

# Connection between the superconducting properties and the structure of "amorphous" low-temperature bismuth films

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We investigate the change of the critical superconducting-transition temperature of "amorphous" bismuth films obtained by condensation of molecular beams on substrates at helium temperature, under the influence of heating (annealing) to various temperatures in the region where the amorphous phase exists. Besides a lowering of the resistivity  $\rho$  [1], we observed a lowering of  $T_C$ . Low-temperature electron-diffraction studies have shown that the coordination structure of amorphous bismuth films is layered by heating (the disorder increases), and also varies in time when kept at the condensation temperature. In the latter case the rearrangement of the structure is accompanied by a small growth of the resistance and of  $T_C$ . Calculations using the data for the structure factor and the atomic-density radial-distribution function make it possible to connect the changes of  $\rho$  and  $T_C$  with the changes of the coordination structure. To determine the character of the behavior of  $T_C$ , calculations are made of the dispersion curves of quasiphonon excitations, and the values of the electron-phonon interaction parameter  $\lambda$  are determined.

We have previously considered [1] the electric properties and structural characteristics of "amorphous" bismuth films obtained by condensing a molecular beam on a substrate cooled to helium temperature. It is known that such films have good electric conductivity (higher than films of the ordinary rhombohedral bismuth modification), as well as superconductivity with  $T_C \sim 5-6^\circ\text{K}$  [2,3]. An investigation of the electric properties of amorphous bismuth films of small thickness has revealed that when the temperature is raised, their resistance decreases noticeably and irreversibly, and that this change is stronger the smaller the film thickness. On the basis of the structure data obtained with the aid of low-temperature electron diffraction, it was possible to show that the change of the resistance upon heating is due to a considerable degree to a realignment of the coordination structure [1]. When the thickness is varied, the structure of films obtained at helium temperatures likewise does not retain the same type. This explains the observed dependence of the resistivity on the thickness.

The electron-diffraction patterns make it possible to obtain both the atomic-density radial-distribution function, which describes the coordination structure, and the structure factor  $a(q)$ :

$$a(q) = \frac{1}{N} \left| \sum_j \exp(iq\mathbf{r}_j) \right|^2 \quad (1)$$

( $N$  is the number of atoms). On the basis of the experimentally obtained structure factor, in accordance with Ziman's theory [4], it is possible to calculate the resistance of noncrystalline matter. Ziman's formula is of the form

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

$$C = 3\pi m \frac{\Omega_0}{8\hbar e^2 \epsilon_F}, \quad \epsilon_F = \frac{\hbar^2 k_F^2}{2m}, \quad k_F = \left( \frac{3\pi^2 Z^*}{\Omega_0} \right)^{1/3}, \quad (3)$$

$\Omega_0$  is the volume per atom,  $w_q$  is the form factor of the local pseudopotential,  $m$  is the electron mass, and  $Z^*$  is the valence. Our calculations [1] have shown that the functions  $\rho(T)$  and  $\rho(L)$  obtained in this manner

agree qualitatively with the experimentally observed ones.

We consider in this paper the superconducting properties of low-temperature bismuth films—mainly the connection between the critical temperature and the coordination structure.

## PROCEDURE AND EXPERIMENTAL OBSERVATIONS

The procedure used to obtain the samples, to perform the electric measurements, and to reduce the diffraction data was similar to that used earlier [1]. Bismuth 99.999% pure was condensed on a substrate of polished sapphire single crystal. The substrate was placed in a vacuum chamber, on the bottom of a copper vessel with liquid helium; thermal contact was via a layer of indium-gallium alloy. A vacuum  $\sim 5 \times 10^{-8}$  Torr was attained in the chamber by means of a condensation helium pump.

The sample configuration (a narrow strip with "whickers" spaced 2 mm apart and extending to the contact areas) ensured the possibility of performing precision measurements of the resistance by a potentiometer method (using a R-345 potentiometer). The sample was a stepped condensate; this made it possible to follow simultaneously the variation of the properties of a series of films of different thickness. The superconducting-transition curves were plotted point by point at temperature intervals  $\sim 0.02-0.05^\circ\text{K}$ . Temperature variation of the small vessel with the substrate contained in it was effected either by pumping off helium vapor (at  $T < 4.2^\circ\text{K}$ ) or by using a heater to balance the cooling action of a large helium vessel that served as a condensation pump (at  $T > 4.2^\circ\text{K}$ ). The substrate temperature was measured with an Allen-Bradley carbon resistor.

