

ELECTRIC AND STRUCTURAL PROPERTIES OF LOW TEMPERATURE BISMUTH FILMS

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The temperature variation of the electric conductivity of thin bismuth films obtained by condensation of molecular beams on a substrate at helium temperatures is investigated. The resistance of the "amorphous" low-temperature phase thus formed decreases appreciably with increase of temperature and increase of film thickness. The phase transition temperature to the rhombohedral phase of bismuth also varies with film thickness. The dependence may be described by a relation which takes into account the effect of surface energy on phase transition temperature in thin layers. A low temperature electron-diffraction study of "amorphous" bismuth films shows that the coordination structure varies with the temperature and film thickness. Data on the structure factor are employed for comparing the observed changes in electrical properties of "amorphous" bismuth films with calculations performed within the framework of the theory of electric conductivity of liquid metals.

WHEN a molecular beam of bismuth is condensed on a substrate cooled to helium temperature, a low-temperature phase is produced, which differs in its properties from the usual rhombohedral phase of bismuth. Experiments performed by Buckel and Hilsch^[1,2] have shown that the low-temperature phase of bismuth in films has a larger conductivity and Hall carrier density than the ordinary modification.

Low-temperature bismuth films exhibit superconductivity with $T_c \sim 5-6^\circ\text{K}$. According to Zavaritskiĭ^[3], the critical temperature of the superconducting transition decreases with decreasing film thickness below 100 Å, and the critical magnetic fields parallel to the film vary with thickness and with temperature in accordance with the Ginzburg-Landau theory (thus, in particular, a critical thickness is observed, below which $H_c \propto (\Delta T)^{1/2}$, and for thicker films a sufficient degree of supercooling one gets $H_c \propto T$). The good agreement with the Ginzburg-Landau theory in a wide range of temperatures is due apparently to the disordered structure of the low-temperature bismuth films and to satisfaction of the relation $l \ll \xi$ (l is the electron mean free path). Lazarev et al.^[4] have shown that bismuth films become superconducting not immediately after condensation, but after a certain period of time. The relatively high critical temperatures are not preserved when the film thickness is increased, and T_c decreases at thicknesses above 1000 Å^[5].

Heating produces at a certain temperature a transition from the low-temperature phase into the ordinary rhombohedral modification of bismuth. This transition is accompanied by a sharp increase of the resistance and of the Hall constant.^[2,6] A phase transition takes place also at helium temperature when the film thickness is increased above 600 Å^[7]. It was noted that low-temperature films of small thickness decrease their resistance with increasing temperature^[8].

Structural investigations of low-temperature films are quite limited. Electron-diffraction observations by Buckel^[9] have shown that the diffraction pattern obtained from low-temperature bismuth films is an aggregate of several strongly smeared lines and recalls

the halo of the amorphous substance. Richter and Steeb^[10] reduced Buckel's diffraction data and plotted the radial distribution of the atomic density. A similar reduction of the electron-diffraction pattern of a film 200 Å thick, undertaken by Fujime^[11], has led to the conclusion that the low-temperature phase is similar in its coordination arrangement to supercooled liquid bismuth.

The available structure data are patently insufficient for a discussion of the features of the physical properties of low-temperature bismuth films. The fact that these objects constitute a strongly disordered phase that comes close in structure to amorphous matter uncovers the possibility of analyzing its electric properties by using the theory of scattering of electrons in liquid and amorphous substances, based on the pseudopotential method^[12]. This approach uses essentially structural data for the investigated objects, particularly the so-called structure factor. Information on the structure factor can be obtained with any diffraction procedure, but the most acceptable for films is electron diffraction, which provides an intense diffraction pattern with small amounts of matter.

The purpose of the present investigation was to obtain with the aid of low-temperature electron diffraction, information on the electric properties of low-temperature bismuth films and their variation with thickness and temperature, as well as data on the structure properties of these objects.

