FEATURES OF TEMPERATURE DEPENDENCE OF THE RESISTANCE OF THIN BISMUTH FILMS

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The following peculiarities of thin bismuth films are observed: 1) with decreasing temperature, the metallic behavior of the resistance gives way to an increase of the resistance, i.e., the resistance goes through a minimum; 2) for very thin films at low temperatures, a maximum of the resistance is observed; 3) at low temperatures the decrease of the film thickness is accompanied by a decrease of the resistivity. The positions of the peculiarities on the temperature dependence of the resistance of bismuth films (the minimum and maximum of the resistance) depend strongly on the film thickness; the resistance minimum is also strongly affected by the degree of structural perfection in the films. These peculiarities follow from the temperature dependence of the carrier density and carrier mobility, the temperature coefficients of which are opposite in sign.

Calculations for the isotropic model assuming conservation of the compensation of the carriers of opposite sign in thin films of bismuth have made it possible to describe qualitatively the appearance of the minimum and maximum of the resistance, and also to reveal a strong dependence of the carrier density on the film thickness, and an effective improvement of the kinetic properties of films with decreasing film thickness. This is apparently due to the influence of the quantum size effect. We investigated the temperature variation of the oscillatory dependences of the resistance of thin bismuth films on the thickness, due to the quantum size effect. The experimental data are satisfactorily approximated by an exponential law for the damping of the oscillation amplitude, but certain difficulties arise when it comes to reconciling the experimental results quantitatively with the existing theories.

I. MINIMUM AND MAXIMUM OF RESISTANCE

THIN bismuth films exhibit an unusual dependence of the resistance on the temperature: unlike bulky bismuth crystals, in which the resistance decreases with decreasing temperature in an almost linear manner, the resistance of Bi films decreases with decreasing T only at high temperatures, and with further decrease of the temperature, a growth of the resistance sets in[1-4]. The minimum of the resistance for films of thickness 2–40 μ was observed in[1] at temperatures 200–400° K; measurements performed in[2,3] on films of thickness smaller than 2,000 Å have shown that the minimum lies above room temperature. In[4] at the same thicknesses (1000–2000 Å) a minimum of the resistance was observed at 100–150°K.

The unusual behavior of the resistance of thin films of bismuth requires a physical interpretation. Kaĭdanov and Regel'[1] proposed that owing to the classical size effect the mean free path of the carriers in Bi films depends on the temperature more strongly than in the bulky crystal, as a result of which the temperature variation of the carrier density in bismuth plays an important role in the temperature variation of the resistance. Assuming the carrier density in the films to be the same as in the bulky crystal, the authors of[1] calculated the electron and hole mobilities at nitrogen and room temperatures and compared the calculated magnetoresistance $\Delta\rho/\rho H^2$ with the experimentally observed value. The discrepancy between the calculated and experimental values of $\Delta\rho/\rho H^2$ increases noticeably with decreasing film thickness.

In[4], the appearance of the minimum of the resistance is connected with the presence in the films of structural imperfections which act as barriers to the electrons. The probability of overcoming these barriers increases with increasing temperature. This leads to a decrease of the resistance; subsequently, however, an important role was assumed by scattering from phonons, which causes the resistance to increase in the same manner as in a metal. Such an explanation seems to us to be insufficiently justified.

The authors of[2] calculated the dependence of the resistance of bismuth films on the temperature (assuming that the carrier densities are equal and that the mobilities remain constant with changing temperature), taking into account the quantum size effect (QSE). It is shown in[2] that the QSE determines the oscillatory character of the dependence of the slope of the experimental curves, when plotted in coordinates $\log(1 - R_T/R_{4.2})$ and $1/T$, on the thickness of the bismuth film. In the assumed model, the linearity in terms of these coordinates corresponds to a decrease of the carrier density with decreasing temperature, in accord with an exponential law. However, the temperature variation of the carrier density takes place not only in films exhibiting the QSE, but also in bulky bismuth (calculations yield a dependence close to $T^{3/2}$[5]). Consequently, the anomalous growth of the resistance of thin films of bismuth with decreasing temperature is not connected with the quantum size effect. We note that for antimony films, which likewise exhibit the QSE[6], the usual metallic course of the resistance with decreasing temperature is observed.

With decreasing thickness of the Bi films, as it turned out, the character of the $\rho(T)$ dependence changes; a resistance maximum was observed at low temperature for very thin films. The minimum and maximum of the resistance were observed earlier by Balla and Brandt[7] for bulky bismuth under pressure, and allowance for this analogy in explaining the properties of films may be useful. In[7], to explain the peculiarities of the temperature variation of the resistance, the influence exerted on the resistance by the temperature change of the carrier density was separated from the influence of the carrier mobility.

The purpose of the present investigation was to study in detail the anomalies of the temperature variation of the resistance of thin films of bismuth of different thicknesses in the interval 1.5–350°K.

Procedure

The bismuth films were prepared by condensing Bi of purity 99.9999% in vacuum ($\sim 10^{-6}$ Torr) on a freshly cleaved surface of mica heated to 80–110°C. The rate of condensation was 50–300 Å/min. Two types of samples were obtained: films of variable thickness (ratio of maximum to minimum thickness ~ 2) and stepwise films with a large range of thickness variation. After condensation, the films were subjected to annealing (at 200–240°C) for several minutes, followed by slow cooling. The films prepared in this manner constitute a mosaic single crystal with orientation of the trigonal axis [111] normal to the plane of the film. At the same time, as shown by electron diffraction, a small fraction of the crystallites was oriented with the [120] direction normal to the substrate, or with the planes ($22\bar{1}$) and (110) parallel to the substrate.

Measurements of the electric conductivity of the films were made by a potentiometric method (with accuracy 10^{-4}) in a cryostat for intermediate temperatures in the interval 1.5–350°K. The accuracy of the measurement and stabilization of the temperature was not worse than 0.1°K. The measurements of the galvanomagnetic characteristics of the films were performed in a cryostat, where the samples were placed in a "finger" between the poles of an electromagnet. The accuracy of the field measurements and its stability were not worse than 10^{-4}. Magnetic measurements at intermediate temperatures were carried out with temperature drifting slowly. The accuracy of temperature measurements was in this case ~ 5°K.

Minimum Resistance for Bismuth Films

As a rule, bismuth films exhibit the quantum size effect[8-11], and therefore the dependence of the film resistance on the thickness has an oscillatory character; for films with thickness larger than 1500 Å, the period of the oscillations is 250–300 Å (a period of about 400 Å was observed earlier[9] for textured bismuth films obtained on neutral substrates). The observed period of the oscillations agrees satisfactorily with estimates that follow from the parameters of the electronic spectrum for bulky bismuth.

