PHYSICAL REVIEW B VOLUME 45, NUMBER 19 15 MAY 1992-I

Magnetic-field dependence of Hall resistance in thin films of pure bismuth

H. T. Chu, P. N. Henriksen, Jing Jing, Hong Wang, and Xiaofeng Xu
Department of Physics, The University of Akron, Akron, Ohio 44325
(Received 18 November 1991; revised manuscript received 13 January 1992)

Hall resistance has been measured in thin films of pure bismuth at 4.2 K in magnetic fields up to about 8 T. Fields were applied parallel to the trigonal axis, which is perpendicular to the plane of the film, and the thicknesses ranged from 30 to 300 nm. In thinner films, the Hall resistance remained in the negative region. In films of intermediate thickness, as the field increased the Hall resistance first decreased, reaching a minimum in the negative region, then increased to enter the positive region at higher fields. For thicker films, except in a narrow range of low fields, the Hall resistance was positive and increased in magnitude with the field. Superimposed on the general trend of the Hall resistance versus magnetic field, Shubnikov–de Haas–type oscillations have also been observed.

I. INTRODUCTION

The Hall effect in semimetal bismuth has been studied in both bulk crystals[1,2] and thin films.[3–6] In bulk bismuth,[1] the Hall resistance at low temperatures (<7 K) is positive for a magnetic field applied along the trigonal axis and negative when the field is along a bisectrix axis, and in either case the Hall resistance generally varies quadratically with applied field. For thin films, most measurements have been at temperatures above 77 K and/or in low magnetic fields. Only for a 142-nm film (mica substrate) at temperatures below 100 K has a negative Hall effect been reported;[3] all other reports have given positive values for Hall measurements in thin films of bismuth. To the best of our knowledge, there has been a lack of Hall measurement for bismuth films at low temperatures ($\lesssim 4.2$ K) or involving high magnetic fields so that the magnetic-field dependence of Hall resistance can be studied.

A recent numerical evaluation[7] of the electric conductivity in thin films of bismuth indicates that at 0 K the electron contribution to the electric conductivity may well surpass the hole contribution, and thus predicts a negative Hall effect. Experimental verification of the negative Hall effect is desirable. Included in the present work are measurements at 4.2 K of the Hall resistance in thin films of bismuth of various thicknesses and the investigation of its dependence on the magnetic field in the range between 0 and 8 T.

Experimental details are outlined in Sec. II, and a theoretical background based upon the energy-band structure in semimetal bismuth is provided in Sec. III. Results and discussion are given in Sec. IV, and a summary in Sec. V.

II. EXPERIMENT

Thin films of bismuth (99.9999% purity) were grown by thermal evaporation onto heated mica substrates in vacuum at a pressure less than 1×10^{-7} Torr. Film thickness was measured and controlled with a quartz crystal microbalance. The mica substrate was preheated to 140 °C and kept at this temperature for about 1 h before the film deposition started. The deposition rate was 4–5 Å/s (during the deposition, the substrate was kept at 140 °C). After the film had reached its desired thickness, and the deposition stopped, the temperature of the mica substrate (thus the temperature of the film) was raised to 160 °C and the film was annealed at this temperature for an hour. Films grown under these conditions were found, as result of surface imaging with an atomic force microscopy,[8] to consist of hexagonal crystallites of the size of 3000×3000 nm^2, with a root-mean-square surface roughness of 1.44 nm. Thus the films were well oriented to have the normal along the trigonal axis. To the best of our knowledge, the size of the grains along with the hexagonal structure has made the films used in this study to possess the best single crystallinity to date in thin films of bismuth on mica.

The electrical resistivity at room temperature and at 4.2 K was measured with a digital ohmmeter. The electric circuit used for the Hall measurement was similar to the one in a previous report[9] where magnetoresistance measurements in thin films of bismuth were made. During measurements, a film of known thickness was placed in the magnetic center of a 35.2-mm-bore superconducting solenoid immersed in liquid helium. Fields were applied perpendicular to the plane of the film, and ramped up and down between 0 and 8 T. The Hall voltages were measured with a Keithley (model 148) nanovoltmeter. After initial setting, all data were computer acquired.

