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A two-band model for the galvanomagnetic properties of thin semimetal films

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A two-band model is proposed to describe the galvanomagnetic properties in thin samples of transition metals or of semimetals such as bismuth which are characterized by two overlapping partially filled bands. The formalism proposed by Sondheimer and Wilson for transition metals and the Cottey model of carrier scattering at the external surfaces are used to solve size effect problems in a thin film subjected to a transverse magnetic field. The general case where the number of carriers per unit volume differs for the two bands is studied. The influence of the temperature is accounted for introducing a parameter x which corresponds to the fraction of the current carried by the conduction electrons. The results of these calculations are presented within the limit of low magnetic fields. Compared with the classical F-S theory, the variation of the Hall effect with film thickness is found to be determined by three essential parameters: the specularity parameter p, the ratio, y, of the number of carriers in the two bands, and the temperature-dependent parameter x. A large scatter of theoretical results is reported; in particular for typical sets of values for p, x and y the size effects can be exactly opposite to those predicted by one-carrier models. Tentative attempts to fit previously published data on the basis of the present model are undertaken. Qualitative agreement is observed, the theory is found to be able to explain the change in the sign of the Hall coefficient with increasing thickness sometimes observed in bismuth films. Difficulties in controlling morphology and geometrical surface properties of films with various thicknesses are outlined. As a consequence, one may find here a possible explanation for quantitative differences between theory and experiments.

1. Introduction

There have been a number of experimental studies [1–3], on the electrical and galvanomagnetic transport properties of thin metal films. Examination of the literature shows that, in general, the results of these studies have been compared with the predictions of the geometrical surface scattering theories of either Fuchs–Sondheimer (F–S) [4, 5] or Cottey [6] which assume a simple free-electron model of the metal. But many works have also been published on the electrical properties of bismuth [7–14] or of nickel and nickel-based [15–17] thin films.

Let us examine the case of the Hall coefficient, R_{Hf}, of films. Hoffman and Frankl [13] measured the galvanomagnetic coefficients of well-ordered bismuth films between 1.15 and 300 K. In the low-temperature region, the classical F–S theory was found to explain crudely the observed thickness dependence, even if R_{Hf} increased with decreasing thickness more rapidly than that predicted by the theory. Data on transport properties of bismuth films published by Inoue *et al.* [12] showed a different behaviour. The Hall coefficient changed its sign in the range 77 to 300 K whereas the absolute value of R_{Hf} at 77 K decreased with decreasing thickness. This observation was in qualitative agreement with the measurement of R_{Hf} on bismuth films by Garcia *et al.* [11]. Effectively, at low temperatures, the Hall coefficient exhibited a size effect exactly opposite to that predicted by the F–S theory; R_{Hf} increased with increasing thickness. Kochowski and Opilski [10] also observed a similar behaviour when they investigated the thickness dependence of the Hall coefficient of thin evaporated bismuth films at 80 K. In contrast, at room temperature, Kochowski and Opilski reported a change in the sign of R_{Hf} together with changes in R_{Hf} with thickness which appeared to be very roughly consistent with theoretical F–S predictions. Enhanced size effects in the ordinary Hall coefficient were observed by Ghosh and Pal [15] in nickel films; the departure from the F–S theory was particularly marked in the low thickness range. Chaudhuri and Pal [17] interpreted their results on the ordinary Hall effect in ferromagnetic copper–nickel films only in terms of the conduction in both the s and d bands; the F–S theory failed to explain the observed behaviour.

It is clear from the preceding discussion that a comparison with the classical F–S theory or the Cottey model is not meaningful. Effectively, nickel is known as a transition metal with a partially filled d

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band [18]; consequently, carriers of both the s and d bands can contribute to the conduction processes. In bismuth, an interesting element belonging to the so-called semimetals, the electrical transport properties are due to a small number of electrons at the bottom of the conduction band and an equal number of holes at the top of the valence band [19]. Thus nickel and bismuth are both characterized by an overlap, Δ, of the s and d bands or of the conduction band and the valence band and by the fact that two different types of carrier contribute to the galvanomagnetic effects. Hence models based on a single conduction band can fail to explain the observed size effects. Let us recall that a two-band model [20, 21] which consists of two overlapping bands of normal form is commonly used [22, 23] to interpret experimental results on the magnetoresistance and Hall effects in bulk materials such as bismuth and transition metals.

In view of the data on the thickness dependence of R_{Hf} in bismuth and nickel films it was felt necessary to derive theoretical expressions of the Hall coefficient of thin samples of semimetal incorporating a surface scattering model. In our solution we have chosen to use a method developed by Cottey [6] which leads to analytical expressions for the galvanomagnetic coefficients and which under the assumption of a free-electron model is known to give reasonable fits of the thickness dependence of the transport properties of thoroughly annealed metal films [3].

2. Theory

2.1. Solving the transport equation

We deal with the model in which there are two overlapping partially filled bands, namely the s and d bands, of standard form, i.e. in each band the energy, W, is proportional to the square of the wave vector, $\boldsymbol{k}$. Assuming that the s–d transitions are negligible, the behaviour of the carriers in each band remains independent of what happens in the other band. Now if, to avoid confusion, we essentially use in this paper the notation and the formalism proposed several years ago by Sondheimer and Wilson [20, 21] we can write the energy level in the s band as

$$W = \frac{\hbar^2|\boldsymbol{k}|^2}{2m_s} \tag{1}$$

where $\boldsymbol{k}$ is the wave vector with components k_x, k_y and k_z. m_s is the effective mass of the s electron, and $\hbar$ is the Planck's constant. The corresponding relation for the energy level in the d band is

$$W = \Delta - \frac{\hbar^2|\boldsymbol{k}|^2}{2m_d} \tag{2}$$

where Δ is the band overlap and m_d is the effective mass of d carriers.

Explicit expressions for the distribution functions of the carriers can be obtained using the Sondheimer formalism [20, 21]. They are

$$f_s = f_s^0 - (k_x C_{1s} + k_y C_{2s}) \frac{\partial f_s^0}{\partial W} \tag{3}$$

$$f_d = f_d^0 + (k_x C_{1d} + k_y C_{2d}) \frac{\partial f_d^0}{\partial W} \tag{4}$$

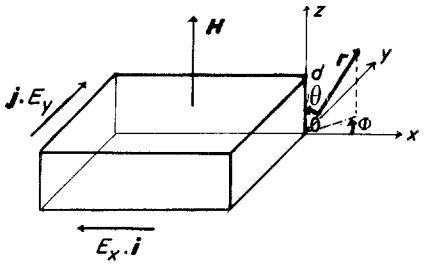

Figure 1 The geometry of the model.

where C_{1s}, C_{1d}, C_{2s} and C_{2d} are functions of the energy W, and the subscripts s and d refer to the carriers of the s and d bands, respectively; f_s^0 indicates the distribution function in the absence of any perturbation.

