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Graphical determination of the energy dependence of the thermoelectric power of thin monocrystalline metal films

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Some theoretical results of the conductivity dependence of the thermoelectric power and of the difference in thermoelectric power are explained in the framework of the bi-dimensional model of conduction for monocrystalline metal films. Thermoelectric power data on thin metal films previously reported by different authors allow an accurate calculation of the energy dependence of the mean free-path, μ, and Fermi-surface area, v.

1. Introduction

Size-effects in thermoelectric power (TEP) of thin metal films have been investigated theoretically [1–20] and experiments [2, 4–10, 16–41] have been interpreted because they provide useful information about the distortions of the Fermi surface (see Ziman [1]) and the energy dependence of the electron mean free path, μ, where

$$\mu = (\partial \ln l_0 / \partial \ln \epsilon)_{\epsilon=\epsilon_F}, \qquad (1)$$

where l_0 is the bulk mean free path and ϵ_f is the Fermi energy.

Even if the Fuchs–Sondheimer (F–S) theory [42] fails to explain, at small thickness, the observed behaviour of transport parameters [43] such as the film resistivity [36, 38], the thickness dependence of the thermoelectric power (TEP) is compared with the prediction of this model. Only one attempt has been made to interpret the results within the framework of a grain-boundary theory and no estimate of μ has been reported. We recall that in comparing the observed size effects with the F–S theory the term μ is generally determined by analysing the film thickness, a, dependence of the difference in TEP, ΔS, [22, 23, 27, 29, 30, 31, 33, 37] or by studying the temperature coefficient of resistivity, β_F, dependence of ΔS [25, 28, 30, 33, 36, 38, 39]. Once μ is determined the energy dependence of the Fermi surface area, $v = (\partial l nA / \partial l n\epsilon)_{\epsilon=\epsilon_F}$ is calculated from the bulk TEP [24, 25, 27–29, 31, 37, 39]. The accuracy of these two methods may be questionable. In the first method it is necessary to know the film thickness and specularity parameter, p, [42] and to use some well-known size effect approximation [21]. In the second method it is necessary to measure the temperature coefficient of resistivity, β_F, of thin metal film and it is well established that the experimental determination of β_F could be subjected to quite significant errors due to the slight value of β_F [21] and in some cases to the mismatch in thermal expansion coefficients of the film and its substrate [44, 45].

2. Theory

Narasimha Rao *et al.* [36, 38] have proposed an other method for determining μ: they obtained a value of μ from a resistivity measurement and then evaluated v in the usual way using the known value of bulk TEP, S_0; however, this method is derived from the F–S theory and is only valid for relatively thick films ($k \geqslant 0.5$); moreover, the interpretation is surprising since, after evaluating μ and v for films of different thicknesses from size effects terms it is found that both μ and v vary with film thickness.

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An original procedure based on annealing phenomena has also been implemented [10, 26] but the calculations must be re-examined since the effects of grain boundaries were omitted.

It has been recently shown that the change with thickness in monocrystalline film resistivity may be interpreted from the bi-dimensional model of grain-boundaries [46]; an interesting result of this model [46] is that, in very large ranges of the reduced thickness, k, of the specularity parameter, p, and of the transmission coefficient of electrons across the grain-boundary, t, [46, 47] a simple relation exists [20] between the conductivity, σ, and β, i.e.:

$$\beta_{\mathrm{Fm}}/\beta_0 \approx \sigma_{\mathrm{Fm}}/\sigma_0, \tag{2}$$

where the subscripts Fm and 0 refer to the monocrystalline film and bulk metal. For example, for $t = 0.4$ and $p = 0.5$ we obtain a deviation less than 1% for $k \geqslant 0.01$.

A method to determine the terms μ and v by studying the size and grain-boundary effects in thin monocrystalline metal films can consequently be proposed.

Alternative models [48, 49] have been presented for representing monocrystalline film conductivity but only the bi-dimensional model [46] gives convenient relations between TEP and conductivity.

Moreover, it has been pointed out in a recent paper [50] that some models which had been obtained using analogous procedures were theoretically questionable.

More complex analytical expressions can also be derived [51] from a modified [47] conduction model [52] for infinitely thick films.

The theoretical expression of the monocrystalline film TEP, S_{Fm}, in the framework of the bi-dimensional model [46] can be expressed as:

$$S_{\mathrm{Fm}} = -S\left\{v + \mu\,\frac{\beta_{\mathrm{Fm}}}{\beta_0}\right\} \tag{3}$$

with

$$S = \frac{\pi^2 k_0^2 T}{3e\epsilon_{\mathrm{F}}}, \tag{4}$$

where k_0 is the Boltzmann constant, T is the absolute temperature, $-e$ is the electron charge and ϵ_{F} is the Fermi energy.

