curves would coincide with the experimental curve at 24.9 eV, i.e., the maximum atomic recoil energy which corresponds to an 0.4-MeV irradiation. The step function, it is clear from the figure, provides a very poor fit. However, the linear function departs from the experimental graph only at the highest energies. As with other metals, the poor agreement of the simple step function probably indicates that atoms in the bulk material should be described in terms of an anisotropic function.[5]

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[1]P. G. Lucasson and R. M. Walker, Phys. Rev. 127, 485 (1962).

[2]W. Bauer, K. Herschback, and J. J. Jackson, Phys. Rev. 185, 924 (1969).

[3]G. R. Fletcher (unpublished).

[4]W. A. McKinley and H. Feshback, Phys. Rev. 74, 1759 (1948).

[5]A. Sosin and W. Bauer, *Studies in Radiation Effects in Solids*, edited by G. J. Dienes (Gordon and Breach, New York, 1969).

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Galvanomagnetic Studies of Bismuth Films in the Quantum-Size-Effect Region*

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Bismuth films (200–1400 Å) were grown epitaxially on freshly cleaved mica substrates. These films consisted of a mosaic of equally oriented crystallites averaging several microns in diameter. The plane of the films coincided with the trigonal plane of Bi. We have studied the thickness dependence of the resistivity, the Hall coefficient, and the transverse magnetoresistance, by gradually varying the thickness of a single film which was kept under high vacuum during the entire experiment. The resistivity at 360 and 77 °K is a smooth monotonic function of the thickness. At 12 °K, we observed small oscillations in the resistivity and in the magnetoresistance. These oscillations are regarded as probable manifestations of the quantum size effect (QSE). The thickness dependence of the Hall coefficient is in striking disagreement with the predictions of the infinite-potential-well model. Better agreement between the theory and experimental results is obtained when we assume a less rigid boundary condition. Also for several films we have investigated the temperature dependence of these three transport coefficients and found it to be quite different from that of bulk bismuth. We have attempted to explain these results in terms of the behavior of the carrier concentration and of the different scattering mechanisms that can come into play in these films.

I. INTRODUCTION

There are two types of size effect in thin metallic films, each one characterized by a specific parameter. The classical size effect, which has been the subject of numerous investigations, appears in solids whose thickness is comparable to the electron-transport mean-free path. Recently, the quantum size effect (QSE) has aroused considerable interest; it appears when the sample thickness is comparable to the de Broglie wavelength of the conduction electrons. The QSE manifests itself in the oscillatory behavior of the electron density of states. These oscillations can be observed in the thermodynamic properties and the kinetic coefficients of the solid when the thickness of the film is varied continuously.

In principle, the QSE can be observed in any metal. In practice, the experimental observation in most solids is rather difficult because the electronic de Broglie wavelength is only of the order of a few angstroms. In Bi, however, the Fermi energy of the electrons is only 25 meV, and the effective mass along some crystal orientations is two or three orders of magnitude smaller than the free-electron mass. Consequently, the electronic

de Broglie wavelength can be as large as 300 or 400 Å. Several authors have claimed to have observed the size quantization in Bi thin films.[1] However, in much of the work published, there are several disturbing features which are in contradiction with the theoretical predictions. In the work of Ogrin *et al.*[1] the amplitude of the oscillations in the resistivity increases with increasing thickness; extrapolation to thick samples would lead to unrealistic results. Moreover, the oscillations at 77 °K are almost as pronounced as those at 4.2 °K. The source of many of the discrepancies present in their work and that of several authors stems, we believe, from the method of varying the thickness. A very important question must be answered when comparing the transport properties of two films of different thickness: Are the observed changes due to size quantization or are they the results of difference in the film structure? This question will be considered in some detail in Sec. III of this paper.

We have reinvestigated the thickness dependence of the galvanomagnetic coefficients using a completely different experimental approach; instead of studying a large number of films, the thickness of a single film was varied by progressively depositing 50-Å-thick layers. Moreover, in order to prevent surface contamination, the film was never removed from the high vacuum during the course of the entire experiment.

II. THEORY

A. Carrier Statistics in a Thin Film

The main features of size quantization can be derived from a simple model in which the electrons and the holes are regarded as independent particles moving in an infinite-square-well potential. Lifshitz and Kosevich[2] have obtained similar results from more general considerations. The single-particle wave function for a film of thickness a can be written as

$$\Psi_{nk_xk_y}=\left(\frac{2}{aL_xL_y}\right)^{1/2}\sin\left(\frac{n\pi z}{a}\right)e^{ik_xx+ik_yy}\ , \qquad (1)$$

where $0\le z\le a$. The corresponding energy spectrum is

$$E_{nk_xk_y}=n^2E_0+\hbar^2k_x^2/2m_x+\hbar^2k_y^2/2m_y\ , \qquad (2)$$

where $E_0=\hbar^2\pi^2/2m_za^2$. Thus while in a bulk crystal, the electron states are given by points which fill the Fermi sea quasicontinuously; in a thin film the Fermi surface breaks up into allowed subsheets parallel to the k_x-k_y plane. Each subsheet corresponds to a discrete value of the wave vector along the quantized direction of the film. This phenomenon is similar to the quantization into "Landau levels" by the magnetic field. Both types of quantization are illustrated in Fig. 1.

The density of electrons resulting from this discrete energy spectrum is an oscillatory function of the thickness and is given by[1]

$$N(a,T)=\frac{(m_xm_y)^{1/2}}{(a\pi\hbar^2)}kT\sum_{n=1}^{\infty}\ln(1+e^{(\eta-n^2E_0)/kT})\ , \qquad (3)$$

where η is the Fermi energy.

In order to understand the oscillatory nature of $N(a,T)$, let us consider the case of complete degeneracy, i.e., $T=0$, and let a be such that $s^2E_0<\eta<(s+1)^2E_0$; in such case, only the first s terms contribute to the summation in (3) since all higher-order terms in the sum are zero. When $\eta=s^2E_0$, the sth term ceases to contribute to the sum and the density of states undergoes a relative minimum. This can be seen physically by referring to Fig. 1(b). As the thickness of the film decreases, the sheets within the Fermi surface move further apart. When the sth energy level moves across the Fermi energy, the density of states at the Fermi level undergoes an oscillation.

We should note that the minima in (3) occur when $\eta=s^2E_0$, i.e.,

$$a_{\min}=s\hbar\pi(2m_z\eta)^{-1/2}=\tfrac{1}{2}s\lambda_F\ , \quad s=1,2,3,\ldots, \qquad (4)$$

where λ_F is the de Broglie wavelength at the Fermi level.

