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INFLUENCE OF SIZE EFFECT UPON THERMAL AND ELECTRICAL CONDUCTIVITY OF THIN FILAMENTS AND WIRES WITH COATING

JÚLIUS KREMPASKÝ, PETER DIEŠKA, Bratislava

The paper deals with the influence of the size effect upon the thermal and electrical conductivity of thin wires and filaments, coated by another layer of thermally or electrically conductive material. An „exchange“ of phonons or electrons at a boundary is considered. It is shown that the surface layer can exert a considerable influence upon the values of thermal or electrical conductivity in the range of size effects in uncoated wires or filaments. By this fact a change of transport parameters, observed after a period of time, as well as a change of these parameters caused by an appropriate coating can be explained.

1. INTRODUCTION

A size effect arises at low temperatures, when the mean free path of phonons or electrons is comparable with at least one dimension of a sample. That means those transport parameters as thermal and electrical conductivity, respectively, depend upon the dimensions of the sample (layer thickness, diameter of wire etc.). The first papers dealing with this dependence were published by Casimir [1], de Haas and Biermasz [2], but the problem was formulated more exactly for the first time by Fuchs [3]. His paper and the following papers, concerning the electrical conductivity of this layers and wires [4—6], are based on the solving of the Boltzmann equation at appropriate boundary conditions.

A phenomenological parameter, characterizing the so-called specular reflexion is introduced into the boundary conditions instead of a detailed examination of electron scattering at the sample surface. Ziman [7], Berman et al. [8], Gurži, Ševčenko [9] and others used this concept when solving the problem of the transport of thermal energy by a crystalline lattice.

All the above mentioned papers solve the problem of insulated thin layers and uncoated wires. This is justified in the case of electrical conductivity as the base under the thin layer can be made of an almost perfect insulator. However, there is no perfect thermal insulator, hence there is not much use in solving

the problem of heat transport by a thin layer if we do not take the basis into consideration. Conditions at the boundary of two thermal conductors which enable a mathematical solution of the problem of thermal conductivity of the system thin layer — base, thin wire — coating etc., are formulated in paper [10]. It can be shown [11] that analogical conditions can be used also when solving electron transport — the corresponding coefficients of „reflection“ and „transmission“ are connected with the potential barrier existing at a boundary.

This paper deals with thermal and electrical conductivity of thin filaments or wires coated by a thermally or electrically conductive layer. It can be either an artificial layer or a layer arising at the surface of any material by an absorption of molecules of the surrounding medium. It is shown in some papers (e.g. [12]) that there were changes of thermal conductivity of thin filaments caused by a surface modification and changes observed after period of time. We assume that in the latter an observed layer can play a significant role. We shall show that the influence of such a layer upon the parameters of the transport in the range of the size effect can be considerable also at a relatively small thickness of layer.

The Boltzmann equation for the stationary-state distribution functions of phonons (electrons) was used as the starting equation for the analysis.

2. BASIC EQUATIONS AND BOUNDARY CONDITIONS

The Boltzmann kinetic equation for a set of particles or quasiparticles in a relaxation time approximation is of the form

$$\mathbf{v}\,\mathrm{grad}_r f + \frac{\mathrm{d}\mathbf{k}}{\mathrm{d}t}\,\mathrm{grad}_k f = -\frac{f - f_0}{\tau}, \tag{1}$$

where $f = f(\mathbf{r}\,.\,\mathbf{k})$ is the distribution function, $f_0(\mathbf{k})$ the equilibrium distribution function, $\mathbf{v}$ the velocity vector, $\mathbf{k}$ the wave vector, $\mathbf{r}$ the radius vector, τ the relaxation constant. In the case of electrons in an electric field of strength E, we can write $\mathrm{d}\mathbf{k}/\mathrm{d}t = eE/\hbar$, where $\hbar = h/2\pi$ and h is the Planck constant, if the relation between their energy and wave number $\mathbf{k}$ is of the type $E = \hbar^2\mathbf{k}^2/2m$. In the case of phonons $\mathrm{d}\mathbf{k}/\mathrm{d}t = 0$, but the first member in equation (1) gives

$$\mathrm{grad}_r = (\mathrm{grad}_r)_{T=const} + \mathrm{grad}\,T\,\frac{\partial}{\partial T}.$$

We assume that the values grad $Tg(\mathbf{r}, \mathbf{k})$ and $Eg(\mathbf{r}, \mathbf{k})$ where $g(\mathbf{r}, \mathbf{k})$ is defined by a substitution

$$f(\mathbf{r}\,.\,\mathbf{k}) = f_0(\mathbf{k}) + g(\mathbf{r}, \mathbf{k}) \tag{2}$$

are small. Then equation (1) will have the form

$$\mathbf{v}\,\mathrm{grad}_r f + \frac{g}{\tau} + \mathbf{v}A = 0\,, \tag{3}$$

where $A = \mathrm{grad}\, T \partial f_0/\partial T$ for phonons and $A = eE\partial f_0/\partial E$ for electrons. Based on this form we can solve the problem of electrical conductivity and thermal lattice conductivity simultaneously. For the sake of simplicity we shall later write only the relations for phonons.

