

Size effect of kinetic coefficients in polycrystalline bismuth films

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The influence of the thickness of a bismuth film and of the size of its crystallites on the thermal conductivity, electrical conductivity and thermoelectric power is studied theoretically and experimentally. The size effect of the thermal conductivity appears in thicker bismuth films than those required for the observation of the size effect of the electrical conductivity and thermal emf coefficients. The thermoelectric quality factor Q as a function of the film thickness reaches a maximum for a film thickness of 1500 Å, which is 2.2 times greater than the quality factor of bulky bismuth samples.

It is well known that if the mean free path of charge and energy carriers is comparable with the thickness of a film, then it is possible to observe significant anomalies in its kinetic characteristics. The external surfaces act then as effective scattering surfaces and the mean free path of the carriers is determined essentially by the film thickness. Such a behavior of the physical properties as a function of the film thickness is known as the "classical size effect." Moreover, if the mean free path of the carriers is comparable with the dimensions of the film crystallites, then it is necessary, in the study of the size effect, to take into account their scattering by the intercrystallite boundaries.^[1]

The calculation of the kinetic coefficients of polycrystalline bismuth films with arbitrary shape and orientation of the crystallites, with account of charge carriers of both signs and of the phonons, represents an extraordinarily complicated physical and mathematical problem. However, under certain simplifications based on the studied crystal structure of the films under investigation, one can construct a simple film model which gives the correct description, in its basic characteristics, of the process of scattering of the carriers by the boundaries of its crystallites.^[2] The scattering by the external surfaces of the film can be taken into account by means of the boundary conditions imposed on the distribution function.^[3-5] Such an approach allows us to take into account the real structure of the film in some approximation and to reduce appreciably the mathematical difficulties encountered in the solution of the problem.

Studies of the crystal structure of bismuth films have shown that its crystallites have a continuous lattice in directions normal to the plane of the substrate. In such a film, the intercrystallite boundaries can be approximated by two uncorrelated types of randomly arranged planes, parallel and perpendicular to the temperature gradient and the electric field.

When the carrier wavelength is large in comparison with the layer in which the crystal structure cannot be regarded as ideal, the grain boundaries can be approximated by mathematical surfaces without thickness.^[6] Such a condition is satisfied in bismuth for electrons and holes as well as for phonons, owing to the low Fermi level and the low Debye temperature.^[7] In this case, the planes parallel to the direction of the temperature gradient and the electric field, which reflect the carriers specularly, do not make a contribution to the kinetic coefficients and therefore can be eliminated from consideration.

To take into account the contribution of the scattering

of charge carriers and phonons to the kinetic coefficients, we calculate the probability $P_{kk'}$ of transition of the carriers from the state $|k\rangle$ to $|k'\rangle$, where $|k\rangle$ and $|k'\rangle$ are the wave functions of the unperturbed problem (plane waves). For simplicity, the dispersion law is assumed to be isotropic, because qualitative results pertaining to thin films are not generally sensitive to the shape of the equal-energy surfaces, since the basic role in the transition processes is played by a small group of carriers traveling almost parallel to the surfaces.^[5,8-10] Here we take into account only the acoustic phonons with linear dispersion laws.

We choose a set of coordinates such that the x axis lies in the plane of the film perpendicular to the scattering planes, the z axis coincides with the direction of the normal to the film, and the y axis completes the rectangular system. In such a set of coordinates, the contribution to the Hamiltonian of the unperturbed system of carriers takes the form

$$u(x) = S \sum_n \delta(x - x_n), \quad (1)$$

where S is the "potential strength" (the product of the barrier width by its height), and x_n is the location of the plane n . The quantities x_n have a distribution of the form

$$f(x_1 \dots x_N) = \frac{1}{L_x (2\pi s^2)^{(N-1)/2}} \exp \left[- \sum_{i=1}^{N-1} (x_{i+1} - x_i - a)^2 / 2s^2 \right], \quad (2)$$

where L_x is the length of the film in the x direction, N is the number of scattering planes, a is the average size of the crystallites, and s is the dispersion.

