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Energy dependence of the theoretical expressions of Ziman transport parameters in the Mayadas–Shatzkes model

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The macroscopic transport parameters K_n ($n = 0, 1, 2$) defined by Ziman are calculated in the framework of the Mayadas–Shatzkes model from two opposite assumptions: whether or not the reflection coefficient depends on electron energy. In the case of metal and semi-metal films asymptotic formulations are given. It is only in the case of fine-grained film that the equations strongly differ whether or not R is energy dependent. A comparison with several experiments related to the thermoelectric power of noble metal films and the temperature coefficient of resistivity of semi-metal films suggests that R must be physically regarded as energy independent.

1. Introduction

The Mayadas–Shatzkes model, M–S model, [1] was the earliest model proposed for describing the effect of grain boundaries of thin metal films on the electrical conductivity. Alternative models have been proposed recently [2–6] and it then appeared that the M–S model was not a convenient tool for calculating the Hall coefficient [7]. Moreover, some implicit assumptions were required [6] for the validity of the M–S model, which is, in fact, a unidimensional representation of multidimensional phenomena [6]. In this way, a physical relation could be found [5, 8] between the reflection coefficient of the M–S model, R, and the statistical electronic transmission coefficient at grain boundaries, t, introduced later by several authors [2–6]. Variation in t with electron energy does not seem physically acceptable because t describes the roughness of the grain boundary, the same assumption is also valid for R, starting from the relation [8]:

$$\frac{R}{1-R} = \log \frac{1}{t} \tag{1}$$

This assumption was used for calculating directly the thermoelectric power of thin films in the M–S model [9].

However, the mathematical expression for the ratio $R(1-R)^{-1}$ given by Mayadas and Shatzkes is [1]:

$$\frac{R}{1-R} = \frac{2m}{\hbar^3} \frac{s^2}{V_F K_F} \tag{2}$$

where m is the electron effective mass, V_F the Fermi velocity, $\hbar$ is Planck's constant, $K_F = m\hbar^{-1} V_F$ and s is the magnitude of the Dirac potential which represents any grain-boundary in the M–S model.

Hence if s is defined as a constant value (independent from electron energy E), the formal equation used for calculating the thermoelectric power, S_f, is [10, 11]:

$$S_f = -AT \left. \frac{\partial \ln \sigma_f}{\partial \ln E} \right|_{E=E_F} \tag{3}$$

where E_F is the Fermi energy, A a constant for a given material, and σ_f, the electrical conductivity of the film, must be used by introducing the relation:

$$\left. \frac{\partial \ln \left(\frac{R}{1-R} \right)}{\partial \ln E} \right|_{E=E_F} = -1 \tag{4}$$

One must not overlook the fact that this relation

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is valid if s is independent of E, i.e. if any grain boundary can be identified with a potential hill; in our opinion this assumption is not easily justified.

In order to answer the question "does it work?" from a general point of view, we have calculated the macroscopic transport coefficients of Ziman [10, 12] in the framework of the M–S model, using either Equation 4 or the following equation:

$$\frac{\partial \ln\left(\frac{R}{1-R}\right)}{\partial \ln E} = 0 \tag{5}$$

2. Theory

2.1. The macroscopic transport coefficients

Three transport coefficients K_n ($n = 0, 1, 2$) are defined from the relation [12]:

$$K_n = \frac{1}{e^2}\int (E - E_F)^n \sigma_f(E) \frac{\partial F_0}{\partial E}\, dE$$

$$n = 0, 1, 2 \tag{6}$$

where F_0 is the equilibrium distribution function of electrons.

Expanding the integrand in Taylor development in the vicinity of E_F gives [12, 13]:

$$K_0 = \frac{1}{e^2}\left[\sigma_f(E) + \frac{(\pi BT)^2}{6}\frac{\partial^2 \sigma_f(E)}{\partial E^2}\right]_{E=E_f} \tag{7}$$

$$K_1 = \frac{1}{e^2}\left[\frac{(\pi BT)^2}{3}\frac{\partial \sigma_f(E)}{\partial E} + \frac{7}{90}(\pi BT)^4 \frac{\partial^3 \sigma_f(E)}{\partial E^3}\right]_{E=E_F} \tag{8}$$

$$K_2 = \frac{1}{e^2}\frac{(\pi BT)^2}{3}\left[\sigma_f(E) + \frac{7}{10}(\pi BT)^2 \frac{\partial^2 \sigma_f(E)}{\partial E^2}\right]_{E=E_F} \tag{9}$$

where B is the Boltzmann constant and T the absolute temperature.

