JOURNAL OF MATERIALS SCIENCE 21 (1986) 469–474

Electrical conduction and ordinary Hall effect in thin nickel films

C. R. PICHARD, M. BEDDA, M. LAHRICHI*, A. J. TOSSER
*Laboratoire d'Electronique, and *Laboratoire de Physique des Dépôts Métalliques, Université de Nancy I, BP 239, 54506 Vandoeuvre les Nancy Cedex, France*

A new interpretation is proposed for the size effects in the electrical resistivity of thin nickel films and in the temperature coefficient of resistivity, starting from theoretical equations, recently published. The size effect in the ordinary Hall coefficient is satisfactorily interpreted in the framework of a polycrystalline model; the agreement is questionable in the framework of a columnar model and the assumption of polycrystalline structure is retained.

1. Introduction

The transport properties of nickel films deposited in high vacuum have been examined recently by De Groot [1] in order to measure the effects of CO superfical adsorption; the experimental data have been interpreted in the terms of the partial theoretical results which have been published to date [2, 3].

Further systematic studies have now been published [4–12] and new interpretations can be proposed for the variation in the film resistivity, ϱ_f, the temperature coefficient of resistivity (t.c.r.), β_f, $= \mathrm{d}\ln\varrho_f/\mathrm{d}T$ (where T is temperature), and the ordinary Hall coefficient, R_{H_f}, with film thickness, d. For this purpose, preliminary theoretical results [4–12] are summarized in the following section.

2. Preliminary results

2.1. Theoretical linear variations in ϱ_f and β_f^{-1} with d

Whatever the film structure (polycrystalline, monocrystalline or columnar) and whatever the model of the grain boundary [13–15], the following equations hold [8, 9, 16, 17]

$$d\varrho_f = \varrho_\infty[d + H(d, D_g, p, t, \lambda_0)], \qquad d\lambda_0^{-1} > 0.1 \tag{1}$$

$$d\beta_f^{-1} = \beta_\infty^{-1}[d + H(d, D_g, p, t, \lambda_0)], \quad d\lambda_0^{-1} > 0.1 \tag{2}$$

where $\varrho_\infty(\beta_\infty)$ is the resistivity (t.c.r.) of the infinitely thick film, λ_0 the electron mean free path in the bulk material and H an analytical function of d, of the grain diameter, D_g, of the electron specular reflection coefficient at film surface, p [18], of the statistical transmission coefficient of electron flow at grain boundary, t [19, 20], and of λ_0.

When the Mayadas–Shatzkes conduction model [13] is used, the transmission coefficient, t, can be replaced by the so-called reflection coefficient, R [13], whose physical interpretation has been discussed previously [8].

In the case of the polycrystalline films, three components of the grain diameter must be used, but it has been established [21] that the assumption of a cubic shape of the grain remains valid even if the deviation from such a shape is very marked; hence, for the sake of simplicity we put

$$D_{g_x} = D_{g_y} = D_{g_x} = D_g \tag{3}$$

In the case of columnar and monocrystalline films the same reason holds and we put

$$D_{g_x} = D_{g_y} = D_g \tag{4}$$

assuming that the thickness lies in the z direction.

One must not overlook the fact that the Mayadas–Shatzkes model [13] gives a unidimensional representation of three-dimensional transport properties [8] and therefore cannot be used for describing the Hall effect [8]. This is the reason why we restrict our attention to multidimensional statistical models [8] based on the statistical representation of a grain boundary [8].

In the case of monocrystalline and columnar films, a simple linearized term is [8, 22, 23]

$$\varrho_\infty H(d, D_g, p, t, \lambda_0) = C_1 D_g^{-1}\lambda_0\varrho_0 \ln\left(\frac{1}{t}\right) + C_2\lambda_0\varrho_0\ln\left(\frac{1}{p}\right), \quad p > 0.3 \tag{5}$$

where ϱ_0 is the bulk resistivity with $C_1 = 1.144$, $C_2 = 0.36$, $D_g < d$ for columnar films, and $D_g \geqq d$ for monocrystalline films.

In the case of polycrystalline films with large grains, one can write [8, 10]:

$$\varrho_\infty H(d, D_g, p, t, \lambda_0) = C_3\lambda_0\varrho_0\ln\left(\frac{1}{p}\right), \quad p > 0.3 \tag{9}$$

where $C_3 = \frac{3}{8}$.