The critical temperature was determined from the transition curves in accordance with the criterion  $R/R_H = 1/2$ . We note that the other method employed, namely extrapolation of the transition curve to the point where the conductivity vanishes, gives values of  $T_C$  that are close to those obtained in accordance with the chosen

criterion. The homogeneity of the transition in amorphous bismuth films was demonstrated by our earlier results [5].

The films for the electron-diffraction studies were condensed inside an electron-diffraction apparatus equipped with low-temperature attachment. The substrates were oxidized aluminum films. The apparatus was evacuated with a condensation pump to  $\sim 8 \times 10^{-7}$  Torr. In a number of cases, a sample for electric measurements was condensed simultaneously with the sample for the structure investigation. The temperature- and resistance-measurement techniques were similar in this case to those described above.

The purpose of the experiments was to determine the character of the variation of the critical temperature in connection with the irreversible changes of the coordination structure of amorphous bismuth films in the course of heating. These changes are difficult to discern directly on the diffraction pattern, inasmuch as the distributions of the electron-scattering intensity  $I(q)$  are of the same type for films heated to different temperatures. The difference becomes appreciable for the coherent intensity  $I_k$  normalized to the squared atomic factor  $f^2$ , i.e., for the function  $a(q) = I_k/f^2$ .

By using the function  $i(q) = a(q) - 1$  it is possible to reconstruct the radial distribution of the atomic density of the amorphous substance

$$4\pi r^2 u(r) = 4\pi r^2 u_0 \left\{ 1 + \frac{1}{2\pi^2 u_0} \int_0^\infty q^2 i(q) \frac{\sin(qr)}{qr} dr \right\} \quad (4)$$

$$= 4\pi r^2 u_0 \{1 + g(r)\}$$

( $u_0$  is the average atomic density).

Figure 1 shows the variation of the atomic-density radial-distribution curves with increasing temperature, for a bismuth film 32 Å thick. The initial state for small-thickness films is characterized by the presence of a number of clearly pronounced coordination spheres (the oscillation amplitude of the function  $g(r)$  is large). This is evidence of the existence of a rather high degree of structure order in the immediate atomic environment. With increasing temperature, the degree of structure ordering decreases, the first coordination maximum broadens noticeably, and the coordination number changes. In this state, the structure is similar to the typical stationary structure existing in thicker bismuth films ( $L > 100$  Å). The low-thickness films were heated in a wide range (up to 100–150°K at  $L < 50$  Å); this led to a strong smearing of the coordination structure. Information on the change of the coordination numbers and on the half-width  $A_{1/2}$  of the first maximum is given for a number of samples in Table 1. For thicker layers, the temperature region where the amorphous state exists is limited, but even in these limits (up to 30–40°K), a certain smearing of the coordination structure accompanies the heating, but without a change in the principal characteristics of the structure.

To determine the influence of the structure on the critical temperature of the superconducting transition, we heated a series of films of different thicknesses to different annealing temperatures. After each rise in temperature, the sample was cooled to determine  $T_c$ , followed by a new heating to a higher temperature. In all experiments of this type we observed a lowering of the critical temperature under the influence of the

FIG. 1. Plots of the radial distribution of the atomic density in a low-temperature bismuth film 32 Å thick at temperatures: 1–5.4, 2–33, 3–41, 4–96°K.

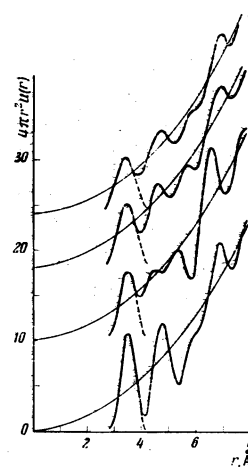


TABLE I. Radii  $r$  of coordination spheres and coordination numbers  $n$  for low-temperature bismuth films.

