

$$\frac{\partial n}{\partial t} = a \frac{\partial^2 \ln n}{\partial z^2}, \quad a = \frac{0,917^{3/2}}{M^{1/2} k^2 \Lambda e^4}, \quad (5)$$

where  $e$  is the electron charge and  $\Lambda$  the Coulomb logarithm. For an initial condition in the form  $n = n_0(1 + z^2/a^2)^{-1}$  the solution of Eq. (5) is

$$n = n_0 (1 + 2at/a^2 n_0) [z^2/a^2 + (1 + 2at/a^2 n_0)^2]^{-1}.$$

#### QUANTUM SIZE-EFFECT SEMIMETAL-SEMICONDUCTOR TRANSITION IN ULTRATHIN BISMUTH FILMS

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A semimetal-semiconductor transition in films with decreasing thickness was theoretically predicted in [1, 2]. If the film potential is approximated by a square well, then this transition in bismuth films should occur at thicknesses  $L_t \sim 300 \text{ \AA}$  for textured samples [3] and  $L_t \sim 200 \text{ \AA}$  for non-textured samples [4].

Textured Bi films were investigated down to a thickness  $L \sim 170 \text{ \AA}$  [5, 6], but no semimetal-semiconductor transition was observed. The shift of the red absorption edge in Bi films [7] is no evidence of a transition, owing to the large temperature smearing ( $T = 300^\circ\text{K}$ ). The indicated existence of a transition in cleaved  $\text{Bi}_2\text{Te}_3\text{S}_5$  [8] cannot be regarded as convincing, since the carrier concentration was not determined in the cited paper, and the resistance does not increase as  $T \rightarrow 0$ .

The absence of a transition down to a thickness  $170 \text{ \AA}$  is apparently connected with the inaccuracy of the film-potential model. Allowance for the electron interaction should lead to a lowering of the film levels, i.e., to a decrease of the expected  $L_t$  [9].

We have investigated the thickness dependences of the conductivity  $\sigma$ , of the Hall coefficient  $R$ , and of the magnetoresistance  $\Delta\rho/\rho_0$  in ultrathin Bi films at  $T = 4.2^\circ\text{K}$ , for the purpose of observing the semimetal-semiconductor transition. We used for the measurements non-textured polycrystalline films with thicknesses from 60 to  $400 \text{ \AA}$ , obtained by electric explosion on glass substrates, using a previously described procedure [4]. The critical film thickness was decreased by using extremely high condensation rates (up to  $10^3 \mu/\text{sec}$ ) [10]. The solidity of the films was determined by electron microscopy, and also by the absence of a sharp growth in the resistivity down to  $L \sim 50 \text{ \AA}$ . The film thickness was determined photometrically by optical absorption, with absolute standardization by the interferometer method of bands of equal chromatic order [11], with accuracy  $\pm 5 \text{ \AA}$ . Measurements of  $\sigma$ ,  $R$ , and  $\Delta\rho/\rho_0$  were made by a null method, the sample was placed directly in the liquid helium, and the magnetic field intensity was  $5000 \text{ Oe}$ .

A decrease of the gap with decreasing  $L$  was not observed earlier [4], apparently because of the temperature smearing, which at temperatures  $78 - 300^\circ\text{K}$  is of the order of the band overlap in Bi,  $\Delta = 4.3 \times 10^{-14} \text{ erg}$ . At  $T = 4.2^\circ\text{K}$  the temperature smearing is negligible.

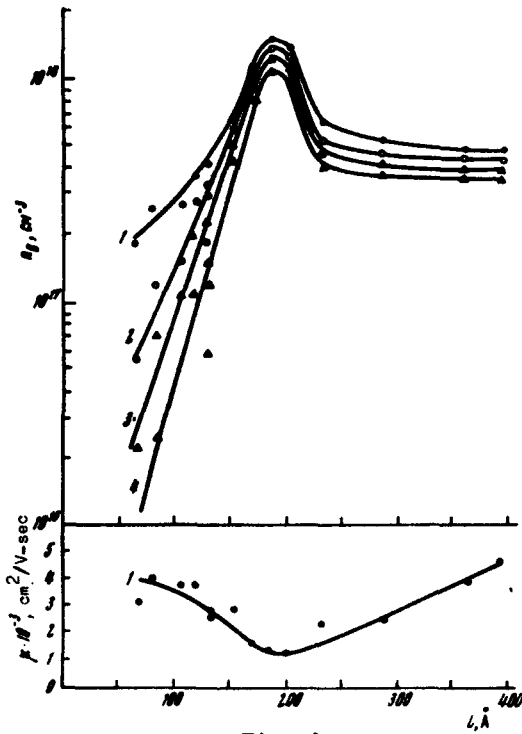


Fig. 1

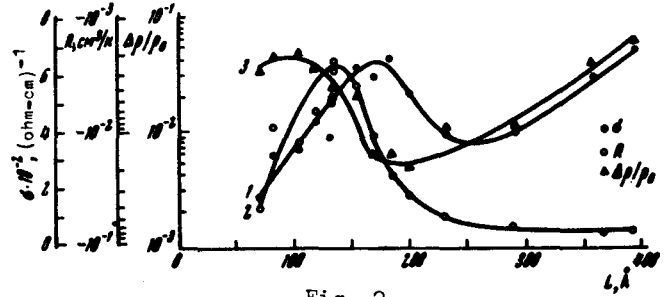


Fig. 2

Fig. 1. Dependence of the conductivity (1), the Hall coefficient (2), and the magnetoresistance (3) on the film thickness.