B. Solution of Neutrality Equation for Semimetals

In the preceding one-carrier model we have assumed that η is a constant function of the thickness. This, of course, is not true for semimetals. In a semimetal, such as Bi, the Fermi level is determined by the charge-neutrality condition that the electron concentration $N_e(a,T)$ must be equal to the hole concentration $N_h(a,T)$. If the electron- and the hole-energy spectra are both quantized, we will have to use Eq. (3) for N_e and N_h, respectively. However, in Sec. III, we will see that the experimentally observed direction of quantization coincides with the trigonal axis. Along this direction, the electron effective mass m_{ez} is much smaller than the hole effective mass m_{hz} ($m_{hz}\approx m_0$ and $m_{ez}\approx 0.02m_0$,[3] where m_0 is the free-electron mass). Consequently, the separation between the hole-energy states is much less than that between the electronic states. For the range of thicknesses that we have studied (200–1400 Å), we will assume that the spectrum for the holes is quasicontinuous. Thus N_h is given by the familiar expression

$$N_h(a,T)=N_vF_{1/2}(\eta_h/kT)\ , \qquad (5)$$

where N_v is the effective density of states and $F_{1/2}$ is the Fermi function. When we take account of the known Fermi topology for Bi (three electron ellip-

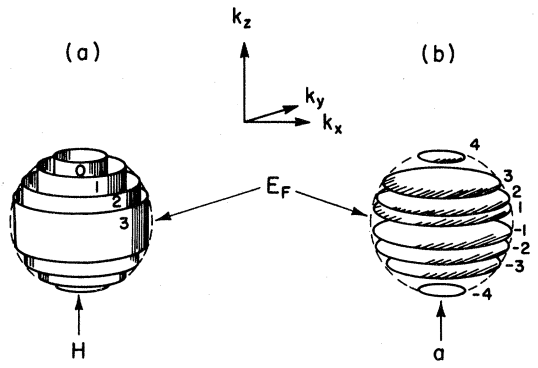

FIG. 1. Quantization of the electron orbits in momentum space: (a) by the magnetic field, (b) by the size.

$$E_n k_z = (n+\tfrac{1}{2})\hbar\omega_c + \frac{\hbar^2 k_z^2}{2m_z} \qquad E_{n k_x k_y} = \frac{n^2\hbar^2\pi^2}{2m_z a^2} + \frac{\hbar^2 k_x^2}{2m_x} + \frac{\hbar^2 k_y^2}{2m_y}$$

soids and one hole ellipsoid), the neutrality equation becomes

$$\frac{3kT(m_{ex}m_{ey})^{1/2}}{\pi\hbar^2 a}\sum_{n=1}^{\infty}\ln(1+e^{(\eta_e - n^2E_0)/kT}) = \left(\frac{2^{1/2}}{\pi^2\hbar^3}\right)(m_{hx}m_{hy}m_{hz})^{1/2}F_{1/2}(\eta_h/kT)\ . \quad (6)$$

This equation can now be solved for either η_e or η_h making use of the fact that $\eta_e + \eta_h = \Delta$, where Δ is the band overlap. Subsequently we can solve for N_e. The computer-calculated results for the thickness and the temperature dependence of the carrier concentration and the Fermi energy are shown in Figs. 2 and 3, respectively. The oscillatory character of $N(a)$ will manifest itself in the thickness dependence of the resistivity, the magnetoresistance, or any other parameter which depends on the carrier concentration or on the density of states.

The effect of size quantization should also manifest itself in the temperature variation of the transport coefficients. For instance, the temperature dependence of the carrier concentration $N(T)$ obtained from the temperature-dependent Fermi energy by solving Eq. (6) will exhibit a significant difference from that in thick films where the QSE can be neglected. For the purpose of comparing experimental results with the theory, Ogrin *et al.*[1] have indicated that between 80 and 300 °K, $N(T)$ can be approximated by the expression

$$\ln\left(1-\frac{N(0)}{N(T)}\right) = \frac{C}{T}\ . \quad (7)$$

This approximate empirical relation was also borne out in our computation using Eq. (6). $N(T)$ satisfying the neutrality condition is plotted in Fig. 4 as $\ln(1-N(10\ ^\circ\mathrm{K})/N(T))$ vs $1/T$, and it can be seen that (7) represents a good fit of the computed carrier concentration.

III. EXPERIMENTAL PROCEDURE

In the previous work[1] on the quantum size effect, several films of different thicknesses, or a number

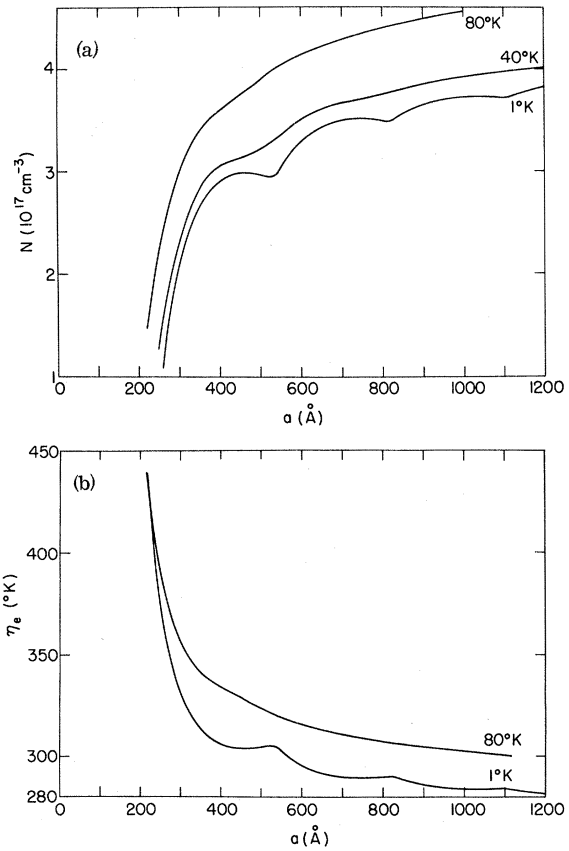

FIG. 2. (a) Computer calculation of the thickness dependence of the carrier concentration using the infinite-potential-well model. (b) Computer calculation of the thickness dependence of the electron Fermi energy using the infinite-potential-well model.