It is known that the probability $P_{kk'}$ in the principal approximation in the interaction is proportional to the square of the modulus of the matrix element of the perturbation operator. Using the explicit form of the wave functions of the unperturbed problem (plane waves) and the perturbation operator with account of the distribution (2), we get in the limit of continuous values of k ,

$$P_{kk'} = \frac{(2\pi)^2 S^2}{V a \hbar} \mathcal{E}(k_x) \delta(\epsilon(k) - \epsilon(k')) \delta(k_x - k'_x), \quad (3)$$

$$\mathcal{E}(k_x) = \frac{1 - \exp(-4k_x^2 s^2)}{1 + \exp(-4k_x^2 s^2) - 2 \exp(-2k_x^2 s^2) \cos 2k_x a}$$

where k_x is the projection of the wave vector on the plane of the film, V the volume of the film, and $\epsilon(k)$ the carrier energy.

The transition probability for a specific form of the carriers is obtained if we take into consideration the corresponding dispersion law.

For electrons and holes, it is possible to write down the relation in the form

$$P_{\mathbf{k}\mathbf{k}'}^h = \frac{(2\pi)^3 m_{e,h}^* S_{e,h}^2}{V a \hbar |k_x|} \mathcal{E}(k_x) \delta(k_i - k_i') \delta(k_x + k_x'), \quad (4)$$

where the indices e and h denote electrons and holes, respectively, and $m_{e,h}^*$ their effective masses.

We obtain the following expression for the probability $P_{\mathbf{q}\mathbf{q}'}$ of phonon scattering by the boundaries of film crystallites;

$$P_{\mathbf{q}\mathbf{q}'} = \frac{(2\pi)^3 S_q^2 q}{V \hbar^2 c a |q_x|} \mathcal{E}(q_x) \delta(q_i - q_i') \delta(q_x + q_x'), \quad (5)$$

here \mathbf{q} is the wave vector of the phonon, and c is the sound velocity in the material.

ELECTRON THERMAL CONDUCTIVITY

Let the temperature gradient ∇T be identical in direction with the x axis, and let the external electric and magnetic fields be absent. Then, assuming that the processes of scattering of carriers by the boundaries of the crystallites and inside them take place independently of one another, we write down the linearized Boltzmann equation for the electron distribution function in the form

$$v_x \frac{\partial f^0}{\partial x} + v_z \frac{\partial g_{\mathbf{k}}}{\partial z} - \frac{eE^x}{m_e^*} \frac{\partial f^0}{\partial v_x} = -\hat{j}_e g_{\mathbf{k}} + \frac{V}{(2\pi)^3} \int_{\mathbf{k}'} P_{\mathbf{k}\mathbf{k}'}^e (g_{\mathbf{k}'} - g_{\mathbf{k}}) dk', \quad (6)$$

where f^0 is the equilibrium value of the Fermi distribution function, $g_{\mathbf{k}}$ the deviation of the distribution function from equilibrium, and E^x the electric field generated by the temperature gradient. The first term of the right side of Eq. (6) describes the scattering inside the crystallites, and the second the scattering by their boundaries. Integration is carried out over the volume of the first Brillouin zone.

Equation (6) is a complicated integro-differential equation, which is impossible to solve in general form. However, as was mentioned earlier, the principal contribution to the transport processes is made by groups of carriers which travel almost parallel to the surface of the film. Here $g_{\mathbf{k}}$ is a "sharp" function of the angle θ (the angle between the normal to the film and the wave vector of the carrier) and the relaxation time can be introduced.^[5] Taking this into account, we can rewrite Eq. (6) in the following fashion:

$$v_x \frac{\partial f^0}{\partial x} + v_z \frac{\partial g_{\mathbf{k}}}{\partial z} - \frac{eE^x}{m_e^*} \frac{\partial f^0}{\partial v_x} = -\frac{g_{\mathbf{k}}}{\tau_e^*}, \quad (7)$$

Here

$$\hat{j}_e g_{\mathbf{k}} = g_{\mathbf{k}} / \tau_e, \quad (7a)$$

$$\frac{1}{\tau_e^*} = \frac{1}{\tau_e} + \frac{2m_e^* S_e^2}{a \hbar^3 |k_x|} \mathcal{E}(k_x). \quad (7b)$$

Scattering of the carriers by the external surfaces of the film is taken into account by the boundary conditions imposed on the distribution function:

$$\begin{aligned} g(v_z, 0) &= pg(-v_z, 0) \quad \text{for } v_z > 0, \\ g(v_z, d) &= pg(-v_z, d) \quad \text{for } v_z < 0, \end{aligned} \quad (8)$$

where p is the specularly parameter and d is the film thickness.