The dependences of the film resistance on the temperature have a minimum in the interval 4.2–350°K only in those cases when the films have a perfect structure; otherwise the minimum lies above 350°K, and thus, growth of the resistance is observed upon cooling. Figure 1 shows plots of $R_T/R_{4.2}$ against the temperature for a series of bismuth films of different thicknesses, obtained in one cycle under equal conditions. We see that for films having identical structure properties, the position of the minimum is determined by the thickness of the film, namely, the temperature of the minimum drops with increasing L.

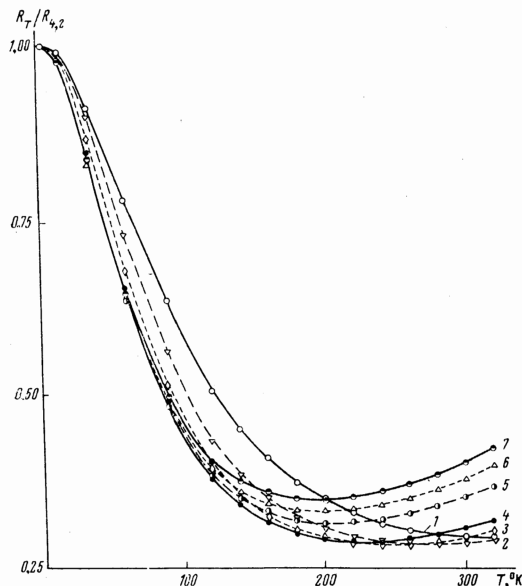

FIG. 1. Change of resistance of epitaxial bismuth films with changing temperature. Sample thickness (Å): curve 1–750, 2–1170, 3–1830, 4–2350, 5–3300, 6–4800, 7–4950.

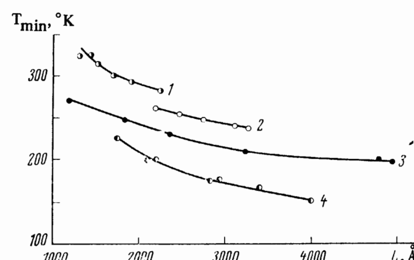

FIG. 2. Plots of the temperature of the minimum resistance against the film thickness for bismuth, obtained in series differing in their structure characteristics. Resistance of films of thickness 2000 Å at 4.2°K, $\rho_{4.2} \times 10^4$ (Ω-cm): curve 1–8.87; 2–7.25; 3–6.65; 4–3.25.

For films of equal thicknesses, the temperature of the minimum is in distinct correlation with the parameters determining the structure characteristics of the films. Thus, for textured films obtained on a neutral substrate (glass, quartz, acetate lacquer) the temperature of the minimum is, as a rule, higher than for epitaxial films obtained on mica. The perfection of the film structure increases with increasing temperature of the substrate during condensation, with decreasing rate of condensation, with improvement of vacuum, and also under the influence of annealing. Adoption of these measures shifts the minimum towards lower temperatures. The minimum of the resistance turns out to be in this case less deep relative to the resistance at 4.2°K; at the same time, $R_{4.2}/R_T$ decreases.

Figure 2 shows plots of the temperature of the minimum against the thickness for several series of films obtained under different conditions. The quantity characterizing the structural properties of the film is taken to be the resistivity $\rho_{4.2}$ of the films of thickness 2000 Å, which are represented in all the series of the samples.

The growth of the resistance of the bismuth film with decreasing temperature occurs under the influence of a decrease of the concentration of the carriers. In bulky bismuth crystals, this decrease of the concentration of the electrons and holes overlaps the growth of the mean free path time, and this on the whole leads to a lowering of the resistance. In bismuth films, the temperature dependence of the mobilities is not so strong, for various reasons, as in a single crystal, and the change of the concentration exerts a decisive influence on the temperature variation of the resistance. An increase of the carrier density in bismuth at temperatures on the order of the Fermi energy occurs as a result of the redistribution of the carriers among the electron and hole bands. Calculations for bismuth under conditions of equal carrier densities and with allowance for the nonparabolicity and nonellipsoidality of the conduction bands[5] leads to the following relation:

$$n = p = \frac{3}{2} p_0 \left(\frac{kT}{\Delta - \varepsilon_F} \right)^{3/2} F_{1/2} \left(\frac{\Delta - \varepsilon_F}{kT} \right), \qquad (I.1)$$

where Δ is the band overlap, ϵ_F is the electron Fermi energy, p_0 is the carrier density at 0°K, and $F_{1/2}$ is the Fermi integral.

The experimental data for bismuth single crystals[7,12] show that at relatively high temperatures (>100°K) the $T^{3/2}$ law is adequately satisfied, and at lower temperatures the change of the concentration is slower. It follows from[5] that, in spite of the change of the carrier density, the Fermi energy of the electrons and of the holes for bulky bismuth is almost constant in the temperature interval 0–400°K. Allowance for the quantization of the spectrum in bismuth films should apparently not change these results, so that there are no grounds for assuming that a dependence of the band overlap on the temperature will appear under the influence of the QSE.

To verify the assumptions concerning the causes of the appearance of the minimum on the $\rho(T)$ curves for bismuth films, we measured the magnetoresistance $\Delta\rho/\rho$ and the Hall constant R_x and performed calculations for the carrier density n and the electron and hole mobilities μ_e and μ_h, by solving the system of equations

$$\sigma = \rho^{-1} = en(\mu_e + \mu_h), \quad R_x = \frac{1}{en} \frac{\mu_h - \mu_e}{\mu_h + \mu_e}, \quad \Delta\rho/\rho H^2 = \mu_e \mu_h. \qquad (I.2)$$

It turned out that $\Delta\rho/\rho H^2$ increases with decreasing temperature and with increasing film thickness. The Hall constant has a positive sign and decreases with decreasing film thickness and with increasing temperature. For example, at room temperature R_x is of the order of 1×10^{-7} unit (all units are in the International System), and at 4.2°K for films of thickness 2000–3000 Å of the order of $(20-30) \times 10^{-7}$ unit, and for films of thickness 300 Å about 0.2×10^{-7} unit, i.e., smaller by two orders of magnitude.

Relations (I.2) are valid for a model that is isotropic in the plane of the film, provided the carrier densities are equal. Allowance for the anisotropy is apparently unnecessary, since the azimuthal orientation turns out to be the same for epitaxial films on a single substrate, in which connection a comparison of the properties of t the films within one series with changing thickness or temperature is perfectly correct. A comparison of films of different series is also permissible, since in most experiments mica plates with identical orientation were used, and in addition, the anisotropy of the magnetoresistance of bismuth in a plane perpendicular to the ternary axis, along which the magnetic field is directed, is small.

