Superconductivity in polycrystalline bismuth films

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Polycrystalline bismuth films (50–200 Å) possessing superconductivity with $T_c \sim 5$–6 °K are obtained by electric explosion and investigated. The mechanism of formation and stabilization of the superconducting phase is studied. Analysis of the structure and the electrical properties of the films shows that the superconductivity is due to the appearance during crystallization of layers of amorphous bismuth at the grain boundaries, forming a netlike superconducting structure in the plane of the film. Such structures behave like continuous superconducting films.

1. INTRODUCTION

We have observed superconductivity in a number of cases in the study of thin bismuth films produced by the electric-explosion method.[1,2,3] It is well known that ordinary bismuth with its rhombohedral lattice, Bi I, is not a superconductor. The crystalline modifications Bi II – Bi VI, which are formed under pressures above 25 kbar, possess superconductivity with critical temperatures T_c in the interval 3.95 – 8.55°K.[4-6]

Crystalline films of bismuth obtained by thermal evaporation onto substrates that are at room temperature do not exhibit superconductivity. Superconducting transitions with $T_c \sim 6$°K were observed in amorphous bismuth films condensed on a substrate cooled to the temperature of liquid helium.[7,8] Upon heating above a certain temperature determined by the thickness of the film (4.2 – 190°K for L = 200 – 15 Å[9] and for T = 4.2°K L > 600 Å[10]), the amorphous phase is unstable and undergoes an irreversible transition to the nonsuperconducting modification Bi I.

Bismuth films obtained by the electric-explosion method at room substrate temperature had $T_c \sim 5 - 6$°K. The superconducting transitions were completely reversible in multiple heatings to 300°K and coolings to 2.5°K. Our purpose here was to study the superconducting properties of the films and clarify the nature and mechanism of formation and stabilization of the superconducting phase under conditions of film formation by electric explosion.

2. EXPERIMENTAL METHOD

To obtain films by the electric-explosion method, we used a Bi wire (99.9999%) of diameter 0.1 – 0.2 mm and length 30 – 40 mm. Condensation was carried out in a vacuum of $10^{-5} - 10^{-6}$ Torr on unheated (300°K) 10 × 80 mm glass substrates. The treatment of the substrates, the measurement of film thickness, and the electric-explosion regime were described previously.[11] The directivity diagram of the dispersion of the vapors in the electric explosion assured the formation of samples of varying thickness in the form of wedges with a taper $\Delta L \sim 300$ Å. The range of thicknesses investigated was 50 – 700 Å.

Preparation of the samples for the electric measurements was by the method used earlier.[11] The resistance of the films was measured by a null method for currents no larger than 100 μA. The temperature dependences of the specific resistance ρ and the magnetoresistance $\Delta\rho_H/\rho_0$ were obtained in the temperature range 2.5 – 300°K at magnetic fields H ≤ 4000 Oe. Temperatures were measured accurate to 0.01°K or better with a germanium transducer.

The structure of the films was investigated on a JEM-7A electron microscope. For analysis of the relief of the surface, we used carbon replicas shadowed with gold; the bulk of the film was studied with the help of transmission microscopy and microdiffraction.

3. EXPERIMENTAL RESULTS

a) The superconducting properties of the films. The temperature dependences $\rho(T)/\rho(6°K)$ are shown in Figs. 1 and 2. Upon lowering the temperature to 6°K, ρ increases monotonically for all films. The films are divided into two types according to the character of the dependence ρ(T) in the range T < 6°K. In films of type I (curve 1, Fig. 1), the monotonic increase in ρ extends to 2.5°K. In films of type II at T ~ 5 – 6°K, the jumps of ρ(T) are spread out over a range ΔT ~ 1 – 3°K (curves 2 – 6 in Figs. 1 and 2). Both complete transition into the superconducting state (Fig. 2) and incomplete transitions with different sizes of the jump in ρ (Fig. 1) are observed. As studies have shown, the incomplete transitions are connected with the non-continuous nature of the superconducting phase in the films and the differ-

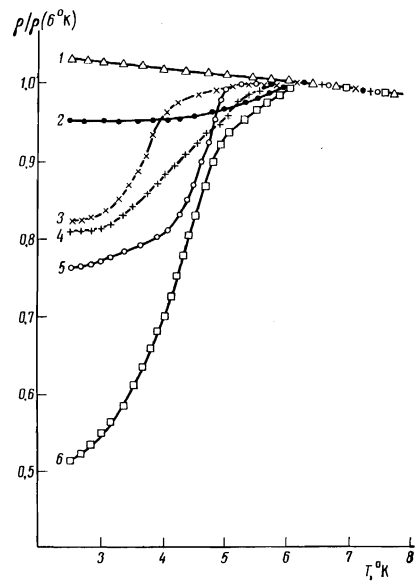

FIG. 1. Dependence of ρ (T)/ρ (6°K) in nonsuperconducting (1) and superconducting (2) bismuth films: The thickness L in Å: 1) 150, 2) 165, 3) 65, 4) 100, 5) 125, 6) 170. Resistance ρ (6°K) × 10^3 Ω-cm: 1) 1.22, 2) 1.65, 3) 2.72, 4) 1.47, 5) 1.73, 6) 1.32.