Solving Eq. (7) with the boundary conditions (8) and substituting the resultant solution in the relation for the current density, averaging it over the film thickness, and equating it to zero, we obtain the expression for the field E^x :

$$E^x = -\frac{1}{eT} \left(\frac{I_{e,h}^e}{I_{e,h}^e} - \mu_e \right) \nabla T - \frac{1}{e} \frac{\partial \mu_e}{\partial x}. \quad (9)$$

In (9), we have introduced the following notation for convenience:

$$\begin{aligned} I_n^e &= \int_0^{\infty} \int_0^{\pi/2} \int_0^{2\pi} e^n \tau_e^* F(\epsilon) \sin^3 \theta \cos^2 \varphi (1 - \alpha_+) d\varphi d\theta d\epsilon \\ &+ \int_0^{\infty} \int_0^{\pi/2} \int_0^{2\pi} e^n \tau_e^* F(\epsilon) \sin^3 \theta \cos^2 \varphi (1 - \alpha_-) d\varphi d\theta d\epsilon, \\ F(\epsilon) &= \left[\exp\left(\frac{\epsilon - \mu_e}{kT}\right) + 1 \right]^{-2} \exp\left(\frac{\epsilon - \mu_e}{kT}\right), \\ \alpha_+ &= \frac{(1-p)\xi^{-1}(1-e^{-\epsilon})}{1-pe^{-\epsilon}}, \\ \alpha_- &= -\frac{(1-p)\xi^{-1}(1-e^{\epsilon})}{1-pe^{\epsilon}}, \quad \xi = \frac{d}{\tau_e^* v_z}. \end{aligned} \quad (10)$$

Here τ_e^* is a function of the energy ϵ , μ_e is the Fermi energy, k is the Boltzmann constant, and the index e denotes that all the quantities are taken for electrons. Then, with account of (9), the coefficient of the electronic component of the thermal conductivity is written in the form

$$\lambda_e = \frac{\sqrt{m_e^*}}{\sqrt{2} \pi^3 \hbar^3 (kT)^2} \frac{I_{e,h}^e I_{e,h}^e - (I_{e,h}^e)^2}{I_{e,h}^e}. \quad (11)$$

The expression for the hole component of the thermal conductivity is obtained by replacement of the index e by h.

LATTICE THERMAL CONDUCTIVITY

As has been pointed out above, we consider only acoustical phonons, since just these are responsible essentially for the heat transfer.^[6] Using the above discussion, it is easy to write out the linearized kinetic equation for the phonons:

$$v_x \frac{\partial g}{\partial x} + v_z \frac{\partial n^0}{\partial T} \nabla T = -\frac{g}{\tau_q^*}, \quad (12)$$

where n^0 is the equilibrium Planck distribution function, g the deviation of the phonon distribution function from equilibrium and

$$\frac{1}{\tau_q^*} = \frac{1}{\tau_q} + \frac{2S_q^2 q}{\hbar^2 c a |q_x|} \mathcal{E}(q_x). \quad (12a)$$