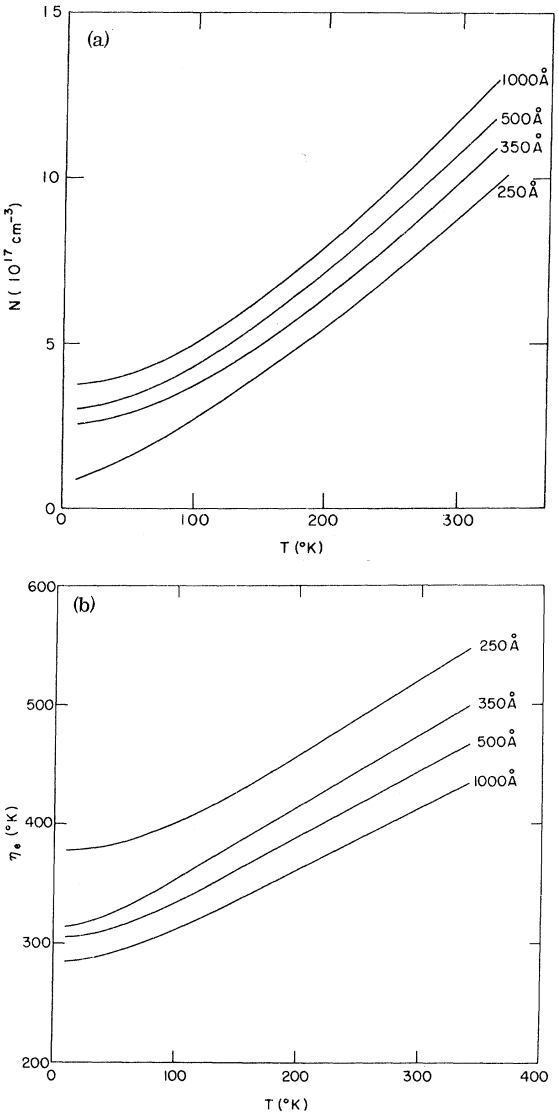

FIG. 3. (a) Computer calculation of the temperature dependence of the carrier concentration using the infinite-potential-well model. (b) Computer calculation of the temperature dependence of the electron Fermi energy using the infinite-potential-well model.

of films in the form of steps, were prepared and removed from the evaporator in order to perform the measurements. It has been our experience that this method has serious drawbacks. First, we have found that the film properties changed drastically when the film was removed from high vacuum. The resistance R of the film increased considerably, especially for the thinner films. In one specific case, R increased by 30% for a film 330 Å thick, whereas for a 1000-Å film, we observed only a 3% increase. This is an obvious effect since the increase in R is probably due, for instance, to surface oxidation, diffusion of oxygen into the bulk, and formation of grains, and the thinner the film, the greater is the percentage of the total volume affected. Another very important fact is that two films having the same thickness, and having been evaporated under identical conditions (same pressure, same rate of deposition, and same substrate temperature) can have very different resistivity values. In some cases, the resistivity differed by as much as 100%. In fact, the resistivity of different sections of the same film can vary by 5 or 6%. The conclusion of these observations is that in order to observe any genuine oscillatory behavior in the kinetic coefficients of the thin films, an experimental approach must be found which minimizes the above-mentioned difficulties. We have seen in Sec. II that the predicted amplitude of the oscillations is rather small even at 1 °K; it is therefore essential to maintain the variations in the physical properties of the film so that they are smaller than those due to size quantization.

A schematic diagram of our experimental setup is shown in Fig. 5. It is basically an evaporator-cryostat combination in which evaporation and annealing of the films at high temperatures (100–150 °C) and measurements at low temperatures can be performed without removing the film from the high vacuum.

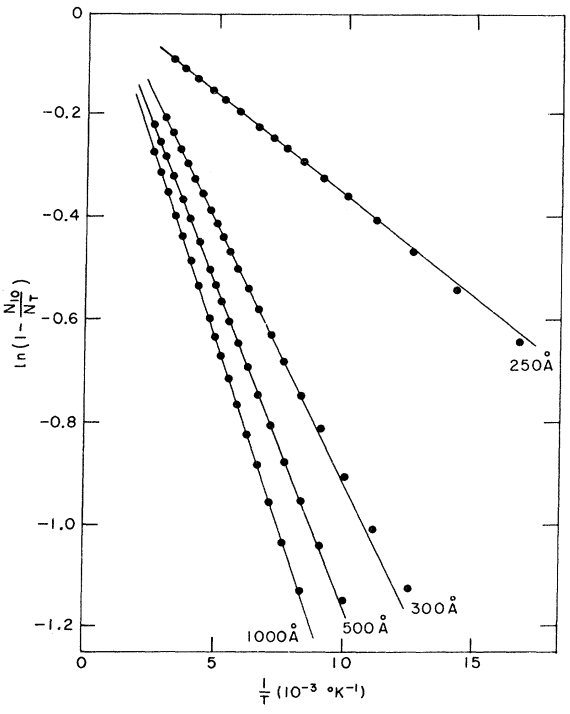

FIG. 4. Computer calculation of the temperature variation of the carrier concentration at high temperatures. For thick enough films, the temperature dependence may be approximated by $\ln(1-N_0/N(T)) \simeq c/T$. We choose N at 10 °K as N_0.

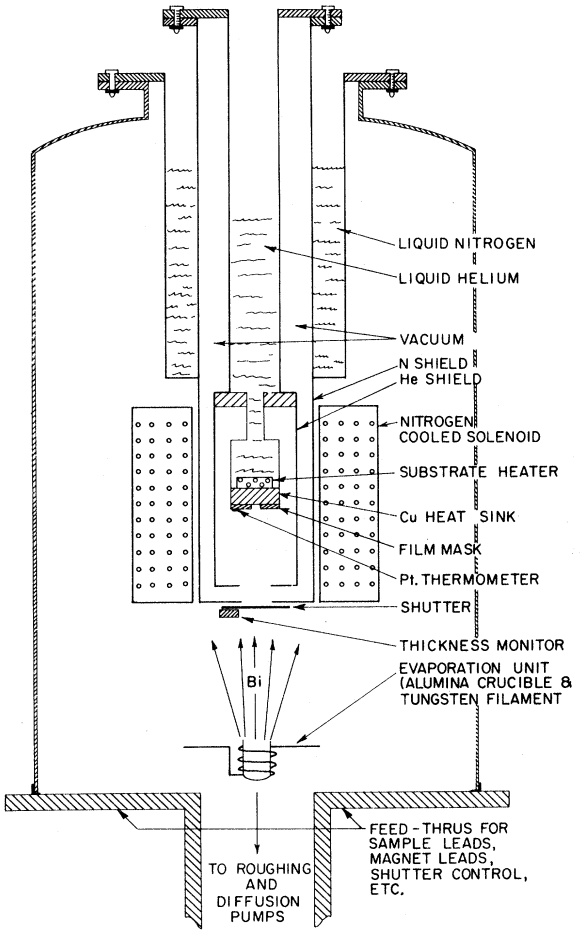

FIG. 5. Experimental setup.