The equality of the carrier densities in bismuth films may become violated if local impurity states of the acceptor or donor type are produced in the films for some reason. Although the reasons for the occurrence of such states are not obvious, it is apparently necessary to take this possibility into account. If it is assumed that the concentration of the impurity states does not depend on the thickness of the films, then introduction into the calculation formulas of a constant coefficient $a = n_p$ leads only to a change of the numerical values of the sought quantities, whereas the general character of the obtained relations remains the same (see also[1]). On the other hand, if the impurity states appear under the influence of the surface, which is more probable, then the concentration of these states per unit volume of the film should increase with decreasing L, and accordingly the difference between the carrier densities should increase. Such a violation of the compensation would lead to an appreciable growth of the Hall constant, but this does not occur in reality. A calculation based on (I.2) shows that the mobilities of the electrons and the holes differ very little from each other and that this difference does not change with changing temperature and decreases with decreasing film thickness. Similarly, calculation of the electron and hole densities under the assumption $\mu_e = \mu_h$, using the system of equations

$$\sigma = \rho^{-1} = e\mu(n + p), \quad R_x = \frac{1}{e} \frac{p - n}{(n + p)^2}, \quad \frac{\Delta\rho}{\rho H^2} = \frac{4np\mu^2}{(n + p)^2}, \qquad (I.3)$$

has shown that the difference of the concentrations n and p is small—smaller by one or two orders of magnitude than the sum of the concentrations, and decreases with decreasing L[1)]. These calculations show that there are no grounds for assuming that the ratio of the electron and hole densities changes appreciably with changing thickness of the Bi films. It therefore suffices in what follows to consider the dependences of n, μ_e, and μ_h on the temperature and on the thickness of the films, as obtained from relation (I.2) assuming that the compensation is conserved.

Figure 3a shows plots of the carrier density in bismuth films of different thicknesses against the temperature. At 4.2°K, for films of large thickness, the obtained values of the density ($\sim 2.6 \times 10^{17}$ cm^{-3}) are close to the densities of the electrons and holes in bulky bismuth (2.75×10^{17} cm^{-3} [13]). With increasing

[1)] To simplify the calculations it was assumed that the difference between n and p is not very large and that in (I.3) the arithmetic mean of the densities can be replaced by their geometric mean $(n + p)/2\sqrt{np}$; then $\Delta\rho/\rho H^2 \sim \mu^2$.

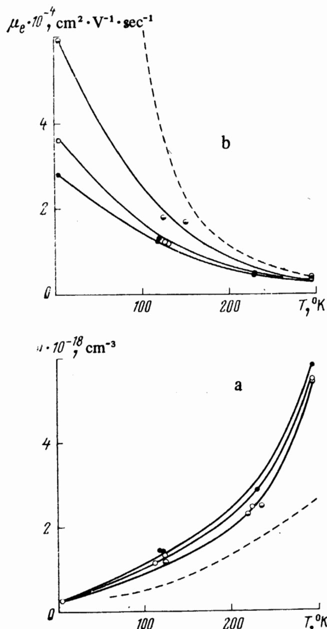

FIG. 3. Plots of the concentration (a) and of the mobility (B) of the carriers in bismuth films against the temperature. Film thickness (Å): ●–1850; ○–2190; ◒–3760 dashed curve–for bulky bismuth.

temperature, the carrier density in the films increases somewhat more strongly than in the bulky crystal. The dashed curve in Fig. 3a gives the N(T) dependence for bulky bismuth in accordance with the data of[12].

In addition, the growth of the carrier mobilities with decreasing temperature in films is slower than in the bulky crystal; this difference becomes more noticeable when the thickness decreases (Fig. 3b)[2)]. For films of thickness more than 1500 Å, the mobilities at room temperature change little with changing film thickness and their mean value is smaller by an approximate factor 2–3 than in the single crystal[12]. At helium temperature, the decrease of the thickness leads to a noticeable lowering of the mobilities. Accordingly, the decrease of μ with increasing temperature in films of thickness 1000–2000 Å turns out to be weaker than in thicker layers. In Fig. 3b, the dashed curve shows the expected change of the electron mobility at lower than room temperature in accordance with the relation $\sim T^{-5/2}$ observed for bulky bismuth[12]. It is possible to approximate the $\mu(T)$ relations for films by means of a power function of the type $T^{-\alpha}$ only in the region of high temperatures, where it turns out that $\alpha \sim 3/2$.

Thus, the minimum on the temperature dependence of the resistance of the bismuth films appears as a result of competition between the temperature dependences of the carrier density and their mobilities, which have different characters and opposite signs. In connection with the change of the temperature variation of the mobitiiies with changing film thickness, the shift of the minimum of the resistance towards higher temperatures with decreasing L becomes understandable. In exactly the same way, the deterioration of the structure characteristics of the films, which leads to a lowering of the mobilities, increases the temperature of the minimum.

An analysis of the data for films having different structure properties is in full agreement with this statement (for example, for sample 4 of Fig. 2, the calculated values of the electron mobility at 4.2°K turned out to be larger by more than 2 times than for sample 2, and accordingly the minimum in the former case was located at lower temperatures, etc.).

Dependence of the Carrier Density and Mobility on the Thickness of Bismuth Films

For bismuth films of thickness L < 1500 Å at low temperatures, a nontrivial increase of the conductivity is observed with decreasing thickness. This peculiarity was pointed out already in investigations of the QSE in textured films of Bi[9]. At room temperature, ρ_{293} is practically independent of the thickness. Calculations performed in accordance with relations (I.2) for several series of samples covering different thickness intervals have revealed L-dependences of the carrier density and mobility that explained this anomalous variation of the conductivity with thickness. It should be noted that this peculiarity is observed not only in the study of the properties of samples with variable thickness, but also when one plots the change of the film conductivity (with the aid of a differentiating scheme) against the change of thickness during the course of condensation of bismuth on cooled substrates[9].

For films of equal thickness, differing in the perfection of their structure and accordingly in the values of the resistivity, calculation gives practically the same values for the carrier density, whereas their mobilities turn out to be noticeably different. Figure 4 shows plots of n(L) for three samples of variable thickness, which are typical and reflect the character of the variation of the carrier density with changing thickness of the bismuth film at 4.2°K (see also[14]). The observed n(L) dependence is very close to

$$n = n_0(1 + 2L_0 / L), \tag{I.4}$$

where $n_0 \sim 2.5 \times 10^{17}$ cm^{-3} and $L_0 \sim$ 500–600 Å.