EXPERIMENTAL PROCEDURE

Bismuth 99.999% pure was condensed on a sapphire substrate placed in a vacuum chamber with cryogenic pumping. The substrate was clamped to a copper plate cooled with liquid helium. To decrease the thermal resistance, the contact surface was coated with a liquid indium-gallium alloy. The substrate temperature was determined with an Allen-Bradley carbon resistor. Evacuation to 2×10^{-6} Torr was with the aid of fore-vacuum and vapor-oil pumps, and from 2×10^{-6} to 4×10^{-8} Torr with the aid of a condensation helium

pump. The molecular bismuth beam was condensed in a vacuum not worse than $(1-2) \times 10^{-7}$ on the substrate at temperature 5–7 and $\sim 55^\circ\text{K}$ (the temperature reached by pumping off nitrogen).

The samples were in the form of stepped condensates (5–6 steps of different thickness). Thus, it was possible to trace in one experiment the temperature variations of the resistance of films that differ noticeably in thickness. The samples were heated at low rate (1–3 deg/min).

Films for the electron-diffraction study were condensed directly inside the EG electronograph on a substrate of helium temperature. The substrates were films of acetate lacquer or, more frequently, aluminum films. Owing to the oxide layer on its surface, the aluminum film serves, like polished sapphire or lacquer, as a neutral substrate. Aluminum oxide and sapphire are the same chemical substance; therefore the physical and chemical properties of these substrates are apparently close, and the structures of the "amorphous" bismuth films condensed on them should not differ noticeably. Control experiments, in which the electric resistance of the bismuth film on a sapphire plate was measured simultaneously with observation of the diffraction pattern, have shown that the transition from the "amorphous" to the crystalline phase occurs on these substrates at the same temperature. An aluminum substrate has the important advantage over a lacquer film that aluminum diffraction pattern consists of a small number of sharp rings, which can be readily excluded from the overall diffraction pattern. The electron diffraction patterns at temperatures above that of helium were obtained by slow temperature drift of the low-temperature attachment. The electronograph was evacuated with a condensation pump to $(1-2) \times 10^{-6}$ Torr.

The film thickness was determined from the optical density. The dependence of the optical density on the thickness was determined with the aid of the multibeam interferometry method.

DEPENDENCE OF THE PHASE-TRANSITION TEMPERATURE ON THE BISMUTH FILM THICKNESS

The temperature of the transition of the low-temperature phase of bismuth into the rhombohedral phase, for films 200–400 Å thick, usually lies in the region $10-20^\circ\text{K}$ ^[1-7]. For films thicker than 100 Å, Zavaritskii^[3] observed an inverse dependence of the phase-transition temperature on the thickness in the indicated range. An investigation of films of smaller thickness has shown that when L decreases the transition temperature increases noticeably. Thus, Fig. 1 shows plots of the resistance of small-thickness films (10–25 Å) against the temperature; the phase transition is observed in them at 130–150°K. (The phase-transition temperature can be defined as the temperature at which the resistance begins to grow intensively or, at the permissible error, the temperature corresponding to the largest slope of the transition curve.) We note that by condensation on a substrate cooled to helium temperature one can obtain conducting layers of negligibly small thickness, down to monatomic, and it turns out here that they have the same conductivity as in the

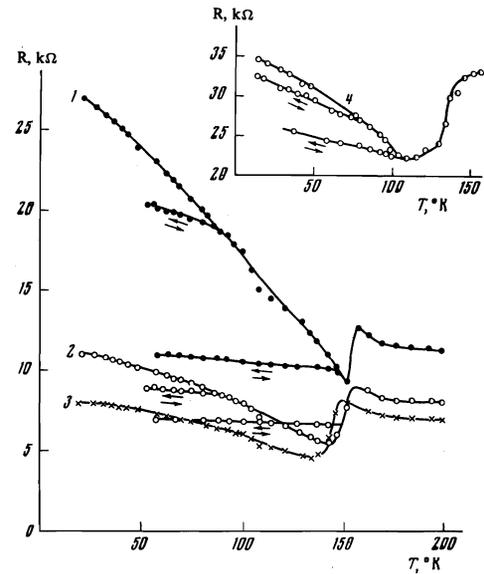


FIG. 1. Temperature dependence of the resistance of thin bismuth films condensed at a substrate temperature 4.5°K . Film thickness (in Å): 1–10, 2–15, 3–25, 4–18.