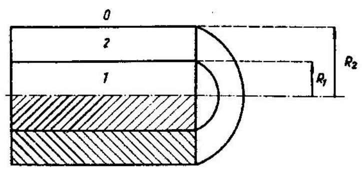

Fig. 1. Schematic diagram of a section of a thin filament wire with coating.

We assume the thin filament to be in the z axis, R_1 is its radius, R_2 is the outer radius of the coating (Fig. 1). To be able to formulate the conditions at the boundary and on the surface we must divide the phonons into:

1. Phonons characterized by the g_1 function — such are all phonons in the filament (each of them can reach the boundary regardless of the direction of its velocity).

2. Phonons characterized by the g_2' function — such are phonons in the coating, the velocity of which has such a direction that they do not reach the surface of the filament (Fig. 2). Projections of their velocity vectors to the

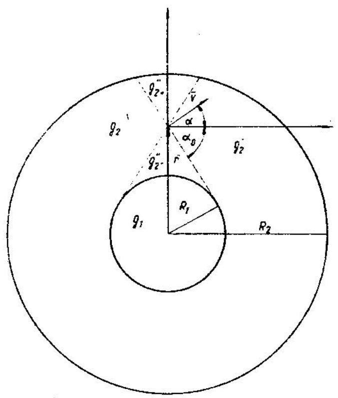

Fig. 2. Distribution of phonons (electrons) in a filament (wire) and in a coating from the standpoint of application of the boundary conditions.

plane perpendicular to the filament axis has an angle α in the intervals $\langle -\alpha_0, \alpha_0 \rangle$ and $\langle \pi - \alpha_0, \pi + \alpha_0 \rangle$, where $\alpha_0 = \arccos R_1/R$.

3. Phonons characterized by the g_2'' function, i.e. the rest of the phonons in the coating. For one part of them the projection of their velocity vectors to the plane perpendicular to the filament axis from the angle α_2 in the interval $\langle \alpha_0, \pi - \alpha_0 \rangle$, for the other part in the interval $\langle -\pi + \alpha_0, -\alpha_0 \rangle$.

Hence the boundary conditions for the above case (according to conditions formulated in papers [3] and [10]) can be written in the forms:

$$R = R_2 \quad g_{2-}' = P_2 g_{2+}' \tag{4a}$$

$$g_{2-}'' = P_2 g_{2+}'' \tag{4b}$$

$$R = R_1 \quad g_{2+}'' = P_{21} g_{2-}'' + Q g_{1+} \tag{5a}$$

$$g_{1-} = P_{12} g_{1+} + Q g_{2-}'' \tag{5b}$$

Quantities marked by $(-)$ differ from those marked by $(+)$ by a substitution between α_1 and $-\alpha_1$ or between α_2 and $-\alpha_2$. The coefficients P_2 and P_{12} characterize the specular reflexion probability on the surface, or at the boundary, respectively, the coefficient Q characterizes the probability of the electron or phonon transition across the boundary. Explicit expressions for these coefficients according to the state of the surface and the boundary as well as for the angle of incidence and the wave vector respectively, are in paper [10]. We shall assume throughout the following calculation that these coefficients are some constants, characterizing a given system.

We wish to point out that conditions (4) and (5) can be considered only in the case, when the wavelengths λ, which characterize phonons or electrons, are much shorter than the dimensions of a particular system. It can be easily shown that in any practical and real case this condition is always fulfilled.