III. HALL RESISTANCE IN ULTRATHIN BISMUTH FILMS

The energy-momentum relationship of charge carriers in crystalline bismuth is rather complicated. According to the nonparabolic ellipsoidal model,[10,11] electrons in bismuth assume the following energy spectrum:

$$E_e(1+E_e/E_g)=\tfrac{1}{2}(P_1,P_2,P_3)\times\begin{bmatrix}\alpha_{11} & 0 & 0\\ 0 & \alpha_{22} & \alpha_{23}\\ 0 & \alpha_{32} & \alpha_{33}\end{bmatrix}\begin{bmatrix}P_1\\ P_2\\ P_3\end{bmatrix}, \qquad (1)$$

where $E_g = 15.3$ meV is the energy gap between the conduction band and the valence band directly beneath it, the α elements form the inverse effective-mass tensor, and the subscripts 1, 2, and 3 refer to the binary, bisectrix, and trigonal axes, respectively. The term involving E_g implies that the energy-momentum dependence is nonparabolic. There are three electron ellipsoids in the conduction band, the other two are obtainable by rotating the first one [Eq. (1)] about the trigonal axis through $\pm 120°$. These three ellipsoids are thus located symmetrically about the trigonal axis. There is only one hole ellipsoid in the valence band that overlaps the conduction band. The hole energy measured from the top of the valence band takes the form

$$E_h = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{P_3^2}{2M_3} , \tag{2}$$

where $M_1 = M_2$ indicating the rotational symmetry of the ellipsoid. The numerical data of the effective masses can be found in Ref. 11.

Consider a bismuth film with the film plane perpendicular to the trigonal axis and assume the film thickness being sufficiently small so that the energy spectra of electrons and holes are quantized into subbands due to the quantum size effect. The size-quantized energy subbands are given for electrons and holes, respectively, by[12]

$$E_e(1+E_e/E_g) = \tfrac{1}{2}\hbar^2 \left\{ \left[\alpha_{11}k_1^2 + \left[\alpha_{22} - \frac{\alpha_{23}^2}{\alpha_{33}} \right] k_2^2 \right] + \alpha_{33} \left[\frac{\pi}{d} n \right]^2 \right\} \tag{3}$$

and

$$E_h = (\hbar^2/2M_1)(k_1^2 + k_2^2) + (\hbar^2/2M_3) \left[\frac{\pi}{d} n \right]^2 , \tag{4}$$

where $n = 1, 2, \ldots,$ indicating the nth subband. Each energy level in Eq. (3) is triply degenerate because of the three symmetrical electron ellipsoids, while the energy levels in Eq. (4) are nondegenerate.

In ultrathin films of bismuth, the separations between subbands are well pronounced and the charge carriers in each of the subbands can be treated as a two-dimensional system at very low temperatures. In a previous work,[13] the electric conductivity and the hall resistance in a two-dimensional bismuth have been studied. Results therefrom may be applied to each of the subbands. The conductivity or the Hall resistance in a bismuth film would then be the sum of the individual contributions of the subbands. The electric conductivity tensors of the electrons and of the holes are scalars[13] owing to the rotational symmetry of the energy bands. The electron conductivity σ_e^0 and the hole conductivity σ_h^0 in zero magnetic field are given by

$$\sigma_e^0 \equiv \tfrac{3}{2} e^2 \tau_e N_e \left[1 + \frac{2E_F}{E_g} \right]^{-1} \left[\alpha_{11} + \left[\alpha_{22} - \frac{\alpha_{23}^2}{\alpha_{33}} \right] \right] , \tag{5}$$

and

$$\sigma_h^0 = e^2 \tau_h N_h M_1^{-1} , \tag{6}$$

where E_F is the Fermi energy, τ_e and τ_h are the relaxation times of electrons and holes, respectively, and N_e and N_h are, respectively, the number densities of electrons and holes. The charge neutrality condition requires that $N_e = N_h$.