The experimental procedure was as follows. A set of six gold contacts (two for the current, two for the voltage, and two for the Hall-voltage leads) were evaporated onto a freshly cleaved mica substrate. Leads were attached to the gold contacts with silver micropaint. The mica substrate with the preset leads was then placed in the high-vacuum evaporator against a copper heat sink which served as the bottom of the He Dewar. A heater placed at the bottom of the He Dewar allowed us to heat the substrate to the desired temperature. High-purity Bi (99.9999%) was evaporated at a rate of about 60 Å/min. The pressure in the evaporator during the evaporation was 1×10^{-7} Torr. We have analyzed some of the films evaporated under these conditions with an RCA EMU-3 electron microscope, and have found that the films are made up of an array of crystallites several microns in diameter. However, almost all these crystallites are identically oriented with the plane of the film corresponding to the trigonal plane. A detailed study of the structure of these films can be found in Ref. 4. After evaporating and annealing the Bi film, the heat sink was gradually cooled. A calibrated platinum resistor placed next to the film was used to measure the temperature of the samples. The resistance of the films was measured by the standard four-terminal method and care was taken to eliminate any thermoelectric voltages by reversing the direction of the current for each measurement. The error in the resistivity measurements was less than 0.2%, and the error in the temperature measurements less than 1 °K. This latter point will be discussed subsequently. A nitrogen-cooled solenoid, capable of yielding a 2-kG field was used to measure the Hall effect and the transverse magnetoresistance. *Once the measurements for a particular thickness were completed, the film was reannealed at* 370 °K *and an additional layer of* Bi *was deposited on top of the previous film.*

Several points concerning the experimental procedure need further discussion. The first one concerns the reliability of the thickness measurements. Thicknesses were determined with a Sloan DTM-2A quartz-crystal-oscillator thickness monitor. The thickness of several films was rechecked with an optical interferometer. The worst disagreement we obtained was 10%. This was also the biggest difference in thickness between sections of the same film and it occurred when the film was less than 200 Å thick. The thicker the film the more uniform they were found to be. We must point out that although the absolute error in the thickness may be as high as 10%, the relative error between two adjacent thicknesses was much less. Thus, in a resistivity vs thickness curve we might have to shift the whole curve by 10%, but the relative shift of adjacent points will be much less.

Another point which deserves consideration is the reliability of the temperature measurements. As we mentioned before, the temperature was measured via a calibrated platinum resistor, which, although ideal for high-temperature measurements, becomes rather insensitive below 77 °K. In our case, an accuracy of 1 °K or better could be obtained down to 4.2 °K. The real question, however, is not the lack of sensitivity of the thermometer, but rather the possible discrepancies between the temperature of the platinum resistor and the actual temperature of the film due to radiation effects. The platinum resistor was perfectly shielded against any thermal radiation, but the substrate had to be left partially exposed. Two copper shields, one in contact with the nitrogen bath and the other in contact with the helium bath, reduced this radiation problem. In an independent experiment we placed a calibrated Ge resistor against the mica substrate, and we were able to compare the temperature of the substrate against that measured by the Pt resistor. We did find some discrepancies between the temperature of the substrate (and hence of the film) and

that of the platinum resistor. However, the largest observed difference, which occurred at 10 °K, was 1 °K. The effect of thermal radiation also manifests itself in the fact that the lowest temperature to which we can cool our film is 10 °K. One poor feature of our setup was that once the helium or the nitrogen boiled off, the temperature could not be kept constant for the period of time necessary to measure the magnetoresistance and the Hall voltage of the film. As a consequence, this evaporator cryostat was used only to measure the Hall effect and the magnetoresistance at 77 and at 12 °K, as well as the temperature dependence of the resistivity (the rate of change of T could be controlled to be as slow as 1 °K every 4 min). The results which we report here on the temperature dependence of the transverse magnetoresistance and of the Hall effect were performed by removing the films from the evaporator and placing them into a vacuum-sealed sample holder. Since exposure to air affects the film properties, in analyzing these data we will concentrate on the temperature characteristics of individual films, and comparison between different films will be carried out in a general way only.

Finally a few words should be said about the quality of the films after many layers have been deposited. Over the time of the run (about 24 h), at 10^{-7} Torr, significant amounts of gaseous impurities might deposit on the surface of the film. Hence, when the next layer of metal is evaporated, there may be monolayers of gas. We think that this is unimportant for two reasons. Before a new layer of Bi is evaporated, the film is reheated to 370 °K; this should drive off most of the gases on the surface which at this temperature should not be soluble in the new Bi layer. But most important is the fact that experimentally we have found that the mean-free path is much greater than the thickness of the individual layers. This could not be so if monolayers of gaseous impurities were trapped between the layers of Bi. Finally, one may wonder what happens to the structure of the films after many layers have been deposited at intervals of 24 h. The analysis of several such films reveals that their crystal structure is qualitatively identical to that of the films formed by a single evaporation.

IV. RESULTS AND DISCUSSION

A. Thickness Dependence of the Resistivity, Hall Coefficient, and Magnetoresistance

We have studied the thickness dependence of the resistivity and the Hall coefficient at 360, 77, and 12 °K. We have also measured the transverse magnetoresistance at 77 and 12 °K. As we have indicated previously during all these measurements the film was kept under vacuum and its thickness was gradually increased in 50-Å steps.

The thickness dependence of the resistivity at 360 °K is shown in Fig. 6(a). The smooth monotonic decrease of ρ with thickness stands in sharp contrast with other published results[1] where the random scattering of the points is as large as 20–30%. At 360 °K, the thermal broadening of the energy subbands is comparable to the separation between the levels; consequently the carrier concentration should be independent of the thickness. This conclusion will be substantiated by the Hall-effect data. The change in ρ is due to the variation of the transport mean-free path l, with thickness. This dependence of ρ on the thickness does not mean that collisions with the surface constitute the main scattering mechanism. The value of the resistivity of bulk Bi at room temperature is approximately 1.2×10^{-4} Ω cm; this corresponds to a mean-free path of several microns.[5] If we assume that $\rho \sim 1/l$ then the mean-free path of our films (for $a > 500$ Å) is only 2 or 3 times smaller than the bulk value instead of 10 or 20 times smaller as would be the case if surface scattering were predominantly diffuse. The limit on the mean-free path of these films, particularly when $a < 400$ Å, seems to be the size of the crystallites which make up the film, and we think that the surface scattering is essentially specular. This is also supported by our magnetoresistance data. We have observed experimentally that below 400 Å the size of the crystallites increases rapidly with thickness. But we should point out that the scattering by the lattice can also be responsible for the dependence of the mean-free