Introducing the M–S function, $f(\alpha)$, defined by:

$$f(\alpha) = \sigma_f/\sigma_0 \tag{10}$$

where σ_0 is the conductivity of the bulk material and [1]:

$$\alpha = \lambda_0 D_g^{-1} R(1-R)^{-1} \tag{11}$$

where λ_0 is the electron mean free path in the bulk material and D_g the average grain size, Equations 7 to 9 go to the following forms [14]:

$$\frac{e^2}{\sigma_0}K_0 = f(\alpha) + \tfrac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2\left[16(s+\tfrac{1}{2})(s+\tfrac{3}{4})f(\alpha) - 12(s+\tfrac{1}{2})(s+\tfrac{3}{4})\frac{1}{1+\alpha} - 3(s+\tfrac{1}{2})^2\frac{1}{(1+\alpha)^2}\right] \tag{12}$$

$$\frac{e^2}{\sigma_0}K_1 = \frac{(\pi BT)^2}{3E_F}\left\{(4s+3)f(\alpha) - 3(s+\tfrac{1}{2})\frac{1}{1+\alpha} + \frac{7}{30}\left(\frac{\pi BT}{E_F}\right)^2(s+\tfrac{1}{2}) \times \left[(64s^2+64s+12)f(\alpha) - 3(16s^2+16s+3) \times \frac{1}{1+\alpha} - 9(s+\tfrac{1}{2})^2\frac{1}{(1+\alpha)^2} - 6(s+\tfrac{1}{2})^2\frac{1}{(1+\alpha)^3}\right]\right\} \tag{13}$$

$$\frac{e^2}{\sigma_0}K_2 = \frac{(\pi BT)^2}{3}\left\{f(\alpha) + \frac{7}{10}\left(\frac{\pi BT}{E_F}\right)^2 \times \left[16(s+\tfrac{1}{2})(s+\tfrac{3}{4})f(\alpha) - 12(s+\tfrac{1}{2})(s+\tfrac{3}{4})\frac{1}{1+\alpha} - 3(s+\tfrac{1}{2})^2\frac{1}{(1+\alpha)^2}\right]\right\} \tag{14}$$

assuming the validity of Equation 5 and:

$$\frac{e^2}{\sigma_0}K_0 = f(\alpha) + \tfrac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2\left[4s(4s-1)f(\alpha) - 3(s-\tfrac{1}{2})(4s+1)\frac{1}{1+\alpha} - 3(s-\tfrac{1}{2})^2\frac{1}{(1+\alpha)^2}\right] \tag{15}$$

$$\frac{e^2}{\sigma_0}K_1 = \frac{(\pi BT)^2}{3E_F}\left\{4sf(\alpha) - 3(s-\tfrac{1}{2})\frac{1}{1+\alpha} + \frac{7}{30}\left(\frac{\pi BT}{E_F}\right)^2(s-\tfrac{1}{2})\left[16s(4s-1)f(\alpha) - 12s(4s-1)\frac{1}{1+\alpha} - 9(s^2-\tfrac{1}{4})\frac{1}{(1+\alpha)^2} - 6(s-\tfrac{1}{2})^2\frac{1}{(1+\alpha)^3}\right]\right\} \tag{16}$$

$$\frac{e^2}{\sigma_0} K_2 = \frac{(\pi BT)^2}{3} \left\{ f(\alpha) + \frac{7}{10} \left(\frac{\pi BT}{E_F} \right)^2 \times \left[4s(4s-1) f(\alpha) - 3(s-\tfrac{1}{2})(4s+1) \frac{1}{1+\alpha} - 3(s-\tfrac{1}{2})^2 \frac{1}{(1+\alpha)^2} \right] \right\} \quad (17)$$

assuming the validity of Equation 4, with:

$$s = \frac{\mathrm{d} \ln \tau_0}{\mathrm{d} \ln E_F} \quad (18)$$

where τ_0 is the electron relaxation time in the bulk material.