At low reduced thickness, $d\lambda_0^{-1}$, when the electronic specular reflection coefficient takes value lower than 0.3, the discrete variations in the electron flow cannot be accurately represented by an exponential law [8], an alternative expression can be proposed, by substituting $2[(1 - p)/(1 + p)]$ for $\ln(1/p)$ in Equations 5 and 6 [23]. Except in this case, the above theoretical relations hold [22].

0022–2461/86 \$03.00 + .12

One can observe that the expression of Equations 5 and 6 clearly shows that

$$\frac{\partial}{\partial T}\varrho_{\infty} H(d, D_{\mathrm{g}}, p, t, \lambda_0) \approx 0$$

where T is temperature. Consequently, the presence of the same analytical function, H, in Equations 1 and 2 is not surprising since

$$\frac{\partial}{\partial T}\varrho_{\mathrm{f}} = \beta_{\mathrm{f}}\varrho_{\mathrm{f}} \tag{7}$$

2.2. Calculations of t and p

From the values of λ_0, cited in the literature [24, 25], the slopes of the linearized equations 1 and 2 gives the values of ϱ_{∞} and β_{∞}^{-1}; if they markedly deviate from ϱ_0 and β_0^{-1}, the ratios $\varrho_{\infty}/\varrho_0$ and β_0/β_{∞} can be expressed in terms of the transmission coefficient [8], whose experimental values are thus available.

The values of p are then calculated from the slope of the linear curves $(\varrho_{\mathrm{f}}/d^{-1})$ and $(\beta_{\mathrm{f}}^{-1}/d^{-1})$ [8].

2.3. Theoretical expression for the Hall coefficients, $R_{\mathrm{H_f}}$

In the absence of impurities within the film a general expression for the Hall coefficient, $R_{\mathrm{H_f}}$, of a metal film is [7, 8, 10, 12, 26, 27]

$$R_{\mathrm{H_f}}/R_{\mathrm{H_0}} = \beta_{\mathrm{f}}\varrho_{\mathrm{f}}/\beta_0\varrho_0 \tag{8}$$

where $R_{\mathrm{H_0}}$ is the Hall coefficient of the bulk material. This equation has been established [8] by following the Sondheimer procedure [18] for solving the Boltzmann equation in the presence of a longitudinal electric field and a transverse magnetic field and by assuming that the only thermal variation in the electrical parameter is that in the bulk mean free path. Cottey [28] has shown that the Sondheimer procedures holds, as long as the direction of the electron velocity in the film plane does not vary with surface scattering; furthermore, the validity of the partial derivatives with respect to temperature does not require knowledge of the relationship between ϱ_0 and λ_0, and thus is not altered in the case of non-spherical Fermi surface.

The simplest equations for the Hall coefficient are [7, 10]

$$R_{\mathrm{H_f}}/R_{\mathrm{H_0}} \approx \frac{2}{3}A(\gamma)/[B(\gamma)]^2 \tag{9}$$

where

$$A(\gamma) = \gamma^{-1} - 2 + 2\gamma\ln(1 + \gamma^{-1}) \tag{10}$$

$$B(\gamma) = \gamma - \frac{1}{2} + (1 - \gamma^2)\ln(1 + \gamma^{-1}) \tag{11}$$

with

$$\gamma = \left(1 + \frac{C^2}{\nu}\right)\left(\frac{1}{\mu} + \frac{1 - C}{\nu}\right)^{-1} \tag{12a}$$

for polycrystalline films

$$\gamma = \left(1 + \frac{C^2}{\nu}\right)\left(\frac{1}{\mu} - \frac{C}{\nu}\right)^{-1} \tag{12b}$$

for columnar and monocrystalline films where

$$\nu = D_{\mathrm{g}}\lambda_0^{-1}\left(\ln\frac{1}{t}\right)^{-1} \quad t > 0.3 \tag{13}$$

$$\mu = \mathrm{d}\lambda_0^{-1}\left(\ln\frac{1}{p}\right)^{-1} \quad p > 0.3 \tag{14}$$

$$C = \frac{4}{\pi} \tag{15}$$

In the case where p takes values lower than 0.3 and at low film thickness, $2[(1 - p)/(1 + p)]$ is substituted for $\ln(1/p)$, as above [23].

It has been shown [27] that the presence of impurities, randomly distributed within the film, leads to the expression

$$\frac{R_{\mathrm{H_{fi}}}}{R_{\mathrm{H_{0i}}}} = \frac{\beta_{\mathrm{f}}\varrho_{\mathrm{f}}}{\beta_0\varrho_0} \tag{16}$$

where the index i marks the presence of impurities similarly distributed at any film thickness.