metallic state. This is apparently due to the small diffusion mobility of the atoms, as a result of which the condensation proceeds via uniform filling of the substrate with metallic atoms. The phase transition in extremely thin layers was revealed by the jump of the electric conductivity at temperature 200–250°K and higher (up to room temperature). Similar observations were made also with the aid of electron diffraction (thus, at a thickness ~ 16 Å, the halo of the "amorphous" phase was preserved up to 200°K, after which the diffraction pattern of the rhombohedral crystalline bismuth appeared).

Figure 2 shows the experimental points characterizing the dependence of the phase-transition temperature on the bismuth film thickness. This dependence is due, in our opinion, to the influence of the surface energy on the conditions of the thermodynamic equilibrium of the two phases. At the equilibrium point, the condition for the equality of the free energies of the two phases in a film or in a small crystal, with allowance for the surface energy, takes the form

$$U_1 - TS_1 + \sigma_1 A / V = U_2 - TS_2 + \sigma_2 A / V \quad (1)$$

(A is the surface and V the volume of the crystal, and S is the entropy). For a bulky crystal

$$U_1 - T_0 S_1 = U_2 - T_0 S_2 \quad (2)$$

Substituting in (1) the quantity $S_1 - S_2 = (U_1 - U_2)/T_0$, from (2), we get

$$(U_1 - U_2) (1 - T/T_0) = (\sigma_2 - \sigma_1) A / V,$$

where $U_1 - U_2 = Q$ is the heat of transition. For a film we have $A/V = 2/L$ (L is the thickness). The final relation is

$$T_0 - T = \frac{2(\sigma_2 - \sigma_1) T_0}{QL} \quad (3)$$

In relation (3), an important feature in the character of the deviation of the transition temperature in the

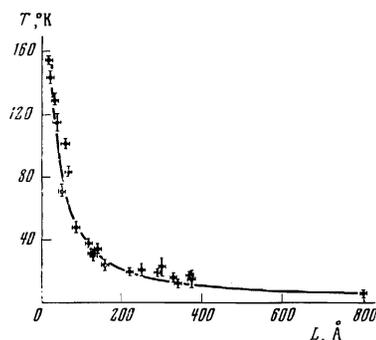


FIG. 2. Dependence of the temperature of the phase transition from the "amorphous" phase to the crystal on the thickness of bismuth films. The values of the transition temperature were obtained from electrical measurements and with the aid of low-temperature electron diffraction.

film from T_0 is the sign of the change of surface energy. Physically this means that if the transition is accompanied by a decrease in the surface energy, the phase-transition temperature in the film turns out to be lower than in the bulk crystal. Precisely such a change with decreasing L was observed for the melting temperature of bismuth and tin films^[13]. If the transition is accompanied by an increase in the surface energy, such as in our case, the transition temperature increases.

T_0 in (3) should be taken to be the temperature below which the low-temperature phase can be preserved in films of arbitrarily large thickness. As an estimate we assume $T_0 \sim 1^\circ\text{K}$. The curve drawn in Fig. 2, which agrees well with the experimental points, corresponds to $Q^{-1}\Delta\sigma \approx 2 \times 10^{-5}$ cm. This is much higher than the value $Q_S^{-1}\Delta\sigma \approx 1.2 \times 10^{-8}$ cm obtained in analogous calculations for the dependence of the melting temperature on the thickness of thin films of bismuth^[13]. If we assume $\Delta\sigma \sim 10^2$ erg/cm², then we obtain in this case $Q \sim 5 \times 10^5$ erg/g, and for melting we get $Q_S \sim 5 \times 10^8$ erg/g (a value close to the heat of melting of bulky bismuth). In accordance with the relations written out above, we should compare not the heats of transition, but the jumps in the entropy. The quantity Q/T assumes close values; thus, in the considered case $Q/T_0 \sim 5 \times 10^5$ erg/g-deg, and for melting $Q_S/T_S \sim 9.8 \times 10^5$ erg/g-deg. We note that relation (3) presumes that the jump of the surface energy in the transition does not depend significantly on the temperature and on the film thickness. This means above all that the structure of the low-temperature phase near the transition temperature should not change noticeably with film thickness. This assumption, as will be shown below, is confirmed by structure investigations.