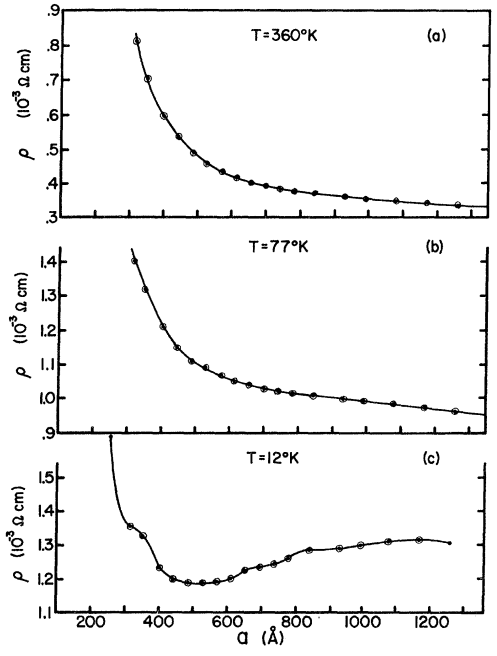

FIG. 6. Thickness dependence of the resistivity ρ at (a) 360 °K, (b) 77 °K, and (c) 12 °K.

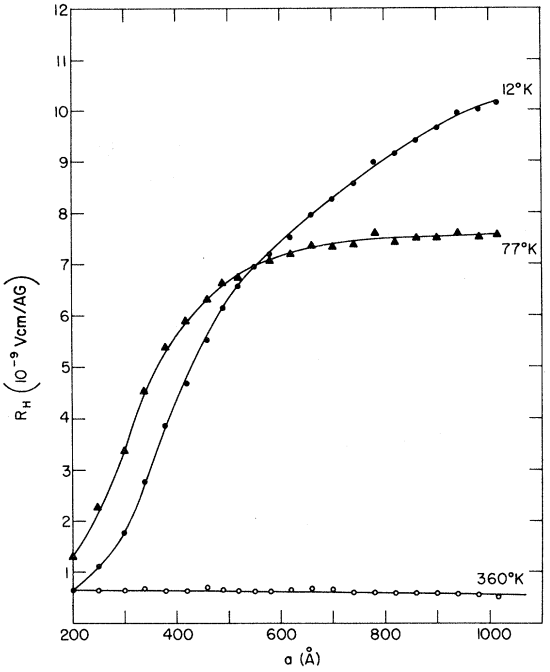

FIG. 7. Thickness dependence of the Hall coefficient.

path on the thickness. Iogansen[6] has shown that at high temperatures, when the electron-energy spectrum is quantized, the relaxation time associated with the scattering of the conduction electrons by phonons is proportional to the thickness.

In contrast to the monotonic behavior of ρ at 360 °K, the resistivity measured at 12 °K exhibits some interesting features [see Fig. 6(c)]. After an initial decrease, ρ unexpectedly increases with thickness. The reason for the minimum is not yet understood. We also see some evidence of oscillations although their amplitude is very small. The experiment was repeated twice and the same anomalous minimum as well as the small oscillations were observed in both cases. One may wonder whether these effects are not due to progressive deterioration of the films upon cooling, possibly due to differential contraction between the film and substrate. If such were the case, we should expect similar effects at 77 °K, as most of the thermal contraction takes place between room temperature and liquid-nitrogen temperature. Figure 6(b) shows that at 77 °K, ρ is still a smooth function of the thickness.

The thickness dependence of the Hall coefficient R_H is given in Fig. 7. The three curves show a clear and consistent trend: R_H tends to level off at certain thickness which decreases with increasing temperature. In fact, at 360 °K, R_H is independent of the thickness. In the simple model of one isotropic Fermi surface, R_H is a function of the carrier density N only, and is given by $R_H = 1/Nec$.

For nonspherical Fermi surfaces or in the presence of several types of carriers, R_H depends also on the mobilities. But even in this case, Sandomirskii[7] has shown that the dependence of R_H is approximately contained in the factor $N(a)$. With this in mind, it is easy to understand the information contained in Fig. 7. When kT is less than the separation between the energy subbands, the carrier concentration will vary with thickness; as kT becomes comparable to the spacing between the levels, variations of the thickness will not affect the carrier concentration. Since the separation between the levels goes as $1/a^2$, the lower the temperature the larger the thickness at which $N(a)$ will taper off. There is however a striking disagreement between the observed behavior of R_H and the predictions of the infinite-potential-well model. Our computer calculations based on this model predicted that the carrier concentration should increase with thickness and consequently $R_H \sim 1/N(a)$ should decrease with a. This is exactly the opposite of what we observed. Although it is difficult to pinpoint the exact cause for this disagreement, there are some possible explanations that we can offer. In the first place, the impurity states have been completely neglected in our calculations. Variations in the local potential near the grain boundaries of the crystallites will affect considerably the density of states. These impurity states will play a more important role when the film is very thin, because, as we have indicated previously, the crystallites are then smaller and more numerous. However, even for a perfect single-crystal film with no impurities, we can obtain a thickness dependence for $N(a)$ which agrees with the experimental results for R_H. This is achieved by replacing the boundary condition that the wave function vanishes at the surface by the one that the gradient of the wave function vanishes at the surface. This condition does not imply an infinite-potential well and allows the wave function to be nonzero outside the film. At the same time, it maintains the reasonable physical fact that there is no net flow of electrons at the surfaces of the film. Paskin and Singh[8] have indicated that while the vanishing wave function might be expected to be a good approximation at the boundary for a perfect metal surface, the vanishing gradient might be expected to be a better approximation at the rough boundaries which usually occur in thin films. This new boundary condition introduces an additional subband, corresponding to the quantum number $n = 0$, whose position does not change with thickness. We have solved the neutrality equation for this new condition. The results for $\eta_e(a)$ and $N(a)$ at 80 °K are shown in Fig. 8. The similarity between these results and the Hall-effect data is evident. This qualitative agreement is considered as an indication of the inconsistency of the previously used condition $\Psi = 0$; the actual boundary conditions in real films

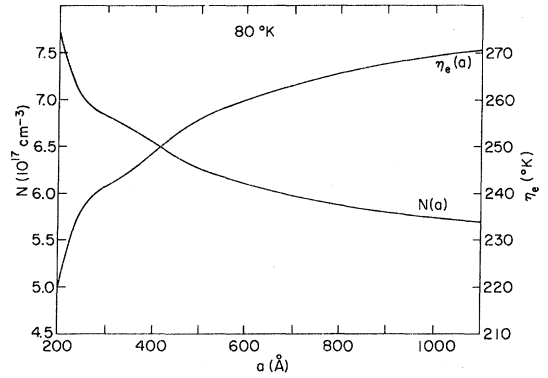

FIG. 8. Computer-calculated thickness dependence of the carrier concentration and of the Fermi energy assuming $\nabla\Psi = 0$ instead of $\psi = 0$ at the boundary.

may be much more complex than these simple forms.