All the noted facts, namely the equality of the calculated values of n for films of equal thickness but having noticeably different resistances, the correct asymptotic value of n as $L \to \infty$, the single n(L) dependence in the

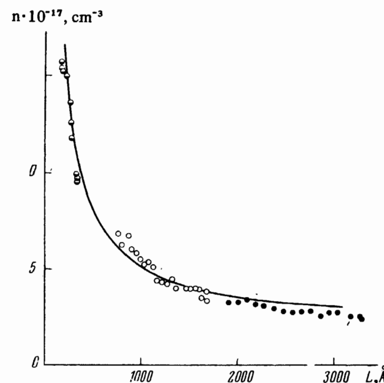

FIG. 4. Carrier density in bismuth films at 4.2°K against thickness. The solid curve is drawn in accordance with relations (I.8) and (I.9) at L_0 = 500 Å. Points of different form correspond to different samples of variable thickness.

[2)]For films thicker than 1500 Å, the hole mobility is ~15% higher than the electron mobility, but with decreasing L this difference becomes quite small. The relations given in Fig. 3b and following are therefore only for μ_e.

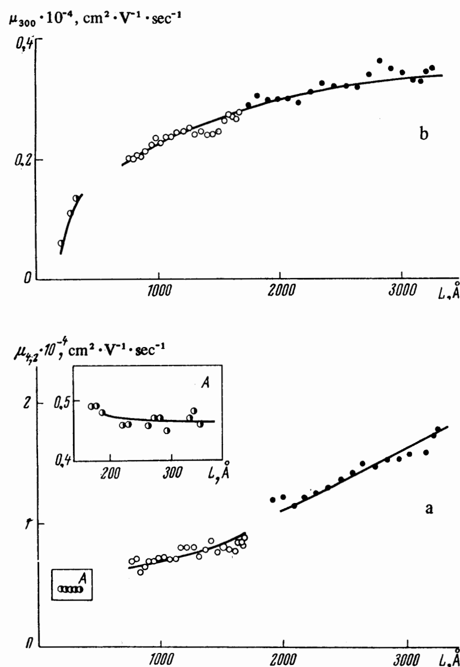

FIG. 5. Dependence of electron mobility on the bismuth film thickness at 4.2°K (a) and 300°K (b). Points of different type correspond to different samples of variable thickness.

entire investigated thickness interval, give grounds for seeking for the causes of the observed dependence.

The character of the variation of the carrier density in bismuth films with changing thickness is not the one expected from the theory of the quantum size effect. According to[15,16], in films of semimetals exhibiting the QSE, there should be observed a weak decrease of the carrier density with decreasing L, followed by an abrupt vanishing of the electron and hole bands at $L/\Delta L = 1$. The calculations for the anisotropic model[16] show that the characteristics of the spectrum should change with decreasing thickness; in particular, it turns out that the Fermi energy of the electrons increases. Theoretical models[15,16] start with a homogeneous distribution of the electron density and an invariant structure of the spectrum as a function of the film thickness. These assumptions seemingly do not reflect the real situation in films of semimetals with small thicknesses, where the surface influence can become appreciable. If it is assumed that the reciprocal dependence of the increment of the carrier density on the thickness is connected with the contribution of surface states, then we should write in lieu of (I.4)

$$n = n_0 + n_s/L, \qquad (I.5)$$

where the density of the surface states n_S turns out to be approximately equal to 2.75×10^{12} cm^{-2}. The surface should give rise to a distortion of the carrier spectrum, and this should hinder the observation of the quantum size effect at small film thickness, as is indeed the case.

The electron and hole mobilities decrease with decreasing thickness of the Bi films (Fig. 5). At 4.2°K in the region of large thicknesses, a practically linear dependence of μ_e and μ_h on the thickness is observed. The change of mobility with changing film thickness above 2000 Å can be quite appreciable (for example, for one of the samples, when L varied in the interval from 2000 to 3500 Å, we observed a change in mobility from 30,000 to 60,000 cm²/V-sec, etc.). The reason for the appearance of the $\mu(L)$ dependence is probably the classical size effect[17]. It should then be assumed that the mean free path l of the electrons and holes in the investigated films is much larger than 4000 Å, for within the limits of these thicknesses no saturation on the $\mu(L)$ dependences, a saturation characteristic of the classical size effect at thicknesses $L \sim l$, was observed. Another cause for the appearance of the dependence of the mobilities on L is the deterioration of the film structure with decreasing thickness. We note, however, that both causes should lead, at small thicknesses, to a steeper decrease of the mobility with decreasing L, than in the region of large thicknesses. Just such a curve was obtained for the mobility as a function of L at room temperature (Fig. 5b). At low temperatures, however, it turned out that the experimental curve has an inverse curvature and in the region 200—500 Å the mobility does not change at all with changing film thickness (it is known that the change of the quality of the film structure near the critical thickness is the most appreciable). This means that when the thickness decreases, a certain additional factor comes into play and cancels out in part or fully the expected decrease of the mobility at small L. This factor, in our opinion, is connected with the quantum size effect and consists in the fact that the appearance of size quantization and the associated decrease in the number of allowed states in the energy spectrum impose additional limitations on the frequency of the electron-phonon collisions; this is equivalent to an effective "improvement" of the kinetic properties of the films.

Estimates from the relation $kt \sim hcq$ (c—speed of sound in bismuth $\sim 2.5 \times 10^5$ cm/sec, q—phonon momentum) for the thicknesses of interest to us ($L < 10^{-5}$ cm) show that already at $T \approx 7-10$°K there are no phonons capable of realizing the transfer of electrons between the size-quantized sub-bands, i.e., having a momentum $q \sim \pi/L$. Actually, the influence of this circumstance comes into play at much higher temperatures, since an important role in the transfers between the sub-bands is played by the magnitude of the z-component of the phonon momentum and, in addition, the phonon momentum should have a definite magnitude ensuring the transfer of the electron to the strip produced by the intersection of the corresponding sub-band with the Fermi surface. Another explanation, in which account is taken of the scattering of the carriers by the screened Coulomb potential, is given in[18].

We note that the indicated "size-quantized" compensation for the "structural" deterioration of the mobility need not necessarily always take place, and consequently the dependence of the resistance on the thickness of the bismuth films can also have the usual form (as, for example, in[11]).

