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XVII-6. Electron Transport Phenomena in Thin Films of Bismuth

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Resistivity, Hall coefficient and magnetoresistance of Bi films at 300°K, 77°K and 4.2°K are studied. The size dependence of effective mobilities of electrons and holes is demonstrated. Employing a simple computation method, the carrier concentration is found in agreement with values given in the literatures. The size dependence of resistivity of a single crystal has also been investigated. In a longitudinal magnetic field, the resistivity shows a maximum around 10 gauss at 4.2°K, from this result a value of Fermi momentum is estimated.

§ 1. Introduction

Bismuth is generally known as a semimetal. The small overlap (~37 meV) between the conduction and the valence bands results in equal number of electrons and holes with low Fermi energies. If the overlap diminishes, as has been found in Bi-Sb alloys, Bi will become a semiconductor. In many respects, however, pure Bi exhibits physical properties very much similar to those of semiconductors. In particular, for Bi films several microns thick prepared by evaporation, the temperature coefficient of resistivity is negative. In the present investigation, we have attempted to study the effect of sample thickness on some transport properties in Bi films.

§ 2. The Size Effect

It has been known for many years that a specimen having dimensions comparable to the bulk mean free path of charge carriers, boundary scattering will influence its transport properties. This size effect has been demonstrated by many experimental observations.[1,2] On the other hand, most of the theoretical work up to date are based upon oversimplified models, primarily because of so little is known about the surface potential which is responsible for the boundary scattering of electrons.

Owing to its unusually long electron mean free path, Bi is a suitable material for the study of size effects.[3–6] However, the presence of two components of charge carriers and the highly anisotropic Fermi surfaces have made detailed comparison between theory and experiment difficult. In the present work, we shall be mainly concerned with the gross features of the size effects in Bi films. A simple method will be used to deduce the average mobilities of electrons and holes.

For an isotropic two-component system consisting of equal number of electrons and holes, the resistivity (ρ), the Hall coefficient (R) and the magnetoresistance coefficient ($B=\{\rho(H)-\rho(0)\}/\rho(0)H^2$) are given by:[7]

$$\frac{1}{\rho}=Ne(\mu_1+\mu_2)\,, \tag{1}$$

$$R=\frac{1}{Nec}\,\frac{\mu_2-\mu_1}{\mu_2+\mu_1}\,, \tag{2}$$

$$B=\frac{\mu_1\mu_2}{c^2}\,, \tag{3}$$

where N is the concentration of electrons ($N=P=$hole concentration), μ_2 and μ_1 are the mobility of electrons and holes, respectively. For a given sample, measured values of ρ, R and B can be used to solve for the three unknowns μ_1, μ_2 and N by employing eqs. (1)–(3).

In our investigation of the Bi films, samples are all polycrystals with a large number of grains, we may use eqs. (1)–(3) to analyze ρ, R and B provided μ_1 and μ_2 are taken as the average mobilities. We shall use this simple method to deduce μ_1 and μ_2 and N for different thicknesses. It was expected that when the thickness becomes comparable to the bulk mean free path of electrons or the size of grains, the μ's will become size-dependent and shall be interpreted as the "effective mobilities." We may define this effective mobility by $\mu_i=e\tau_i/m_i (i=1, 2)$, where m_i is the density-of-state mass and τ_i the average time between collisions by taking the boundary scattering into account.

It is worth noting that the Hall coefficient R depends only on N, μ_2/μ_1 in accordance with eq. (2). Hence R will be insensitive to size variation. Measurements of this coefficient are insufficient to reveal the nature of size effect. Furthermore, from eqs. (1) and (3) we observe that

$$(Ne\rho)^{-2}-4Bc^2=(\mu_2-\mu_1)^2\geq 0\ . \qquad (4)$$

Thus, for a set of measured values of ρ and B, eq. (4) places an upper limit for the carrier concentration N. This relation can be used as a check for the approximations assumed in our computation.

§ 3. Experimental

Bi films (1 cm$\times$3 cm$\times d$, $d\sim$several microns) were prepared by evaporating pure Bi (99.9999%) onto glass substrates in a vacuum of 10^{-5}–10^{-6} mm.Hg. Sample thickness was determined by weighing, the systematic error was estimated to be several percent. X-ray pictures showed that these films are all polycrystals. Single crystal samples were grown from melt on a hot plate. Crystal orientation was determined by chemical etching and x-ray examination. Samples (0.5 cm $\times$1.5 cm$\times d$, $d\sim$0.14–1.8 mm) were first shaped using a spark cutter and then etched in 35% HNO_3. Successive reduction of thickness between measurements was done by chemical etching in a solution of '6 parts of fuming nitric acid+6 parts of glacial acetic acid+1 part of water'. Measurements of ρ, R and B were made by the conventional 6-terminal method in a standard stainless-steel dewar.