Assuming a magnetic field H is applied along the trigonal axis and perpendicular to the film plane, and an electric field $\mathbf{E}$ is applied in the film plane resulting in a current also in the film plane, the current density $\mathbf{j}$ can be given by

$$\mathbf{j} = \overleftrightarrow{\sigma}(H) \cdot \mathbf{E} = [\overleftrightarrow{\sigma}_e(H) + \overleftrightarrow{\sigma}_h(H)] \cdot \mathbf{E} , \tag{7}$$

where $\overleftrightarrow{\sigma}_e(H)$ and $\overleftrightarrow{\sigma}_h(H)$ are the conductivity tensors of electrons and holes, respectively, and

$$\overleftrightarrow{\sigma}_e(H) = \frac{\sigma_e^0}{1+(\omega_e\tau_e)^2} \begin{bmatrix} 1 & -A\omega_e\tau_e \\ A\omega_e\tau_e & 1 \end{bmatrix} \tag{8}$$

and

$$\overleftrightarrow{\sigma}_h(H) = \frac{\sigma_h^0}{1+(\omega_h\tau_h)^2} \begin{bmatrix} 1 & \omega_h\tau_h \\ -\omega_h\tau_h & 1 \end{bmatrix} , \tag{9}$$

where the effective cyclotron frequencies are

$$\omega_e = \frac{eH}{C} \left[\alpha_{11} \left[\alpha_{22} - \frac{\alpha_{23}^2}{\alpha_{33}} \right] \right]^{1/2} \left[1 + \frac{2E_F}{E_g} \right]^{-1} \tag{10}$$

and

$$\omega_h = eH/M_1C , \tag{11}$$

and the constant A is the result of the anisotropy of the α tensor,

$$A = 2 \left[\alpha_{11} \left[\alpha_{22} - \frac{\alpha_{23}^2}{\alpha_{33}} \right] \right]^{1/2} \Big/ \left[\alpha_{11} + \left[\alpha_{22} - \frac{\alpha_{23}^2}{\alpha_{33}} \right] \right] . \tag{12}$$

The matrix $\sigma(H)$ in Eq. (7) is apparently independent of a rotation about the trigonal axis, indicating that the transport properties in the film do not depend on the orientation of the current. Taking the x direction for the current, the Hall resistance is simply

$$R_H = E_y / j , \tag{13}$$

where $j = j_x$ is the current density. Substituting Eqs. (8)–(11) in Eq. (7), an explicit expression of R_H can be obtained, of which the low-magnetic-field limit is

$$R_H \cong (\sigma_h^0 \omega_h \tau_h - A \sigma_e^0 \omega_e \tau_e)/(\sigma_e^0 + \sigma_h^0)^2 , \tag{14}$$

and the high-magnetic-field limit is

$$R_H \cong \frac{H}{NeC} (\omega_h^2 \tau_h^2 - \omega_e^2 \tau_e^2)/(\omega_e\tau_e + \omega_h\tau_h/A)^2 , \tag{15}$$

where $N = N_e = N_h$ is the density of either electrons or holes.

IV. RESULTS AND DISCUSSION

The current density $j = i/ld$ in a film (where l and d are width and thickness, respectively) is inversely proportional to the thickness when a constant current is passed through the film. The Hall resistance (actually resistivity) R_H, as defined by Eq. (13), is $R_H = (V_H/i)d$, where V_H is the measured Hall voltage across the film width. For a given film, V_H (and thus R_H) is a function of the magnetic field H.