Taking into account that the TEP of the bulk metal is written as [1]

$$S_0 = -S(\mu + v) \tag{5}$$

and combining Equations 2, 3 and 5 gives

$$\Delta S = S_{\mathrm{Fm}} - S_0 = S\mu - S\mu\,\frac{\sigma_{\mathrm{Fm}}}{\sigma_0} \tag{6}$$

and

$$S_{\mathrm{Fm}}/S_0 = -\frac{Sv}{S_0} - \frac{S\mu}{S_0}\cdot\frac{\sigma_{\mathrm{Fm}}}{\sigma_0}. \tag{7}$$

Equation 6 has been previously studied [20]; it was shown that a plot of ΔS against $\sigma_{\mathrm{Fm}}/\sigma_0$ is a straight line with an abscissa intercept of unity and an ordinate intercept of $S\mu$ (note that in this analysis the impurity contribution to resistivity, and then to the TEP, is neglected).

Noting that, in the limit of large thickness, the conductivity ratio, $\sigma_{\mathrm{Fm}}/\sigma_0$, approaches 1 then it appears from Equation 7 that a plot of S_{Fm}/S_0 against $\sigma_{\mathrm{Fm}}/\sigma_0$ should yield a straight line with an ordinate intercept $-Sv/S_0$ and a slope of $-S\mu/S_0$ which must pass through the point $\{S_{\mathrm{Fm}}/S_0 = 1, \sigma_{\mathrm{Fm}}/\sigma_0 = 1\}$.

As S_0 is a known quantity, both μ and v can be easily determined from the plots of S_{Fm}/S_0 against $\sigma_{\mathrm{Fm}}/\sigma_0$. Further, as the S_{Fm}/S_0 and ΔS against $\sigma_{\mathrm{Fm}}/\sigma_0$ plots should yield the same μ value it is possible to evaluate v with a better accuracy.

Measurements of the TEP on silver and copper films by Narasimha Rao *et al.* [36, 38], as well as previously reported results on potassium films by Jain and Verma [8], illustrate the adequation of the proposed model. Previous studies [18, 46] of the thickness dependence of the silver and copper film resistivity and its temperature coefficient of resistivity have shown that the size effect can be understood in term of the bi-dimensional effect. Note that, in the case of silver films, the apparent size effect has been attributed [18] to a thickness dependence of the average grain size for films of thickness greater than 20 nm.

The ΔS and S_{Fm}/S_0 against $\sigma_{\mathrm{Fm}}/\sigma_0$ plots of copper films are given in Figs 1 and 2. As expected, straight lines exhibiting the theoretical features noticed in the above section are obtained (it is assumed, as suggested previously [45], that the experimental errors are more marked at larger thicknesses). The best fit in Fig. 1 yields

$$\mu \approx -0.819;$$

whereas Fig. 2 yields

$$\mu \approx -0.746$$

and

$$v \approx -0.824.$$

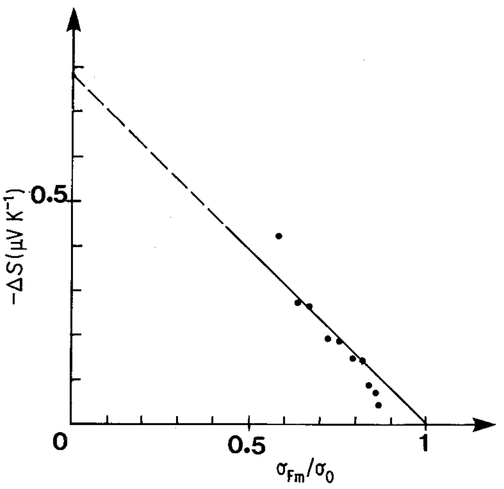

Figure 1 Variation of $-\Delta S$ with the conductivity ratio $\sigma_{\mathrm{Fm}}/\sigma_0$ (experimental data of Narasimha Rao *et al.* [36] for copper films).

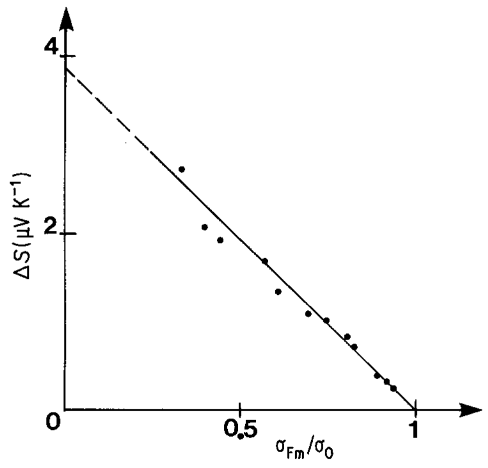

Figure 3 Variation of the difference in thermoelectric power, ΔS, with the conductivity ratio, $\sigma_{\mathrm{Fm}}/\sigma_0$, for silver films (experimental data of Narasimha Rao *et al.* [38]).