One can immediately predict the deviations in the two expressions of the usual transport parameters obtained in this way, since the electrical conductivity σ_f, the thermoelectric power S_f, and the thermal conductivity C_f are expressed by [6, 10, 11]:

$$\sigma_f = e^2 K_0 \quad (19)$$

$$S_f = -\frac{1}{eT} \frac{K_1}{K_0} \quad (20)$$

$$C_f = \frac{1}{T} \left(K_2 - \frac{K_1^2}{K_0} \right) \quad (21)$$

2.2. The case of metal films

In the case of pure metal films,

$$\pi BT/E_F \ll 1 \quad (22)$$

and the approximate equations for K_0, K_1, and K_2 are:

$$\frac{e^2}{\sigma_0} K_0 \approx f(\alpha) \quad (23)$$

$$\frac{e^2}{\sigma_0} K_1 \approx \frac{(\pi BT)^2}{3E_F} \left[(4s+3) f(\alpha) - 3(s+\tfrac{1}{2}) \frac{1}{1+\alpha} \right], \quad \frac{\mathrm{d} \ln \left(\frac{R}{1-R} \right)}{\mathrm{d} \ln E} = 0 \quad (24')$$

$$\frac{e^2}{\sigma_0} K_1 \approx \frac{(\pi BT)^2}{3E_F} \left[4s f(\alpha) - 3(s-\tfrac{1}{2}) \frac{1}{1+\alpha} \right], \quad \frac{\mathrm{d} \ln \left(\frac{R}{1-R} \right)}{\mathrm{d} \ln E} = -1 \quad (24'')$$

$$\frac{e^2}{\sigma_0} K_2 \approx \frac{(\pi BT)^2}{3} f(\alpha) \quad (25)$$

For low values of α, i.e. for grains of large size, the above expression for $(e^2/\sigma_0)K_1$ become:

$$\frac{e^2}{\sigma_0} K_1 \approx \frac{(\pi BT)^2}{3E_F} [s + \tfrac{3}{2} - 3(s+1)\alpha], \quad \frac{\mathrm{d} \ln \left(\frac{R}{1-R} \right)}{\mathrm{d} \ln E} = 0 \quad (26')$$

$$\frac{e^2}{\sigma_0} K_1 \approx \frac{(\pi BT)^2}{3E_F} [s + \tfrac{3}{2} - 3(s+\tfrac{1}{2})\alpha], \quad \frac{\mathrm{d} \ln \left(\frac{R}{1-R} \right)}{\mathrm{d} \ln E} = -1 \quad (26'')$$

and [1, 6]:

$$f(\alpha) \approx 1 - \tfrac{3}{2} \alpha \quad (27)$$

For high values of α, i.e. for fine-grained films, the above expressions for K_1 become:

$$\frac{e^2}{\sigma_0} K_1 \approx \frac{(\pi BT)^2}{3E_F} \left[\frac{3}{4\alpha} + \tfrac{3}{5} (s-\tfrac{1}{2}) \frac{1}{\alpha^2} \right], \quad \frac{\mathrm{d} \ln \left(\frac{R}{1-R} \right)}{\mathrm{d} \ln E} = 0 \quad (28')$$

$$\frac{e^2}{\sigma_0} K_1 \approx \frac{(\pi BT)^2}{3E_F} \left[\frac{3}{2\alpha} + \tfrac{3}{5} (s-\tfrac{5}{2}) \frac{1}{\alpha^2} \right], \quad \frac{\mathrm{d} \ln \left(\frac{R}{1-R} \right)}{\mathrm{d} \ln E} = -1 \quad (28'')$$

and [1, 6]:

$$f(\alpha) \approx \frac{3}{4\alpha} - \frac{3}{5\alpha^2} \quad (29)$$

The last equations show that a marked variation in the behaviour of transport parameters can occur for fine-grained films, whether the assumption of energy independence of $R(1-R)^{-1}$ is retained or not; for instance, the absolute magnitude of the thermoelectric power of fine-grained films is multiplied by a factor, 2, when an energy dependence of the ratio $R(1-R)^{-1}$ is retained, as shown by introducing Equations 28′ and 29, or Equations 28″ and 29 in Equation 20:

$$S_f \approx -\frac{(\pi B)^2 T}{3eE_F}\left[1+\tfrac{4}{5}(s+\tfrac{1}{2})\frac{1}{\alpha}\right], \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E}=-0 \qquad (30')$$

$$S_f \approx -\frac{(\pi B)^2 T}{3eE_F}\left[2+\tfrac{4}{5}(s-\tfrac{1}{2})\frac{1}{\alpha}\right], \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E}=-1 \qquad (30'')$$