Figures 1 and 2 show the H dependence of R_H in the films of various thicknesses. A few points may be worth mentioning in regard to the general features of the curves shown. The linear portion in the R_H-versus-H dependence in low fields seems very narrow, if it exists at all. The dependence exhibits a somewhat parabolic (or quadratic) variation in fields $H \lesssim 3$ T. There are Shubnikov–de Haas oscillations superimposed upon the general trend or the envelope; these oscillations are more visible on curves for films of 3001, 1504, 801, and 303 Å. Identifying the peaks and valleys corresponding to the Shubnikov–de Haas oscillations and taking the inverse of the field intensities at which two consecutive valleys (or peaks) occur, the period in H^{-1} of the oscillations can be obtained. The period depends on the effective masses and, if the masses do not vary appreciably with the film thickness, then the respective periods for films of different thickness should not differ from each other appreciably. The periods for the first three films mentioned above are, respectively, $\Delta(1/H) = 0.73$, 0.82, and 0.67 T^{-1}. This suggests that the effective masses may not vary appreciably with the film thickness. The fact that the Shubnikov–de Haas effect has been observed provides additional evidence of the quality (single crystallinity) of the films.

For a couple of thicknesses, films of similar thickness have been used to reproduce the measured result. Similar results also imply that the Hall voltage in bismuth films normal to the trigonal axis is independent of the orientation of the electrical current flowing in the film plane. This is in agreement with the theory sketched in Sec. III, where an orientation-independent Hall effect has been predicted based upon the rotational symmetry about the trigonal axis of the energy-band structure.

The Hall voltage for films in this study is always negative in low magnetic fields. In films as thick as 300 nm, the negative hall voltage appears only at very low fields. We may thus conclude that at low temperatures and in sufficiently low magnetic fields, the Hall effect is negative, and thus the electron contribution to the electric conductivity predominates over that of holes in thin films of bismuth with film plane normal to the trigonal axis.

In Fig. 1, the Hall resistances in thinner films are shown. In the 303-Å film, after peeling off the Shubnikov–de Haas oscillations, the general trend (see the Appendix), shown in dotted line, seems roughly parabolic and R_H decreases with the increasing field. In films of 404 and 801 Å, R_H remains in the negative and becomes almost stationary in higher fields.

Figure 2 shows the R_H in intermediate and thicker films. The Hall resistance enters in the positive region in higher fields after being negative in lower fields. The field intensity at which the Hall effect becomes positive decreases with increasing film thickness. In the film of 1002 Å, R_H is again nearly stationary in higher fields. In thicker films, the general trends of R_H (see the Appendix) are again roughly parabolic and R_H increases in magnitude with the film thickness.

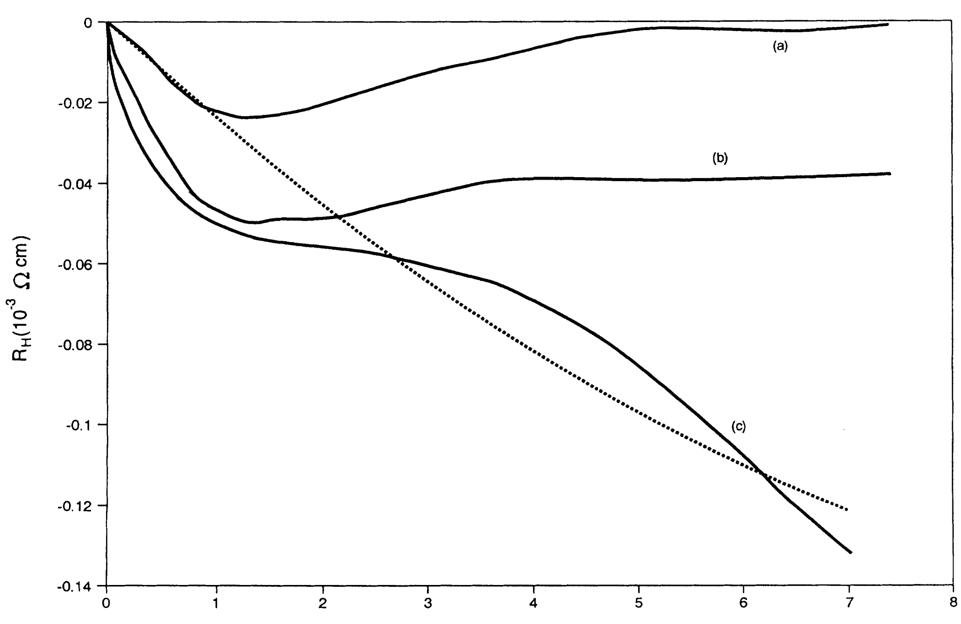

FIG. 1. Hall resistance vs magnetic field in thin films of bismuth ($T = 4.2$ K, film plane perpendicular to the trigonal axis and the magnetic field). Film thickness: (a) 80.1 nm, (b) 40.4 nm, (c) 30.3 nm.