Equation 8 also holds in the case of magnetic metal films, restricting the attention to the ordinary Hall coefficient [8]; this feature has been verified in the case of iron films [29].

Recent theoretical studies [10] have shown that the behaviour of the Hall coefficient can be an efficient tool for checking the assumptions related to the film structure because the Hall coefficient is sensitive to the grain boundary scattering. In the case of polycrystalline films a linear plot for the variations in the reduced Hall coefficient with reciprocal thickness is [10]

$$R_{\mathrm{H_f}}/R_{\mathrm{H_0}} \approx 1 - C_0\left(\frac{C - 1}{C^2 + \nu}\right) + \left(\frac{C_0\nu}{C^2 + \nu}\right)\left(\frac{1}{\mu}\right) \tag{17}$$

where $C_0 = 0.04$, and $C = 4/\pi$, and μ and ν are defined by Equations 13 and 14 respectively, provided that γ (Equations 12a and b) takes values between 0.04 and 0.4 [10].

Since

$$\frac{C - 1}{C^2 + \nu} < \frac{C - 1}{C^2} = 0.163 \tag{18}$$

one can say that the ordinate intercept defined by Equation 17 is close to unity.

In the case of monocrystalline or columnar film, a linearized expression for the reduced Hall coefficient is [10]

$$R_{\mathrm{H_f}}/R_{\mathrm{H_0}} \approx 1 + C_0\left(\frac{\nu}{\mu} - \mathrm{C}\right)\left(\frac{1}{\nu + C^2}\right) \tag{19}$$

Since

$$\frac{C}{C^2 + \nu} < \frac{1}{C} = \frac{\pi}{4} \tag{20}$$

the ordinate intercept defined by Equation 19 is close to unity in the case of columnar films ($D_{\mathrm{g}} < d$) whereas it is not the case for monocrystalline films, with $D_{\mathrm{g}} = d$, since the ratio ν/μ is thickness independent [10].

3. Comparison with experiments [1]

3.1. Correlated variations in $R_{\mathrm{H_f}}$ and $\beta_{\mathrm{f}}/\varrho_{\mathrm{f}}$

The correlation in the variations of $R_{\mathrm{H_f}}$ and of the product $(\beta_{\mathrm{f}}\varrho_{\mathrm{f}})$ is clearly seen (Fig. 1) ([1] Fig. 35]).

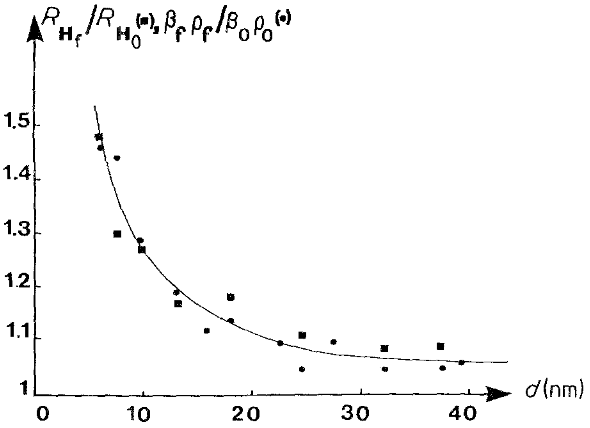

Figure 1 Compared size effect in the reduced Hall coefficient R_{H_f}/R_{H_0} and in the reduced product resistivity × t.c.r. (from [1]) at 273 K.

At large thickness, the product $\beta_f\varrho_f$ takes values near to that of the bulk material

$$\beta_f\varrho_f|_{d\to\infty} = 40 \times 10^{-11}\,\Omega\mathrm{mK}^{-1}$$

whereas, from the values cited in literature [1, 24, 25]

$$\beta_0\varrho_0 = 46.9 \times 10^{-11}\,\Omega\mathrm{mK}^{-1}$$

Hence no impurity effect can be retained.

Moreover, the asymptotic value for R_{H_f} is

$$R_{H_f}|_{d\to\infty} = 0.63 \times 10^{-10}\,\mathrm{m}^3\mathrm{C}^{-1}$$

whereas the set of values for R_{H_0} lies from 0.55×10^{-10} to $0.66 \times 10^{-10}\,\mathrm{m}^3\mathrm{C}^{-1}$ [1]. Consequently the assumption of negligible impurity effects seems adequate [28].