3. SOLUTION OF EQUATION (3)

According to Chambers [13] the general solution of equation (3) can be written in the form

$$g(\mathbf{R}, \mathbf{v}) = -\mathbf{v}\mathbf{A}\left\{1 + \exp\left[-\frac{|\mathbf{R}_s - \mathbf{R}|}{\tau v_R}\right]\right\}, \tag{6}$$

where $\mathbf{v}_R$, $\mathbf{R}_s$ and $\mathbf{R}$ are projections of the vectors $\mathbf{v}$, $\mathbf{r}_s$ and $\mathbf{r}$ into the plane perpendicular to the z axis and where $\mathbf{r}_s$ is the radius vector of a point on the surface, which is obtained by shifting the velocity vector against its direction. As we are interested in longitudinal conductivity only, we can put $E = E_z$, $\mathrm{grad}\, T = \partial T/\partial z$ and write the expression $\mathbf{v}\mathbf{A}$ in the form $v_z(\partial T/\partial z)\,(\partial f_0/\partial T)$ for phonons and in the form $eE_z\partial f_0/\partial E$ for electrons. Thus we get for the above mentioned functions g_1, g_2', g_2'' the expressions

$$g_1 = v_1 A_1 \cos\beta_1 \left\{1 + C_1 \exp\left[-\frac{R\sin\alpha_1 + (R_1^2 - R^2\cos^2\alpha_1)^{1/2}}{l_1\sin\beta_1}\right]\right\} \quad (7a)$$

$$g_2' = v_2 A_2 \cos\beta_2 \left\{1 + C_2 \exp\left[-\frac{R\sin\alpha_2 + (R_2^2 - R^2\cos^2\alpha_2)^{1/2}}{l_2\sin\beta_2}\right]\right\} \quad (7b)$$

$$\alpha_2 \in \langle -\alpha_0, \alpha_0\rangle \text{ and } \alpha_2 \in \langle \pi - \alpha_0, \pi + \alpha_0\rangle$$

$$g_{2-}'' = v_2 A_2 \cos\beta_2 \left\{1 + C_{2-}'' \exp\left[-\frac{R\sin\alpha_2 + (R_2^2 - R^2\cos^2\alpha_2)^{1/2}}{l_2\sin\beta_2}\right]\right\} \quad (7c)$$

$$\alpha_2 \in \langle -\pi + \alpha_0, -\alpha_0\rangle$$

$$g_{2+}'' = v_2 A_2 \cos\beta_2 \left\{1 + C_{2+}'' \exp\left[-\frac{R\sin\alpha_2 - (R_1^2 - R^2\cos^2\alpha_2)^{1/2}}{l_2\sin\beta_2}\right]\right\} \quad (7d)$$

$$\alpha_2 \in \langle \alpha_0, \pi - \alpha_0\rangle$$

where l_1 and l_2 are relaxation lengths. Index 1 denotes the filament, index 2 the coating. The angles $\alpha_1, \alpha_2, \beta_1, \beta_2$ are interrelated by the law of refraction. To respect this relation would complicate very much the computation and therefore we shall assume that phonons and electrons cross the boundary without changing their direction and therefore $\alpha_1 = \alpha_2$ and $\beta_1 = \beta_2$. Hence according to [10] $P_{12} = P_{21} = P$ holds.

Writing

$$-a = \frac{2(R_1^2 - R^2\cos^2\alpha)^{1/2}}{l_1\sin\beta}$$

$$-b = \frac{2(R_2^2 - R^2\cos^2\alpha)^{1/2}}{l_2\sin\beta}$$

$$-c = \frac{(R_2^2 - R^2\cos^2\alpha)^{1/2} - (R_1^2 - R^2\cos^2\alpha)^{1/2}}{l_2\sin\beta}$$

and using the conditions (4) and (5), we obtain for the constants C_1, C_2, C_{2+} and C_{2-} the following expressions

$$C_1 = \frac{-(1-P) + \dfrac{Q}{1 - PP_0 e^{2c}}\left[\dfrac{A_2}{A_1}(1 - e^c)(1 + P_0 e^c) + QP_0 e^{2c}\right]}{1 - P e^a - \dfrac{Q^2 P_0}{1 - PP_0 e^{2c}} e^{a+2c}} \quad (8a)$$

$$C_2' = -\frac{1 - P_0}{1 - P_0 e^b} \quad (8b)$$

$$C_{2+}'' = \frac{P - 1 + P e^c(P_0 - 1) + \dfrac{Q}{1 - P e^a}\left[\dfrac{A_1}{A_2}(1 - e^a) + Q e^a(1 - e^c + P_0 e^c)\right]}{1 - PP_0 e^{2c} - \dfrac{Q^2 P_0}{1 - P e^a} e^{a+2c}} \quad (8c)$$

$$C_{2-}'' = \frac{P_0 - 1 + P_0 e^c(P - 1) + \dfrac{QP_0 e^c}{1 - P e^a}\left[\dfrac{A_1}{A_2}(1 - e^a) + Q e^a\right]}{1 - PP_0 e^{2c} - \dfrac{Q^2 P_0}{1 - P e^a} e^{a+2c}} \quad (8d)$$

where P_0 means the coefficient of „reflexion“ on the outer side of the coating.