If the background scattering and the carrier scattering at the film surfaces are assumed to occur independently, Matthiessen's rule [24] applies in each band separately and a resultant time of relaxation can be defined for each type of carrier. Let τ_s^* and τ_d^* be the total relaxation time describing the simultaneous background and external surface scatterings for, respectively, the s and d bands. Suppose now that the perturbing fields are sufficiently small to induce effects which can be represented by a first-order perturbation of the equilibrium distribution, the calculation can be carried out by introducing

$$f_i = f_i^0 + f_i^1(\boldsymbol{k}) \qquad i = s, d \tag{5}$$

in which $f_s^1(\boldsymbol{k})$ and $f_d^1(\boldsymbol{k})$ are the small deviations from equilibrium caused by the external fields. Then in presence of an electric field, $\boldsymbol{E}$ (E_x, E_y, 0) and a transverse magnetic field, $\boldsymbol{H}$ (0, 0, H) (Fig. 1) the Boltzmann transport equations are finally expressed in the following condensed form

$$f_i^1 = \frac{e}{\hbar}\tau_i^*(\mathrm{E} + \boldsymbol{v} \wedge \boldsymbol{H})\frac{\partial f_i(\boldsymbol{k})}{\partial \boldsymbol{k}} \qquad i = s, d \tag{6}$$

where v is the velocity of either the s or the d carriers.

Let us recall that the functions C_{1i} and C_{2i} (i = s, d) do not depend explicitly on v_x and v_y. Thus making use of Equations 3 and 4, neglecting the terms containing products of $\boldsymbol{E}$ with $f_i^1(\boldsymbol{k})$ but retaining the terms related to the products $(\partial f_i/\partial W)C_{1i}$ and $(\partial f_i/\partial W)C_{2i}$, alternative expressions for the deviation functions f_s^1 and f_s^1 are readily found to be

$$f_s^1 = \tau_s^* \frac{\hbar}{m_s}\frac{\partial f_s^0}{\partial W} \times \left[e(k_x E_x + k_y E_y) + \frac{eH}{\hbar}(k_x C_{2s} - k_y C_{1s})\right] \tag{7}$$

$$f_d^1 = \tau_d^* \frac{\hbar}{m_d}\frac{\partial f_d^0}{\partial W} \times \left[-e(k_x E_x + k_y E_y) + \frac{eH}{\hbar}(k_x C_{2d} - k_y C_{1d})\right] \tag{8}$$

Now to solve the Boltzmann transport equations we need only to determine the functions C_{1i} and C_{2i}, comparing Equations 3 and 4 with Equations 7 and 8,

respectively, one obtains the following formulae

$$C_{1s} = -\frac{e\hbar}{m_s}\tau_s^*\left(\frac{E_x - \alpha_s^* E_y}{1 + \alpha_s^{*2}}\right) \quad (9a)$$

$$C_{2s} = -\frac{e\hbar}{m_s}\tau_s^*\left(\frac{\alpha_s^* E_x + E_y}{1 + \alpha_s^{*2}}\right) \quad (9b)$$

for the s electrons. In a similar way expressions for C_{1d} and C_{2d}

$$C_{1d} = -\frac{e\hbar}{m_d}\tau_d^*\left(\frac{E_x + \alpha_d^* E_y}{1 + \alpha_d^{*2}}\right) \quad (10a)$$

$$C_{2d} = \frac{e\hbar}{m_d}\tau_d^*\left(\frac{\alpha_d^* E_x - E_y}{1 + \alpha_d^{*2}}\right) \quad (10b)$$

are at once also obtained. In the above equation, the α_i^* parameters are written as

$$\alpha_i^* = \frac{eH\tau_i^*}{m_i} \qquad i = s, d \quad (11)$$

and with our convention take always positive values.

2.2. Relations for the electrical current density and the Hall coefficient

Before deriving the expressions for the components J_x and J_y of the current density $\boldsymbol{J}$ it seems of interest to pause here to focus attention on the definition of the background mean-free paths of the s and d carriers. Let us recall that under the assumption of a quasi-free model the background mean-free path of an s electron is given by [3, 24]

$$\lambda_{0s} = \tau_{0s} v_F = \tau_{0s}[2W_F/m_s]^{1/2} \quad (12)$$

where τ_{0s} is the background relaxation time and W_F the Fermi energy.

Turning to the carriers of the d band one can see that at high temperatures where a background relaxation time τ_{0d} exists, we may attribute a background mean-free path

$$\lambda_{0d} = \tau_{0d}[2(\Delta - W_F)/m_d]^{1/2} \quad (13)$$

to a d carrier where we have taken as our zero energy the bottom of the s band. Obviously there is no reason to assume equal background relaxation times and the mean-free paths for the two bands.

As outlined in Section 1, the main feature of the classical F–S theory which holds when the material can be regarded as an isotropic material with a single type of carrier is, within the limit of small magnetic fields, to predict a pronounced increase in various transport parameters such as the film resistivity and the Hall coefficient with decreasing film thickness, d, or with roughening of the film surfaces [1–3]. Because the F–S theory leads to analytical expressions for the electrical resistivity of thin films in the limits only of very thick and very thin films an overview of the theoretical F–S size effect requires, in general, computational techniques.

Moreover, it must be borne in mind that even for bulk isotropic material with two different types of carrier, the expressions for the galvanomagnetic coefficients become more complicated showing in particular that the Hall coefficient may be very sensitive to small differences in the number of s and d carriers and to differences in the carrier mobilities. Thus we can anticipate some theoretical results by noticing that moreover the size effects in the galvanomagnetic coefficients of tin semimetal films are partially determined by the differences in the mean-free paths of the two types of carrier. In these conditions the behaviour appears more and more complex and the effects of the carrier scattering can no longer act in many ways analogously to the predictions of the classical F–S theory. In particular, the possibility to derive approximate expressions for the electrical resistivity and the Hall coefficient of semimetal films in reduced thickness ranges which are sufficiently large to provide convenient fits of experimental data, seems in fact to be very restricted. For these reasons, in this paper we opt for a Cottey-like representation of the carrier scatterings at external surfaces rather than for a representation based on the F–S model. The choice is motivated by the fact that in this manner we avoid some cumbersome numerical computations and proceed always with analytical relations which permit a rapid evaluation of the galvanomagnetic coefficients. Moreover it is now well established that although the case of totally diffuse scatterings at the film surface is consequently omitted the Cottey model seems adequate [3] for partially specular scatterings, i.e. for values of the specularity parameter, p, greater than 0.4, and that its validity can be extended over the almost entire p range under special conditions [25].