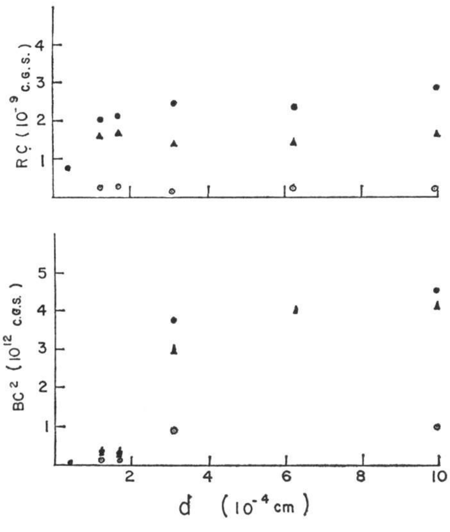

Fig. 1. The size dependence of resistivity (ρ), Hall coefficient (R) and magnetoresistance coefficient (B) of Bi films.

§ 4. Results and Discussion

The measured values of resistivity, Hall coefficient and magnetoresistance coefficient of evaporated films are shown in Fig. 1. Data were taken at 300°K, 77°K and 4.2°K and are plotted against the film thickness d. Because of the limits of accuracy and insufficient number of data points, we have made no attempt of fitting our size effect results into any model so as to determine the functional dependence of resistivity on thickness.

We first note that when temperature is reduced from 300°K to 4.2°K, the resistivity in all films increases. In this respect, the Bi films behave more like a semiconductor. It is believed that in these films, the electron-phonon interaction plays only a minor role in determining the resistivity. However, because of the low Fermi energies, the temperature dependence of charge concentration can become predominant. Hence when temperature is reduced, the decrease in number of charge carriers will surpass the increase in mean free path, thereby results in an increase of resistivity.

When the thickness is decreased, the resistivity starts to increase for $d\leq 2-3\times 10^{-4}$ cm. Also, the magnetoresistance coefficient B starts to decrease as an indication of reduction of effective mean free path. The Hall coefficient remains essentially constant. This indicates that the ratio of μ_2/μ_1 is almost independent of d or the surface scattering has similar effects on both the electrons and holes. From these results, we shall regard the measured values for $d\geq 3\times 10^{-4}$ cm as those characterizing the bulk properties.

Using eqs. (1)–(3), we can solve for $N(=P)$ and the effective mobilities μ_1 and μ_2. We also note that eqs. (1)–(3) are based on the assumption that the surface scattering is negligible and these equations are not strictly valid for thin films with $d\leq 3\times 10^{-4}$ cm. To calculate N, we use only the values of ρ, R and B for $d\geq 3\times 10^{-4}$ cm. From eq. (4), we obtain the upper limits for carrier concentration $N_{\max}$ at three different temperatures. Using the density-of-state mass obtained elsewhere[8] ($m_1=0.15\, m_0$ for holes and $m_2=0.052\, m_0$ for electrons), we can compute the relaxation times τ_1 and τ_2 for holes and electrons. These results are summarized in Table I. The

Table I.

T	$N(10^{17}/\text{c.c.})$	$N_{max}(10^{17}/\text{c.c.})$	$\tau_1(10^{-13}\text{ sec})$	$\tau_2(10^{-13}\text{ sec})$
300°K	25.5±1.0	26.1	2.2	1.1
77°K	5.0±0.5	5.60	3.7	2.7
4.2°K	3.3±0.5	3.70	3.6	3.1

calculated values for μ_1 and μ_2 are shown in Fig. 2.

We have also measured the magnetoresistance in a longitudinal as well as a transverse field. In a longitudinal field, the magnetoresistance $\rho(H)$ increases as H^2. For a field as high as 10 kG, no sign of saturation has been found. The magnetoresistance coefficient increases as temperature is reduced, similar to the transverse case. In a transverse field of H=9 kG, the angular variation of $\rho(H)$ is shown in Fig. 3. Anisotropy of a few percent was found and it increases as temperature is decreased. One striking feature is that $\rho(H)$ is minimum when H is perpendicular to the film surface and is maximum when H is in the plane of film. These features may be due to the special size effects in a magnetic field.

In single crystals of Bi, we have measured the size dependence of ρ_{yy}^0, the resistivity for current in the bisectrix-axis direction in zero magnetic field, at three different temperatures. The results are shown in Fig. 4. Size dependence is clearly demonstrated. We estimated from this result that at 4.2°K, the mean free path of charge carriers is around 1 mm. However, in the plot as shown, the residual resistance ratio $\rho_{300}/\rho_{4.2}$ decreases monotonically as the thickness is reduced. At this time, we do not have enough data to ascertain whether the points should level off at lower values of d or not, more measurements will be attempted.

