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Identification of imperfections contribution to electronic conductivity in monocrystalline metal film

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Résumé. — Une nouvelle méthode est proposée pour analyser les effets sur la conductivité et le pouvoir thermoélectrique des imperfections fixées dans des couches minces métalliques monocrystallines. Des résultats expérimentaux antérieurs relatifs à des couches de cuivre et d'argent sont ainsi interprétés. Cette méthode permet de mettre en évidence la présence d'imperfections, mais elle permet aussi d'analyser des effets dimensionnels anormaux dus aux imperfections.

Abstract. — A new method based on simultaneous measurements of thermoelectric power and conductivity is proposed for analysing the contribution to electron scattering of imperfections frozen in thin monocrystalline metal films; previously reported data on copper and silver films are examined. It is shown that the procedure is efficient for identifying the presence of imperfections but could also give information on anomalous size effects due to impurities.

1. Introduction. — Size effects (due to the geometrical limitation of the carrier mean free path, by the film surfaces) in the electrical, thermal and galvanomagnetic transport properties of thin metal films have been extensively investigated in the past few years [1-11]. Thermoelectric power (t.e.p.) studies are particularly interesting because such studies could give valuable information on the distortions of the Fermi surface [12]. Furthermore some authors [3-5] have suggested that the observed anomalous thickness dependence of the t.e.p. can be attributed to structural defects frozen-in the metal films [3-5]. Particularly we must keep in mind that the scattering of carriers by grain boundary surfaces can significantly modify the size dependence of the transport properties [13-15]; for this purpose an attempt is made in this paper to report a new method for analysing the thermopower in monocrystalline metal films whose grain size a_g are greater or equal to the film thickness a .

2. Theoretical. — **2.1 T.E.P. AND MATTHIESENS'S RULE.** — The electrical transport properties of thin monocrystalline films can be understood in terms of the Mayadas-Shatzkes model (M.-S. model) [13] or in terms of the bidimensional model recently proposed by Tellier and Tosser [15]. In the case of the M.-S. model it has been shown that the thin monocrystalline

film resistivity ρ_{Fm} obeys, under some conditions established by Thieme and Kierstein [16], the Matthiessen's rule [12], i.e.

$$\rho_{Fm} \approx \rho_0 + \rho_g + \rho_s \quad (1)$$

where ρ_0 is the bulk resistivity, ρ_g and ρ_s are respectively the resistivities due to the grain boundaries and the external surfaces scatterings. Furthermore by considering the numerical values of the resistivity ratio ρ_{Fm}/ρ_0 as evaluated on the basis of the bidimensional model [15] it can be easily shown [15, 17] that a relation of type (1) yields a fair agreement with the observed size effect in thin monocrystalline thin films in large grain parameters and reduced thickness k ranges.

Further considering the additional contribution ρ_i of other imperfections to the total monocrystalline film resistivity it follows that

$$\rho_{Fm}^* \approx \rho_0 + \rho_g + \rho_s + \rho_i \quad (2)$$

The total thermopower S_{Fm} can be derived from the general law [18]

$$S_F = \rho^{-1} \cdot \sum_i \rho_i S_i \quad \text{with} \quad \rho = \sum_i \rho_i$$

where S_F is the total film thermoelectric power, ρ_i

and S_i are the components of resistivity and thermoelectric power due to the i -th scattering process.

Hence

$$S_{Fm} = \frac{S_0 \rho_0}{\rho_{Fm}^*} + \frac{S_g \rho_g}{\rho_{Fm}^*} + \frac{S_s \rho_s}{\rho_{Fm}^*} + \frac{S_i \rho_i}{\rho_{Fm}^*} \quad (3)$$

where S_0 , S_i , S_g , S_s are the contributions to the ther-

moelectric power from bulk material, imperfections (grain boundaries excluded), grain boundaries and surface scatterings.