Thickness, Å	T, °K	$r_1$	$n_1$	$r_2$	$n_2$	$r_3$	$n_3$	$r_4$	$n_4$	$A_{1/2}^\infty$
16	4.6	3.8	9	—	—	5.1	11	6.6	~21	—
	22	3.53	8	4.6	9	5.5	5	6.6	~18	0.68
	92	3.65	5.5	4.8	10	6.6	—	7.3	—	1.29
	151	3.8	6	4.8	—	—	—	—	—	1.63
32	5.4	3.55	7	4.78	9	5.9	9	7	~24	0.63
	33.5	3.53	5.8	4.6	7	5.5	10	6.7	~20	0.87
	41	3.5	6.1	4.7	8.8	5.8	12	7	~25	0.96
	96	3.5	5.5	4.7	9	5.9	12	7	~22	1.05
70	4.5	3.45	6	4.67	8.4	5.7	8	6.7	~20	0.9
120	4.6	3.42	6.2	4.6	8	5.5	7.8	6.7	~20	0.76
	17.5	3.47	5	4.63	8	5.5	8	6.7	~19	0.63
	24.5	3.43	5.8	4.67	8.5	5.5	8	6.6	~19	0.9
	35	3.43	6	4.6	7.4	5.5	8	6.7	~20	0.96
	39.5	3.45	5.9	4.62	7.5	5.45	8	6.7	~20	1.09
290	4.65	3.5	5.3	4.7	8	5.7	10	6.9	~22	0.78
	4.7; 0'	3.55	7	4.5	8	5.5	9	6.6	~18	—
450	12'	3.43	4	4.5	6	5.3	7	—	—	—
	18'	3.53	4.7	4.57	7.2	5.3	7.5	6.6	—	—
	30'	3.5	4.4	4.5	6.8	5.5	10	6.5	~22	—

\*Holding time (minutes).

TABLE II. Change of critical temperature of amorphous bismuth films after heating to different temperatures.

Thickness, Å	Heating temperature, °K			
	4.2 (initial)	22	40	68
194	6.0	—	—	—
124	5.78	5.65	—	—
110	5.73	5.63	—	—
50	5.25	5.22	5.21	—
14	4.22	4.17	4.16	4.12

heating. The results of one of the experiments are shown in Table 2.

The problem under discussion includes also the interesting phenomenon of the time variation of  $T_c$ . Lazarev et al. [6] have observed that superconductivity in low-temperature bismuth films becomes manifest not immediately after condensation, but after holding at temperature for a certain period of time. We have also observed this phenomenon. Postnikov [7] investigated the dependence of the required holding time on the film thickness. It turned out that with increasing  $L$  the time required for superconductivity to appear increases (2, 4, and 22 min at  $L \sim 400, 500,$  and  $1000$  Å, respectively). The appearance of superconductivity, in our opinion, is connected with the growth of  $T_c$  with time under the influence of the structure realignment. At some instant of time,  $T_c$  reaches a value exceeding the

substrate temperature in this experiment, and the film becomes superconducting.

Evidence of the structure changes in thick bismuth films after holding at temperature is found in a noticeable change in the diffraction pattern. Figure 2 shows the time variation of the  $I(q)$  curves. The structural changes are accompanied by an increase in the coherent background and by a change in the relative intensity of the diffraction maxima. This is evidence that the new coordination structure does not appear simultaneously in the entire volume, and that the intermediate state is inhomogeneous. The plots of the radial distribution have shown that the initial structure, similar to the structure in thin layers, is gradually converted into a typical structure. Naturally, this restructuring should be accompanied by a change in resistivity.

We recorded the time variation of the resistivity of films obtained in the electron-diffraction apparatus simultaneously with the films used for the diffraction study. From the function  $a(q)$  determined from the diffraction pattern (Fig. 2b) it is possible to determine the theoretical values of the resistivity as given by Ziman's formula (2).

Figure 3 shows plots of resistivity against time, registered either by direct measurements (dashed curves) or calculated from formula (2) (solid curves), for samples 375 and 450 Å thick. The relative changes of the resistivity differ somewhat in these cases, but the general character of the variation of  $\rho$  is similar. We can therefore conclude that the time variation of the film resistivity and accordingly the growth of  $\rho$  are determined by the realignment of the coordination structure.

It can be noted that the changes of  $T_C$  correlate with the changes of the resistivity, both in structural changes under the influence of annealing and in processes that occur during the holding at temperature. One can, however, cite an example in which this correlation is violated. Thus, the resistivity of amorphous bismuth films

increases with decreasing thickness (at  $L < 200$  Å)<sup>[11]</sup>, yet the critical temperature decreases<sup>[3,5,7]</sup> (see also Table 2). As a possible explanation of this phenomenon, we resorted in<sup>[5]</sup> to the notion that  $T_C$  is influenced by fluctuations of the order parameter and of the electromagnetic field. According to Kulik<sup>[8]</sup>, the influence of fluctuations of the electromagnetic field may turn out to be quite appreciable, and at the observed film resistances, according to the estimates of<sup>[5]</sup>, the fluctuations lower  $T_C$  by an amount close to that observed in experiment, but still insufficient to describe fully the  $T_C(L)$  dependence.