At this point we must recall that in the framework of the Cottey model the relaxation time, $\tau(\theta)$, associated with the scattering at the external surfaces expressed as [3, 6]

$$\tau(\theta) = \frac{d}{|\boldsymbol{v}|\,|\cos\theta|\,\ln(1/p)} \quad (14)$$

in polar coordinates $(\boldsymbol{k}, \theta, \Phi)$ (Fig. 1) for a carrier moving with a velocity $\boldsymbol{v}$ remains explicitly independent of the type of the carrier until one assumes that the phenomenological reflection parameter, p, which describes the average effect of roughness of the film surfaces, is the same for the two types of carrier.

Assuming further that the background and surface scatterings occur independently, the total relaxation time, τ_i^*, describing these two simultaneous scattering processes

$$\frac{1}{\tau_i^*} = \frac{1}{\tau_{0i}} + \frac{1}{\tau(\theta)} = \frac{1}{\tau_{0i}}\left[1 + \frac{\tau_{0i}|\boldsymbol{v}|\ln(1/p)}{d}|\cos\theta|\right] \quad (15)$$

$$(i = s, d)$$

depends on the type of carrier. Here it must be pointed out that using the term $2(1 - p)/(1 + p)$ instead of the term $\ln(1/p)$ in Equation 15 the model remains valid for more and more diffuse surface scatterings [25].

To calculate the galvanomagnetic coefficients and especially the Hall coefficient on which emphases is placed, we need the total electrical current $\boldsymbol{J}(J_x, J_y, 0)$ which is the sum of those due to the two bands separately.

The calculation of the electrical density (J_{xi}, J_{yi}, 0) for the two bands is classical. Starting from the formulae

$$J_{xi} = \frac{e\hbar}{4\pi^3 m_i} \iiint k_x^2 C_{1i} \frac{\partial f_i^0}{\partial W} \mathrm{d}^3k \qquad (16a)$$

$$i = s, d$$

$$J_{yi} = \frac{e\hbar}{4\pi^3 m_i} \iiint k_y^2 C_{2i} \frac{\partial f_i^0}{\partial W} \mathrm{d}^3k \qquad (16b)$$

where for a film the functions C_{1i} and C_{2i} are given by either Equations 9 or 10 involving the respective total relaxation times τ_s^* and τ_d^*.

The integration is performed in polar coordinates by using the usual approximate method for integrals involving the Fermi distribution function in which the integrals are expanded as an ascending series in $(k_B T/W_F)^2$ for the s band and as an ascending series in $[k_B T/(\Delta - W_F)]^2$ for the d-band [20, 21].

Retaining only the terms of zero order, it is found that for the d band the current density takes the forms

$$J_{xd} = \tfrac{3}{4}\sigma_{0d} \int_0^\pi \frac{\sin^3\theta[E_x(1 + |\cos\theta|/\mu_d) + \alpha_d^2 E_y}{[1 + |\cos\theta|/\mu_d]^2 + \alpha_d^2} \mathrm{d}\theta \qquad (17)$$

$$J_{yd} = \tfrac{3}{4}\sigma_{0d} \int_0^\pi \frac{\sin^3\theta[-\alpha_d E_x + (1 + |\cos\theta|/\mu_d)E_y]}{[1 + |\cos\theta|/\mu_d]^2 + \alpha_d^2} \mathrm{d}\theta \qquad (18)$$

where, for convenience, the size parameter, μ_d, is defined as

$$\mu_d = \frac{\mathrm{d}}{\lambda_{0d}} \frac{1}{\ln(1/p)} \qquad (19)$$

and where the field parameter α_d is connected with the background relaxation time τ_{0d}

$$\alpha_d = \frac{eH\tau_{0d}}{m_d} \qquad (20)$$

σ_{0d} is the contribution of the d band to the total background conductivity, σ_0

$$\sigma_{0d} = \frac{e^2 n_d \tau_{0d}}{m_d} \qquad (21)$$

where n_d is the number of vacancies in the d band.

Carrying out the integration over the variable θ one finally obtains

$$J_{xd} = \tfrac{3}{2}\sigma_{0d}[\mathscr{A}_d E_x + \alpha_d \mathscr{B}_d E_y] \qquad (22)$$

$$J_{yd} = \tfrac{3}{2}\sigma_{0d}[-\alpha_d \mathscr{B}_d E_x + \mathscr{A}_d E_y] \qquad (23)$$

with

$$\mathscr{A}_d = -\tfrac{1}{2}\mu_d + \mu_d^2 + \frac{\mu_d}{2}(1 - \mu_d^2 + \alpha_d^2\mu_d^2) \times \ln\left[\frac{(1 + \mu_d^{-1})^2 + \alpha_d^2}{1 + \alpha_d^2}\right] - 2\alpha_d\mu_d^3 \tan^{-1}\left(\frac{\alpha_d}{\mu_d} \frac{1}{\alpha_d^2 + 1 + \mu_d^{-1}}\right) \qquad (24)$$

and

$$\mathscr{B}_d = -\mu_d^2 + \mu_d^3 \ln\left[\frac{[1 + \mu_d^{-1}]^2 + \alpha_d^2}{1 + \alpha_d^2}\right] + \frac{\mu_d}{\alpha_d}[1 - \mu_d^2 + \alpha_d^2\mu_d^2] \times \tan^{-1}\left(\frac{\alpha_d}{\mu_d} \frac{1}{\alpha_d^2 + 1 + \mu_d^{-1}}\right) \qquad (25)$$

The corresponding relations for the s electrons are found to be

$$J_{xs} = \tfrac{3}{2}[\sigma_{0s}\mathscr{A}_s E_x - \alpha_s \mathscr{B}_s E_y] \qquad (26)$$

$$J_{ys} = \tfrac{3}{2}[\sigma_{0s}\sigma_s \mathscr{B}_s E_x + \mathscr{A}_s E_y] \qquad (27)$$

where σ_{0s} is the part of the background conductivity associated with the s electrons. The relations for the functions $\mathscr{A}_s$ and $\mathscr{B}_s$ are the same as in Equations 24 and 25 except that we must substitute the subscript s for the subscript d and we must bear in mind that the size parameter

$$\mu_s = \frac{\mathrm{d}}{\lambda_{0s}} \frac{1}{\ln(1/p)} \qquad (28)$$

and the field parameter α_s

$$\alpha_s = \frac{eH\tau_{0s}}{m_s} \qquad (29)$$

differ respectively as μ_d and α_d.