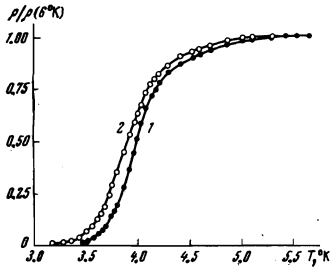

FIG. 2. Superconducting transitions at H = 0 (1) and $H_\perp$ = 4000 Oe (2); L = 95 Å, ρ (6°K) = 1.20 × 10^{-3} Ω-cm.

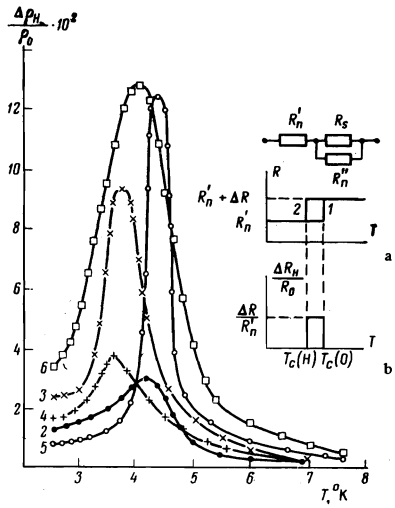

FIG. 3. Curves of magnetoresistance of superconducting films vs. temperature. The film numbers correspond to those in Fig. 1. Resistance (a) and the magnetoresistance (b) of sample composed of superconducting R_S and nonsuperconducting R'_n, R''_n parts as functions of T.

ence in the jumps of ρ is due to the quantity and the inhomogeneous distribution of this phase. Complete transitions were observed over portions of length $\lesssim$ 1 mm. For larger dimensions, the transitions were, as a rule, incomplete. Of 125 films studied, 10% possessed superconductivity. All the superconducting films had thicknesses in the range ~ 50 – 200 Å.

Investigations of the superconducting transitions based on the resistance in magnetic fields up to 4000 Oe, directed perpendicular ($H_\perp$) and parallel ($H_\parallel$) to the plane of the film, showed that the films possess high critical fields. The perpendicular field $H_\perp$ = 4000 Oe shifts the curves of the superconducting transitions by an insignificant amount ($\Delta T \sim 0.1 - 0.2°K$) in the direction of lower temperatures. The parallel field up to 4000 Oe had no effect on the transitions. For films with complete superconducting transitions, the $\rho(T)$ dependences for H = 0 and $H_\perp$ = 4000 Oe are shown in Fig. 2. The curves $\rho(T)$ in $H_\perp$ for films with an incomplete transition were shifted in a similar way.

The effect of $H_\perp$ on the incomplete superconducting transitions is shown most graphically in the dependence of the magnetoresistance $\Delta\rho_H/\rho_0$ on the temperature (Fig. 3). These plots have the characteristic shape of bell curves. This behavior of $\Delta\rho_H/\rho_0$ in films with an incomplete transition can be understood if we consider the temperature dependence of the resistance R and the magnetoresistance $\Delta R_H/R_0$ of a sample that consists, because of the discontinuities of the superconducting phase, of nonsuperconducting parts R'_n, R''_n and a part R_S with a sharp superconducting transition (Fig. 3a, b). Upon cooling of such a sample in zero magnetic field, this resistance undergoes a jump by a value

$$\Delta R = R_s/(1+R_s/R_n'')$$

at $T = T_c(0)$ (curve 1, Fig. 3a). If $H \neq 0$, then the jump will take place at a lower temperature $T_c(H) < T_c(0)$ (curve 2, Fig. 3a). Therefore the magnetoresistance of the sample in the temperature interval $T_c(H) < T < T_c(0)$ has a finite value (Fig. 3b):

$$\frac{\Delta R_H}{R_0} = \frac{R(H)-R(0)}{R(0)} \approx \frac{R_s}{R_n'(1+R_s/R_n'')}.$$