The curve drawn in Fig. 2 pertains to bismuth films condensed on sapphire. When the substrate is changed or when the experimental conditions that determine the formation of the adsorption layers on the substrate surface and the film are altered, the transition temperatures can change somewhat as a result of the influence of the quantity $\Delta\sigma$.

At the chosen experimental conditions, the curve of Fig. 2 is the dividing line between the regions of the existence of the low-temperature and of the rhombohedral phases in bismuth films in processes leading to an increase of the temperature or an increase of the thickness. Regardless of the substrate temperature,

condensation of thin films lying on the T-L diagram below the phase-transition curve (see Fig. 2) leads to the production of the low-temperature phase. Figure 3 shows the temperature variation of the resistance of thin bismuth films condensed at a substrate temperature 55°K . The presence of resistance jumps indicates that a low-temperature phase was produced during the condensation; the registered transition temperatures agree with the data for films condensed at helium temperature. This shows that the onset of the low-temperature phase is not the exclusive result of the features of the kinetics of condensate formation at low temperature¹⁾; the low-temperature phase is apparently a state that is energywise more favorable in samples of small dimensions at low temperature than the crystalline rhombohedral phase. However, the low temperature phase is not restored when crystalline bismuth films are cooled. Such a transition should be accompanied by a disordering of the crystal structure, and this process is apparently hardly possible in the solid state when the temperature is decreased. A restoration of the low-temperature phase is possible only by cooling the disordered high-temperature state, for example when vapor is condensed.

ELECTRIC PROPERTIES OF LOW-TEMPERATURE BISMUTH FILMS

When low-temperature thin films are heated, a noticeable decrease of the resistance is observed (Fig. 1). It turns out here that the smaller the layer thickness, the more appreciable the relative decrease of R . The change of the resistance after a second cooling to 55°K (Fig. 1, curves 1–3) or to 5°K (Fig. 1, curve 4) is linear, but the curves of second cooling and heating do not coincide with the curve of the initial change of the resistance upon heating, namely their negative slope is much smaller and is determined not only by the thickness but also by the temperature reached in the preceding heating. This shows that the temperature variation of the resistance of low-temperature films of bismuth is connected to a considerable degree with irreversible changes of the structure. According to present-day ideas^[12], the temperature variation of the resistance of amorphous and liquid metals is not connected, in contrast to crystals, with temperature variations of different electron scattering mechanisms (by phonons, electrons, impurity atoms, defects, and boundaries), but is determined mainly by the temperature-governed structural changes. This allows us to assume that they cause also the reversible small negative variation of the resistance of films subjected to prior heating.

For low-temperature bismuth films of small thickness, a noticeable dependence of the resistivity on the thickness was also observed (Fig. 4), and this depend-

¹⁾The fact that the formation of the "amorphous" condensate is determined by an atom diffusion mobility that is not small can be illustrated by the following example: when molecular beams of antimony are condensed on neutral substrates at room temperature, an amorphous condensate is produced in thin layers; at the same time, electron-microscope observations of the kinetics of the condensate formation show that the mean free path of the atoms over the substrate surface is of the order of 1000Å.

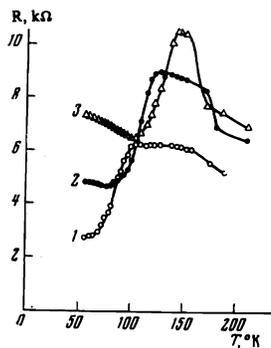


FIG. 3

FIG. 3. Temperature variation of the resistance of bismuth films condensed at 55°K. Film thickness (in Å): 1—36, 2—24, 3—18.