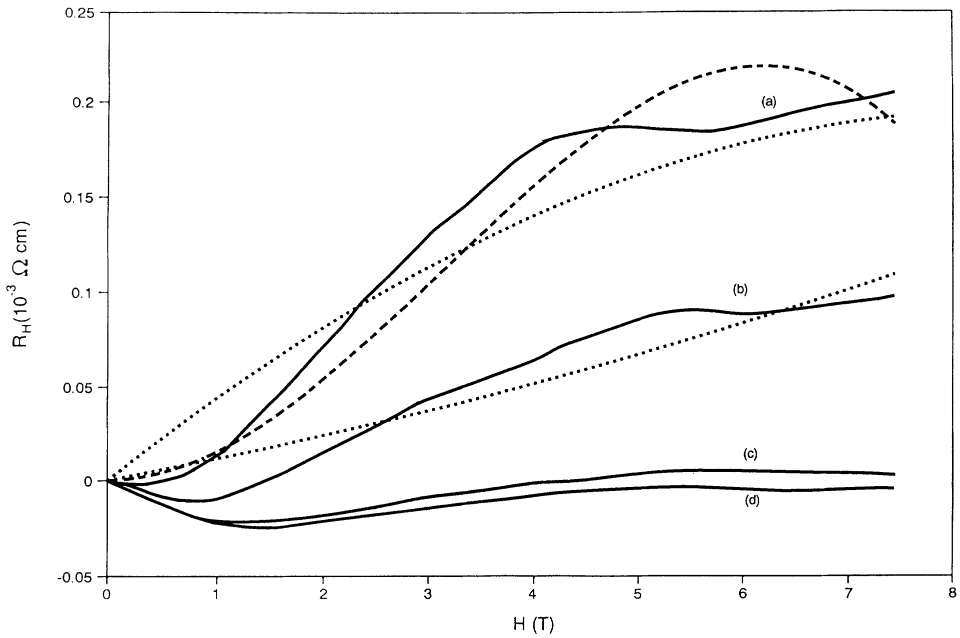

FIG. 2. Hall resistance vs magnetic field in thin films of bismuth ($T = 4.2$ K, film plane perpendicular to the trigonal axis and the magnetic field). Film thickness: (a) 300.1 nm, (b) 150.4 nm, (c) 100.2 nm, (d) 80.1 nm.

The interpretation for the negative R_H in low fields may come from Eq. (14). It has been shown[7] that the electron contribution to the electric conductivity is much greater than the hole contribution at 0 K in zero field. Thus the negative term in Eq. (14) may be larger in lower fields, indicating a negative Hall effect. Since the effective cyclotron mass of electrons is much smaller[11] than that of holes, the cyclotron frequency of electrons is thus much larger. As the magnetic-field intensity increases, the larger cyclotron frequency causes greater scatterings and thus reduces the relaxation time τ_e. If τ_h becomes sufficiently larger than τ_e, the Hall resistance R_H may become positive in view of the expression given in Eq. (15).