Maximum Resistance for Bismuth Films

For bismuth films of very small thickness ($L \lesssim 400$ Å) the temperature dependence of the resis-

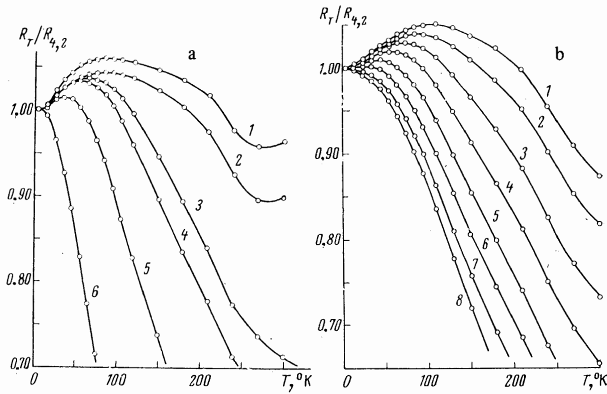

FIG. 6. Temperature dependence of very thin films of bismuth: a—epitaxial films on mica, of thickness (Å): 1—180; 2—188; 3—263; 4—293; 5—348; 6—700; b—films on acetate lacquer, of thickness (Å): 1—180; 2—198; 3—222; 4—252; 5—298; 6—350; 7—415; 8—450.

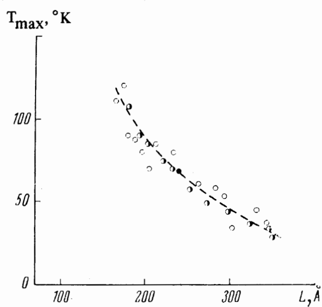

FIG. 7. Dependence of the temperature of the resistance maximum on the thickness of bismuth films condensed on lacquer (○) and on mica (◑, ●).

tance shows a maximum the position of which is determined by the thickness of the film (Fig. 6). With decreasing L, the temperature corresponding to the maximum of the resistance increases. Figure 6 shows examples of the temperature variation of the resistance for bismuth films obtained under different conditions: the films of series a were prepared on a freshly cleaved surface of mica and are single-crystal; the films of series b were prepared on acetate lacquer and constitute a polycrystalline condensate having a texture. The position of the maximum is less sensitive to the change of the structure characteristics of the films than the position of the minimum of the resistance and the decisive factor for the temperature of the maximum is the thickness of the film (Fig. 7).

In Fig. 6a, attention should be paid to the fact that with decreasing film thickness there appears, besides the shift of the maximum towards higher temperatures, also a minimum whose temperature decreases with decreasing L. Consequently, for thick films, the minimum of the resistance shifts towards higher temperatures with decreasing thickness; for intermediate thicknesses ($300 < L < 2000$) the minimum lies outside the investigated temperature interval, and for very thin films the minimum "returns" and appears at $T < 350$°K (it appears, incidentally, precisely for single-crystal films of series a, which have more perfect structure, i.e., in accord with the already noted influence of the structure on the temperature of the minimum).

Recently Garcia et al.[19] reported observation of a broad maximum of resistance for bismuth films of small thickness, and also a series of subtle peculiarities observed in freshly condensed films. The authors of[19] propose that the maximum of the resistance can be explained by analyzing the contributions of different scattering mechanisms, which have different temperature dependences, namely: the scattering of carriers by ionized impurities ($\tau^{-1} \approx T^{-3/2}$) and by phonons ($\tau^{-1} \sim T$). Actually it is possible to explain in this manner the appearance not of a maximum but of a minimum of the resistance, if one disregards the temperature dependence of the carrier density.

The maximum of the resistance for Bi films of small thickness can be explained on the basis of the same concepts which were used to explain the minimum of the resistance. In contrast to films of intermediate thickness (1000—2000 Å), very thin films are characterized by a strong change in mobility at low temperatures. Thus, in the interval 100—300°K, the values of the mobility change by more than a factor of 2; the helium-temperature mobility $\mu_{4.2}$ exceeds μ_{300} by several times; the smaller the film thickness, the more appreciable this growth. The causes for such a growth of μ were discussed in the preceding section and apparently lie in the fact that the quantum size effect improves the kinetic properties of the films effectively.

Figure 8a shows plots of $\mu_{4.2}/\mu_{300}$ against the film thickness for bismuth. The strong growth of the mobility at low temperatures for films of small thickness causes the dependence of $\mu_{4.2}/\mu_{300}$ on L to have opposite signs at large and at small thicknesses. In addition, the relative change of the carrier density in the interval 4.2—300°K decreases monotonically with decreasing L (Fig. 8b). Both factors—the strong growth of μ and the weak variation of n with decreasing temperature for small-thickness films—lead to the appearance of a maximum on the temperature dependence of the resistance. When the temperature drops below a certain value T_{max}, the decisive factor in the temperature variation of the resistance of thin films of bismuth is the growth of the mobility, which ensures the normal

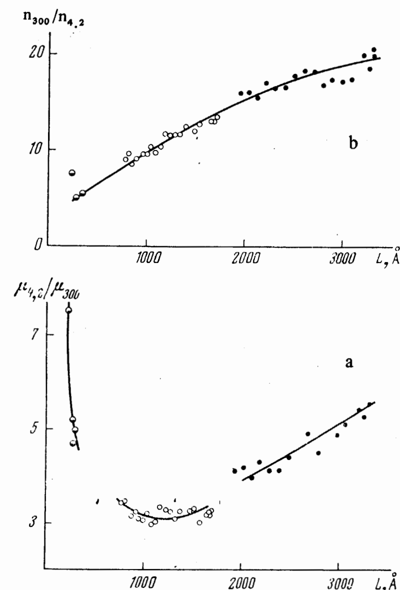

FIG. 8. Variation of the ratios $\mu_{4.2}/\mu_{300}$ (a) and $n_{300}/n_{4.2}$ (b) with bismuth film thickness. Points of different types correspond to different samples of variable thickness.

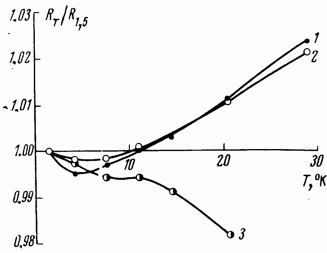

FIG. 9. Temperature variation of the resistance of bismuth films of thickness (Å): 1–222, 2–350, 3–700.

metallic variation of the resistance. Reversal of the sign of the dependence of $\mu_{4.2}/\mu_{300}$ on L for small-thickness films also makes understandable the "return" of the minimum of the resistance and its appearance within the limits of the investigated temperature interval.

A more detailed study of the character of the variation of the resistance of Bi films at temperatures below 4.2°K has shown that in this temperature region there is observed one more minimum of the resistance (Fig. 9). For thicker samples not possessing a resistance maximum, a singularity is observed at these temperatures (curve 3). The appearance of a second minimum is apparently connected with the competition between the contributions of different scattering mechanisms. We plan to investigate these questions in greater detail in the future.