Fig. 2. Dependence of the concentration  $n_b$  and of the mobility  $\mu$  on the thickness  $L$  at: 1 -  $n = p$ , 2 -  $n_s = 3 \times 10^{11} \text{ cm}^{-2}$ , 3 -  $n_s = 5 \times 10^{11} \text{ cm}^{-2}$ , 4 -  $n_s = 10^{12} \text{ cm}^{-2}$ . Owing to the small difference between  $\mu_n$  and  $\mu_p$ , one curve is given for  $\mu$ .

The results of the measurements are shown in Fig. 1. An important factor is the growth of  $|R|$  with decreasing thickness, starting with  $L = 140 \text{ \AA}$ . This was not observed in [4], because of the high temperature; no such thicknesses were attained in other investigations of the quantum size effect. We note also the considerable value of  $\Delta\rho/\rho_0$ , which (see below) is connected with the relatively high mobilities  $\mu_n$  and  $\mu_p$ .

From the measured values of  $\sigma$ ,  $R$ , and  $\Delta\rho/\rho_0$  it is possible to calculate the concentrations  $n$  and  $p$  and the mobilities from the formulas in (1), by assuming some hypothesis concerning the connection between  $n$  and  $p$ :

$$\begin{aligned}
 n\mu_n + p\mu_p &= \frac{\sigma}{e}, & n\mu_n^2 - p\mu_p^2 &= R\sigma^2, \\
 n\mu_n^3 + p\mu_p^3 &= \sigma \left\{ \frac{\Delta\rho c^2}{\rho_0 H^2} + (R\sigma)^2 \right\}.
 \end{aligned}
 \tag{1}$$

In thin films it is necessary to take into account the influence of the surface levels on the carrier concentration. The absence of the field effect, however, did not make it possible to determine the surface concentration  $n_s$ .

The results of calculations by formulas (1), under the assumption  $n = p$ , corresponding to an "ideal" semimetal in the absence of or under complete compensation of the surface states, is shown in Fig. 2. We see that the bulk concentration of the carriers  $n_b$  decreases with decreasing thickness, starting with  $L \sim 180 \text{ \AA}$ , this being due to the transition of the Bi films into the semiconducting state. The thickness interval  $\Delta L$  within which  $n_b$  decreases by a factor  $e$  is  $\sim 50 \text{ \AA}$ . As already noted, the temperature smearing is small here and  $\Delta L$  is determined by the broadening of the levels (by the smoothing of the state-density function) resulting from the carrier scattering. The value of  $\mu$  leads to  $\Delta L$  of the same order.

We also calculated  $n_b$  under the assumption that  $n = p(n_s/L)$  (Fig. 2). At reasonable values of  $n_b$ , the character of the  $n_b(L)$  dependence remains unchanged, the decrease of  $n_b$  begins at the same thickness  $L \sim 180 \text{ \AA}$ , and only  $\Delta L$  varies.

The presence of the transition is evidenced indirectly also by the  $\mu(L)$  dependence. The increase of  $\mu$  starting with  $L \sim 200 \text{ \AA}$  is apparently due to the decrease of the scattering with decreasing concentration of the charged scatterers. Thus, from the  $n_b(L)$  dependence, and also from  $\mu(L)$ , it follows that a semimetal-semiconductor transition occurs in Bi films at  $L_t \sim 180 \text{ \AA}$ . This is somewhat less than the thickness calculated theoretically from the square-well model, owing, as noted above, to the inaccuracy of the model.

An interesting feature of the  $n_b(L)$  dependence is the growth of  $n_b$  when  $L$  changes from 250 to 180  $\text{\AA}$ . A similar rise was observed in [6]. At  $n_s \neq 0$ , the maximum on the  $n_b(L)$  curve decreases somewhat, but does not vanish (Fig. 2). It is difficult to explain satisfactorily this sharp growth of  $n_b$  at present, but it may be connected with the contribution of the surface states. For "thick" films ( $L > 300 \text{ \AA}$ ) far from the transition point  $L_t$ , the value of the concentration  $n_b$  coincides with those given by others [6, 12].

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#### THERMODYNAMICS OF THE MELTING OF ARGON

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We describe here the results of measurements of the volume of argon in the vicinity of the melting point in the temperature region from 197.78 to 323.15°K.