It may be noted that the marked variations in R_{H_f} at low thickness suggests a low value of p, in agreement with extended tabulated data [8, 11] about columnar or polycrystalline structure.

3.2. Experimental values of ϱ_∞, β_∞, p and t

Plotting $d\varrho_f$ and $d\beta_f^{-1}$ against d gives linear curves (Figs. 2 and 3), and constant slopes that can be attributed only to a structural state independent from thickness. From Equations 1 and 2 we deduce $\varrho_\infty = 9.75 \times 10^{-8}\,\Omega\mathrm{m}$ and $\beta_\infty = 3.68 \times 10^{-3}\,\mathrm{K}^{-1}$. These values differ markedly from those of the bulk material, as cited in the literature [24, 25] $\varrho_0 = 6.8 \times 10^{-8}\,\Omega\mathrm{m}$ and $\beta_0 = 6.9 \times 10^{-3}\,\mathrm{K}^{-1}$. It can then again be concluded that the film does not have a monocrystalline structure.

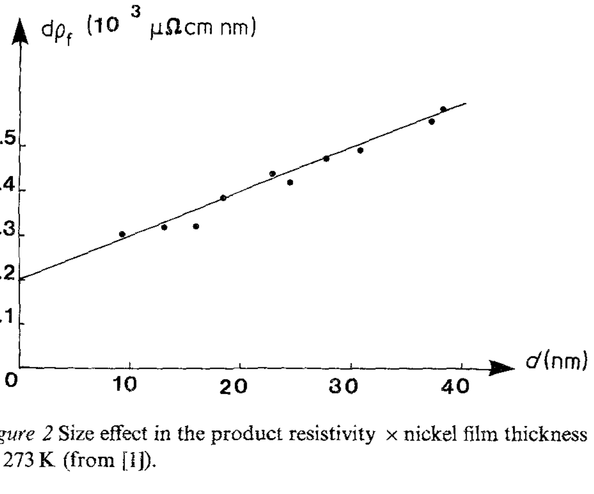

Figure 2 Size effect in the product resistivity × nickel film thickness at 273 K (from [1]).

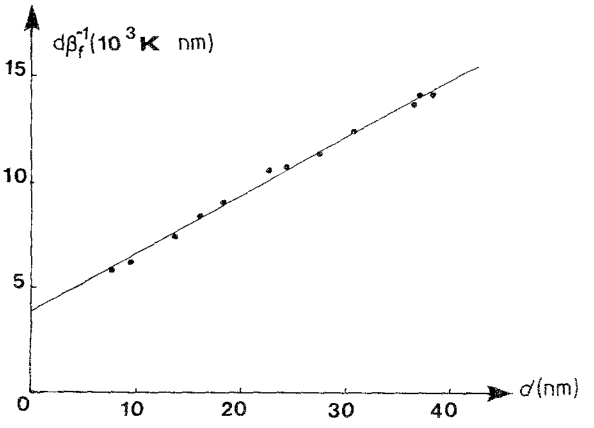

Figure 3 Size effect in the product t.c.r. × nickel film thickness at 273 K (from [1]).

Let us recall that the films were deposited in high vacuum on to a substrate whose temperature was 77 K [1] and that the ageing temperature was 363 K [1]; the procedure was closely similar to that used by other workers who have performed ageing procedures at 293 and 482 K [30–32]; they have shown that the average grain diameter is practically equal to the film thickness if the ageing temperature exceeds 483 K, whereas it is not the case at 293 K ([31], Fig. 3). Since the resistivity varies with the deposition rate before and after ageing we assume that the size of the grains varies with deposition rate, in good agreement with several experiments [24, 33–36]; the presence of impurities cannot be retained because the Hall coefficient of films of large thickness takes values close to the bulk ones without any correcting coefficient due to impurity effect [27].

In order to estimate the grain diameter in the film plane, we have measured the thickness threshold corresponding to an infinite value of the resistivity; this procedure applies both to columnar and polycrystalline structure since the cubic shape of polycrystalline grains is generally satisfactory, as shown previously [21].

Starting from the experimental data [1], the variations in the reciprocal square of the resistivity with thickness (Fig. 4) give a thickness threshold of about 5 nm; hence we put $D_g = 5\,\mathrm{nm}$. This value is in close agreement with the observation of many workers [35, 36].