It is now possible to write the expressions for the components J_x and J_y of the total electrical current density; they are

$$J_x = \tfrac{3}{2}[(\sigma_{0d}\mathscr{A}_d + \sigma_{0s}\mathscr{A}_s)E_x + E_y(\alpha_d\sigma_{0d}\mathscr{B}_d - \alpha_s\sigma_{0s}\mathscr{B}_s)] \qquad (30a)$$

$$J_y = \tfrac{3}{2}[(\alpha_s\sigma_{0s}\mathscr{B}_s - \alpha_d\sigma_{0d}\mathscr{B}_d)E_x + E_y(\sigma_{0d}\mathscr{A}_d + \sigma_{0s}\mathscr{A}_s)] \qquad (30b)$$

This paper is essentially concerned with the investigation by means of the two-band model of the size effect in the Hall coefficient of thin films of metals in which there are two overlapping bands with emphasis on a comparison of the theoretical predictions in the free-electron model [26–29] and in the two-band model. Because the Hall coefficient is defined as the ratio [21, 26]

$$R_{Hf} = -\frac{E_y}{HJ_x}\Bigg\}_{J_y=0} \qquad (31)$$

using the relations for the functions $\mathscr{A}_i$ and $\mathscr{B}_i$ (i = s, d) together with the relations for the field parameters α_i and the contributions σ_{0i} to the bulk conductivity, from Equation 31 one obtains

$$R_{Hf} = \frac{2}{3}\frac{1}{e} \times \frac{\left(\frac{\sigma_{0d}^2}{n_d}\mathscr{B}_d - \frac{\sigma_{0s}^2}{n_s}\mathscr{B}_s\right)}{\left\{[\sigma_{0d}\mathscr{A}_d + \sigma_{0s}\mathscr{A}_s]^2 + \left(\frac{H}{e}\right)^2\left[\frac{\sigma_{0d}^2}{n_d}\mathscr{B}_d - \frac{\sigma_{0s}^2}{n_s}\mathscr{B}_s\right]^2\right\}} \qquad (32)$$

whereas the Hall coefficient of the bulk material for the case of a magnetic field of arbitrary magnitude is given by [21]

$$R_{H0} = \frac{1}{e} \times \frac{\left\{\left[\frac{\sigma_{0d}^2}{n_d} - \frac{\sigma_{0s}^2}{n_s} + \left(\frac{H}{e}\right)^2\right]\left[\frac{n_d - n_s}{n_s^2 - n_d^2}\sigma_{0s}^2\sigma_{0d}^2\right]\right\}}{\left[(\sigma_{0s} + \sigma_{0d})^2 + \left(\frac{H}{e}\right)^2 \frac{(n_s - n_d)^2}{n_s^2 n_d^2}\sigma_{0s}^2\sigma_{0d}^2\right]} \quad (33)$$

It is convenient [21] in order to discuss more easily the size effects in the Hall coefficient of transition metal films and especially to focus attention on the changes in the thickness dependence of R_{Hf} with the temperature, T, to write the background conductivity associated with each band in the forms

$$\sigma_{0s} = x\sigma_0, \qquad \sigma_{0d} = (1 - x)\sigma_0 \quad (34)$$

where σ_0 is the conductivity of the bulk material and x corresponds to the fraction of total electrical current which is carried by the s band. Effectively, it is generally usual [21] to account for the temperature variation of R_{H0} by allowing x to vary with temperature.

If, moreover, we consider the more general case where the numbers of the s and the d carriers differ, and introduce the parameter

$$y = n_s/n_d \quad (35)$$

the expression for the Hall coefficient, R_{Hf}, of a thin sample becomes

$$R_{Hf} = \frac{1}{e}\frac{2}{3n_s} \times \frac{(1 - x)^2 y\mathscr{B}_d - x^2\mathscr{B}_s}{[(1 - x)\mathscr{A}_d + x\mathscr{A}_s]^2 + \alpha_s^2\left[\frac{(1 - x)^2}{x}y\mathscr{B}_d - x\mathscr{B}_s\right]^2} \quad (36)$$

and involves parameters α_s, n_s, $k_s = d/\lambda_{0s}$ associated only with the s band, because the field parameter, α_d, and the mean free path, λ_{0d}, can be now rewritten in terms of x and y.

Now the corresponding expression for the Hall coefficient of the bulk material is

$$R_{H0} = \frac{1}{e}\frac{1}{n_s}\frac{[(1 - x)^2 y - x^2] + \alpha_s^2[(1 - y)y(1 - x)^2]}{1 + \alpha_s^2(1 - x)^2(1 - y)^2} \quad (37)$$

To get a general idea of the results it is sometimes assumed that $n_s = n_d$ [21] following this procedure, and putting $y = 1$ into Equations 36 and 37 the ratio of the Hall coefficient for a film of a transition metal to that of the bulk material reduces to

$$R_{Hf}/R_{Ho} = \frac{2}{3}\frac{1}{1 - 2x} \times \frac{(1 - x)^2\mathscr{B}_d - x^2\mathscr{B}_s}{[(1 - x)\mathscr{A}_d + x\mathscr{A}_s]^2 + \alpha_s^2\left[\frac{(1 - x)^2}{x}\mathscr{B}_d - x\mathscr{B}_s\right]^2} \quad (38)$$

because in this particular case the bulk Hall coefficient, R_{H0}, remains independent of H.

2.3. Discussion of theoretical results

The expressions for the Hall coefficient may be evaluated with the aid of no more than a pocket calculator. The Hall coefficient ratio, R_{Hf}/R_{H0}, and the Hall coefficient, R_{H0}, of the bulk material were evaluated assuming that the field parameter, α_s, associated with the s band takes a constant value of 0.01. An impression of the influence of the adjustable parameters x and y can be obtained from Figs 2 and 3 where we have plotted curves of the calculated Hall coefficient ratio (Equations 36 and 37) as a function of the reduced thickness k_s at $p = 0.75$. In each figure the varying parameter for the different curves is x while the parameter y is kept constant in the range 0.5 to 2.

In comparing the results displayed in Figs 2 and 3 with the predictions of one carrier models [26–29] it is clear that there are several interesting differences.

1. The one-carrier model based on the Cottey model [29] gives a decrease of the ratio R_{Hf}/R_{H0} as the film thickness is increased. The classical F–S theory [26] predicts that in the vicinity of $k = 1$ the Hall coefficient ratio falls below that of the bulk; however, this effect is only a few per cent so that it is, in general, ignored. Thus the essential feature of the one-carrier models remains the quasi-monotonic decrease of R_{Hf} to R_{H0} with increasing values of film thickness. As we see, at moderately high k_s the present model gives an opposite dependence on d with a Hall coefficient R_{Hf} which is less than that in the limit $k_s \to \infty$. The fact is that over the k_s range investigated here we find in most cases a Hall coefficient minimum, $[R_{Hf}/R_{H0}]_{min}$; the value of $[R_{Hf}/R_{H0}]_{min}$ as well as its position $[k_s]_{min}$ depending on the parameters x and y.