After some mathematical rearrangements equations (2) and (3) give four alternative expressions for the difference ΔS between the film and bulk material thermoelectric power, in the form $\Delta S = a + b(\rho_{Fm}^*)^{-1}$, i.e.

$$\Delta S = -S_0 + \frac{1}{\rho_{Fm}^*} [\rho_0 S_0 + \rho_s S_s + \rho_g S_g + \rho_i S_i] \quad (4.1)$$

$$\Delta S = (S_i - S_0) + \frac{1}{\rho_{Fm}^*} [\rho_0(S_0 - S_i) + \rho_s(S_s - S_i) + \rho_g(S_g - S_i)] \quad (4.2)$$

$$\Delta S = (S_s - S_0) + \frac{1}{\rho_{Fm}^*} [\rho_0(S_0 - S_s) + \rho_g(S_g - S_s) + \rho_i(S_i - S_s)] \quad (4.3)$$

$$\Delta S = (S_g - S_0) + \frac{1}{\rho_{Fm}^*} [\rho_0(S_0 - S_g) + \rho_s(S_s - S_g) + \rho_i(S_i - S_g)] \quad (4.4)$$

Note that if the grain boundary scattering effect is negligible the bidimensional and M.-S. models tend to the well known Fuchs-Sondheimer model [19] (F.-S. model) and that the number of alternative expressions for ΔS reduces to three; however in their study, during annealing, of the change of t.e.p. on films of given thicknesses Leonard and Lin [8] have proposed one equation only (corresponding to eq. (4.2)) to calculate the S_i contributions.

Equations (4) indicate, as suggested by Leonard *et al.* [7, 8] that, for a given metal film, the plot of ΔS versus $1/\rho_{Fm}^*(T)$ should yield a straight line but it appears from equations (4) that an adequate choice for the true expression of the linear slope is not clear.

2.2 CORRELATED SIZE EFFECT IN T.E.P. AND CONDUCTIVITY RATIO. — We consider in this section the plot of ΔS versus $\sigma_{Fm}(a)/\sigma_0$ obtained for films of different thicknesses exhibiting negligible concentration of imperfections ($\rho_i \approx 0$). Numerical evaluations of S have been obtained from tabulated values of conductivity σ and its t.c.r., β , in the F.-S. model [19] and in the bidimensional model [15] with the aid of the following general expression

$$\Delta S = -S \left(\frac{d \ln l_0}{d \ln E} \right)_{E=E_F} \left(\frac{\beta_F}{\beta_0} - 1 \right)$$

where l_0 is the bulk m.f.p., E the electron energy and E_F the Fermi energy; this equation is valid [20, 21] in the F.-S. conduction model and [22] in grain-boundary conduction models.

We have drawn in figure 1 theoretical plots of ΔS versus σ_F/σ_0 according to the F.-S. theory. Figure 1 shows several features: theoretical plots of ΔS versus $\sigma_F(k)/\sigma_0$ for various values of the specularity parameter p [19] apparently give straight lines if the conductivity ratio σ_F/σ_0 is greater than 0.55. For example, in the case $p = 0.25$ this condition corresponds to

Fig. 1. — Theoretical plot of ΔS versus σ_F/σ_0 according to the F.-S. theory; + $p = 0.75$; o $p = 0.25$; ● $p = 0$.

the reduced thickness range $k \gtrsim 0.4$; at smaller thicknesses significant deviations occur.

Figure 2 shows the theoretical curve of ΔS versus

Fig. 2. — Theoretical variation of ΔS with the monocrystalline film conductivity ratio σ_{Fm}/σ_0 as given by the bidimensional model [15]. ● $t = 0.7$, $p = 0.8$; + $t = 0.6$, $p = 0.5$; * $t = 0.9$, $p = 0.5$.

$\sigma_{\text{Fm}}/\sigma_0$ based on the bidimensional model [15]. For convenience the curves are drawn in the particular case $a \approx a_g$, but it is clear from the following discussion that the conclusion is not modified for $a_g > a$. It must be noted that a unique straight line accurately represents the theoretical variations in large grain parameter (transmission coefficient t [15, 23]) and specularity parameter p ranges.

2.3 IDENTIFICATION OF IMPURITY CONTRIBUTION. — From equation (4.1) it appears that if we consider the plots of ΔS versus $\sigma_{\text{Fm}}/\sigma_0$ (drawn for films of different thicknesses) we do not obtain a straight line if the imperfection contribution to the resistivity depends on thickness. If ρ_i and thus S_i could be neglected a linear relation between ΔS and $\sigma_{\text{Fm}}/\sigma_0$ is obtained provided that the specularity parameter p and transmission coefficient t through grain boundaries [15, 23, 24] do not vary with the film thickness, as assumed in size and grain boundaries effects theories and generally observed [15, 24-27].