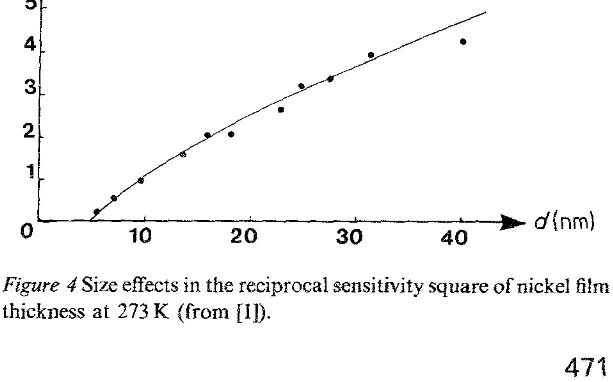

Figure 4 Size effects in the reciprocal sensitivity square of nickel film thickness at 273 K (from [1]).

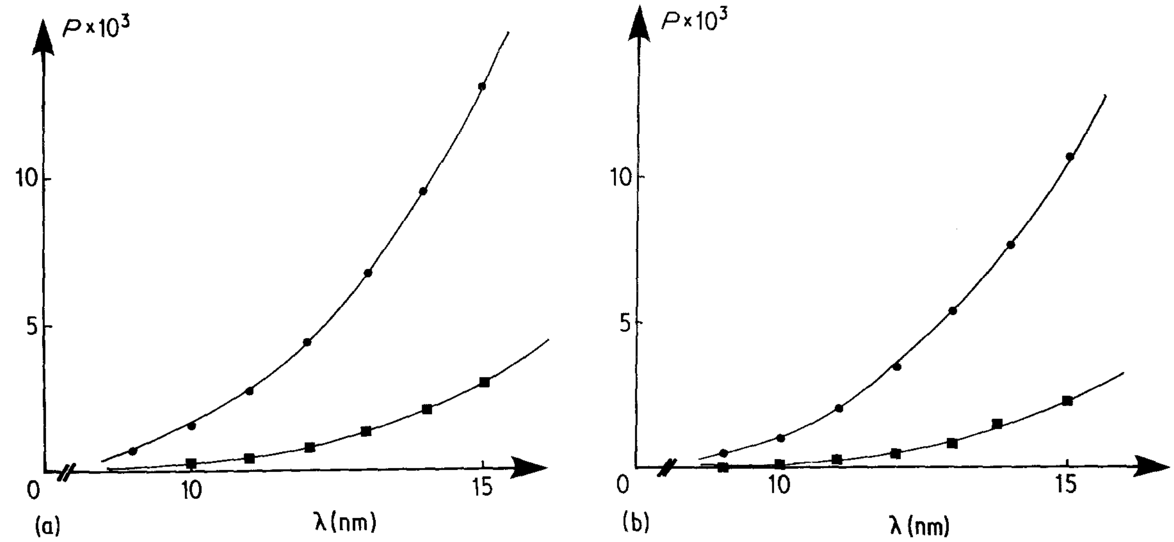

Figure 5 Variations in the specular reflection coefficient, p, with assumed value of the bulk mean free path, λ_0, ■ starting from (ϱ_f, d^{-1}), ● starting from (β_f^{-1}, d^{-1}), assuming (a) a polycrystalline structure, (b) a columnar structure.

From the slopes of the linear plots of ϱ_f against d^{-1} and β_f^{-1} against d^{-1} and for a given value of λ_0, experimental values of p can be found from Equations 5 and 6.

A large number of values for the mean free path in bulk nickel, λ_0, has been proposed [24, 25, 33–36]; however, our attention is focused on experiments using a high vacuum apparatus [36], similar to that used in De Groot's experiments [1]; it leads to data exhibiting a good consistency [1, 36] so that the value $\lambda_0 = 10\,\text{nm}$ seems preferable for interpreting the experiments [1]; it is well known [35, 36] that the value of resistivity markedly depends on the type of vacuum. We thus obtain $p = 1.6 \times 10^{-4}$ and $p = 1.5 \times 10^{-3}$ in the case of polycrystalline film, and $p = 1.1 \times 10^{-3}$ and $p = 1.1 \times 10^{-4}$ in the case of columnar film. These values vary slowly with the assumed value of λ_0 (Figs. 5a and b). The deviation in the values derived from resistivity or t.c.r. plots is marked but it may be observed that the value of p is very low in any case, and the inaccuracy could play an important role.