We note that the obtained electric characteristics of bismuth films of small thickness, down to the smallest thickness of the conducting layer (~ 170 Å), lead to no data confirming the assumption[2] that the band overlap is lifted and that the bismuth film goes over into the dielectric state.

The investigation leads to the conclusion that the complex nonmonotonic temperature dependence of the resistance of thin bismuth films (a minimum of resistance in films of larger thickness and a maximum in films of smaller thickness) can be explained on the basis of allowance for the temperature dependences of the carrier densities and carrier mobilities. The weaker temperature dependence of the relaxation time than in the bulky crystal and the dependence of the mobility on the thickness and on the structure characteristics of the film determine the appearance and position of the minimum on the $\rho(T)$ curve). The same presentations can be used to explain the appearance of the maximum on the temperature dependence of the resistance of bismuth films of small thicknesses. It turns out here that there is an effective improvement of the kinetic properties with decreasing bismuth film thickness; this improvement is apparently connected with the quantum size effects, the influence of which is most appreciable in films of small thickness at low temperatures. The obtained dependences of the carrier density and mobility on the film thickness also make it possible to explain the growth of the conductivity of thin films of bismuth with decreasing thickness, as observed in[9].

II. DAMPING OF QUANTUM OSCILLATIONS OF RESISTANCE

The influence of the quantum size effect on the electric characteristics of thin films of bismuth is most clearly pronounced in the appearance, at low temperatures, of an oscillatory dependence of the resistance and other kinetic properties of the films on their thickness (first demonstrated in[8]). With increasing temperature, the amplitude of the oscillations naturally decreases. According to[21,22], there should be observed an exponential damping of the quantum oscillations, which excludes the possibility of their observation at high temperatures. In a number of papers[10,11,23] it has been reported that the quantum size effect was observed in Bi films at room temperature. The experimental investigation, the results of which are reported in this section, was aimed at a detailed study of the temperature dependence of the amplitude of quantum oscillations of resistance of thin Bi films of different thicknesses L.

The damping of quantum oscillations of the resistance of Bi films should be analyzed independently of the general character of the temperature variation of the resistance, the anomalous course of which, as shown in Sec. I, is not connected with the quantum size effect. The dependence of the oscillating component on L and T is given in the most general form in[22]:

$$\sum_{s=1}^{\infty}\frac{1}{s^2}\,\mathrm{sh}^{-1}\left(\frac{2\pi^2kT}{\Delta\varepsilon_F}\right)\left[\sin\frac{sP_z^e}{\hbar}L+\frac{\hbar}{sP_z^eL}\cos\frac{sP_z^e}{\hbar}L\right], \quad (II.1)$$

where P_z^e is the extremal chord of the Fermi surface, which determines the period of the oscillations of the resistance as a function of the thickness

$$\Delta L = 2\pi\hbar / P_z^e, \quad (II.2)$$

$\Delta\epsilon_F$ is the distance between the size-effect sub-bands near the Fermi level:

$$\Delta\varepsilon_F=\frac{2\pi\hbar}{L}\left(\frac{1}{|v_{z1}|}+\frac{1}{|v_{z2}|}\right)^{-1}, \quad (II.3)$$

v_z is the z component of the electron (or hole) velocity at the points of intersection of the Fermi surface with the extremal chord. For not too thin films one can use only the first term of the sum. According to[24], neglect of all the terms except the first is permissible also at not too low temperatures ($\Delta\epsilon_F/kT < 5.5$).

At temperatures $2\pi^2kT/\Delta\epsilon_F > 1$ one can assume that $\sinh^{-1}z = e^{-z}/2$. Under these conditions, an expression was obtained in[21] for the oscillating component of the resistance:

$$\rho_{osc}=\rho_0\left(\frac{2\pi kT}{\varepsilon_F}\right)\exp\left(-\frac{2\pi^2kT}{\Delta\varepsilon_F}\right)\cos\frac{P_z^e}{\hbar}L=\rho_0A\cos\frac{P_z^e}{\hbar}L. \quad (II.4)$$

On the basis of this expression it is possible to analyze the temperature variation of the amplitude of the quantum oscillations of the resistance and the splitting of the sub-bands $\Delta\epsilon_F$ can be determined. From the period of the oscillations ΔL and from the value of $\Delta\epsilon_F$ it is possible to obtain characteristic parameters of the energy spectrum in the direction of the size quantization, namely, the extremal chord P_z^e and the velocity component v_z (at $v_{z1} = v_{z2}$). Assuming approximate satisfaction of the quadratic dispersion law, relations (II.2) and (II.3) take the form

$$\Delta L = \pi\hbar / \sqrt{2m^*\varepsilon_F}, \quad (II.5)$$

$$\Delta\varepsilon_F=\frac{\pi\hbar}{L}\sqrt{2\varepsilon_F/m^*}, \quad (II.6)$$

	L, Å	$\Delta\epsilon_F \cdot 10^3$, eV	$v_z \cdot 10^{-7}$, cm/sec	From relations (II.5) and (II.6)		$\epsilon_F \cdot 10^3$ eV*
				$\epsilon_F \cdot 10^3$, eV	m^*/m_0	
Parameters of bulky Bi and expected value of $\Delta\epsilon_F$		5 (for L = 3000 Å)	1,3[25]	27,6[12]	0,0204[12]	—
From relation (II.4) for the interval 6–180°K	3000	60	87	300	0,0014	330
From relation (II.4) for the interval 20–50°K	3000	37	54	185	0.002	200
From relation (II.7) for the interval 75–230°K	3000	36	52	180	0,002	—
From relation (II.8) for the interval 20–50°K (sample 1, ΔL = 255A)	2550	6,03	7,4	30,15	0,014	47,5
	2850	6,3	8,7	35,2	0,012	19,2
	3300	5,61	8,9	36,3	0,011	65
From relation (II.8) for the interval 20–50°K (sample 2, ΔL = 260A)	2600	6,6	8,3	33,0	0,017	29,2
	2800	6,55	8,9	35,2	0,016	20,2
	2900	6,79	9,5	37,9	0,014	16,4

*Obtained by extrapolation to T = 0.

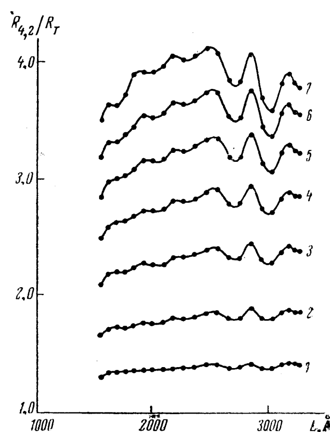

FIG. 10. Dependence of the ratio $R_{4.2}/R_T$ on the bismuth film thickness at different temperature (degrees K): curve 1–51, 2–75, 3–100, 4–125, 5–150, 6–240.

from which we can determine the effective mass m* and the Fermi energy ϵ_F of the carriers.