Solving (12) with the boundary conditions (8), and substituting the resultant solution in the expression for the heat flow, after averaging it over the film thickness we obtain a relation for the coefficient of lattice thermal conductivity:

$$\begin{aligned} \lambda_q &= \frac{3(kT)^3}{(2\pi\hbar)^3 c^2} \int_0^{\Theta_D/T} \frac{\eta^4 e^\eta}{(1-e^\eta)^2} d\eta \left[\int_0^{\pi/2} \int_0^{2\pi} \tau_q^* c \cos^2 \varphi \sin^3 \theta (1 - \beta_+) d\varphi d\theta \right. \\ &\left. + \int_{\pi/2}^{\pi} \int_0^{2\pi} \tau_q^* c \cos^2 \varphi \sin^3 \theta (1 - \beta_-) d\varphi d\theta \right], \end{aligned} \quad (13)$$

where $\eta = \hbar\omega/kT$, Θ_D the Debye temperature,

$$\beta_+ = \frac{(1-p)\xi^{-1}(1-e^{-\eta})}{1-pe^{-\eta}}, \quad \beta_- = -\frac{(1-p)\xi^{-1}(1-e^{\eta})}{1-pe^{\eta}}, \quad \xi = \frac{d}{\tau_q^* v_z}. \quad (14)$$

We note that in (13) τ_q is a power function of η and the principal contribution in the integration is made by $\eta \sim 1$.^[5] For this reason, all the values are taken to mean their "temperature" values taken at $\eta \sim 1$. In such an approximation, the thermal conductivity λ_q is written in the form

$$\lambda_q = 1/3 M c l_{\text{eff}}^*, \quad (15)$$

where M is the specific heat of the material and is given by

$$M = 3R \left[D \left(\frac{\Theta_D}{T} \right) - \frac{\Theta_D}{T} D' \left(\frac{\Theta_D}{T} \right) \right], \quad (15a)$$

R is the number of atoms per unit volume, and $D(x)$ the Debye function; l_{eff}^* can be interpreted as the mean free path of phonons in the film, the explicit form for which is given by

$$l_{\text{eff}}^* = \frac{3}{4\pi} l^* \left[\int_0^{\pi/2} \int_0^{2\pi} \cos^2 \varphi \sin^3 \theta (1 - \beta_+) d\varphi d\theta + \int_0^{\pi/2} \int_0^{2\pi} \cos^2 \varphi \sin^3 \theta (1 - \beta_-) d\varphi d\theta \right], \quad (16)$$

where

$$l^* = \tau_q \cdot c.$$

Thus the expression for the coefficient of total thermal conductivity of the film, with account of two sorts of charge carriers and of phonons, takes the form

$$\lambda = \lambda_e + \lambda_h + T \frac{\sigma_e \sigma_h}{\sigma_e + \sigma_h} (\alpha_e - \alpha_h)^2 + \lambda_q, \quad (17)$$

in which the first two terms are the thermal conductivities due to electrons and holes, respectively, the third term is the thermal conductivity due to bipolar thermal diffusion and the fourth term is the phonon component of the thermal conductivity; the quantities σ_e , σ_h , α_e , α_h are the electron and hole components of the conductivity and thermal emf, respectively, which are determined below.

ELECTRICAL CONDUCTIVITY AND THERMAL EMF

The expression for the coefficient of the electronic component of the thermal emf is obtained directly from the relation (9)

$$\alpha_e = \frac{1}{eT} \left(\frac{I_{1/2}^e}{I_{1/2}^e} - u_e \right). \quad (18)$$

The coefficient of the electronic component of the electrical conductivity can be obtained by setting $\nabla T = 0$ in Eq. (6) and by interpreting E^α as the external field. The final expression is

$$\sigma_e = \frac{e^2 \sqrt{m_e}}{\sqrt{2} (\pi \hbar)^{3/2} kT} I_{1/2}^e, \quad (19)$$

Similar coefficients for the holes are obtained by replacement of the index e by h. The following well-known relations are valid for the total coefficients of thermal emf and electrical conductivity:

$$\sigma = \sigma_e + \sigma_h, \quad (20)$$

$$\alpha = \left(\frac{\sigma_e}{\sigma_h} \alpha_e + \alpha_h \right) / \left(\frac{\sigma_e}{\sigma_h} + 1 \right). \quad (21)$$