2. The plots of R_{Hf}/R_{H0} against the reduced thickness k_s at $p = 0.5$ are collected in Fig. 4 for some typical values of the parameters x and y. One can see that at first sight the influence of the specularity parameter, p, is particularly marked in the region

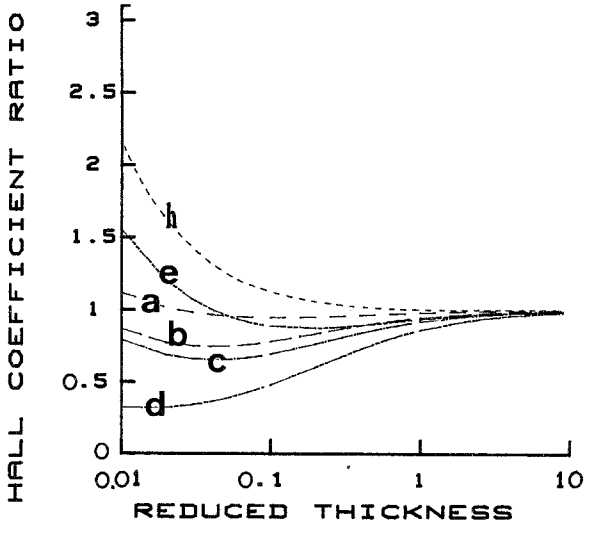

Figure 2 The Hall coefficient ratio, R_{Hf}/R_{H0}, plotted against the reduced thickness, k_s, assuming $p = 0.75$ and $y = 0.5$. (a), (b), (c), (d), (e) Theoretical curves for the respective x values of 0.88, 0.69, 0.55, 0.45 and 0.3. (h) Theoretical Cottey curve for $p = 0.75$ [29].

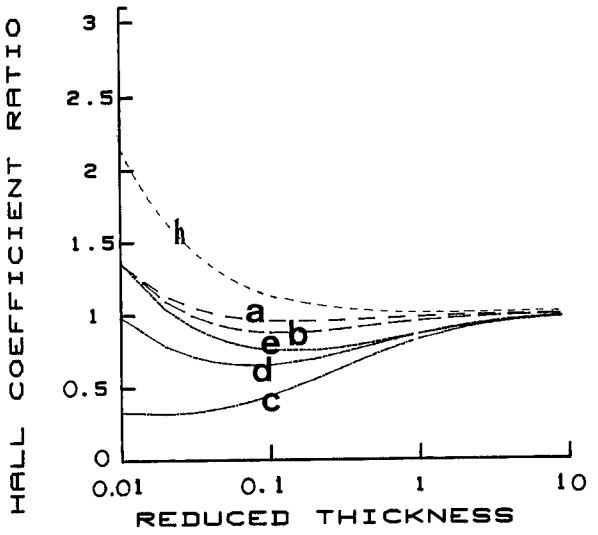

Figure 3 The Hall coefficient ratio, R_{Hf}/R_{H0}, plotted against the reduced thickness, k_s, assuming $p = 0.75$ and $y = 2$. (a), (b), (c), (d), (e) Theoretical curves for the respective x values of 0.88, 0.69, 0.55, 0.45 and 0.3. (h) Theoretical Cottey curve for $p = 0.75$ [29].

corresponding to very thin films. Moreover an obvious result of the two-band model is the more or less pronounced shifting of the Hall coefficient minimum to higher k_s values as p decreases. This movement is more conveniently illustrated in Table I where some tabulations concerned with R_{Hf}/R_{H0} have been inserted. From an experimental point of view this feature may become important. Effectively one might imagine the same type of movement could occur for any values of x and y so that as p is lessened we can see either an increase or a decrease in R_{Hf}/R_{H0}. Let us recall that changes in the transport properties of thin films with annealing can be partially ascribed [3, 30–35] to a mechanical reordering of the external film surface which evidently induces an increase in the specularity parameter p. Hence, care must be taken that as the R_{Hf}/R_{H0} against k_s plots for different values of p cross each other, the size effect can be considered as singular

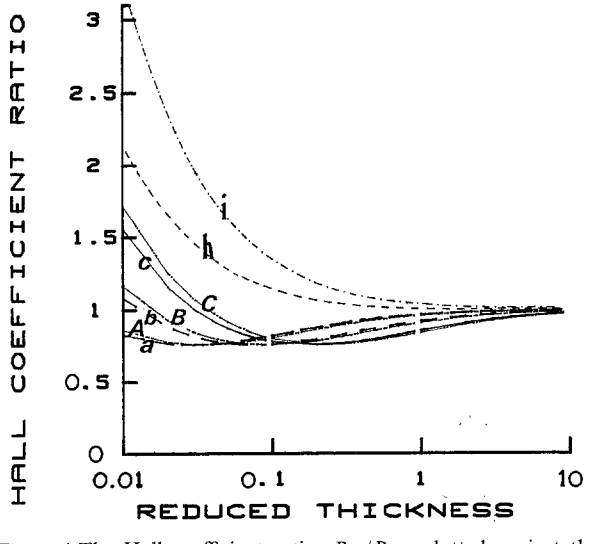

Figure 4 The Hall coefficient ratio, R_{Hf}/R_{H0}, plotted against the reduced thickness, k_s, assuming $p = 0.5$. (a), (b), (c) Theoretical curves for $y = 1$ and for the respective x values of 0.3, 0.55 and 0.88. (A), (B), (C) Theoretical curves for $y = 2$ and for the respective x values of 0.3, 0.55 and 0.88. (h), (i) Theoretical Cottey curves for the respective p values of 0.75 and 0.5 [29].

TABLE I Numerical values of the reduced Hall coefficient, R_{Hf}/R_{H0}, calculated for $y = 1$ according to Equation 38

k_s	$x = 0.45$			$x = 0.55$		
	$p = 0.9$	$p = 0.75$	$p = 0.5$	$p = 0.9$	$p = 0.75$	$p = 0.5$
0.01	0.8595	1.1632	1.7176	0.8265	1.0806	1.5578
0.02	0.7746	0.9267	1.2524	0.7640	0.8811	1.1569
0.04	0.7591	0.8028	0.9775	0.7645	0.7830	0.9232
0.08	0.7911	0.7589	0.8272	0.8058	0.7578	0.8012
0.1	0.8076	0.7580	0.7989	0.8237	0.7617	0.7800
0.2	0.8649	0.7852	0.7854	0.8811	0.7991	0.7581
0.4	0.9164	0.8388	0.7742	0.9286	0.8557	0.7861

for some typical measuring temperatures (MT) as soon as we are concerned with films annealed at various annealing temperatures (AT).