4. THERMAL AND ELECTRICAL CONDUCTIVITY

The total thermal conductivity of the filament-coating system is defined by the expression

$$\lambda = \frac{\pi R_1^2 \lambda_1 + \pi(R_2^2 - R_1^2)\lambda_2}{\pi R_2^2}, \quad (9)$$

where λ_1 is the thermal conductivity of the filament, λ_2 the thermal conductivity of the coating. These thermal conductivities can be calculated by means of the g_1, g_2', g_{2+}'' and g_{2-}'' functions. As the functions characterizing the coating are complicated, we shall do the computation only for the filament.

The mean density of the thermal flux through the filament is defined by the expression

$$\langle j_z\rangle = \frac{1}{\pi R_1^2}\int_0^{R_1} j_z 2\pi r\, dr, \quad (10)$$

where

$$j_z = \frac{3}{8\pi^3} \int_0^{k_m} \int_0^{\pi} \int_0^{2\pi} \hbar\omega v g_1(\alpha, \beta)\, k^2 \sin\alpha \cos\beta \, dk\, d\beta\, d\alpha .$$

The computation can be simplified by assuming the special cases: $Q \to 0$ and $Q \to 1$. In the first case we use the Taylor series of the function $C_1(Q)$ in the neighbourhood of $Q = 0$ and we take into account only the first terms. To simplify we shall denote the first member in the relation (8a) by C_{10}, the second by δC_1, so that $C_1 = C_{10} + \delta C_1$. When we substitute this expression into the function (7a) and then into the relation (9), we shall find that the ratio of the thermal conductivity of the coated filament and the thermal conductivity of the bulk material can be expressed as

$$\frac{\lambda_1}{\lambda_{1\infty}} = \frac{\lambda_{10}}{\lambda_{1\infty}} + \frac{12}{\pi R_1^2} \int_0^{R_1} R\, dR \int_0^{\pi/2} \sin\beta \cos^2\beta \, d\beta \int_0^{\pi/2} \delta C_1 \times$$
$$\times \exp\left[- \frac{(R_1^2 - R^2 \cos^2\alpha)^{1/2}}{l_1 \sin\beta} \right] \mathrm{ch} \left[\frac{R \sin\alpha}{l_1 \sin\beta} \right] d\alpha, \qquad (11)$$

where $\lambda_{10}/\lambda_{1\infty}$ is the ratio of the thermal conductivity of the uncoated wire and the bulk material calculated in paper [5]. We shall denote the difference of thermal conductivity between the coated and the uncoated filament by $\delta\lambda_1 = \lambda_1 - \lambda_{10}$. Then the relation (11) can be written in the more simple form

$$\frac{\delta\lambda_1}{\lambda_{1\infty}} = p, \qquad (12)$$

where

$$p = \frac{12}{\pi R_1^2} \int_0^{R_1} R\, dR \int_0^{\pi/2} \sin\beta \cos^2\beta \, d\beta \int_0^{\pi/2} \delta C_1 \times$$
$$\times \exp\left[- \frac{(R_1^2 - R^2 \cos^2\alpha)^{1/2}}{l_1 \sin\beta} \right] \mathrm{ch} \left[\frac{R \sin\alpha}{l_1 \sin\beta} \right] d\alpha .$$

For $Q \to 1$ we shall do the computation in a similar way, only the Taylor series is in the neighbourhood of $Q = 1$. We shall present the results of only more interesting cases, in which $(R_2 - R_1)/l_2 \ll 1$ and $(R_2 - R_1)/l_2 \ll 1$. We shall obtain

$$\frac{R_2 - R_1}{l_2} \ll 1; \quad Q \to 0; \quad p \approx 0 \qquad (13a)$$

$$Q \to 1; \quad p \approx \frac{\lambda_{10}(P_0)}{\lambda_{1\infty}} - \frac{\lambda_{10}(0)}{\lambda_{1\infty}} \qquad (13b)$$

$$\frac{R_2 - R_1}{l_2} \ll 1; \quad Q \to 0; \quad p = \frac{A_2 Q}{A_1(1 - P)} \left[1 - \frac{\lambda_{10}(P)}{\lambda_{1\infty}} \right] \qquad (14a)$$

$$Q \to 1; \quad p = \frac{A_2}{A_1} \left[1 - \frac{\lambda_{10}(0)}{\lambda_{1\infty}} \right], \qquad (14b)$$