When a longitudinal magnetic field is applied to the single crystals at 4.2°K, the magnetoresistance first increases and then decreases after reaching a maximum at $H\sim$10 G. The position and width of this maximum was found to depend on the sample thickness, but the accuracy of our

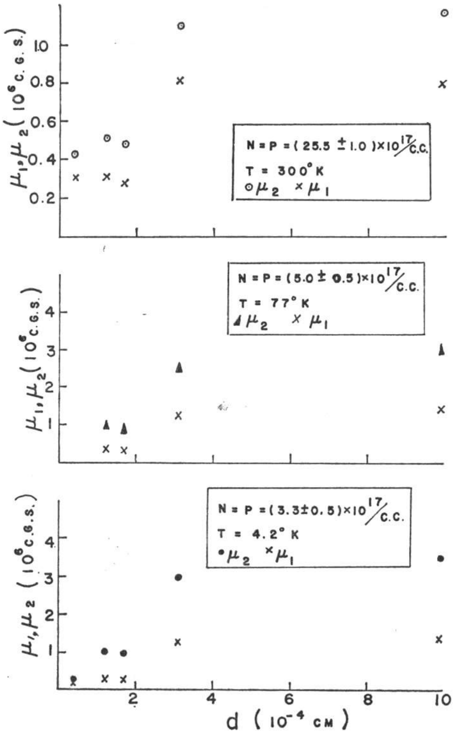

Fig. 2. The size dependence of effective mobilities of electrons and holes.

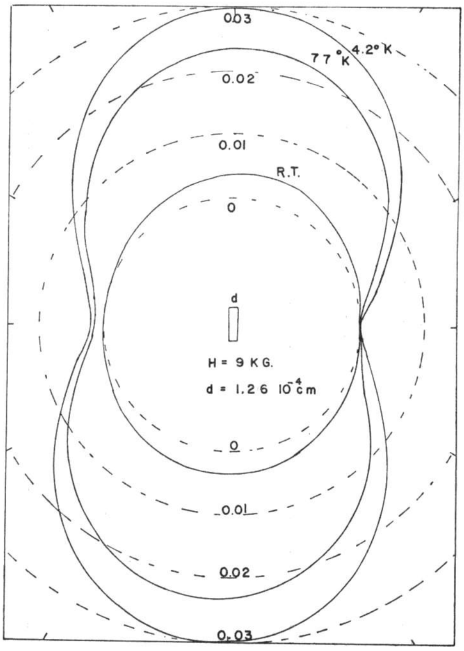

Fig. 3. The angular variation of transverse magnetoresistance of a Bi thin film at room temperature (R.T.), 77°K and 4.2°K. H=9KG. $(\rho(\theta)-\rho(\theta=0))/\rho(\theta=0)$ is plotted as a function of θ, which is the angle between H and the normal of the film.

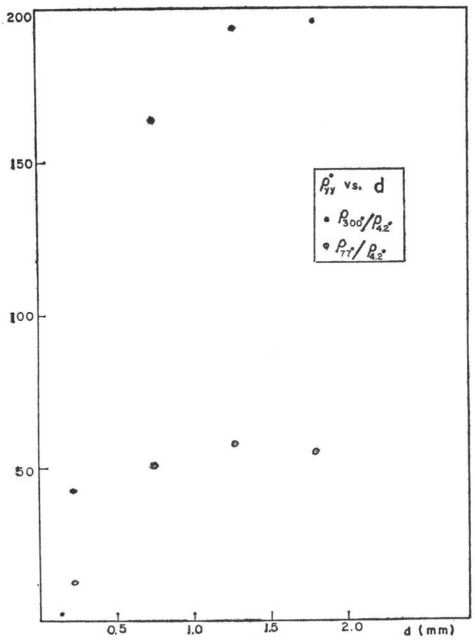

Fig. 4 The variation with sample thickness of $\rho_{300°}/\rho_{4.2°}$ and $\rho_{77°}/\rho_{4.2°}$ of a Bi single crystal.

results is not good enough for us to make any quantitative conclusion. Using the results of a theoretical work on the magnetoresistive size effect assuming single spherical Fermi surface and diffuse scattering of electrons at the boundaries,[9] we expect to see a peak at $H\sim 1.3\,m^*Vc/de$ for d roughly equal to the bulk mean free path. For $H=10$ G and $d\sim 1.0$ mm, we obtain $m^*V\sim 1.2\times 10^{-20}$ g cm/sec. Although this number is too high by a factor of about 5, but considering the rather idealized model used in the computation, it seems at least to indicate that the mechanism which is responsible for this type of longitudinal magnetoresistance as discussed in ref. 9) is a plausible one.

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