dependence of the mobility at 4.2 K calculated from the experimental values of the resistivity, Hall coefficient, and magnetoresistance coefficient. It is seen that the mobility also oscillates with thickness with a period of about 400 Å as predicted by the theory. The mobility oscillations increase with increasing thickness since the oscillatory behavior is superimposed upon a general increase in mobility due to the ordinary size effect. Comparison of Figs. 5 and 9 shows that the maxima in the resistivity-ratio oscillations occur at the minima of the mobility oscillations as would be expected.

The quantum size effect was first observed in thin bismuth films by Ogrin, Lutskii, and Elinson.[15] They found oscillations in the resistivity, Hall coefficient, magnetoresistance, and mobility with a period of about 400 Å. Duggal and Rup[19] confirmed the quantum size-effect oscillations, with a period of 400 Å, in thin bismuth films, but there appeared to be an extra oscillation at a thickness of about 800 Å. Finally, Fesenko[28] observed that the period of the oscillations in the resistivity varied with sample thickness being about 250 Å at a thickness of 2000 Å, about 100 Å at 1000 Å, and about 40 Å at 500 Å. He attributed the difference in the period for the thicker films, 250 Å as compared to 400 Å for other workers, to differences in the carrier concentration due to different growth conditions. The present results appear to be in good agreement with those of the majority of the other authors, although they disagree with those of Fesenko.

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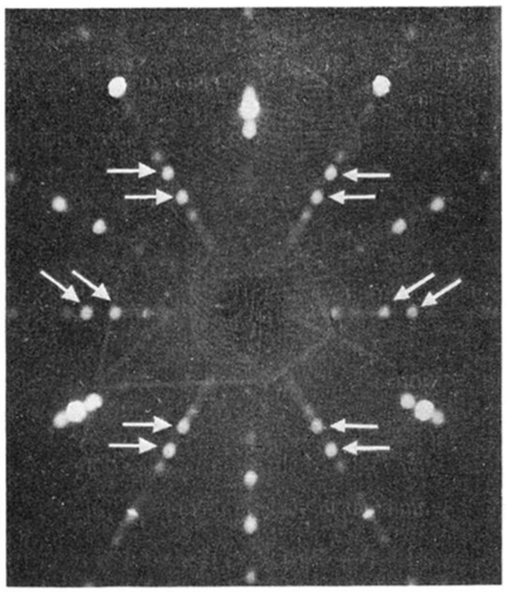

FIG. 1. Laue back-reflection x-ray diffraction pattern of a twinned bismuth film on a mica substrate. The bismuth spots are indicated by arrows.