When $\omega_c \tau \ll 1$ (ω_c = cyclotron frequency and τ = relaxation time), the transverse magnetoresistance $\Delta\rho(H)$ is a quadratic function of the magnetic field for an ideal semimetal. The combination of a long mean-free path (at 4.2 °K, l a few millimeters[5]) and small effective masses account for the fact that in bulk Bi the condition $\omega_c \tau \ll 1$ breaks down for very small fields. The deviation from quadratic behavior at 4.2 °K begins for $H > 4$ G.[9] The mean-free path in our films is severely reduced by crystal imperfections and as a consequence, even at 12 °K $\Delta\rho(H) \sim H^2$ holds up to 1 kG. The importance of the magnetoresistance when the quadratic dependence is obeyed stems from the fact that $\Delta\rho(H)/\rho(0)H^2$ is a function of the transport mobilities only.[9] The detailed determination of the mobility requires the experimental measurement of several of the 12 independent components of the galvanomagnetic tensor for Bi.[9]

For a qualitative argument, we may borrow the well-known result for an ideal semimetal containing isotopic electrons and holes; the quantity $\Delta\rho(H)/\rho(0)H^2$ is simply $\mu_e \mu_h / c^2$, where μ_e and μ_h are the mobilities of electrons and holes, respectively. From the fact that $\Delta\rho(H)/\rho(0)H^2$ was independent of H up to ~1 kG in our films, in contrast to ~4 G for the bulk samples, the electron mean-free path could be estimated to be around 10^{-2} to 10^{-3} times that in the bulk. This result is consistent with our earlier estimate of the mean-free path of about 1 μ from the resistivity data.

However, even without making all the anisotropy measurements, we can conclude from Fig. 9 that at 12 °K the mobilities oscillate when the thickness is varied. The oscillatory character of the mobilities can be related to their dependence on the Fermi energy. As we have indicated, one of the most important scattering mechanisms in these films is impurity scattering. This is particularly true at 12 °K. If we assume that this type of scattering is

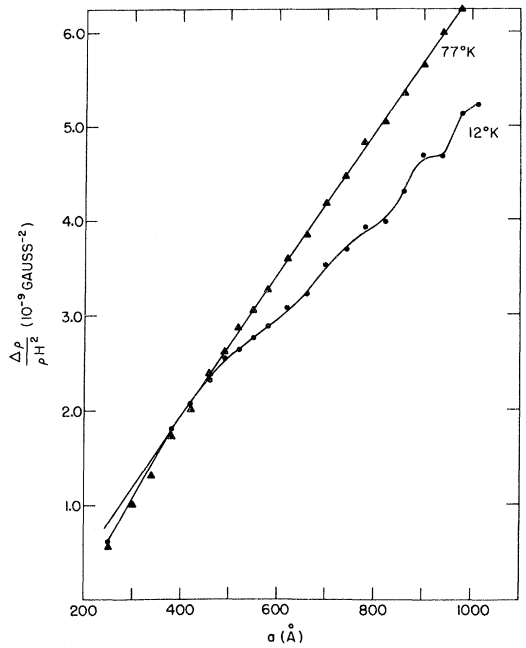

FIG. 9. Thickness dependence of the magnetoresistance coefficient $\Delta\rho/\rho H^2$.

Coulombic in nature,[10] we get a differential cross section $\sigma \sim 1/\eta^2$. We therefore have $\mu \sim \tau \sim \eta^{3/2}$. One interesting feature in these oscillations is that the period is not constant. The separation between the first and the second minima is ~190 Å, between

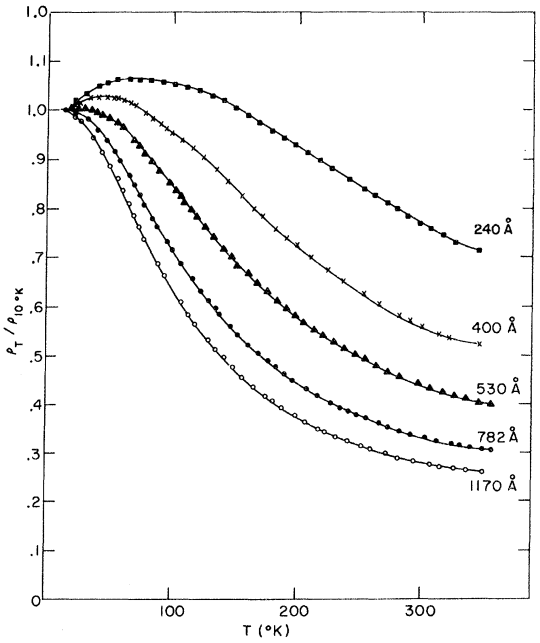

FIG. 10. Temperature dependence of the resistivity.

the second and the third only ~140 Å. The variation in the period may originate from the thickness dependence of the Fermi energy and of the effective mass. The Fermi energy changes with thickness because of the neutrality condition which must be satisfied in a semimetal. The thickness variation of the effective mass arises from the nonparabolic band structure[11] of Bi. Detailed quantitative analysis will require numerical computation as well as more accurate experimental work. Nevertheless, the period in the order of 170 Å is in good agreement with our estimate using the known band parameters and the approximate thickness dependence of the Fermi energy.

B. Temperature Dependence of Galvanomagnetic Coefficients

Most of the studies made thus far on the QSE have been concerned with the thickness dependence of the galvanomagnetic coefficients. To our knowledge, nobody has yet investigated the temperature dependence of the magnetoresistance and, except for the work of Ogrin *et al.* and that of Hoffman *et al.*,[1] the temperature dependence of the resistivity and of the Hall coefficient has been equally neglected. This is not at all surprising: The experimental observation of oscillations in the transport coefficients of the film when its thickness is varied is the best and most convincing evidence of size quantization. On the other hand, the variation of the carrier concentration with temperature is not an exclusive property of thin films. In bulk Bi, the carrier density decreases by a factor of 2 or 3 in going from room temperature to 4.2 °K.[12] This variation is much smaller than the predictions of our calculations for the very thin films ($a < 300$ Å) but it is comparable to the changes predicted for $a > 1000$ Å. However, the temperature dependence of the transport coefficients of these films is so different from that of the bulk as to warrant careful study.