From the experimental values of ϱ_∞ and β_∞ and taking $\lambda_0 = 10\,\text{nm}$ and $D_g = 5\,\text{nm}$, the values of the parameter v are calculated, and the values of t are derived (Equation 13). It yields $t = 0.86$ and $t = 0.74$ in the case of polycrystalline structure, and $t = 0.83$ and $t = 0.68$ in the case of columnar structure. Variations with the assumed value of λ_0 are slight (Fig. 6a and b).

4. Discussion

In the general linearized expressions for the resistivity and the t.c.r., the bulk mean free path, λ_0, is introduced [8]; its definition is based on the assumption of isotropic scattering over the Fermi surface; this procedure seems inadequate for nickel films, since nickel has a very markedly non-spherical Fermi surface [24, 36] but it only alters the validity of the physical interpretation of λ_0; moreover, the expressions of the transport properties in the presence of several sources of electronic scattering are obtained [8] by assuming the superimposed effects of the sources of scattering. It is then concluded that the non-spherical shape of the Fermi surface alters the quantitative results but not the qualitative interpretation.

The very low value of p could be seen as somewhat surprising. However, it is in agreement with the fact that an ageing temperature of 363 K does not allow

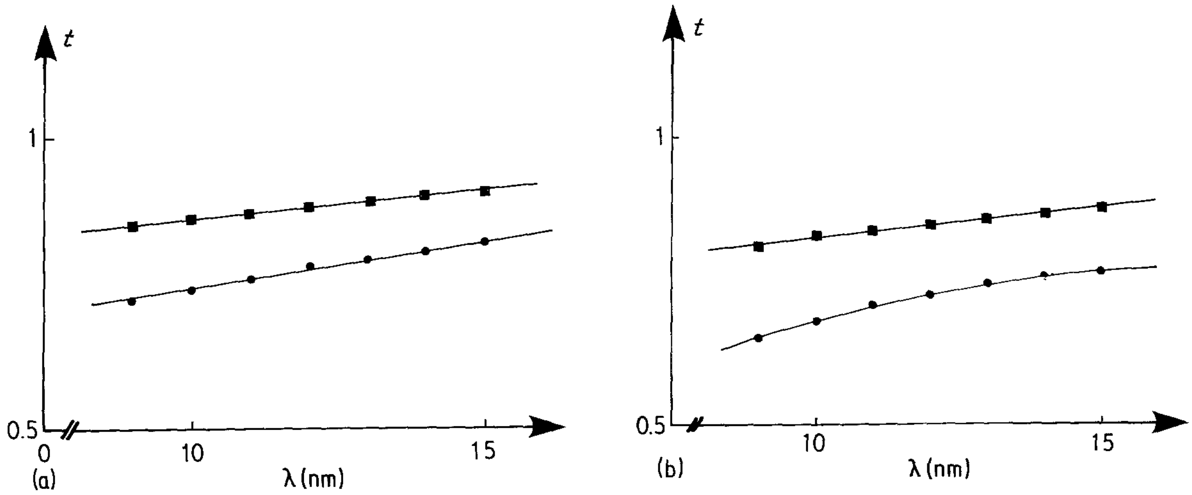

Figure 6 Variations in the transmission coefficient, t, with assumed value of the bulk mean free path, λ_0, ■ starting from (ϱ_f, d^{-1}), ● starting from (β_f^{-1}, d^{-1}), assuming (a) a polycrystalline structure, (b) a columnar structure.