Plots of the silver film data in the form ΔS against $\sigma_{\mathrm{Fm}}/\sigma_0$ and S_{Fm}/S_0 against σ_{Fm} are drawn respectively in Figs 3 and 4. The thermoelectric power behaviour shows the best agreement with the bi-dimensional model and we easily deduced from the ΔS against $\sigma_{\mathrm{Fm}}/\sigma_0$ plot that

$$\mu \approx 3.17;$$

whereas, from the plot of Fig. 4 we obtain

$$\mu \approx 3.19$$

and

$$v \approx -4.35,$$

in good agreement with the value of μ evaluated in Fig. 3. Note that the very small departure from the bi-dimensional model which occurs in Figs 3 and 4 is surely due to inaccuracies and uncertainties in the measurements; thus, the reasonable agreement between the observed behaviour and the theoretical predictions of the bi-dimensional model contradicts the conclusion proposed by Narasimha Rao *et al.* [38], namely, the thickness dependence of the terms μ and v.

The case of potassium is however more complicated to interpret because Jain and Verma [8] have omitted to report the value of the conductivity and TEP of an infinitely thick film. However, as

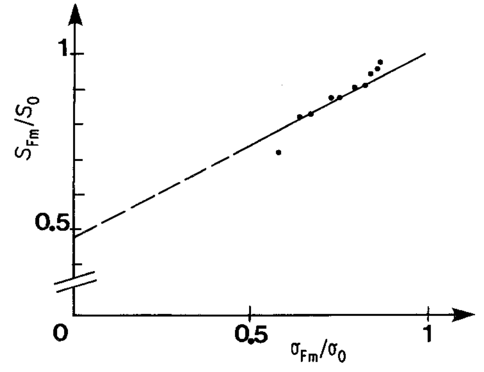

Figure 2 Variation of S_{Fm}/S_0 with $\sigma_{\mathrm{Fm}}/\sigma_0$ for copper films (experimental data of Narasimha Rao *et al.* [36]).

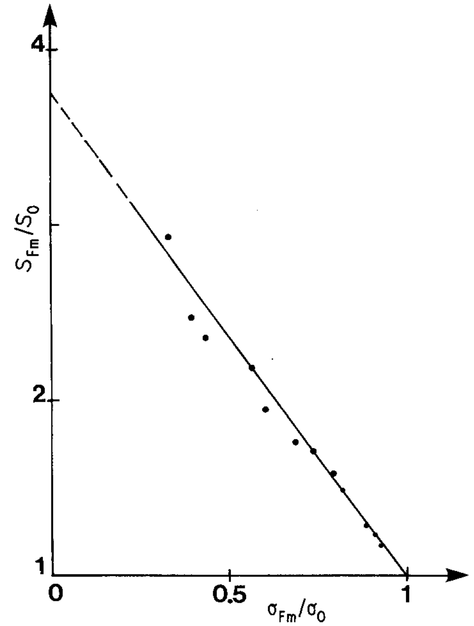

Figure 4 Variation of S_{Fm}/S_0 with $\sigma_{\mathrm{Fm}}/\sigma_0$ for silver films (experimental data of Narasimha Rao *et al.* [38]).

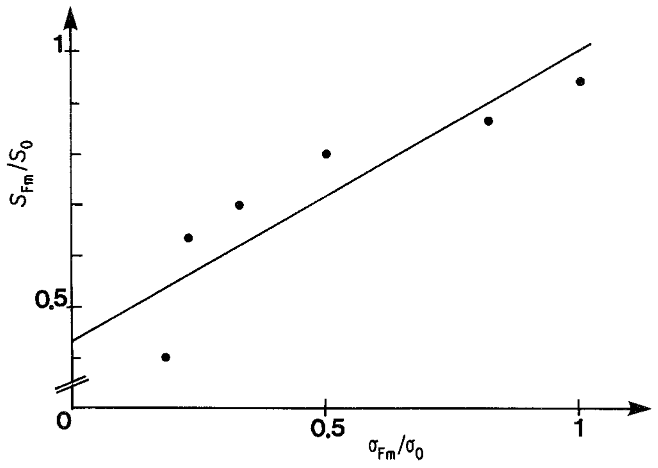

Figure 5 Variation of S_{Fm}/S_0 with σ_{Fm}/σ_0 for potassium (experimental data reported by Jain and Verma [8]).

seen in Fig. 5 the best fit of S_{Fm}/S_0 against σ_{Fm}/σ_0 yields

$$\mu/v \approx 0.57/0.43 \approx 1.33$$

with μ positive if S_0 exhibits a negative sign. Assuming that $v = 1$ (free electron model) gives $\mu = 1.33$, i.e., $l_0 \sim \epsilon^{1.33}$. Since the electron velocity is proportional to the square-root of the energy, the corresponding variation of τ with energy is $\tau \sim \epsilon^b$ where $b = 0.83$. This result markedly departs from the result $b \approx 1.5$ obtained by Jain and Verma [8] in their tentative fit to their data.

3. Conclusion

When the grain-boundary and external-surface scatterings which occur simultaneously in thin monocrystalline metal films are described in terms of the bi-dimensional model, the study of the conductivity dependence of the thermoelectric power and of the difference in thermoelectric power allows simple determination of the terms μ and v representing the energy dependence of the mean free path and Fermi surface area. Previously published data on silver, copper and potassium films show a good agreement with the predictions of the theory.

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