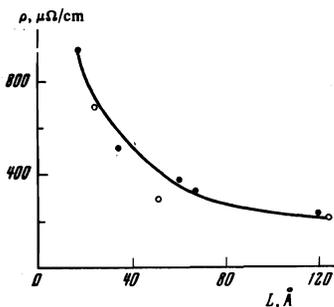


FIG. 4

FIG. 4. Resistivity vs. film thickness for bismuth condensed at a substrate temperature ~4.5°K.

ence is certainly not connected with a decrease in the solidity of the films, since low-temperature condensates continue to conduct down to monolayer thickness. After the thin films are heated to temperatures below the phase-transition temperature, the dependence of the resistivity on the thickness is weaker or is practically nonexistent. These peculiarities of the electric properties can be explained on the basis of an electron-diffraction structure investigation.

STRUCTURE OF LOW-TEMPERATURE BISMUTH FILMS

The reduction of the electron-diffraction patterns yields information on the structure of amorphous substances. The latter is described by the radial distribution function of the atomic density. This function can be constructed with the aid of the Fourier-transform of the electron-scattering intensity distribution $I(q)$ ($q = 4\pi\lambda^{-1} \sin \vartheta$, 2ϑ is the scattering angle, and λ is the electron wavelength).

A feature of electron diffraction is the presence of an incoherent background, which must be excluded from the calculations. If an experiment yields an intensity I_c connected with only the coherent scattering and expressed in units of f^2 (f is the atomic factor of electron scattering), then we can, after finding the function $i(q) = I_c/f^2 - 1$, plot the atomic-density radial distribution function^[14]

$$4\pi r^2 u(r) = 4\pi r^2 u_0 + \frac{2r}{\pi} \int_0^\infty qi(q) \sin(qr) dq; \quad (4)$$

u_0 is the average atomic density.

Thus, the operation preceding the integration consists of eliminating the diffraction from the substrate, as well as the incoherent background, and normalization of the coherent-scattering intensity to f^2 . The sharp diffraction maxima from the aluminum substrate could be easily excluded in our experiments from the common diffraction pattern, and the incoherent background from the aluminum was eliminated in accordance with a procedure described below, together with the incoherent background from the bismuth. This has greatly increased the accuracy of the calculations in comparison with earlier papers^[10,11], in which the con-

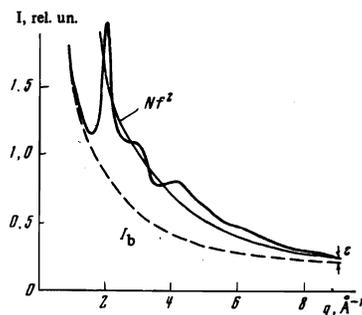


FIG. 5. Distribution of the intensity on the diffraction pattern from an "amorphous" bismuth film 140Å thick.

tribution of the amorphous substrate was not excluded in practice.

Further calculations were performed with a computer using a special program. We solved the following mathematical problem: find the background curve $I_b(q)$ specified in analytic form by the function $aq^{-\alpha}$. The advantages of describing the background by means of a power-law function are demonstrated in^[15]. The two unknown parameters contained in this function have made it possible to satisfy the requirement that the background pass through two points: one of them at low values of q ($q = 0.4-0.8$) coincides with the total intensity (this ensures a decrease of the coherent scattering to zero as $q \rightarrow 0$), and the second point, at large q ($q \approx 9$), was chosen such that the background intensity was lower than the summary intensity by an amount ϵ , which is also a sought parameter (this satisfied the requirement that the background not coincide with the envelope of the diffraction curve). In addition, the following condition was satisfied: a certain curve

$$I_0(q) = I_b(q) + cf^2(q),$$

crossing the diffraction maxima (Fig. 5) coincides with the intensity curve at large q , and the function $I_c = [I(q) - I_b(q)]/c$ ensures satisfaction of the equation^[16]

$$\int_0^\infty i(q) q^2 dq = 0. \quad (5)$$

Thus, all the known properties of the background and of the coherent electrons were satisfied in the calculation, and the intensities of the latter were simultaneously normalized to f^2 .