It must be pointed out that the observed more marked thickness dependence of the resistivity with decreasing film thickness is generally attributed to thickness dependent concentration of imperfections [3, 25] provided that the value of the thick film resistivity approaches the bulk value. This marked dependence may also be understood in term of grain boundaries scattering effects [15]. To reconcile one of these two alternative interpretations with the experimental data and to establish the role of imperfections in determining the size effect, measurements of the difference in t.e.p. are convenient; equations (4) suggest a method to determine if the contribution of imperfections to the resistivity and thus to t.e.p. can be neglected.

It is effectively well established [13, 15, 28] that the contribution ρ_s and ρ_g to the total resistivity ρ_{Fm}^* become negligible in the limit of large thicknesses (i.e. in the limit of large grain size) any equation (4) then reduces to the limiting relation

$$\Delta S|_{a, a_g \rightarrow \infty} \approx (S_i - S_0) \left[1 - \frac{\sigma_{\text{Fm}}^*}{\sigma_0} \right]. \quad (5)$$

Equation (5) indicates that :

a) In presence of large concentration of imperfections, i.e. for $\sigma_{\text{Fm}}^*/\sigma_0 \ll 1$, ΔS becomes equal to zero only if $S_i \approx S_0$.

In the general case where the imperfection concentration is thickness dependent, the plot of ΔS versus $\sigma_{\text{Fm}}^*/\sigma_0$ exhibits a departure from straight line.

b) In absence of imperfections the observed variations in ΔS with $\sigma_{\text{Fm}}/\sigma_0$ are fitted by a straight line with an abscissa intercept ($\Delta S = 0$) equal to unity.

Leonard and Lin [8] have proposed the following equation

$$\Delta S = (S_i - S_0) + \frac{1}{\rho} [\rho_0(S_0 - S_i) + \rho_s(S_s - S_i)] \quad (4.5)$$

for analysing the correlated variations in ΔS and ρ during annealing and derived the value of S_i , S_s , ρ_i and ρ_s ; several remarks can be presented. First no contribution of grain boundaries to the resistivity has been considered whereas the preparation procedure (films evaporated onto unheated glass substrate and then annealed) does not allow [25] to assume that the experimental gold films do not exhibit grain boundary scattering; moreover the experimental variations of reduced film resistivity ρ/ρ_0 with reduced thickness k [8, Fig. 1] are more marked than the variations of the usual asymptotic F.-S. function obtained [19] in the case of diffuse scattering at external surfaces, i.e. $(1 + \frac{3}{8}k^{-1})$, which is valid for $k > 0.5$ [25] (for $k = 4.3$ $(\rho/\rho_0)_{\text{exp}} = 1.11$, $(\rho/\rho_0)_{\text{F.-S.}} = 1.087$); since a partially specular reflection can be predicted (annealing temperature 480 °C (for 2 hours) [25]) the theoretical size effect term must be written [19] $1 + \frac{3}{8}(1-p)k^{-1}$, that enhances the discrepancy between experimental and theoretical F.-S. values.

Consequently a reinterpretation of these experiments must be based on equation (4.2) (instead of equation (4.5)) and analysis in the way proposed by Leonard and Lin [8] therefore requires the validity of the following assumptions :

- 1 — no variations in S_i and S_s during annealing,
- 2 — no variations in S_g during annealing,
- 3 — no variation in ρ_s during annealing,
- 4 — no variation in ρ_g during annealing.

Assumptions 1 and 3 have been previously advanced [8]. It is physically doubtful that assumptions 3 and 4 could be simultaneously valid, an exhaustive discussion would be necessary in a future paper.

3. Comparison with experiments of some authors. —

Let us examine the results of previous studies [1, 2, 3, 5, 29] about t.e.p. of monocrystalline thin metal films.

Suri *et al.* [3] have undertaken systematic studies of the resistivity, t.c.r. and thermoelectric power of unannealed and annealed copper films [3]. They were prepared [3] by thermal evaporation in a vacuum of 2×10^{-6} torr at a rate of 6-8 Å/s; they could be annealed at 250 °C and the substrate could be heated at various temperatures. The difference (at room temperature) between the values of the infinitely thick film and the bulk metal ($\rho_0 \approx 1.7 \mu\Omega \text{ cm}$) resistivity is less than 20 % for unannealed films. Then it is reasonable to expect the film to be monocrystalline [15]. Figure 3 shows that the conductivity ratio $\sigma_{\text{Fm}}^*/\sigma_0$ dependence of the difference ΔS in thermoelectric powers does not correspond to a linear law; it could be advanced, as suggested by Suri *et al.* [3-5] that the observed behaviour is due to the thickness dependent contribution of imperfections, in good agreement with the marked effect of annealing (Fig. 3). From equation (5), the observed increase in ΔS with $\sigma_{\text{Fm}}^*/\sigma_0$ suggests that the thickness dependence is more marked