Resistivities of the various films at room temperature and 4.2 K are shown in Fig. 3 for reference. Dependence of resistivity on thickness due to the quantum-size effect is more pronounced at the lower temperature. The crossing of an energy subband over the Fermi energy as the film thickness is being reduced causes a discontinuity of the slope in the dependence of electron density on film

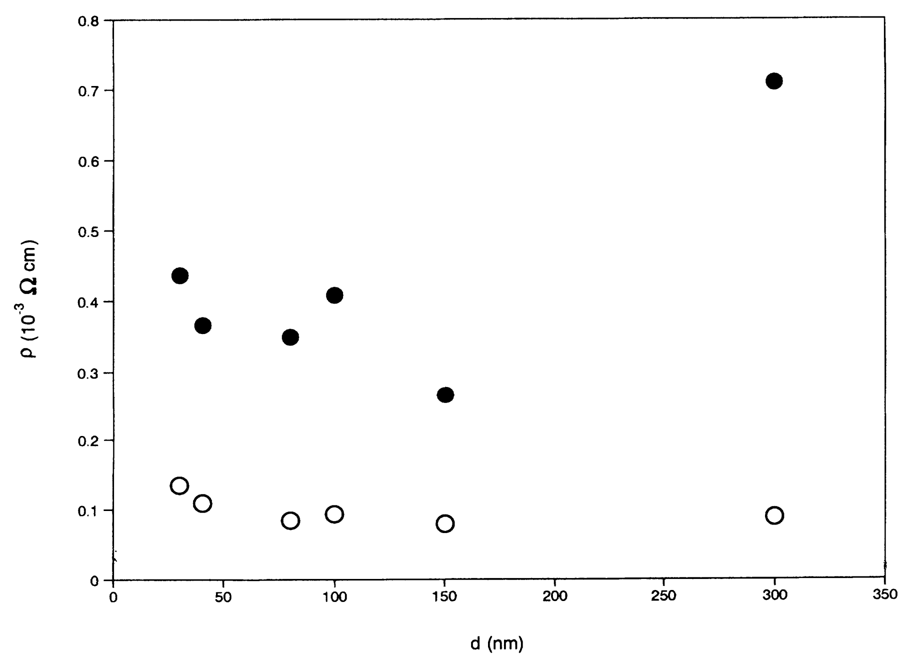

FIG. 3. Electric resistivity vs thickness in thin films of bismuth (zero magnetic field). ●, at $T = 4.2$ K; ○, at room temperature.

thickness, and thus introduces a structure in the resistivity-thickness dependence; e.g., the minimum of resistivity in the 70–80-nm region in Fig. 3 corresponds to the crossover of the third-lowest subband of the electrons.[7]

V. SUMMARY

An atomic force microscope has been used as an aid in fabricating thin films of pure bismuth to obtain high-quality films having uniform thickness and large crystal grains. The Hall resistance in these films (30–300 nm thick) has been measured at 4.2 K as a function of the applied magnetic fields up to 8 T. The magnetic-field dependence of the Hall resistance in thin films of bismuth has been analyzed and reported. The negative Hall effect in low fields agrees that the electron contribution dominates the electric conduction at 0 K in zero field. The period (in H^{-1}) of Shubnikov–de Haas oscillations superimposed upon the R_H-versus-H dependence is nearly equal for films of different thickness, indicating the effective masses may not change appreciably with the thickness of a film. The Hall effect is positive in thicker films in higher fields, indicating a larger hole relaxation time in thicker films and higher fields. This is consistent with the positive Hall coefficient in bulk bismuth.

APPENDIX

The magnetic-field dependence of Hall resistance can be deemed as the superposition of a general trend and Shubnikov–de Haas oscillations. However, it is difficult to have these two components clearly separated. We have tried to approximate the general trend with a short polynomial $aH+bH^2+cH^3+\cdots$. Curve fittings with the experimental data have been carried out with a computer. For Fig. 1(c) and Fig. 2(b), the dotted line is the result of using a two-term polynomial $aH+bH^2$, and the results seem to be satisfactory. For Fig. 2(a), the dotted line is the result of using two terms and the dashed line is from a three-term polynomial; it seems to us that the dashed curve may provide a better approximation for lower and intermediate field intensities ($H<6$ T). Beyond 6 T, the curvature of the dashed line [Fig. 2(a)] must be replaced by a smaller one, e.g., like that of the dotted line.

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