COMPARISON WITH EXPERIMENT

We now carry out a comparison of the theoretical results with the experimental data at room temperature for bismuth films obtained by thermal vaporization of Bi in a vacuum of 10^{-6} Torr with subsequent condensation on a polymer substrate at a rate of $22 \text{ \AA}/\text{sec}$ and a substrate temperature 106°C .^[11] X-ray diffraction, electron diffraction, and electron microscopy studies showed that such films have a polycrystalline structure, and their crystallites are oriented in the (001) plane parallel to the substrate and have an arbitrary azimuthal orientation. With decrease in the film thickness, the degree of perfection of its crystal structure remains unchanged up to $350\text{--}400 \text{ \AA}$ while the mean size of its crystallites decreases (see Fig. 1). A method which allows one to

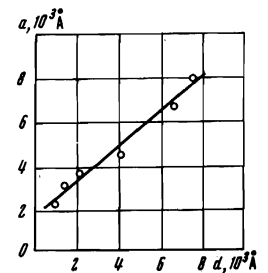


FIG. 1. Dependence of the mean dimension a of the crystallites on the film thickness d .

carry out simultaneously the measurement of the coefficients of thermal conductivity, electrical conductivity and thermal emf on the same sample is set forth in^[12].

To make a comparison of the theoretical and experimental results, it is necessary to estimate a number of parameters that enter into the expression for the kinetic coefficients. For estimates of the effective masses and the relaxation times τ_e and τ_h , we make use of the experimental values of the electrical conductivity and the free path lengths of the electrons and holes, which were obtained for thick films neglecting scattering by the external surfaces and intercrystallite boundaries. Thus, for a film of thickness 8400 \AA at $T = 300^\circ\text{K}$, the free path lengths of the electrons and holes amounted to 2000 \AA and 1300 \AA , respectively while the mean size of the crystallites was 8500 \AA .

Setting $\tau_e = \tau_{e0} \epsilon^r$ and $\tau_h = \tau_{h0} \epsilon^r$ from the expressions for the electrical conductivity and the mean free path lengths of the charge carriers under the assumption $r = 3/2$ (since precisely this value gives the best agreement of the experimental and theoretical results, which is in accord with^[13]), we obtain

$$m_e^* \approx m_h^* \approx 0.5 m_0, \quad \tau_{e0} = 1.45 \cdot 10^6 \text{ erg}^{-3/2} \text{ sec} \\ \tau_{h0} = 0.6 \cdot 10^6 \text{ erg}^{-3/2} \text{ sec}$$

where m_0 is the mass of the free electron.

The free path length of phonons in Bi at a temperature of 300°K amounts to 5000 \AA .

In order to estimate the order of magnitude of S, we use the following considerations. The scattering of the carriers at the boundaries of the crystallites of the film makes a significant contribution to the kinetic coefficients only when the quantity $2\tau m^* S^2 / \hbar k_F \sim 1$, where k_F is the Fermi momentum. We then have for S

$$S_e \approx S_h \sim 10^{-21} \text{ erg-sec}$$

which is of the same order of magnitude as the result for S in films of aluminum and copper,^[2] which were obtained from low-temperature measurements.

The specularity parameter p was chosen from the condition of best agreement of the computed and experimental curves, and had the value $p = 0.6$ for charged carriers and $p = 0.5$ for phonons. Calculation of the integrals $I_n^{e,h}$ and the expression l_{eff}^* was performed by numerical methods on a high-speed computer.

Comparison of the results is most conveniently begun with the coefficient of electrical conductivity. Figure 2 shows the conductivity curves of bismuth films as a function of thickness. Curve 1 corresponds to the Fuchs theory^[3] for $l_e = 2000 \text{ \AA}$, $l_h = 1300 \text{ \AA}$ and $p = 0$. Curve 2 corresponds to the case $p = 1$, i.e., it shows how the conductivity of the film changes with the mean dimension of the crystallites. As follows from Fig. 2, the best agreement of the theoretical results with the ex-

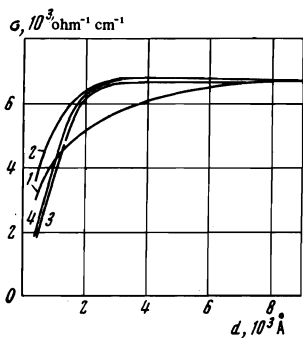


FIG. 2

FIG. 2. Dependence of the coefficient of electrical conductivity σ of a bismuth film on its thickness for $T = 300^\circ\text{K}$: 1—theoretical Fuchs curve for $l_e = 2000\text{\AA}$ and $l_n = 1300\text{\AA}$, $p = 0$; 2—theoretical curve for $p = 1$ and $S_{e,h} = 10^{21}\text{ erg-cm}$; 3—theoretical curve for $p = 0.6$ and $S_{e,h} = 10^{21}\text{ erg-cm}$; 4—experimental curve.