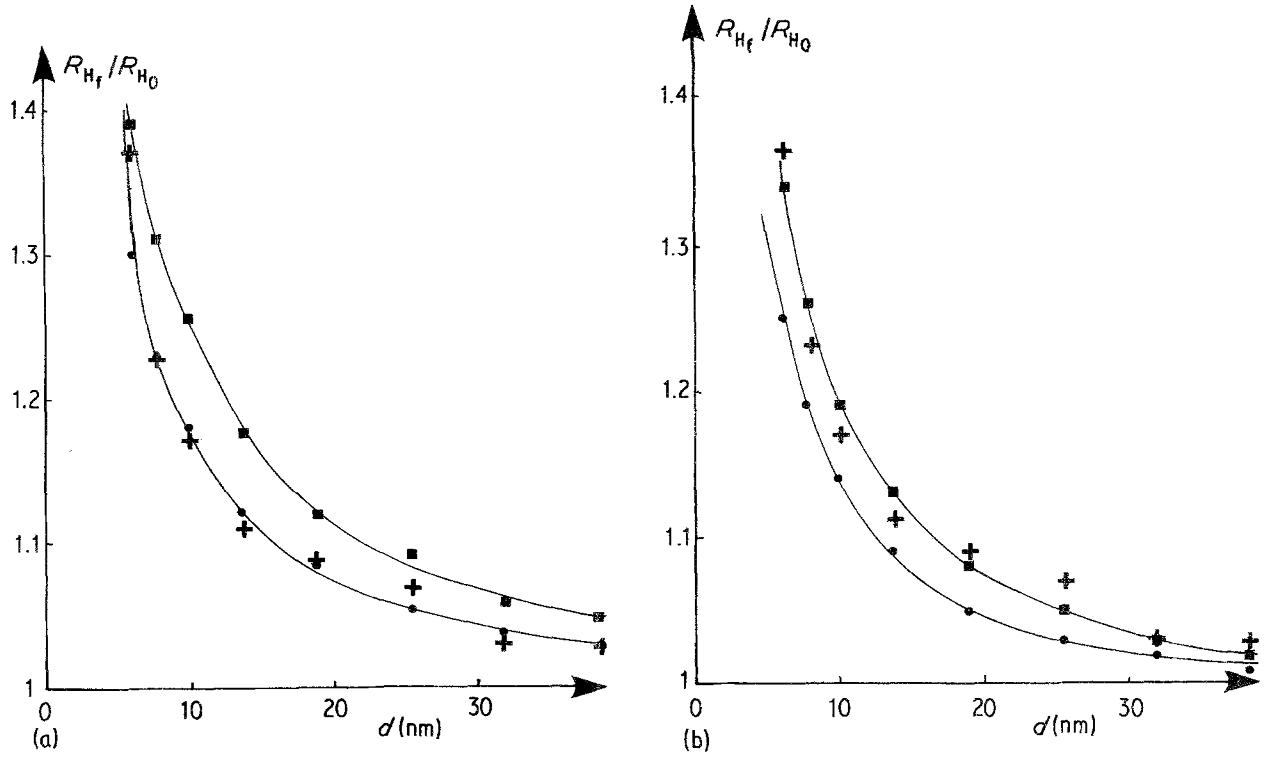

Figure 7 Theoretical and experimental variations in the reduced ordinary Hall coefficient of thin nickel films at 273 K, assuming either (a) a polycrystalline structure, or (b) a columnar structure. Key: (a) + experimental; ● theoretical, $p = 1.5 \times 10^{-3}$; ■ $p = 1.6 \times 10^{-4}$. (b) + experimental; ● theoretical, $p = 1.1 \times 10^{-3}$; ■ theoretical, $p = 1.1 \times 10^{-4}$.

the existence of grains whose thickness is equal to the film thickness [31] and therefore cannot replace the top surface of the polycrystalline layer by a smooth surface.

The unique specular reflection coefficient, p, represents the scattering at both bottom and top surface and can be regarded [37] as the geometrical average of two specular reflection coefficients, p_b and p_t, where $p = (p_b p_t)^{1/2}$. A very low value of p can then take its origin in a practically diffuse reflection at the film surface whose roughness is due to an incomplete reordering of the surface, as suggested above.

Introducing into Equation 9 the experimental value of ν (without any assumption related to λ_0 and D_g) gives theoretical variations for R_{H_f} in the case of a polycrystalline structure (Fig. 7a) and of a columnar structure (Fig. 7b). A better agreement with experimental results is obtained in the case of a polycrystalline structure.

Starting from the Mayadas–Shatzkes model [13], variations in the resistivity has led to [1] $p = 0.5$ and $R = 0.57$, where R is the reflection coefficient of the Mayadas–Shatzkes model. Since the statistical transmission coefficient, t, can be expressed as [8, 38]

$$t = \exp\left(-\frac{R}{1-R}\right),$$

t takes the value 0.27 for $R = 0.57$. For the value of p the deviation is marked, but it may be pointed out that p has been calculated from a linearized equation ([1] Equation 1.28, p. 53) due to Mola and Heras [39] related to monocrystalline film, whereas the film does not exhibit monocrystalline structure.

5. Conclusion

Previous experiments [1] related to the size effects in the resistivity, the temperature coefficient of resistivity and the ordinary Hall coefficient of nickel films can be satisfactorily reinterpreted in terms of a statistical conduction model, suggesting the existence of a polycrystalline structure.