## CONNECTION BETWEEN SUPERCONDUCTING PROPERTIES OF NONCRYSTALLINE SUBSTANCES WITH THE STRUCTURE

The available experimental data<sup>[9-11]</sup> on the tunnelling characteristics of low-temperature amorphous condensates of bismuth offer evidence of the presence of a strong electron-phonon interaction in these objects. This interaction, as is well known<sup>[12-14]</sup>, leads to a renormalization of the states of the electrons, the renormalization coefficient being

$$Z = 1 + \lambda. \quad (5)$$

McMillan<sup>[15,16]</sup> has demonstrated within the framework of the theory of strong-coupled superconductors that

$$\lambda = 2 \int \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega, \quad (6)$$

where  $\alpha^2(\omega)$  is the electron-phonon-interaction parameter,  $F(\omega)$  is the density of states of the lattice-vibration spectrum,

$$T_c = \frac{\langle \omega \rangle}{1.20} \exp \left[ - \frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \quad (7)$$

$$\langle \omega \rangle = \int \alpha^2(\omega)F(\omega) d\omega / \int \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega, \quad (8)$$

where  $\mu^*$  is the dimensionless Coulomb pseudopotential. Formula (7) was obtained by solving the Éliashberg equation; the form of the phonon spectrum was assumed in this case similar to the form of the phonon spectrum of niobium.

It should be noted that the parameters needed to determine  $T_C$  in accordance with formula (7) can be determined from the tunnel characteristics of the metals. The numerical calculations show good agreement between theory and experiment<sup>[9-11, 14]</sup>.

Direct calculation of  $\lambda$  and  $T_C$  in accordance with formulas (6) and (7) is quite difficult, since this calls for knowledge of the total aggregate of the characteristics of the electron-phonon system for a given particular metal. Such a calculation can be carried out, however, for certain simple models of an electron-phonon system. In particular, in the pseudopotential method, assuming a spherical Fermi surface and a local approximation for the pseudopotential, one can obtain<sup>[17,18]</sup>

$$\alpha^2(\omega)F(\omega) = N^{-1} \sum_{\nu} \int \frac{d^3q}{(2\pi)^3} L_{\nu}(q) \delta(\omega - \omega_q^{\nu}), \quad (9)$$

$$L_{\nu}(q) = \frac{1}{4} \frac{m}{M} \frac{|qe(q, \nu)|^2}{k_{\nu} q \omega_q^{\nu}} |w_q|^2, \quad (10)$$

where  $\nu$  is the polarization,  $m$  is the electron mass,  $M$  is the ion mass,  $\epsilon(q, \nu)$  is the polarization vector, and the integral in (9) is taken over the Fermi surface. Using (9) and (10), we can obtain from (6)

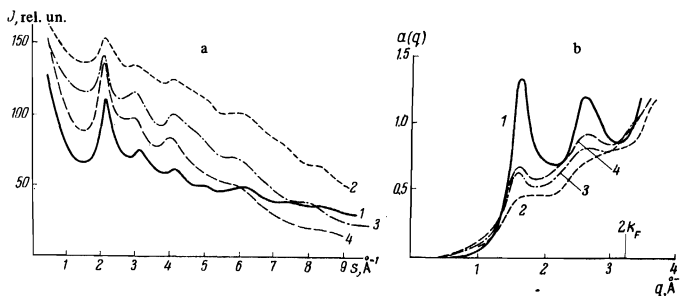


FIG. 2. Time variation of the diffraction pattern (a) and of the structure factor of a bismuth film 450 Å thick (b): 1—immediately after condensation, 2—6 minutes later; 3—12 minutes later, 4—18 minutes later.

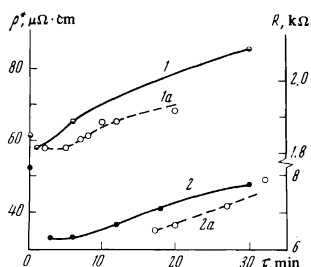


FIG. 3. Change of resistivity with time for bismuth films 375 Å (curve 1a) and 450 Å (curve 2a) thick. The continuous curves 1 and 2 correspond to calculations based on formula (2).

$$\lambda = \frac{N(0)}{2Mk_F^2} \int_0^{2k_F} \frac{|w_q|^2 q^3 dq}{\omega^2} \quad (11)$$

where  $N(0)$  is the density of states on the Fermi surface and  $\omega(q)$  is the frequency of the longitudinal oscillations. In the derivation of (11), only the normal processes in the electron-phonon interaction were taken into account.