These expressions can be compared to the theoretical value of the thermoelectric power in the bulk material, S_0, expressed as [11, 15]:

$$S_0 = -\frac{(\pi B)^2 T}{3eE_F}(U+V) \qquad (31)$$

with:

$$U = \left.\frac{\partial \ln \lambda_0}{\partial \ln E}\right|_{E=E_F} \qquad (32)$$

$$V = \left.\frac{\partial \ln ct}{\partial \ln E}\right|_{E=E_F} \qquad (33)$$

where ct is the area of the Fermi surface.

Under the simplifying assumption of a spherical Fermi surface the value of V is unity. Taking into account the possible energy dependence of the relaxation time (Equation 18), the value of U is:

$$U = s+\tfrac{1}{2} \qquad (34)$$

Hence:

$$S_0 = -\frac{(\pi B)^2 T}{3eE_F}(s+\tfrac{3}{2}) \qquad (35)$$

In the case where the electron relaxation time does not depend on energy, i.e. for $s=0$, it is clear that the thermoelectric power of fine-grained metal film takes an absolute magnitude larger than that of the bulk material. Such a behaviour is somewhat surprising since it is generally reported that the absolute magnitude of the thermoelectric power of pure metal films increases with thickness, [11, 15], in good agreement with the general relation:

$$S_f = -\frac{(\pi B)^2 T}{3eE_F}\left[V+U\frac{\beta_f}{\beta_0}\right] \qquad (36)$$

where β_f and β_0 are the temperature coefficient of the film and the bulk material, respectively.

Many consequences of the above relation have been deduced in the case of polycrystalline and monocrystalline films, in good agreement with the experiments of several authors [11, 15]. Consequently we do not retain the assumption of energy dependence of the ratio $R(1-R)^{-1}$.

It can be objected that our opinion is based on the theoretical values of S_0, whereas several authors have given experimental data which differ markedly [11, 15], except in the case of noble metals where no marked deviation occurs. Moreover it has been shown that some authors did not take into account the effect of grain boundaries that modifies the experimental values of U and V, as recently pointed out [16, 17]. Our opinion can also be sustained by the fact that empirical results related to the conductivity lead to the same conclusion [18]. No verification of the conclusion can be found by studying the behaviour of the thermal conductivity of thin metal films since the role played by K_2^2 is related to a second-order term in the usual assumption of $\pi BT/E_F \ll 1$.

2.3. Semi-metal films

In the case of semi-metal films, the complete expressions of K_0, K_1 and K_2 must be used and in the limiting cases of large and fine grains, the following approximate equations for K_0 and K_1 are obtained, after tedious calculations:

$$\frac{e^2}{\sigma_0}K_0 \approx 1-\tfrac{3}{2}\alpha+\tfrac{1}{6}\frac{(\pi BT)^2}{E_F}(s+\tfrac{1}{2}) \times \left[s+\tfrac{3}{2}-6(s+1)\alpha\right], \quad \alpha \ll 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E}=0 \qquad (37')$$

$$\frac{e^2}{\sigma_0}K_0 \approx 1-\tfrac{3}{2}\alpha+\tfrac{1}{6}\frac{(\pi BT)^2}{E_F}(s+\tfrac{1}{2})\left[s+\tfrac{3}{2}-6s\alpha\right], \quad \alpha \ll 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E}=1 \qquad (37'')$$

$$\frac{e^2}{\sigma_0}K_1 \approx \frac{(\pi BT)^2}{3E_F}\left((s+\tfrac{3}{2})-3(s+1)\alpha+\frac{7}{30} \times \left(\frac{\pi BT}{E_F}\right)^2(s+\tfrac{1}{2})\left[s^2+s-\tfrac{3}{4}-12s(s+1)\alpha\right]\right), \quad \alpha \ll 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E}=0 \qquad (38')$$