The results of the analysis of the plotted atomic-density radial distribution curves for low-temperature bismuth films (see, for example, Fig. 6) with different thicknesses have demonstrated the following:

1. In films of thickness 100–300 Å, a increase of the temperature changes little the configuration of the $4\pi r^2 u(r)$ curves. Such films reveal in a wide range of temperatures and thicknesses a certain "typical" structure, represented in Fig. 6 and in the table. The characteristic features of this structure are that a well-pronounced coordination sphere, of radius 3.2–3.3 Å and containing 4–5 atoms, is followed by a coordination sphere represented by three indistinct maxima containing a total of about 18 atoms, followed in turn by a well-pronounced coordination sphere of radius 6.6 Å containing ~18 atoms.

2. When the crystallization temperature is ap-

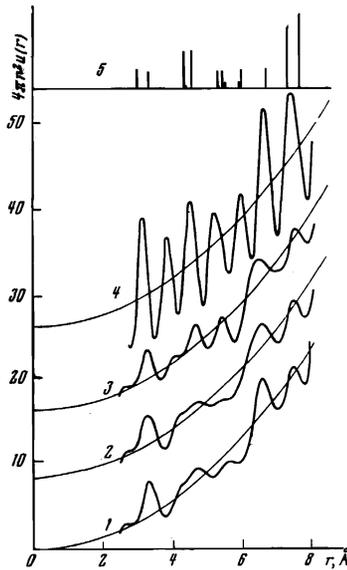


FIG. 6. Radial distribution of the atomic density in an "amorphous" film of bismuth 120 Å thick at temperatures 4.65 (1), 24.5 (2), 35.3 (3), and 39.5°K (4); curve 5 shows the distribution of the atoms over the coordination spheres in crystalline rhombohedral bismuth.

proached, the radial distribution assumes the form of a series of clearly pronounced maxima (curve 4 on Fig. 6, table).

3. In thin layers, $L < 100 \text{ \AA}$, the initial structure produced at helium temperature differs from the "typical" structure (see the table). It is characterized by a small number of clearly pronounced coordination spheres. With increasing temperature, this initial structure changes and goes over into the "typical" structure. As in thicker layer, a pre-crystallization structure is produced near the transition temperature.

4. In thick films ($L \sim 300\text{--}450 \text{ \AA}$) we were able to register at the initial instant of time, after the condensation, a structure that differs from the "typical" and is similar to the initial structure in thin layers. After aging at a constant temperature, this structure changes and goes over into the "typical" structure. Apparently, the distinct coordination in very thin films is a consequence of the tendency towards a certain two-dimensional (surface) ordering in the nearest atomic environment, which vanishes when the temperature or the thickness is increased and the influence of the surface coordination becomes weaker.

Thus, it turns out that the structure of "amorphous" films of bismuth is not of one type; its changes are controlled mainly by two parameters, the temperature

and thickness of the film. This explains qualitatively why we have observed changes in the electric properties of low-temperature bismuth films under the influence of these parameters, and also the previously known facts, namely the dependence of the critical temperature of the superconducting transition on the film thickness, the appearance of superconductivity after storing the film at helium temperature, etc.

DISCUSSION OF THE RESULTS OF THE INVESTIGATION OF THE STRUCTURE AND ELECTRIC PROPERTIES

The electric properties of amorphous metals are best discussed in connection with Ziman's theory of the electric conductivity of liquid metals^[12]. Ziman's theory is based on the assumption that electrons in liquid metals are a weakly-bound gas, i.e., each of the independent particles is described by a space function determined by the wave vector k . In this case there exists a definite spherical Fermi surface of radius k_F .

Within the framework of the pseudopotential theory^[17], the problem is formulated as the scattering of plane waves $|k\rangle = \Omega^{-1/2} \exp(ik \cdot r)$ by the pseudopotential $W(r)$ of the ions. The matrix elements of the pseudopotential between two unperturbed states

$$\langle k + q | W(r) | k \rangle = S(q) \langle k + q | w(r) | k \rangle$$

are determined by the structure factor

$$S(q) = \frac{1}{N} \sum_i \exp(-iqr_i) \tag{6}$$

and by the form factor $\langle k + q | w | k \rangle$, which depends only on the scattering vector q , owing to the locality of the pseudopotential, due to the scattering between states on the Fermi surface; the form factor is the Fourier component w_q of the pseudopotential of the individual ion. Thus, an important role in the scattering process is played by the spatial distribution of the ions and by the scattering ability of the individual ion.