The experimental results of the temperature dependence of ρ, R_H, and $\Delta\rho(H)$ for several films are shown in Figs. 10–12. The first striking difference

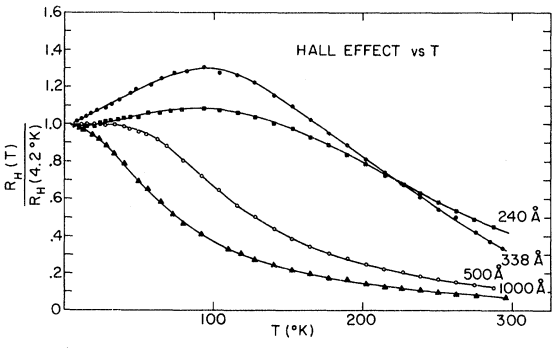

FIG. 11. Temperature dependence of the Hall coefficient.

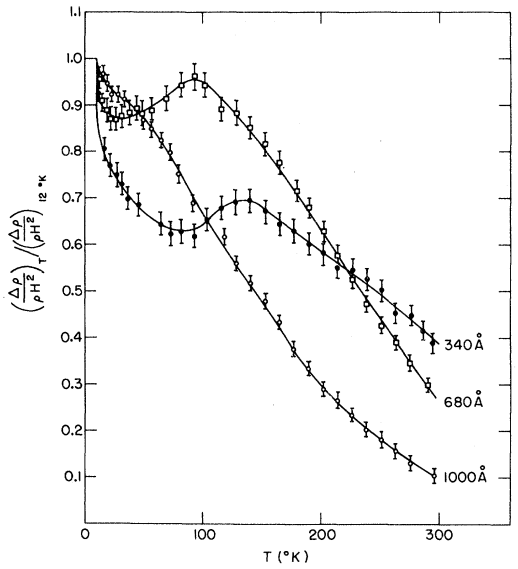

FIG. 12. Temperature dependence of the magnetoresistance coefficient.

between the bulk and the films can be seen in the behavior of $\rho(T)$. In bulk Bi, the resistivity decreases with decreasing temperature [for high purity samples $\rho(300\,°K)/\rho(4.2\,°K)$ can be as high as 400][13]; in thin films this situation is reversed: ρ increases when the temperature is lowered. Moreover, for the thinner films ($a \lesssim 600$ Å), the resistivity as well as the Hall coefficient exhibit a broad maximum whose position moves to lower temperatures as the thickness of the film is increased. The initial rise in ρ and R_H is due to the decrease in the carrier concentration combined with the fact that the mean-free path is restricted by crystal imperfections. The maximum in ρ and R_H cannot be understood in terms of $N(T)$, which we know is a monotonic function of the temperature. The key to this maximum must lie in the behavior of the mobilities. It is important therefore to understand $\Delta\rho(H)/\rho H^2$ which, as we have indicated, is a function of the mobilities only. To understand the peculiar behavior of the magnetoresistance coefficient (see Fig. 12) and hence of the mobilities, we have to consider the different scattering mechanisms that could come into play. In general, the effective mobility of the carriers can be written as

$$(\mu_{\text{effective}})^{-1} = (\mu_{\text{phonon}})^{-1} + (\mu_{\text{electron}})^{-1} + (\mu_{\text{impurity}})^{-1} + (\mu_{\text{surface}})^{-1} + \cdots ,$$

where μ_{phonon} is the mobility associated with the scattering of the electrons by the lattice, etc.

Using the deformation potential method, Iogansen[6] and Ya Demikhovskii and Tavger[14] have shown that in a thin film, the relaxation time associated

with the scattering of the electrons by the accoustical phonons is given by $\tau^{-1}_{\text{phonon}} \sim T$. Impurity scattering is usually assumed to be independent of the temperature. This is true in most metals where the Fermi energy η remains fairly constant. However, in these films our computer calculation shows that for $T > 70\,^{\circ}\text{K}$, $\eta \sim T$. We have also indicated in connection with the thickness dependence of the magnetoresistance that $\tau^{-1}_{\text{impurity}} \sim \eta^{-3/2}$. Consequently, we can write that $\tau^{-1}_{\text{impurity}} \sim T^{-3/2}$. Recent studies[15] have shown that in Bi the electron-electron scattering becomes quite important at low temperatures and that $\tau^{-1}_{\text{electrons}} \sim T^2$. Moreover, Iogansen[6] has also shown that in size-quantized films $\tau^{-1}_{\text{electron}} \sim 1/a^2$. Finally, we can assume that the surface scattering is temperature independent. Combining all this information and remembering that $\tau \sim \mu$, we get the following expression for the temperature dependence of the mobility:

$$(\mu_{\text{effective}})^{-1} = (\alpha T)_{\text{phonon}} + (\beta T^{-3/2})_{\text{impurity}} + (\gamma T^2/a^2)_{\text{electron}} + \cdots .$$

We can now proceed to give a qualitative explanation of the observed behavior of the magnetoresistance coefficient. At high temperatures the scattering is probably due to impurities and phonons, since the average size of the crystallites is comparable to the mean-free path of the carriers in bulk Bi. When the temperature is lowered, the phonon term will cause the mobilities to go up, while the impurity term will make them go down. As the temperature continues to decrease, the scattering by the phonons will become less important and the impurity mechanism will take over, causing the observed decrease in the mobilities. But if we refer to Fig. 3(b), we can see that below $70\,^{\circ}\text{K}$ and the Fermi energy tends to level off, and therefore the impurity scattering should become less and less temperature dependent. The final rise of ρ could be accounted for by the electron-electron scattering term which plays an important role at low temperatures.

Within this context, it is easy to understand why the maximum and the minimum move to lower temperatures when the thickness of the film is increased. The temperature at which the impurity term will dominate the phonon term increases with decreasing thickness because the higher density of impurities in the thinner films results in a greater probability for impurity scattering. Similarly, since the electron-electron scattering coefficient is proportional to $1/a^2$, the thinner the film, the higher the temperature at which this term will come into play. It is the rise in the mobilities associated with the electron-electron scattering which is responsible for the observed maximum in the temperature dependence of the resistivity.

V. CONCLUSION

We have studied the transport properties of single-crystal thin films of Bi between $12\,^{\circ}\text{K}$ and room temperature. Throughout the entire experiment, the films were kept inside the high-vacuum system so that air contamination was minimized. We found that by keeping the samples *in situ*, our results reveal certain outstanding features in contrast to most of the similar work reported previously. One crucial fact is that the thickness dependence of the resistivity, Hall coefficient, and the magnetoresistance coefficient, except in the region where oscillations due to QSE take place, all fall on smooth curves with very little scatter. This is in contrast to the largely scattered data reported previously by measurements with films taken out of the vacuum. By this observation, we feel that the QSE, weak as it is, has been correctly found in our experiment.