To verify the assumption that changes in the coordination structure of amorphous bismuth films influence  $T_C$ , we can use for  $\lambda$  a formula of the type of (11) (we note that it is similar to Ziman's formula (2) for  $\rho$ ). The dependence of  $\lambda$  on the coordination structure is not revealed explicitly in formula (11). It can be assumed, however, that the coordination structure should influence the dispersion of  $\omega_2$  and thus influence also the value of  $\lambda$ .

It should be noted that the structure of amorphous bismuth is similar to the structure of a liquid in the sense that in either case there is no lattice periodicity and there is only a short-range coordination of the atoms. Ordinary phonon theory is not suitable for such systems. In such a medium, only collective excitations with wavelength much larger than the interatomic distances (acoustic waves) can propagate without attenuation. For collective motions with short wavelength, an important role is played by the microscopic structure of the object. The question whether collective motions are possible in disordered systems can be answered by resorting to the experimental data.

Experiments on inelastic neutron scattering [19-21] have shown that coherent scattering from short-wave fluctuations in liquid metals is similar to neutron scattering from a solid near the melting point. The hypothesis was advanced that the observed short-wave elementary excitations in simple liquids are similar to phonons in crystalline bodies. The spectra of elementary excitations have been theoretically investigated most intensively in such disordered systems as quantum liquids or liquid helium [22,23]. At the same time, both experimental [19-21] and theoretical [24-27] studies showed that collective motions in simple liquids have dispersion relations similar to the dispersion law of phonons and rotons for liquid helium (Fig. 4).

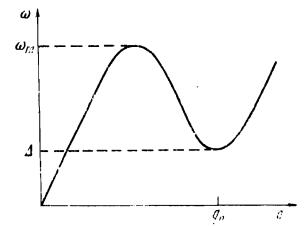
A theoretical analysis of the collective motions in liquids must take two circumstances into account: the absence of order and the self-diffusion of the atoms. In the case of amorphous solids, the second circumstance need not be considered. Under these conditions, theoretical calculations [24-27] performed in the harmonic approximation yield the following expression for the dispersion of the longitudinal excitations

$$\omega_q^2 = \frac{v_0}{M} \int \frac{\partial^2 v}{\partial z^2} g(r) (1 - \cos qz) dr, \quad (12)$$

where  $v(r)$  is the paired interatomic-interaction potential and  $g(r)$  is the radial-distribution function normalized to unity (see formula (4)).

The influence of the degree of order of the atoms in a noncrystalline body on the form of the function  $\omega(q)$  was considered in detail in [27]. In a crystal,  $\omega(q)$  is a periodic function of  $q$  and  $\omega = 0$  at a certain  $q = q_0$  ( $q_0$  is the reciprocal-lattice vector). In the absence of periodicity, however,  $\omega(q)$  remains finite at  $q = q_0$  and equal to  $\Delta$  (Fig. 4). The value of  $\Delta$  decreases with increasing degree of order and becomes equal to zero in

FIG. 4. General form of the  $\omega(q)$  curve for a noncrystalline body.



the limit of total ordering, corresponding to formation of the crystal lattice.

It should be noted that expression (12) or modifications thereof have been obtained by a number of authors by different methods [24,26,27]. This relation clearly points to an influence of the coordination structure, determined by  $g(r)$ , on the form of the dispersion law of the collective excitations. For a crystal, expression (12) goes over into the usual dispersion relation for longitudinal phonons in a crystal. Thus, formula (12) is a general dispersion relation of high-frequency elementary excitations for collective motions of arbitrarily disposed atoms.