$$\frac{e^2}{\sigma_0}K_1 \approx \frac{(\pi BT)^2}{3E_F}\left\{(s+\tfrac{3}{2}) - 3(s+\tfrac{1}{2})\alpha + \frac{7}{30} \times \left(\frac{\pi BT}{E_F}\right)^2 (s^2-\tfrac{1}{4})\left[(s+\tfrac{3}{2}) - 12s\alpha\right]\right\},$$

$$\alpha \ll 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = -1 \qquad (38'')$$

$$\frac{e^2}{\sigma_0}K_2 \approx \frac{(\pi BT)^2}{3}\left\{1 - \tfrac{3}{2}\alpha + \frac{7}{10}\left(\frac{\pi BT}{E_F}\right)^2 (s+\tfrac{1}{2}) \times \left[s+\tfrac{3}{2} - 6(s+1)\alpha\right]\right\}, \quad \alpha \ll 1,$$

$$\mathrm{d}\ln\left(\frac{R}{1-R}\right) = -1 \qquad (39')$$

$$\frac{e^2}{\sigma_0}K_2 \approx \frac{(\pi BT)^2}{3}\left\{1 - \tfrac{3}{2}\alpha + \frac{7}{10}\left(\frac{\pi BT}{E_F}\right)^2 (s+\tfrac{1}{2}) \times \left[s+\tfrac{3}{2} - 6s\alpha\right], \quad \alpha \ll 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = -1\right. \qquad (39'')$$

$$\frac{e^2}{\sigma_0}K_0 \approx \frac{3}{4\alpha} - \frac{3}{5\alpha^2} + \frac{1}{10}\left(\frac{\pi BT}{E_F}\right)^2 (-s^2+\tfrac{1}{4})\frac{1}{\alpha^2}$$

$$\alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = 0 \qquad (40')$$

$$\frac{e^2}{\sigma_0}K_0 \approx \frac{3}{4\alpha} - \frac{3}{5\alpha^2} + \frac{1}{10}\left(\frac{\pi BT}{E_F}\right)^2 \times \left[\frac{5}{2\alpha} + \left(-s^2+4s-\frac{15}{4}\right)\frac{1}{\alpha^2}\right],$$

$$\alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = -1 \qquad (40'')$$

$$\frac{e^2}{\sigma_0}K_1 \approx \frac{(\pi BT)^2}{3E_F}\left[\frac{3}{4\alpha} + \tfrac{3}{5}(s-\tfrac{1}{2})\frac{1}{\alpha^2} + \frac{7}{50}\left(\frac{\pi BT}{E_F}\right)^2 \times (s+\tfrac{1}{2})(s^2+s-\tfrac{3}{4})\frac{1}{\alpha^2}\right], \quad \alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = 0 \qquad (41')$$

$$\frac{e^2}{\sigma_0}K_1 \approx \frac{(\pi BT)^2}{3E_F}\left[\frac{3}{2\alpha} + \tfrac{3}{5}(s-\tfrac{5}{2})\frac{1}{\alpha^2} + \frac{7}{50}\left(\frac{\pi BT}{E_F}\right)^2 \times (s-\tfrac{1}{2})\left(s^2-4s+\frac{15}{4}\right)\frac{1}{\alpha^2}\right],$$

$$\alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = -1 \qquad (41'')$$

$$\frac{e^2}{\sigma_0}K_2 \approx \frac{(\pi BT)^2}{3}\left[\frac{3}{4\alpha} - \frac{3}{5\alpha^2} - \frac{21}{50}\left(\frac{\pi BT}{E_F}\right)^2 \times (s^2-\tfrac{1}{4})\frac{1}{\alpha^2}\right], \quad \alpha \gg 1, \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = 0 \qquad (42')$$

$$\frac{e^2}{\sigma_0}K_2 \approx \frac{(\pi BT)^2}{3}\left\{\frac{3}{4\alpha} - \frac{3}{5\alpha^2} - \frac{21}{50}\left(\frac{\pi BT}{E_F}\right)^2 \times \left[-\frac{5}{2\alpha} + \left(s^2-4s+\frac{15}{4}\right)\frac{1}{\alpha^2}\right]\right\},$$

$$\alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = -1 \qquad (42'')$$

It may be observed anew that the main deviations in the formulations of a given K_n occur in the case of fine-grained films, especially for K_1, as in the preceding case of metal films, and for the extra term in the brackets (typical of semi-metals) in the expressions of K_0 and K_2; it appears that the extra term varies as α^{-1} when R depends on energy and as α^{-2} when R does not.