where

$$\frac{\lambda_{10}(x)}{\lambda_{1\infty}} = \frac{1 + x}{1 - x} \frac{2(R_2 - R_1)}{l_1} - \frac{3(R_2 - R_1)^2}{2 l_1^2} \times$$
$$\times \left[\frac{1 + 4x + x^2}{(1 - x)^2} \left(\ln \frac{l_1}{2(R_2 - R_1)} + 1{\cdot}059 \right) - (1 - x)^2 \sum_1^{\infty} m^3 x^{m-1} \ln m \right] -$$
$$- \frac{2}{15} \left[\frac{8(R_2 - R_1)^3}{l_1} \right] \frac{1 + 11x + 11x^2 + x^3}{(1 - x)^3},$$

hence

$$\frac{\lambda_{10}(0)}{\lambda_{1\infty}} = \frac{2(R_2 - R_1)}{l_1} - \frac{3(R_2^2 - R_1)^2}{3 l_1^2} \left(\ln \frac{l_1}{2(R_2 - R_1)} + 1{\cdot}059 \right) -$$
$$- \frac{2}{15} \left[\frac{2(R_2 - R_1)}{l_1} \right]^3 .$$

Writting $R_2 - R_1 = a$ (thickness of the planparallel layer) and $x = \varepsilon$, the last two relations are identical with those derived in paper (5).

5. DISCUSSION

Not knowing the coefficients P and Q, we are not able to analyse quantitatively the obtained results, yet we can deduce from the derived relations some interesting conclusions. The authors regard as very important the results in (13), valid for a vera thin coating. They are written in the form of the ratio of thermal conductivities, but as mentioned above, they can be applied withhout change to electrical conductivities.

It is evident above all that for the case of $Q = 0$ there is no contribution to the size effect observed on an uncoated wire. That is a selfevident consequence. But in the case when $Q \to 1$, i.e. the phonons are able to pass from filament to coating or vice versa (or the electrons from wire to coating and vice versa) almost without limits, the ratio of the thermal (electrical) conductivity of a thin filament and the thermal conductivity of the bulk material can be expressed according to the relation (13b) by the relation

$$\frac{\lambda_1}{\lambda_{1\infty}} \approx \frac{\lambda_{10}(P_0)}{\lambda_{1\infty}}; \qquad p_0 < 1 \tag{15a}$$

and the relation

$$\frac{\lambda_1}{\lambda_{1\infty}} \approx 1; \qquad P_0 = 1. \tag{15b}$$

We can see that when $P_0 = 1$, there does not appear any size effect, although the size effect could be considerable in the same wire without coating. The observed changes depend upon the difference of coefficients of the specular reflexion on the surface of the uncoated wire and on the surface of the coating, respectively. There is only a small probability for this coefficient to be of the same value for the surface of the layer arising from molecule adsorption as for the originally clean surface of the wire. That is, according to our oppinion, the reason, why after a period of time different changes of conductivity, caused by a size effect, were measured in the same samples.

The presented result could be utilized. If a layer were found, or a technology of the production of a layer with $P_0 \approx 1$ on its surface, this layer could „protect" thin conductors from the size effect, which fact could be of great importance in low temperature technique.

According to the relation (15b), the presence of a surface layer modifies the size effect on an uncoated wire or filament, even when $P_0 < 1$. Although the value of the thermal conductivity λ_{10} could fall due to the size effect to zero, a certain remnant thermal conductivity $\lambda_{10}(P_0) > \lambda_{10}(0)$ would remain of a surface layer.

The presented considerations are more real in the case of the thermal conductivity, since in the case of the electrical conductivity of metals there is almost always a diffused scattering observed on the surface ($P = 0$).

Relations (14) can be interpreted in a similar way, but it is necessary to take into consideration that instead of a coefficient of reflexion on the surface of the layer, there is a coefficient of specular reflexion at the boundary in relation (14a). The ratio of constants $A_2/A_1 = (\partial f_0/\partial T)_2/(\partial f_0/\partial T)_1$ is equal to one for thermal conductivity, A_2/A_1 for electrical conductivity can be found

by means of the Boltzmann or the Fermi-Dirac distribution. It is determined by the position of the Fermi levels in connected media. In the majority of practical cases this effect is of no great importance, as the transport of phonons or of the electric charge in a thin filament or wire will not play a significant role compared to the transport in a bulky coating.

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Katedra fyziky
Elektrotechnickej fakulty SVŠT,
Bratislava