We have investigated the temperature dependence of the amplitude of the resistance oscillations on several samples with variable thickness. The procedure of preparing the samples is described in Sec. I. From the parameters of the electron spectrum of bulky bismuth (see the table), one should expect according to (II.5) and (II.6) for the main orientation—the direction [111] perpendicular to the plane of the film—a period $\Delta L \approx 260$ Å and a sub-band splitting $\Delta\epsilon_F \approx 5 \times 10^{-3}$ eV. In most cases the observed period of the oscillations was very close to the value $\Delta L = 260$ Å, and in accordance with (II) this gives for the extremal chord of the electronic ellipsoid in the direction of the trigonal axis $P_z^e = 2.55 \times 10^{-21}$ g-cm/sec.

Using the method of variable-thickness samples, which ensured the most accurate construction of the "thickness" dependences of the film properties, we verified that the amplitude of the oscillations depends on the perfection of the film structure; as a rule, it is larger for sections near the maximum thickness, where the quality of the films is better because of the perpendicular incidence of the molecular beam. Independently of this, the amplitude of the oscillations for films of thickness less than 1000 Å decreases noticeably with decreasing L in place of the appreciable growth predicted by the theory. In many cases, the oscillations have the form of beats. The damping of the oscillations with decreasing film thickness is apparently closely connected with the deformation of the spectrum near the surfaces under the influence of the surface states. In addition, the presence of the accompanying orientations (see Sec. I) characterized by smaller values of the period ΔL can lead to a decrease in the period of the oscillations and to the appearance of beats.

Figure 10 shows plots of $R_{4.2}/R_T$ against L for different temperatures; these plots demonstrate the temperature variation of the oscillation amplitude. The need for constructing the plots of $R_{4.2}/R_T$ against L is brought about by the fact that calculation of the specific resistance of the films cannot be made without introducing additional errors connected with the errors in the determination of the geometric dimensions of individual sections of a sample of variable thickness. Therefore the reduction must be carried out by using only the ratios of the resistances at different temperatures, ratios independent of the geometry. The principal possibility of obtaining the temperature variation of the amplitude of the oscillations of $\rho(L)$ from the plots of $R_{4.2}/R_T$ against L was demonstrated by us in[6]. The growth of the amplitude A* of the oscillations of the ratio $R_{4.2}/R_T$ corresponds to a decrease of the sought amplitude A with increasing temperature. The temperature dependence of the amplitude A* has the form of a curve with saturation in the region of temperatures where the amplitude A is vanishingly small. Further, using the fact that $A^* = (A_{4.2} - A_T)/(1 - A_{4.2}^2) \approx A_{4.2} - A_T$ (see[6]) and choosing for $A_{4.2}$ the value of A* in the saturation region, we can obtain directly the values of the sought amplitude A at all temperatures. The reduction of the experimental data was carried out with a computer; the relative error in the resistances did not exceed 10^{-4}. In connection with the difficulties that exist in quantitative matching of the results with the existing theories[21,22], we present numerical values of the amplitude of the quantum oscillations of the resistance at different temperatures for one of the samples (thickness 2900 Å):

T, °K:	4.2	14.5	30	51	75	100	124.5	150	180	210	240
$A \cdot 10^2$:	5.0	4.9	4.43	3.78	2.95	2.13	1.81	1.32	0.92	0.53	0.25

The temperature dependence of the amplitude of the

oscillations of the resistance is described satisfactorily by an exponential law, but is slower than expected in accordance with formula (II.4) and with the foregoing estimates of $\Delta\epsilon_F$. Good linearity of the obtained relations in the coordinates log(A/T) vs. T is observed in the temperature interval 60—180°K, and a somewhat poorer linear approximation, with a larger slope, is observed in the interval 20—50°K. In the former case $\Delta\epsilon_F$ turns out to be higher by one order of magnitude than the expected value, and further processing in accordance with formulas (II.3) (II.5), and (II.6) leads to values that deviate from the parameters of bulky bismuth by one order of magnitude (see the table).

For the expected values of $\Delta\epsilon_F \approx 5 \times 10^{-3}$ eV, formula (II.4) can be used almost down to helium temperatures (the condition $2\pi^2 kT/\Delta\epsilon_F > 1$ is satisfied for $T > 3°K$). In the region 20—50°K, the satisfactory linearity in coordinates log(A/T) vs. T (Fig. 11a) gives a lower value of $\Delta\epsilon_F$ than at high temperatures (see the table), and accordingly somewhat more reasonable values of m* and ϵ_F. According to (II.4), the value of ϵ_F can also be obtained by extrapolating the straight lines plotted in coordinates log (A/t) vs. T to T = 0. Both methods give close values of ϵ_F, but in the second case the scatter is quite large, since an important role in such an estimate of ϵ_F is played by the absolute values of the amplitude, which can be strongly influenced by the degree of the structure perfection of the films, etc. We note that the closeness of the values of ϵ_F obtained in a simultaneous solution of (II.5) and (II.6) and by extrapolation to T = 0, offers evidence of the internal consistency of the numerical coefficients in relation (II.4).

At high temperatures ($\pi kT/\epsilon_F \gtrsim 1$, i.e., $T > 100°K$) the thermal smearing of the spectrum turns out to be of the order of the Fermi energy. This brings about essentially different situations in films of bismuth and antimony at the same temperature and having equal splitting of the sub-bands $\Delta\epsilon_F$ (we note that according to (II.6), the thicknesses that are equivalent with respect to the equality of $\Delta\epsilon_F$ are close for films of Bi and Sb, in spite of the different values of ϵ_F and m*). The change of the amplitude and phase of the oscillations of the thermodynamic potential, which are connected with spatial quantization of the spectrum, was considered for a wide temperature interval in a paper by Nedorezov[22]. It turned out that at temperatures $\pi kT/\epsilon_F > 1$ the damping of the oscillations should indeed occur more slowly than at lower temperatures, this being essentially connected with the non-equidistant distribution of the quantum energy levels. Calculation for a two-band model of a semimetal has shown that at high temperatures the period of the oscillations and the value of $\Delta\epsilon_F$ differ from the corresponding quantities at low temperatures by a factor

$$\frac{\sqrt{1+\varepsilon_g/\varepsilon_F}}{1+\varepsilon_g/2\varepsilon_F}$$

(ϵ_g is the energy gap between the conduction band and the valence band). For bulky bismuth, however, this factor is close to unity, since $\epsilon_g/\epsilon_F \gtrsim 0.5$. In films, apparently, the situation remains essentially unchanged, since it is seen from Fig. 10 that the period of the oscillations remains practically constant in the entire investigated region of temperatures.