FIG. 3. Dependence of the coefficient of thermal conductivity λ of a bismuth film on its thickness for $T = 300^\circ\text{K}$: 1—theoretical curve of the thermal conductivity, due to charge carriers and bipolar diffusion; 2—theoretical curve of the thermal conductivity corresponding to the phonon component, for $p = 0.5$ and $S_q = 0$; 3—phonon thermal conductivity for $p = 0.5$ and $S_q = 10^{22}\text{ erg-cm}$; 4—theoretical curve of the total thermal conductivity; 5—experimental curve of the total thermal conductivity.

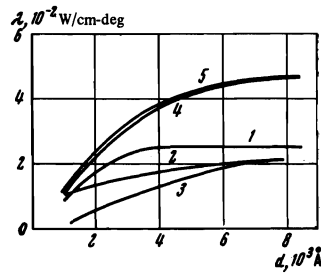


FIG. 3

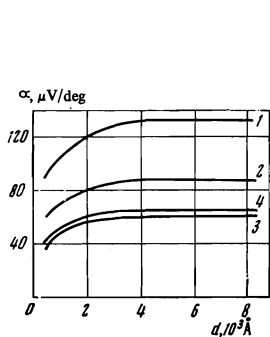


FIG. 4

FIG. 4. Dependence of the thermal-emf coefficient α of a bismuth film on its thickness for $T = 300^\circ\text{K}$: 1—theoretical curve of the electron thermal emf; 2—theoretical curve of the hole thermal emf; 3—theoretical curve of the total thermal emf; 4—experimental curve.

FIG. 5. Dependence of the thermoelectric quality factor Z of a bismuth film on its thickness for $T = 300^\circ\text{K}$: 1—theoretical curve; 2—experimental curve.

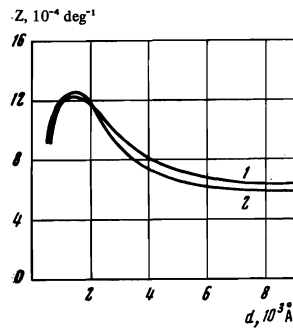


FIG. 5

perimental data is observed with account of both mechanisms of scattering for $p = 0.6$, $S \approx 10^{24}\text{ erg-cm}$ and $r = \frac{1}{2}$ (curve 3).

The experimental and computed curves of the thermal conductivity are shown in Fig. 3. The behavior of the thermal conductivity, which is due to electrons and

holes, is represented by the curve 1. A barely noticeable decrease in the coefficients σ_e , σ_h , α_e , α_h , beginning with 4000\AA , leads to a significant decrease in the bipolar term of the thermal conductivity ($\lambda_{e,h} \sim \alpha^2 \sigma$), which is very large in absolute value. As a result, the thermal conductivity due to the charge carriers falls off, beginning with 4000\AA . Curve 2 takes into account the scattering of the phonons only on the surface of the film ($p = 0.5$, $S_q = 0$). Curve 3 represents the dependence of the phonon component of the thermal conductivity for $p = 0.5$ and $S_q = 10^{22}\text{ erg-cm}$. Curve 4 corresponds to the total thermal conductivity. Curve 5 is the experimental curve.

Figure 5 shows the calculated and experimental dependences of the thermal emf coefficient on the film thickness ($p = 0.6$, $S_{e,h} = 10^{22}\text{ erg-cm}$). The dependence of the thermoelectric quality factor of the bismuth film on its thickness is shown in Fig. 5. Curve 1 was computed from the experimental data. Curve 2 is calculated. As follows from the drawing, there is excellent agreement between the experimental and theoretical curves.

The excellent agreement of the theoretical and experimental results allow us to confirm the validity of the premises that form the basis of the calculation.

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