We note that formula (11) also follows from the relation obtained by Maksimov [28] for  $\lambda$  in the case of a crystal with defects:

$$\lambda = \frac{N(0)}{\hbar} \int_0^{2k_F} \frac{|w_q|^2 q dq}{k_F^2} \int_0^\infty \frac{S_1(q, \omega) d\omega}{\omega}, \quad (13)$$

$S_1(q, \omega)$  is that part of the dynamic structure factor  $S(q, \omega)$  which takes into account phonon creation and annihilation processes. For an ideal crystal we have [29]

$$S_1(q, \omega) = \sum_{\nu} \frac{\hbar}{2M\omega_q^{\nu}} |qe(q, \nu)|^2 [\delta(\omega + \omega_q^{\nu}) n_q^{\nu} + \delta(\omega - \omega_q^{\nu}) (n_q^{\nu} + 1)], \quad (14)$$

$$n_q^{\nu} = \left[ \exp\left(\frac{\hbar\omega_q^{\nu}}{kT}\right) - 1 \right]^{-1}.$$

According to (24), a contribution to  $S_1(q, \omega)$  of a noncrystalline body is made only by longitudinal modes, with

$$S_1(q, \omega) = \frac{\hbar q^2}{2M\omega_q} \{ (n_q + 1) \delta(\omega - \omega_q) + n_q \delta(\omega + \omega_q) \}. \quad (15)$$

When either (14) or (15) is substituted in (13), we obtain relation (11) for  $\lambda$ . This was the formula we used for the numerical calculation of  $\lambda$ .

## CALCULATION RESULTS AND DISCUSSION

We calculated with the computer the dispersion curves  $\omega(q)$  in accordance with formula (12) for a series of amorphous bismuth films. For the functions  $g(r)$  we used curves plotted from the electron-diffraction data. The functions  $g(r)$ , plotted in steps of  $\Delta r = 0.1 \text{ \AA}$ , were specified in the interval from 2.8 to 6  $\text{\AA}$ , i.e., the calculations covered three coordination spheres (see Fig. 1). For the function  $v(r)$  we chose the paired potential of the interaction between the ions [30]:

$$v(r) = \frac{\Omega_0}{\pi^2} \int_0^\infty F(q) \frac{\sin qr}{qr} q^2 dq + \frac{Z^2 e^2}{r}, \quad (16)$$

where  $F(q)$  is a characteristic function whose values, calculated with the aid of the Heine-Abarenkov model potential, were taken from [31].

The results of the calculations of the dispersion curves are illustrated by two examples in Fig. 5. The form of the obtained curves corresponds to the previ-

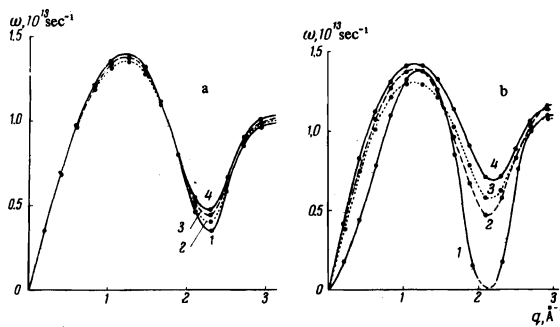


FIG. 5. Plot of  $\omega(q)$  calculated from formula (12) on the basis of the plotted atomic-density radial distributions  $g(r)$ . a—Film 120 Å thick; curves 1, 2, 3, 4 correspond to temperatures 4.6, 24.5, 35, and 39.5 °K. b—Film 16 Å thick; curves 1, 2, 3, and 4 correspond to temperatures 4.5, 22, 92, and 151 °K.

ously described predictions of the theory. The quantitative parameters of the curves do not contradict the known experimental data. Thus, the maximum frequency turned out to be  $(1.4-1.5) \times 10^{13} \text{ sec}^{-1}$ , and according to Zavaritskiĭ's tunnelling data<sup>[9]</sup>, the end point of the reconstructed phonon spectrum corresponds to  $\omega_m \sim 1.8 \times 10^{13} \text{ sec}^{-1}$ , while Ewert<sup>[32]</sup> cites for amorphous bismuth films a Debye temperature 77 °K, corresponding to  $\omega_D \sim 1 \times 10^{13} \text{ sec}^{-1}$ . The slope of the initial linear section yields a sound velocity  $s \sim 1.9 \times 10^5 \text{ cm/sec}$ , which seems reasonable.