References

1. P. DE GROOT, thesis, Fakultät Physik Techniche Universität München (1980).
2. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *J. Mater. Sci.* **15** (1980) 2236.
3. *Idem, J. Phys. F Met. Phys.* **10** (1980) L101.
4. *Idem, J. Mater. Sci.* **16** (1981) 451.
5. A. J. TOSSER, C. R. TELLIER and C. R. PICHARD, *ibid.* **16** (1981) 944.
6. *Idem, Phys. Status Solidi (a)* **68** (1982) K171.
7. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *J. Mater. Sci. Lett.* **1** (1982) 260.
8. C. R. TELLIER and A. J. TOSSER, "Size effects in thin films" (Elsevier, Amsterdam, 1982) Chs. 1, 2.
9. C. R. TELLIER, C. R. PICHARD, V. I. VATAMANYUK and A. J. TOSSER, *J. Mater. Sci. Lett.* **2** (1983) 579.
10. C. R. PICHARD, A. KHALID-NACIRI and A. J. TOSSER, *ibid.* **3** (1984) 455.
11. C. R. PICHARD, V. I. VATAMANYUK, A. KHALID-NACIRI, C. R. TELLIER and A. J. TOSSER, *ibid.* **3** (1984) 447.
12. C. R. PICHARD, C. R. TELLIER, M. BEDDA and A. J. TOSSER, *ibid.* **3** (1984) 783.
13. A. F. MAYADAS and M. SHATZKES, *Phys. Rev. B* **1** (1970) 1382.
14. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *Thin Solid Films* **62** (1979) 189.
15. C. R. TELLIER and A. J. TOSSER, *ibid.* **70** (1980) 225.
16. C. R. TELLIER, C. R. PICHARD and A. J. TOSSER,

ibid. **76** (1981) 129.

17. C. R. PICHARD, Y. F. KOMNIK, B. I. BELEVTSEV and A. J. TOSSER *J. Mater. Sci. Lett.* **2** (1983) 360.
18. E. H. SONDHEIMER, *Adv. Phys.* **1** (1952) 1.
19. F. WARKUSZ, *Electrocomp. Sci. Technol.* **5** (1978) 197.
20. C. R. TELLIER, C. R. PICHARD and A. J. TOSSER, *Thin Solid Films* **61** (1979) 349.
21. C. R. PICHARD, C. R. TELLIER, L. OUARBYA and A. J. TOSSER, *Le Vide* **210** (1982) 3.
22. C. R. TELLIER, C. R. PICHARD and A. J. TOSSER, *J. Mater. Sci. Lett.* **1** (1982) 271.
23. J. FLECHON, S. KARBAL and G. MBEMBA, *Mater. Chem. Phys.* in press.
24. K. L. CHOPRA, "Thin Films Phenomena" (McGraw Hill, New York, 1969) ch. VI.
25. "Handbook of Chemistry and Physics", (Chemical Rubber, Cleveland, Ohio, 49th Edn. 1969).
26. C. R. PICHARD, A. J. TOSSER, C. R. TELLIER and K. C. BARUA, *J. Mater. Sci.* **16** (1981) 2480.
27. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *J. Mater. Sci. Lett.* **1** (1982) 423.
28. A. A. COTTEY, *J. Phys. C Sol. Stat. Phys.* **6** (1973) 699.
29. C. R. PICHARD, C. R. TELLIER, A. J. TOSSER and C. VAUTIER, *Rev. Phys. Appl.* **15** (1980) 1303.
30. G. WEDLER and P. WISSMAN, *Naturforsch.* **23a** (1968) 1537.
31. *Idem, ibid.* **23a** (1968) 1544.
32. P. WISSMANN, *Thin Solid Films* **5** (1970) 329.
33. M. A. ANGADI and L. A. UDACHAN, *ibid.* **79** (1981) 149.
34. E. I. TOCHITKII and N. M. BELYAUSKII, *Phys. Status Solidi (a)* **61** (1980) K21.
35. G. GOUREAUX, thesis, University of Caen (1960).
36. J. LE BAS, thesis, University of Rouen (1971).
37. L. GUENDOUZ, C. R. TELLIER, A. J. TOSSER and C. R. PICHARD, *J. Mater. Sci. Lett.* **3** (1984) 377.
38. C. R. PICHARD, C. R. TELLIER and A. J. TOSSER, *Le Vide* **35** (1980) 207.
39. E. E. MOLA and J. M. HERAS, *Thin Solid Films* **18** (1973) 137.

Received 19 February
and accepted 13 March 1985