The oscillation in resistivity [Fig. 6(c)] and magnetoresistance coefficient (Fig. 9) at $12\,^{\circ}\text{K}$ are ascribed to the effect due to size quantization. Quantitative comparison between our observed oscillation period and the computed ones was not attempted, since more accurate measurements seem desirable. However, the observed periods $\Delta a \sim 140$–190 Å are in good agreement with our estimate.

The broad minimum in the resistivity curve [Fig. 6(c)] seems very interesting. Its cause is not clearly known. We may speculate that it might arise from a possible semimetal-semiconductor transition.

From the Hall-effect study (Fig. 7), we concluded that the infinite-potential-well model, with the boundary condition that the wave function vanishes at the film surfaces, doe not predict a correct thickness dependence. However, replacing the boundary condition by $\nabla\Psi = 0$ does give the thickness variation in accord with our data.

The magnetoresistance coefficient gives the thickness dependence of the mobilities. We found from these measurements that in Bi films, the Fermi energy varies with the film thickness.

In an effort to sort out the various scattering mechanisms in these films, we have made temperature-dependence studies of the transport properties. Since some of the films had to be taken out of the vacuum in order to use a high-field magnet, the temperature dependence of the Hall effect and the magnetoresistance is inconclusive. It seems that impurity scattering in these films plays a dominant role in determining the temperature dependence, in contrast to the temperature-independent scattering by impurities in a bulk metal. Consequently, the variation of the Fermi energy becomes very important in understanding the temperature dependence of the transport phenomena, in particular

at low temperatures.

It is clear that the transport studies of thin films in the QSE region contains a whole wealth of intriguing physical problems, the problem of boundary conditions, the problem of various scattering mechanisms, and the problems associated with the feasible semimetal-semiconductor transition, etc. More accurate measurements in still better vacuum and quantitative-model computations are highly desirable.

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[1]Yu F. Ogrin, V. N. Lutskii, and M. I. Elinson, Zh. Eksperim. i Teor. Fiz. Pis'ma v Redaktsiyu 3, 114 (1966) [Sov. Phys. JETP Letters 3, 71 (1966)]; V. N. Lutskii, D. N. Korneev, and M. I. Elinson, *ibid.* 4, 267 (1966) [4, 179 (1966)]; Yu F. Ogrin, V. N. Lutskii, M. U. Arifova, V. I. Kovalev, V. B. Sandomirskii, and M. I. Elinson, Zh. Eksperim. i Teor. Fiz. 53, 1218 (1967) [Sov. Phys. JETP 26, 714 (1968)]; V. P. Duggal and Raj Rup, J. Appl. Phys. 40, 492 (1969); Jong Min Lee *et al.*, J. Korean Phys. Soc. 3, 27 (1970); R. A. Hoffman and D. R. Frankl, Phys. Rev. B 3, 1825 (1971).

[2]I. M. Lifshitz and A. M. Kosevich, Izv. Akad. Nauk SSSR, Ser. Fiz. 19, 395 (1955) [Bull. Acad. Sci. USSR, Phys. Ser. 19, 353 (1955)].

[3]Y. H. Kao, R. D. Brown, and R. L. Hartman, Phys. Rev. 136, A858 (1964).

[4]N. Garcia, Y. H. Kao, and O. F. Kammerer, Thin Films (to be published).

[5]W. S. Boyle and G. E. Smith, Progr. Semicond. 7, 1 (1963).

[6]L. V. Iogansen, Zh. Eksperim. i Teor. Fiz. 50, 709 (1966) [Sov. Phys. JETP 23, 470 (1966)].

[7]V. B. Sandomirskii, Zh. Eksperim. i Teor. Fiz. 52, 158 (1967) [Sov. Phys. JETP 25, 101 (1967)].

[8]A. Paskin and A. D. Singh, Phys. Rev. 140, A1965 (1965).

[9]R. Zitter, Phys. Rev. 127, 1471 (1962).

[10]J. M. Ziman, *Principles of the Theory of Solids* (Cambridge U.P., New York, 1964).

[11]See, for example, a review by L. A. Falkovski, Usp. Fiz. Nauk 94, 3 (1968) [Sov. Phys. Usp. 11, 1 (1968)].

[12]Y. H. Kao (unpublished).

[13]A. N. Friedman and S. H. Koenig, IBM J. Res. Develop. 4, 158 (1960).

[14]V. Ya Demikhovskii and B. A. Tavger, Fiz. Tverd. Tela. 6, 960 (1964) [Sov. Phys. Solid State 6, 743 (1964)].

[15]A. N. Friedman, Phys. Rev. 159, 553 (1967); R. Hartman, *ibid.* 181, 1070 (1969); E. W. Fenton, J. P. Jan, A. Karlson, and R. Singer, *ibid.* 184, 663 (1969); V. Chopra, R. K. Ray, and S. M. Bhagat, Phys. Status Solidi 4(a), 205 (1971); H. D. Drew and U. Strom, Phys. Rev. Letters 25, 1755 (1970); F. C. Chen, Jay Kirschenbaum, and Y. H. Kao (unpublished).

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Longitudinal Magnetoresistance of Thin Metallic Films with Partially Specular Boundary Scattering

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The longitudinal magnetoresistance of a thin metal film has been calculated using Chambers's method. It is assumed that the electron Fermi surface as well as the bulk mean-free path are spherically symmetric. Contrary to previous work based on the assumption of wholly diffuse surface scattering, we consider that scattering of electrons at the boundaries is partially specular. Explicit magnetoresistance curves have been calculated by numerical integration. It is found that low-field magnetoresistance depends quite sensitively on the fraction of specularly reflected electrons at the boundaries (ϵ). The resistance may change an order of magnitude between $\epsilon = 0$ and $\epsilon = 0.9$ in contrast to the corresponding $\sim 10\%$ variations in surface impedance associated with the anomalous skin effect. It is proposed that direct comparison between experimental data and the computed curves will yield information on the nature of boundary scattering.

I. INTRODUCTION

The behavior of free electrons in thin metallic films has been a subject of long-standing experimental and theoretical interest.[1] Owing to the presence of boundary scattering, the dynamics of conduction electrons in these films will differ significantly from that in the bulk material when the electronic mean-free path (mfp) becomes comparable to the film thickness. The first rigorous