We are interested primarily in the change in the shapes of the dispersion curves when the coordination structure is changed. Figure 5a shows plots of  $\omega(q)$  for a bismuth film 120 Å thick at different temperatures. It is seen from the figure that with increasing temperature, the ascending and descending branches of the  $\omega(q)$  curves remain practically unchanged, but that differences appear in the regions of the maximum and of the minimum, namely, the frequency  $\omega_m$  decreases somewhat, while  $\Delta$  increases. This change in the dispersion curves reflects the smearing of the coordination structure of amorphous bismuth films when heated. These changes turned out to be more substantial in thinner samples. Figure 5b shows plots of  $\omega(q)$  for a film  $\sim 16$  Å thick. Curve 1 corresponds to the initial state and has a configuration corresponding to a rather ordered structure ( $\Delta \sim 0$ ). With increasing temperature,  $\Delta$  increases. This change of the  $\omega(q)$  curves should lead, in accordance with (11), to a decrease of  $\lambda$ , since the changes of  $\omega_q^2$  are more significant at large  $q$  (owing to the factor  $q^3$ ).

These assumptions were confirmed by direct computer calculations in accordance with formula (11). The results of the calculations of  $\lambda$  for films with different thicknesses are given in Table 3. For all three thicknesses represented here,  $\lambda$  decreases with increasing annealing temperature. The decrease of  $\lambda$ , in accordance with (7), should lead to a lowering of  $T_c$ . Thus, the experimentally observed decrease of  $T_c$  after the heating of the bismuth films to different temperatures is explained by the fact that small changes in the coordination structure alter the characteristics of the phonon spectrum.

We present the calculated values of  $\lambda$  for bismuth films 450 Å thick held for a time  $\tau$  at the condensation temperature (4.55 °K):

$\tau, \text{min} = 0$	6	12	18	30
$\lambda = (14.1)$	1.04	2.2	2.08	2.27

TABLE III. Values of the parameter  $\lambda$ , calculated from formula (11) on the basis of data for the coordination structure of amorphous bismuth films.

$L, \text{Å}$	$T, \text{°K}$	$\lambda$	$L, \text{Å}$	$T, \text{°K}$	$\lambda$	$L, \text{Å}$	$T, \text{°K}$	$\lambda$	$T_c$ (calculated)
16	4.55	(9.38)	32	5.4	2.7	120	4.65	2.51	5.53
	22	2.18		33	2.02		24.5	2.32	5.24
	92	1.90		41	1.84		35	2.23	5.14
	151	1.47		96	1.78		39.5	2.04	4.84

We see that in this case the values of  $\lambda$  increase noticeably with increasing holding time, resulting in an increase of  $T_c$  and explaining the appearance of superconductivity after a certain time interval following the end of the condensation.

The values of  $\lambda$  obtained in the calculation for the initial structure of the bismuth films turned out to be anomalously high and did not agree with the realistically possible ones (which are given in parentheses). It appears that the model of almost free electrons does not apply to the initial structure, and furthermore that other quantities (besides the phonon spectrum), such as  $N(0)$  and  $k_F$ , i.e., the electron-spectrum characteristics that enter in formula (11), can also be different for such a structure.

The values of  $\lambda$  obtained by us for the typical structure of amorphous bismuth films agree well with the values determined in tunnelling experiments. Thus, for amorphous bismuth films  $\lambda = 2.7$  and  $\mu^* = 0.1$  according to<sup>[9]</sup>,  $\lambda = 2.46$  and  $\mu^* = 0.1$  according to<sup>[10]</sup>, and  $\lambda = 1.85$  and  $\mu^* = 0.01$  according to<sup>[11]</sup>.

From the obtained values of  $\lambda$  and from formula (7) it is also possible in principle to calculate the critical temperature. But this calls for knowledge of  $\langle \omega \rangle$  and  $\mu^*$ , which are unknown and possibly change with changing coordination structure. We have estimated  $T_c$  only for a sufficiently thick bismuth film, inasmuch as in this case it appears that the published data<sup>[9-11]</sup> for the values of  $\langle \omega \rangle$  and  $\mu^*$  can be used. The calculated  $T_c$  at  $\mu^* = 0.1$  and  $\langle \omega \rangle = 0.434 \times 10^{13} \text{ sec}^{-1}$  are given in Table 3 for a film 120 Å thick. The decrease of the calculated  $T_c$  with increasing annealing temperature agrees qualitatively with the experimental results, although its change turned out to be much more appreciable than experimentally observed.

In Table 3 one can note also the existence of a thickness dependence of  $\lambda$  for annealed bismuth films; this dependence agrees qualitatively with the experimental observations<sup>[3,5,7]</sup>. It appears that the lowering of  $T_c$  with decreasing film thickness is governed not only by the influence of the fluctuations, as noted above, but also contains a structural contribution.

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