Equation 37 related to the bulk material can easily interpret some complicated processes such as the inversion temperature at which the Hall coefficient, R_{H0}, of a semimetal changes sign. In practice this is usually attributed to a variation of the parameter x with temperature. Because this typical behaviour is also met [10, 12] in thin samples of semimetal at specific MT, it is interesting to investigate if we are able to determine the ranges of values of x and y for which the theoretical Hall coefficient of thin films shows a change from positive to negative or vice versa with increasing film thickness. Looking back to Equation 37 we see that the Hall coefficient of bulk material changes its sign for critical values of x and y, denoted for convenience x_c and y_c, satisfying approximately the relation

$$y_c = [x_c/(1 - x_c)]^2 \tag{39}$$

We believe that we can use values close to x_c and y_c to determine the expected behaviour. Further confirmation comes from Fig. 5 which illustrates at a fixed x_c the variation of the Hall coefficient ratio, R_{Hf}/R_{H0}, with the parameter y for different values of the reduced thickness k_s. As expected, the sign of the Hall coefficient ratio changes rapidly as the parameter y passes through the critical value y_c. Moreover the range of y values where the reduced Hall coefficient, R_{Hf}/R_{H0}, falls to a negative value depends markedly on the film thickness. We can also plot R_{Hf}/R_{h0s} against

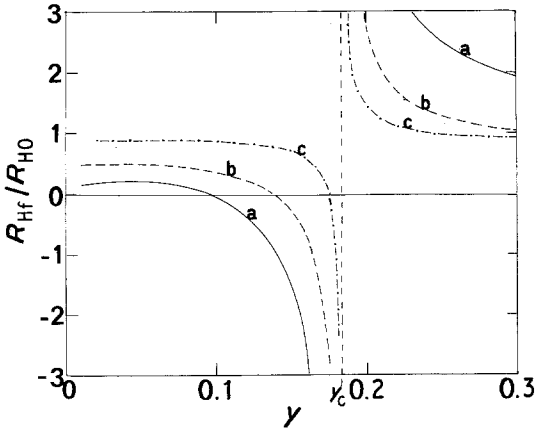

Figure 5 The Hall coefficient ratio, R_{Hf}/R_{H0}, plotted against the parameter y for different values of the reduced thickness, k_s, assuming $x = 0.3$ and $p = 0.75$. (a), (b), (c) Theoretical curves for the respective k_s values of 0.01, 0.1 and 1.

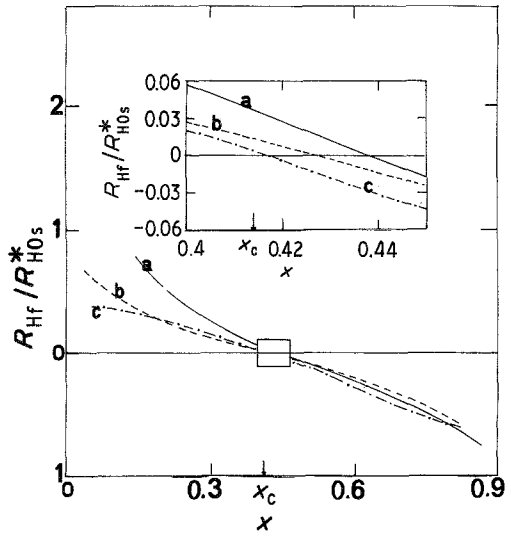

Figure 6 The Hall coefficient ratio, R_{Hf}/R_{H0s}, plotted against the parameter x for different values of the reduced thickness, k_s, assuming $y = 0.5$ and $p = 0.75$. (a), (b), (c) Theoretical curves for the respective k_s values of 0.01, 0.1 and 1. Inset: variation of R_{Hf}/R_{H0s} for x in the vicinity of $x_c = 0.414$.

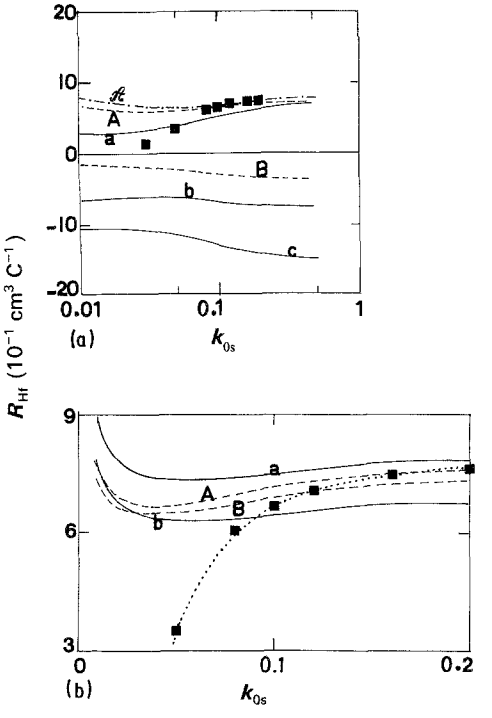

Figure 7 (a) Theoretical fit of published data (■) on bismuth films for MT = 77 K [11] assuming $p = 0.9$ and $\lambda_{0s} = 1\,\mu$m. (a), (b), (c) Theoretical curves for $x = 0.55$ and for respective y values of 2.1 and 0.5. (A), (B) Theoretical curves for $x = 0.55$ and for respective y values of 1 and 0.5. $\mathscr{A}$ is the theoretical curve for $x = 0.4$ and $y = 0.7$. (b) Experimental determination of the parameters x and y for data (■) on bismuth films [11] and for MT = 77 K. (a), (b) Theoretical curves for $y = 0.7$ and for respective x values of 0.39 and 0.4. (A), (B) Theoretical curves for $y = 1$ and for respective x values of 0.445 and 0.447.

x at a fixed critical y_c (Fig. 6) where R_{H0s} is the absolute value of the bulk Hall coefficient when we neglect the effect on the transport properties of adding d-like carriers to a metal (i.e. $R_{H0s} = 1/en_s$). The results undoubtedly indicate that the Hall coefficient reverses its sign with increasing film thickness in a small range of x around x_c. It can be seen that in this range the Hall effect is indeed small, it has the sign of conduction by holes for thinner films and leaves the hole-like sign for thicker films.

3. Discussion of experimental results on bismuth and conclusions

As noticed in Section 1 there is a relatively large number of papers [7–17] dealing with experimental studies of the Hall effect in thin samples of transition metals or of a semimetal such as bismuth. In most cases the fundamental origin of the size effect has remained far from complete. This is at least partially due to the lack of a coherent set of experimental data. In various papers the relevant properties were not measured in the same material so that, except for bismuth [7–14], it is difficult to obtain an overall picture. Effectively it is possible to collect a set of different experimental data on the electrical properties of bismuth films which can be analysed in the framework of the present model.