Fig. 3. — Plot of ΔS versus σ_{Fm}^*/σ_0 for annealed and unannealed copper films [3]; ● unannealed films; ○ annealed films.

in ΔS than in σ_{Fm}^*/σ_0 , since both ΔS and σ_{Fm}^*/σ_0 increase with increasing thickness [5]; this prediction agrees with the calculated variation in S_i with thickness [4], which is qualitatively valid for thicker films but cannot be considered as a true quantitative result since it starts from equation (4.5), previously proposed [8] and somewhat questionable as shown in previous paragraph; new interpretations of data about Cu films [3, 4, 5, 29] are then required.

The simultaneous measurements of the resistivity ρ_{Fm} and its t.c.r. β_{Fm} in copper films by Narasimha Rao *et al.* [2] have been recently analysed with a satisfactory agreement on the basis of the bidimensional model [15]; results in thermoelectric power were also available [2]. A plot (Fig. 4) of the data in the form ΔS versus σ_{Fm}^*/σ_0 yields a straight line but it appears that the intersection with the abscissa axis occurs for $\sigma_{Fm}^*/\sigma_0 \approx 0.95$. This behaviour is somewhat surprising since we previously [15] observed the thickness dependence of ρ_{Fm}^* and β_{Fm} to show good agreement with the prediction of the bidimensional model even if small departure occurred in the limit of large thicknesses. It should be pointed out that another straight line with unity intercept (dotted line) may be also obtained by assuming that the experimental accuracy decreases at large thicknesses where smaller values of ΔS were measured.

But several remarks concerning the preparation

Fig. 4. — Plot of ΔS versus σ_{Fm}^*/σ_0 for annealed copper films [2].

procedure can be made. The films were evaporated in a vacuum of 5×10^{-6} torr onto cleared mica substrates and annealed *in situ* at 130-160 °C; the annealing temperature is lower than those generally used: 300 °C [9], 480 °C [7]; we can then assume that the thicker films are not firmly annealed that can modify the magnitude of ΔS and induce a deviation from the theoretical law.

Fig. 5. — Plot of ΔS versus σ_{Fm}^*/σ_0 for annealed silver films [1].

Narasimha Rao *et al.* [1] have also reported data in resistivity and t.e.p. of silver films. As shown in figure 5 a straight line exhibiting an abscissa intercept equal to unity is obtained down to $k \approx 0.3$; thus we may easily conclude that these silver films are free of imperfections. However the F.-S. model as well as the bidimensional model in the case $a \approx a_g$ fails to explain the observed size effect in resistivity and its t.c.r. A tentative was made to fit the experimental

Fig. 6. — The variation of grain size a_g with film thickness a according to previous published results on permalloy films [30].

Fig. 7. — Comparison of experimental data [1] with theoretical variations of conductivity with film thickness : full line : bidimensional model [15]; dotted line : F.-S. model [18], curve A $p = 0.5$; curve B $p = 0$.

data with the theoretical data deduced from the bidimensional model by assuming that :

a) at small thicknesses the grain size a_g is equal to the film thickness a ;

b) at larger thicknesses the variations in grain size with thickness are linear (Fig. 6); the linear plot was taken similar to that obtained in the case of permalloy films [30].

Since the silver films were obtained by evaporation in a vacuum better than 10^{-6} torr and firmly annealed

Fig. 8. — Comparison of experimental data [1] with theoretical variations of t.c.r. with film thickness : full line : bidimensional model; dotted line : F.-S. model, curve A $p = 0.5$; curve B $p = 0$.

in situ [31] the above assumptions have physical consistency.

We have drawn in figures 7 and 8 the corresponding theoretical plots; as expected, satisfactory fits of the reduced thickness ($l_0 \approx 523 \text{ \AA}$ [22]) dependence of the conductivity and temperature coefficient of resistivity ratio are observed down to $k \sim 0.3$.

4. Conclusion. — A convenient way to analyse the role played by imperfections in thin monocrystalline metal film is proposed by determining the size effect in thermoelectric power. The experimental results reported by different authors allow then to make a suitable choice of the adequate conduction theory (F.-S. or bidimensional).

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