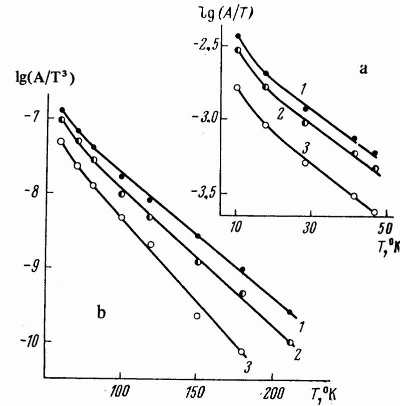

FIG. 11. Temperature dependence of the amplitude of the oscillations in linearizing coordinates: a—at low temperatures ($\pi kT/\epsilon_F < 1$), b—at high temperatures ($\pi kT/\epsilon_F > 1$). Film thickness (Å): curve 1—2300, 2—3600, 3—2550.

According to[22], the amplitude of the oscillations at high temperatures is proportional to

$$\frac{\pi(kT)^3}{\varepsilon_F(\varepsilon_F+\varepsilon_g)}\exp\left(-\frac{2\pi^2 kT}{\Delta\varepsilon_{\text{eff}}}\right). \tag{II.7}$$

Accordingly, we have plotted the experimental results in coordinates log(A/T³) vs. T (Fig. 11b). Satisfactory linearity is attained in the interval 75—230°K. $\Delta\epsilon_{eff}$ turns out to be the same as obtained from formula (II.4) at low temperatures (see the table).

Thus, owing to allowance for the results of[22], it is possible to explain the transition from the rapid to the slower damping of the resistance oscillations on going from low temperatures ($\pi kT/\epsilon_F < 1$) to higher ones ($\pi kT/\epsilon_F > 1$), and also the fact that in these temperature regions the damping is determined by the equal splittings of the sub-bands $\Delta\epsilon_F$. Yet the numerical discrepancy between the obtained values of $\Delta\epsilon_F$ and the estimates is quite appreciable and is possessed not only by bismuth films. Thus, the value $\Delta\epsilon_F \sim 0.1$ eV obtained in the analysis of the damping of the resistance oscillations of antimony films[6] at a thickness ~ 350 Å and at ΔL = 25 Å yields, in accordance with (II.5) and (II.6), $\epsilon_F \approx 0.6$ eV and $m_{33}^* \approx 0.1m_0$; extrapolation of the curves to T = 0 yields $\epsilon_F \approx 0.55$ eV. For bulky antimony, according to[26], we have $\epsilon_F \sim 0.1$ eV and $m_{33}^* \sim (0.1-0.6)m_0$. Account must be taken here of the fact that the difference between the obtained values of ϵ_F and m_{33}^* and the parameters of the bulky antimony increases even more if the Dingle factor is taken into account; this factor leads to a decrease in the amplitude of the oscillations[6] [3]).

Thus, besides the good agreement between the period of the oscillations ΔL and the parameters of the spectrum of the bulky bismuth, a strong discrepancy is observed for the quantity $\Delta\epsilon_F$. Possible reasons may be

[3])Epitaxial bismuth films have a much more perfect structure and better kinetic characteristics than antimony films. Estimates show that for Bi flims the relaxation time is larger by at least one order of magnitude than in Sb films, so that the Dingle factor is less significant for them.

the strong deformation of the spectrum in the films and the deviation from the quadratic dispersion law. Calculations for a non-quadratic model[22] show that the discrepancies between the observed quantities ΔL and $\Delta\epsilon_F$ and those calculated from the quadratic dispersion law, ΔL_0 and $\Delta\epsilon_{F_0}$, are determined by the relationships

$$\Delta L = \Delta L_0\left(1+\frac{\varepsilon_F}{\varepsilon_g}\right)^{-1/2},$$
$$\Delta\varepsilon_F = \Delta\varepsilon_{F0}\left(1+\frac{\varepsilon_F}{\varepsilon_g}\right)^{3/2}\left(1+\frac{2\varepsilon_F}{\varepsilon_g}\right)^{-1}.$$

In the case $\epsilon_g/\epsilon_F \sim 0.5$, the corresponding corrections are close to unity. If, on the other hand, it is assumed, for example, that $\epsilon_g/\epsilon_F = 0.1$, then it turns out that $\Delta L = 0.3\ \Delta L_0$ and $\Delta\epsilon_F = 1.7\ \Delta\epsilon_{F_0}$; further, from (II.5) and (II.6) we obtain for bismuth films 3000 Å thick $\epsilon_F = 36 \times 10^{-3}$ eV and $m_{33}^* = 0.0014 m_0$, which differs strongly from the effective mass of the electrons in bulky bismuth; moreover, it turns out that $\Delta\epsilon_F \approx \epsilon_F$. Consequently, such an explanation cannot be regarded as satisfactory.

The optimal description of the obtained experimental results gives the following empirical relation for the relative amplitude of the oscillations:

$$A = \left(\frac{kT}{\varepsilon_F}\right)\exp\left(-\frac{\pi kT}{\Delta\varepsilon_F}\right), \qquad (II.8)$$

which differs from (II.4) in that the factor 2π is missing from the pre-exponential coefficient and from the argument of the exponential; this factor appears when the nonmonotonic dependence of the thermodynamic or kinetic characteristics of the films on the thickness is expanded, in the case of size quantization, in a harmonic series. Since the amplitude of the oscillations is relatively large, (5%) and the waveform of the oscillation curves differs strongly from sinusoidal (unfortunately, we do not have enough points for a detailed investigation of the waveform of the curves), such an expansion and discarding of all the harmonics except the first, leads to underestimates of the amplitude of the oscillations in the theoretical calculations. The table lists examples of the reduction of the experimental data for two samples of bismuth in accordance with relation (II.8). The obtained quantities are close to the parameters of the bulky bismuth.

Thus, the features of the energy spectrum of bismuth, particularly the relatively small value of the Fermi energy ϵ_F, explain the transition from the fast to the slow regime of damping of the quantum oscillations of the resistance in Bi films on going from low ($\pi kT/\epsilon_F < 1$) to high temperatures ($\pi kT/\epsilon_F > 1$); the exponential law of damping of the oscillations in these temperature regions is characterized by the same value of $\Delta\epsilon_F$. But the numerical values of $\Delta\epsilon_F$ turn out to be higher than would follow from estimates in accordance with the parameters of the electronic energy spectrum of bulky bismuth, whereas the observed period of the oscillations is in good agreement with these parameters.

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