At this point it should be noticed that the two-band model gives the ratio R_{Hf}/R_{H0s}. Hence, before a comparison between this theoretical work and previous experimental works [7–14] is carried out, a corrective factor, $\mathscr{C}$, must be chosen, which constitutes a measure of the magnitude of $1/en_s$. After a rapid comparison of published data we have decided, in order to obtain a general correlation between the various experimental works, to use the same $\mathscr{C}$ for results at the measuring temperature (MT) of about 80 K. Further the corrections at different MT are calculated using published values [13, 19] of the ratio $N(\mathrm{MT})/N(80\,\mathrm{K})$, $N(\mathrm{MT})$ being the number of carriers per unit volume at MT assuming the carrier concentrations are the same for the two bands. This procedure provides theoretical values of R_{Hf}.

First let us consider experimental works [11, 12] concerned with one of the characteristic situations for the Hall coefficient outlined in the preceding section so that one-band models fail partly to explain the observed size effects in R_{Hf}. Garcia *et al.* [11] studied the thickness dependence of the resistivity, the Hall coefficient and the magnetoresistance of thin bismuth films consisting of identically oriented crystallites. After a detailed examination of their data Garcia *et al.* argued that the electron mean free path could be estimated to be around 10^{-2} and 10^{-3} times that in the bulk. Taking into account this last argument and the fact that because the films were very carefully annealed the surface scattering is not great enough to be essentially significant [3], tentative assumptions are made to fit their data at 77 K in the form R_{Hf} against k_{0s} (Fig. 7a) assuming $\lambda_{0s} = 0.5\,\mu$m and $p = 0.9$. Clearly a reasonable fit of the thickness dependence of the Hall coefficient of films at 77 K is obtained only for either $y = 1$ and x near 0.45 or $y = 0.7$ and x near 0.4. We have now to adjust the parameter x. It can be seen in Fig. 7b that the theoretical curves for $x = 0.447$ and $y = 1$ and for $x = 0.395$ and $y = 0.7$ may represent accurately the data for $d > 40$ nm but at smaller values of d there is a discrepancy. Because at $d < 40$ nm the size of crystallites depends on the film thickness, the value of the bulk mean free path of $0.5\,\mu$m cannot still be valid for the whole thickness

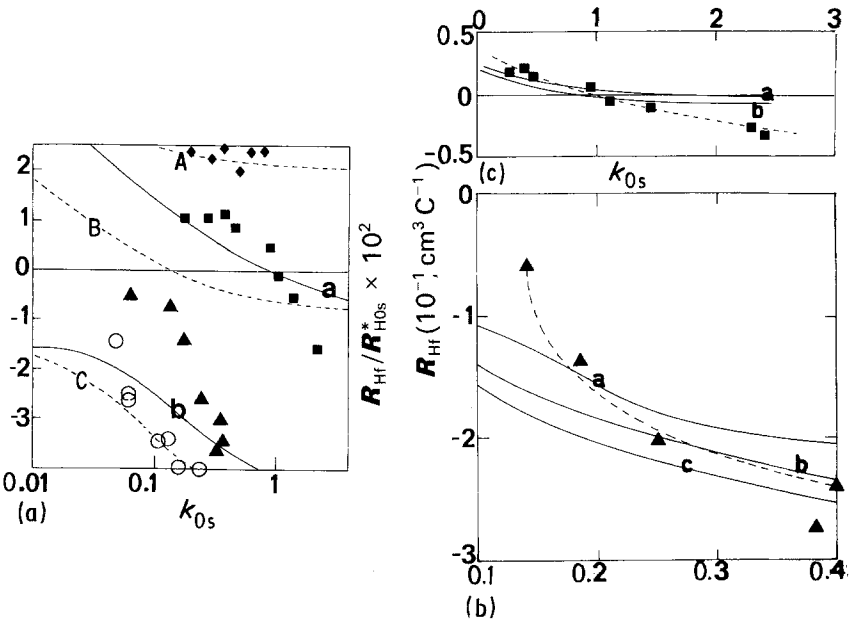

Figure 8 (a) Theoretical fit of published data on bismuth films by Inoue *et al.* [12] for MT = (■) 80 K and (▲) 300 K and by Kochowski and Opilski [10] for MT = (○) 80 K and (◆) 293 K. (a), (b) Theoretical curves for $p = 0.5, y = 0.5$ and for respective x values of 0.42 and 0.45. (A), (B), (C) Theoretical curves for $p = 0.9$. $y = 0.5$ and for respective x values of 0.4, 0.42 and 0.45. (b) Experimental determination of the parameter x for data (▲) on bismuth films [12] and for MT = 80 K. (a), (b), (c) Theoretical curves for $p = 0.7$, $y = 0.5$ and for respective x values of 0.42, 0.445 and 0.447. (c) Experimental determination of the parameter x for data (■) on bismuth films [12] and for MT = 300 K. (a), (b) Theoretical curves for $p = 0.7, y = 0.5$ and for respective x values of 0.416 and 0.418.

range investigated here, and thus some deviations may be expected for thinner films.

Inoue *et al.* [12] obtained an interesting set of experimental data on the Hall effect in polycrystalline bismuth films at MT ranging from 80 to 300 K: (i) at MT = 80 K R_{Hf} is always negative and its absolute value increases with d; (ii) for MT = 300 K a reversal of the Hall coefficient is observed, R_{Hf} is negative for thicker films and becomes positive at $d < 50$ nm. Inoue *et al.* argued the presence of local acceptor states to explain the temperature dependence of the Hall coefficient.

Because the introduction of acceptor levels near the top of the hole band will cause a reduction in the number of electrons and an increase in the number of holes, the parameter y will no longer be equal to 1. If we repeat the above procedure to compare the theoretical plots of R_{Hf} against k_s (Fig. 8a) with the experimental data at 80 and 300 K, we observe that the thickness dependence of R_{Hf} can be qualitatively described in terms of the two-band model with $y = 0.5$ and with x, respectively, near 0.45 and 0.42. We note that a value of 0.5 for y is by no means unreasonable if the acceptor states are responsible for the reduction in the number of electrons. Adjusting the value for x at MT = 80 K (Fig. 8b) and at MT = 300 K (Fig. 8c) the proposed model gives a reasonable qualitative agreement with experiments even if at 300 K the theoretical magnitude of R_H remains too small. In particular, it appears that the theoretical and experimental reversals of R_{Hf} occur approximately at the same thickness. If, however, a correction for the factor $\mathscr{C}$ is accepted it is possible to arrive at a fair fit of data. But it seems more appropriate to note that the bismuth films have a fine-grained structure and thus we may partially ascribe the deviations to scattering at grain boundaries.