Consequently the magnitude of the extra term in the film conductivity σ_f (Equation 19) would be much more important when R depends on energy as shown by the expressions of σ_f:

$$\sigma_f \approx \sigma_0\left\{\frac{3}{4\alpha} - \frac{3}{5\alpha^2}\left[1 + \tfrac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2 (s^2-\tfrac{1}{4})\right]\right\},$$

$$\alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = 0 \qquad (43')$$

$$\sigma_f \approx \sigma_0\left\{\frac{3}{4\alpha}\left[1 + \tfrac{1}{3}\left(\frac{\pi BT}{E_F}\right)^2\right]\right\},$$

$$\alpha \gg 1, \quad \frac{\mathrm{d}\ln\left(\frac{R}{1-R}\right)}{\mathrm{d}\ln E} = -1 \qquad (43'')$$

Neglecting $(\pi BT/E_F)^2$, equations 43′ and 43″ reduce to previously proposed equations [19].

The film temperature coefficient of resistivity, β_f, defined by:

$$\beta_f = -\partial \ln \sigma_f / \partial T \tag{44}$$

can be calculated from Equation 43″, and gives:

$$-\beta_f \approx \frac{\partial}{\partial T} \ln \left[1 + \tfrac{1}{3}\left(\frac{\pi BT}{E_F}\right)^2\right] \tag{45}$$

Equation 45 can be written as:

$$\beta_f \approx -\tfrac{2}{3}\left(\frac{\pi B}{E_F}\right)^2 T, \quad \alpha \gg 1 \tag{46}$$

Similarly Equation 43′ gives:

$$\beta_f \approx -\frac{\partial}{\partial T} \ln \left\{1 - \frac{4}{5\alpha}\left[1 + \tfrac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2 (s^2 - \tfrac{1}{4})\right]\right\} \tag{47}$$

that roughly reduces to:

$$\beta_f \approx -\frac{4}{5\alpha}\left\{\beta_0\left[1 + \tfrac{1}{6}\left(\frac{\pi BT}{E_F}\right)^2 (s^2 - \tfrac{1}{4}) + \tfrac{1}{3}\left(\frac{\pi B}{E_F}\right)^2 T(s^2 - \tfrac{1}{4})\right]\right\}, \quad \alpha \gg 1 \tag{48}$$

In the case of antimony films low negative values of β_f have been observed [20] for fine-grained films, that can be regarded as compatible with both Equations 46 and 48. Simultaneously it was observed [19] that the variations in the conductivity with temperature [12, Fig. 2] were less marked than with grain size, for fine-grained films (grain diameter = 20 nm). Hence Equation 43′ seems more adequate. We consequently assume that the R coefficient of the M–S model [1] can be regarded as independent of electron energy.

The fact that R could be regarded as energy dependent from a mathematical point of view is due to the modelling of the grain-boundary by Mayadas and Shatzkes in the framework of the dislocation model of Ziman [21]; the existence of a Dirac potential hill of given "strength" [1] for representing a grain boundary [1] is unusual since it is well known that in the case of very thin potential barrier the tunneling procedure [22] is markedly determined by the image force which lowers the barrier [21]. Therefore this mathematical model of the grain boundary must be regarded as a mathematical tool whose physical interpretation must be emphasized from experiments.

Some unattempted features of the M–S model have been presented previously [6] and also suggested a mathematical point of view.

5. Conclusion

The general calculations of the macroscopic transport parameters of thin metal and semi-metal films in the framework of the Mayadas–Shatzkes model and comparison with experiments suggests that the reflection coefficient at grain-boundaries must be regarded as independent of electron energy.

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