Outside of this range, it is equal to zero, since superconductivity is lacking for $T > T_c(0)$ and for $T < T_c(H)$ the superconductivity is not destroyed by the magnetic field. In connection with the smearing out of the superconducting transition in the films studied, the temperature dependence of $\Delta\rho_H/\rho_0$ is smoothed out; however, the characteristic maximum on the curves is preserved. The magnetoresistance is maximal at the temperature corresponding to the inflection point on the curves of the superconducting transitions in a magnetic field.

b) Structure of the films. According to electron-microscopy data, the films are of both types—polycrystalline and of single-layer thickness. Analysis of a large number of electron micrographs has shown the presence of rhombohedral Bi I only. At the same time,

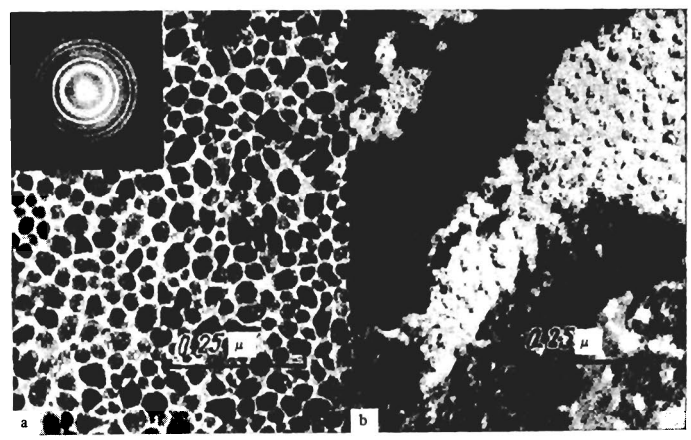

FIG. 4. Structure of nonsuperconducting films: a) transmission picture and microdiffraction; b) replica from surface (dark regions—replica with stripping).

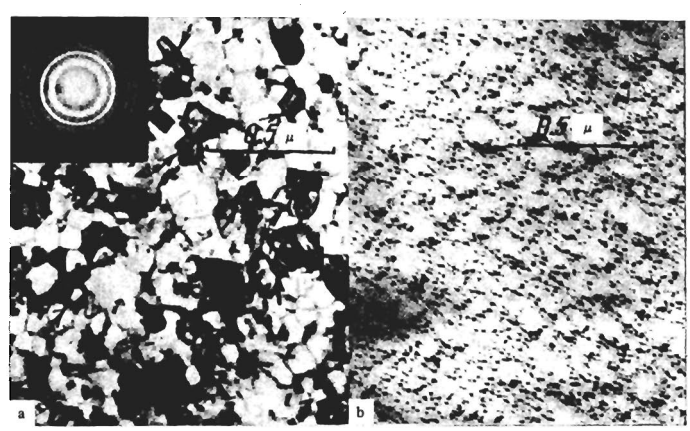

FIG. 5. Structure of superconducting films: a) transmission picture and microdiffraction (the arrows indicate grains with closed extinction contours); b) replica from surface.

the two types of films differ materially in the micromorphology of the crystallites.

In films of type I, the grains had predominantly oval shapes in the plane of the substrate (Fig. 4a) and, judging from the contrast on the replicas with extraction, the surface of such grains is nearly spherical (Fig. 4b). With increase in film thickness, the dimensions of the crystallites increased from 50 – 70 Å at L ≈ 50 Å to 400 – 500 Å at L ≈ 150 Å. A small fraction of the grains in films of this type have crystallographic faceting.

For films of type II, the grain faceting is characteristic, (Fig. 5a). The contrast on the replicas (Fig. 5b) and the extinction thickness contours parallel to the lateral faces of the grains (shown by arrows in Fig. 5a) indicate relatively planar surfaces of the crystallites and the formation of narrow grooves with small dihedral angles along the grain boundaries. It is difficult to estimate the fraction of grains with thickness contours, inasmuch as the appearance of the contours is strongly dependent on the mutual positions of the electron beam and the crystallites. The grooves on the boundaries are absent for some of the faceted crystallites. Moreover, a small fraction of the grains have the shape which is characteristic for the crystallites in films of type I. With increase in the thickness, the dimensions of the faceted crystallites with grooves on the boundaries increase from 200 – 400 Å for L ≈ 50 Å to 900 – 1200 Å for L ≈ 200 Å. For the same thicknesses, the size of the faceted grains without grooves on the boundaries is 2 – 3 times greater, and that of the oval ones smaller 1/4 to 1/8 as large.

Inasmuch as the crystalline structure of the interior of the grains in films of both types corresponds to Bi I, we can assume that the superconducting properties of films of type II are due to the features of the structure of the grain boundaries. Judging by the closeness of the values of T_c in amorphous[7,8] bismuth films and in the films studied, in our case the amorphous phase of Bi is evidently formed along the grain boundaries and stabilized at room temperature. It has not been possible to establish the presence of the amorphous phase along the grain boundaries by means of microdiffraction, because of its relatively small volume. However, the grooves on the grain boundaries indirectly demonstrate their presence.