We now turn our attention to previous works [10, 13] for which attempts to fit data in terms of the classical F–S model can, at first sight, be made. Hoffman and Frankl measured [13] at MT = 4.2 K the Hall coefficient of well-ordered bismuth films: the Hall coefficient has the sign of the conduction by holes and decreases with increasing thickness. Because the films were deposited at 330 K and then annealed at the same temperature for only $\frac{1}{2}$ h, the anneal is certainly not complete and one can reasonably assume partially diffuse surface scattering (i.e. $p \simeq 0.6$ at MT = 300 K [13]). Thus assuming $p = 0.5$ at MT = 4.2 K and retaining for λ_{os} the value of 8 μm determined earlier by Hoffman and Frankl [13], a qualitative and quantitative agreement between the theoretical and experimental results is obtained for the two following sets of x and y values

$$x \simeq 0.47 \quad \text{and} \quad y = 1$$

$$x \simeq 0.43 \quad \text{and} \quad y = 0.7.$$

The discrepancies between theory and experiment do not, in general, exceed 5% except for the thickest film for which a more serious departure of about 30% is observed. Thus the correct choice for x and y remains difficult because firstly we note that the value of 1 for y agrees with the common assumption that in pure bulk bismuth the concentration of holes is equal to the concentration of electrons [19], and secondly we believe that for films suffering an anneal during a short time, impurities may play a role in determining the value for y.

Also interesting is the study for thin evaporated bismuth films made by Kochowski and Opilski [10] where the dependence of the Hall coefficient on thickness is essentially determined by the value of the measurement temperature. In fact at MT = 293 K, R_{Hf} was found to be practically independent of d whereas at MT = 80 K obvious similarities between the works on the Hall effect in bismuth films by Inoue *et al.* [12] (see Figs 8a, b) and by Kochowski and Opilski [10] were observed. Hence assuming again that $y = 0.5$, the experimental behaviour of R_{Hf} as a function of d at 80 K conforms nearly to the theoretical features obtained for $x = 0.45$ and $p = 0.7$. A reanalysis of the data at 293 K with $x = 0.4$ shows that the calculated and the experimental values of R_{Hf} are of comparable order of magnitude over a very large thickness range.

TABLE II Values of x and y calculated in the framework of the two-band model using data from the literature; when possible, alternative values of x and y are also indicated

x	y	MT (K)	Reference
0.47 or 0.43	1 or 0.7	4.2	[13]
0.447 or 0.39	1 or 0.7	80	[11]
0.447	0.5	80	[12]
0.45	0.5	80	[10]
0.4	0.5	293	[10]
0.418	0.5	300	[12]

All the values of parameters x and y obtained from these reanalyses of previous experiments are collected in Table II. At this point it appears to be necessary to use another simple experimental test to establish the validity of the model. We can, for example, compare values of the background carrier mobility previously published in the literature [7, 10, 19] with the present ones. For this purpose, as usual for bismuth, let us denote n, the number of electrons (i.e. n corresponds to n_s in Equation 32) and p, the number of holes (i.e. $p = n_d$). It readily appears from Equations 34 and 35 that the ratio, $\mu_{p\infty}/\mu_{n\infty}$, of the hole mobility to the electron mobility is expressed as

$$\mu_{p\infty}/\mu_{n\infty} = y(1 - x)/x \quad (40)$$

for an infinitely thick film. The actual values of the mobility ratio are also listed in Table II. If we compare our values with data selected from the literature [7, 10, 19] (Table III), it will be seen that our results in no way seem unreasonable. Firstly, we note that there is a relatively large scatter between the results from different authors; this situation reflects some uncertainties in determining the electrical properties of an infinitely thick film. For example, from the work on single crystal of bismuth by Abeles and Meiboom [19] the mobility ratio was found firstly to be always smaller than 0.5 and secondly to increase slightly with increasing MT. This last feature, although more pronounced, was also observed by Asashi and Kinbara [7] but the quantitative result at 77 K of their analysis (Table III) disagrees with that of Abeles and Meiboom. Our results give a mobility ratio whose variation with measurement temperature follows the expected behaviour. Moreover, at 80 K, our values as evaluated from [10] and [12] lie midway between the values quoted by other authors [7, 19].

However, to assess the validity of the present model several other remarks can be made.

1. When available for films prepared and annealed under the same conditions, the study of the thickness dependence of R_{Hf} at various MT gives, at a fixed y, a value of x which decreases moderately with increasing MT, in agreement with the work of Abeles and Meiboom (Table II).

2. The present model has the advantage to be capable of explaining qualitatively the reversal, at a fixed MT, of the sign of the Hall coefficient which occurs with increasing thickness.

3. The two-band model is, to our knowledge, the only model which gives a fair agreement with experiment when the observed size effect is just opposite to that predicted by the classical F–S theory, i.e. when the Hall coefficient increases with increasing thickness.

TABLE III Values of the mobility ratio, $\mu_{p\infty}/\mu_{n\infty}$, as determined from the present model using data from the literature. For comparison, previously published values for the mobility ratio are also given

$\mu_{p\infty}/\mu_{n\infty}$		MT (K)	Reference
Calculated	Published		
1.127 or 0.927	–	4.2	[13]
1.237 or 1.09	–	80	[11]
0.618	–	80	[12]
0.611	–	80	[10]
0.75	–	293	[10]
0.696	–	300	[12]
–	0.615	4.2	[7]
–	0.864	77	[7]
–	0.432	80	[19]
–	0.472	300	[19]

We can thus conclude that the model proposed here is the simplest one, giving a reasonable agreement with experiments. However, because a two-band model involves at least four important physical parameters, namely x, y, λ_0 and p, the following points must be taken into account.

1. A serious analysis of the role and an identification of the nature of frozen-in impurities is necessary to be able to establish the relative importance of impurities in the transport properties of thin films and to make a meaningful estimate of the parameter y.

2. The morphology of films needs to be carefully analysed in order to determine the size of crystallites when present. This point is essential to evaluate the background mean free path.

3. Because both the average grain size and the concentration of impurities may vary with film thickness, the simplest experimental procedure to estimate the changes of the parameter x with temperature is to perform measurements of the Hall effect on the same thoroughly annealed film whose morphology is known.

Tables II and III show that we have not completely succeeded in placing the qualitative correlation between theory and experiments on a quantitative basis. We can "force" the present model to fit the data by an appropriate choice of x, y, λ_0 nd p, but in view of the preceding remark it does not seem fruitful to speculate about such refined choices.

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