Ziman's formula for the resistivity is

$$\rho = CN \frac{1}{k_F^4} \int_0^{2k_F} |S(q)|^2 |w_q|^2 q^3 dq, \tag{7}$$

$$C = 3\pi m \Omega_0 / 8\hbar e^2 v_F, \tag{8}$$

where N is the number of ions in the crystal, and Ω_0 is the volume per atom. Using the diffraction data for the structure factor, we can calculate ρ in accordance with formula (7). We used for the form factor the tables of Animalu and Heine^[17], constructed for the model potential of Heine and Abarenkov. The form factor for bismuth is shown in Fig. 7.

To calculate C , we used for m , as in calculations

Radii r of the coordination spheres and coordination numbers n for low-temperature bismuth films

Structure	Coordination sphere											
	I		IIa		IIb		IIb		IIIa		IIIb	
	r	n	r	n	r	n	r	n	r	n	r	n
"Typical"	3.25	4.5	4.0	~3.5	4.7	~7.5	5.55	8±1	—	—	6.6	18-22
Initial (in very thin films)	3.35	6±1	~4.4	8±1	~5.0	8±1	—	—	6.2-6.8	24±4	—	—
Pre-crystallization	3.3	4.5	3.95	3.5	4.65	6.5	5.6	5.5	~6.2	7.5	~6.8	12

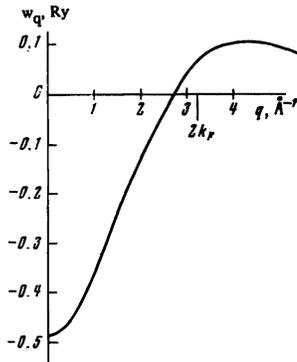


FIG. 7. Dependence of the form factor on the wave vector for bismuth [17].

for liquid metals^[8], the value of the free-electron mass. The quantity $\Omega_0 = 35.35 \text{ \AA}^3$ was obtained from the density of the crystalline bismuth (we used the same value of Ω_0 in^[10,11] to construct the atomic-density radial distribution function). We determined the energy ϵ_F from the formula

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2m}, \quad k_F = \left(\frac{2\pi^2 Z}{\Omega_0} \right)^{1/3}, \quad (9)$$

where Z is the valence. As a result we obtained

$$k_F = 1.61 \text{ \AA}^{-1}, \quad C = 4300 \text{ \mu}\Omega\text{-cm/Ry}.$$

The structure factor is connected with the intensity of the coherently-scattered electrons, normalized with the aid of the square of the atomic factor. Indeed, the scattering intensity is

$$I(q) = Nf^2 \left\{ 1 + \int_0^\infty [u(r) - u_0] \frac{\sin qr}{qr} 4\pi r^2 dr \right\}. \quad (10)$$

From diffraction theory it is known that

$$1 + \int_0^\infty [u(r) - u_0] \frac{\sin qr}{qr} 4\pi r^2 dr = a(q) = \frac{1}{N} \left| \sum_i \exp(iq \cdot r_i) \right|^2 \quad (11)$$

Thus, we write in place of (10)

$$I(q) = Nf^2 a(q).$$

from the determination of $a(q)$ we can easily see the connection with the structure factor (6)

$$a(q) = NS^*(\mathbf{q})S(\mathbf{q}). \quad (12)$$

We can therefore write in place of (7)

$$\rho = C \frac{1}{k_F^4} \int_0^{2k_F} a(q) |w_q|^2 q^3 dq. \quad (13)$$

We calculated ρ^* from formula (13) using a computer, for a number of samples of different thickness. The summation with respect to q was in steps of 0.04168 \AA^{-1} .

Figure 8 shows examples of the $a(q)$ plot. In one case (a) we show the variation of this function with increasing temperature, and in the other case (b) with increasing film thickness. These changes, as shown in the preceding section, are connected with the change of the coordination structure of the "amorphous" bismuth films under the influence of the indicated parameters.

Figure 9 shows plots describing the variation of the calculated values of ρ^* with increasing temperature and film thickness. From a comparison with Figs. 1 and 4 we see that good agreement is observed (at least qualitatively) between the calculated and observed $\rho(T)$ and $\rho(L)$. The numerical discrepancy (by an ap-

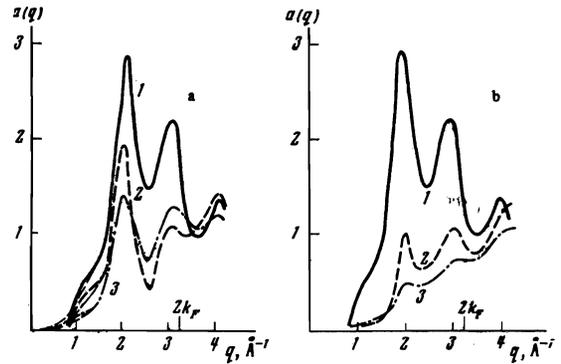


FIG. 8. Variation of the function $a(q)$ with the temperature (a) and with the thickness (b) of low-temperature bismuth films. a—Thickness $\sim 16 \text{ \AA}$, temperature: 1—4.5; 2—22; 3—92°K. b—Temperature 4.5°K, thickness, \AA : 1—16; 2—115; 3—450.

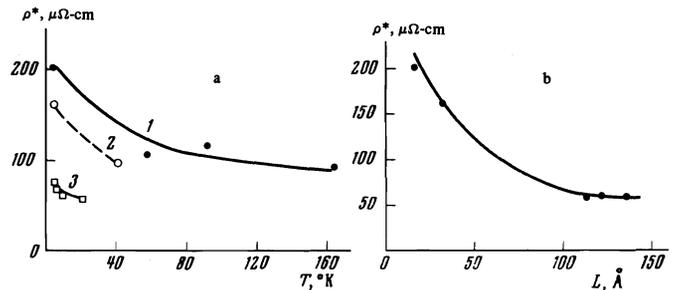


FIG. 9. Dependence of the resistivity on the temperature (a) and thickness (b) of low-temperature bismuth films. The values of ρ^* were calculated from formula (13). a—Thickness, \AA : 1—16; 2—32; 3—290. b—Temperature 4.5°K.

proximate factor of 4) can be due to calculation errors. Among the possible sources of errors are:

- 1) The approximate character of the table for the form factor.
- 2) The use of the value of Ω_0 for crystalline bismuth.
- 3) The deviation of the effective valence from $Z = 5$.
- 4) The vanishing of the function $a(q)$ at $q = 0.4 - 0.8$ rather than at $q \rightarrow 0$, as a result of the peculiarities of the procedure used to eliminate the incoherent background from the diffraction pattern (we note, however, that the absence of an initial section of the function $a(q)$ should not affect the calculations very strongly, since the integrand contains the strong factor q^3 , the integration interval is relatively large and includes two diffraction maxima).

The main cause of the numerical discrepancy between the calculated and experimental values of the resistivity of the investigated objects is, in our opinion, the deviation of the effective mass from the mass of the free electron (the formula for the constant C contains the mass in the form m^2). For the low-temperature phase of bismuth in films, which, as is well known, is a superconductor with a strong electron-phonon interaction, one should expect the effective mass to be larger than that of the free electron. Thus, at $m^* \approx 2m_0$, the discussed numerical discrepancy is eliminated. Zavaritskii obtained^[19] by means of tunnel measurements $m^* \sim 3.7m_0$ for "amorphous" bismuth films.

Thus, our calculations show that irreversible variations of the electric properties of low-temperature bismuth films of small thickness with increasing temperature, and also the dependence of the resistivity on the thickness, are determined mainly by changes in the coordination structure.

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