4. DISCUSSION OF THE RESULTS

The formation of amorphous layers can be explained if we consider the behavior of dislocation centers in the grain boundaries as a function of the temperature. The formation of a liquid phase along the grain boundaries near the melting temperature of bismuth was discovered experimentally by Glicksman and Vold.[12,13] Melting of the grain boundaries is connected with the formation of liquid dislocation centers located on the boundaries, and with their merging at the corresponding angle of disorientation of the grains as a result of the growth of the center radii with approach to the melting point. The radius r_0 of the liquid center is determined as a function of the temperature for an individual rectilinear edge dislocation from the conditions of mechanical and thermodynamic equilibrium of the crystal-dislocation system with the liquid center. Following[13], we can write down the condition of equilibrium in the form

$$P=\frac{\gamma_c}{r_0}-\frac{bE_0}{2\pi r_0^2}, \quad E_0=\frac{Gb}{4\pi(1-\nu)}, \tag{1}$$

$$\int_0^P \Omega_l\, dP=\int_{T_0}^{T} \Delta S_f\, dT, \tag{2}$$

where P is the pressure inside the liquid center at the temperature T, T_0 is the equilibrium temperature, at which P = 0, γ_c is the specific surface energy on the center-crystal boundary, b is the Burgers vector, G the shear modulus, ν the Poisson coefficient, Ω_l the molar volume of the liquid, and ΔS_f the entropy of fusion.

As is seen from Eq. (1), the pressure inside the liquid center is equilibrated by the surface tension on the boundary and the elastic stresses in the crystal outside the dislocation center, which are oppositely directed. It is easy to show that when

$$r_0=r_{0e}=bE_0/2\pi\gamma_c \quad \text{or} \quad r_0\to\infty, \tag{3}$$

these forces cancel one another and the pressure inside the center is equal to zero. Below r_{0e}, the pressure in the center is negative and formation of a Frank dislocation with a hollow center is possible; above, it is positive and the existence of liquid centers is more probable. At $r_{0m} = 2r_{0e}$, the pressure P passes through a maximum. The radii r_{0m} and r_{0e} correspond (see (2)) to a certain extremal temperature T_m and an equilibrium temperature $T_0 = T_e < T_{melt}$, which will be defined later. The temperature T_e was identified in[13] with the melting temperature of the crystal T_{melt}. Such an identification is not physically correct for the following reasons. First, it has been established experimentally by the same authors[12] that melting along the grain boundaries begins at temperatures much lower than the T_{melt} of the crystal as a whole. Second, the existence of liquid dislocation centers of finite radius r_{0e} (see (3)) at T_{melt} is of low probability. It is more natural to assume that an unbounded growth of the liquid centers takes place around T_{melt}, i.e., $r_0 \to \infty$. Moreover, the solution given in[13] for $T \le T_e$ does not follow from the set (1), (2). Therefore, it is necessary to consider the behavior of the center over the whole range of temperatures $T \le T_{melt}$.

Using the values T_e and T_{melt} for T_0 with account of the sign of the derivative dP/dT from (1), (2), we obtain the temperature dependences P(T) and $r_0(T)$:

$$P=\frac{\Delta S_f}{\Omega_l}(T-T_e), \tag{4}$$

$$r_0=\frac{A}{T-T_e}\left[1-\sqrt{1-B(T-T_e)}\right], \tag{5}$$

for $T \le T_m$;

$$P=\frac{\Delta S_f}{\Omega_l}(T_{melt}-T), \tag{6}$$

$$r_0=\frac{A}{T_{melt}-T}\left[1+\sqrt{1-B(T_{melt}-T)}\right], \tag{7}$$

for $T_m \le T \le T_{melt}$.

$$A=\gamma_c\Omega_l/2\Delta S_f, \quad B=2bE_0\Delta S_f/\pi\gamma_c^2\Omega_l.$$

From the condition of the extremum (P) (1) and formula (7) for r_0 we find the temperature

$$T_m=T_{melt}-1/B \tag{8}$$

and the corresponding maximum pressure in the center

$$P_m=\pi\gamma_c^2/2bE_0. \tag{9}$$

Equating (4) and (6) at $T = T_m$, we determine T_e:

$$T_e = T_{melt} - 2/B. \quad (10)$$

For bismuth, taking $T_{melt} = 544°K$, $\Omega_l = 21.3$ cm^3/mole, $\Delta S_f = 2.1 \times 10^8$ erg/mole-deg, $\gamma_c = 54.5$ erg/cm^2, $b = 4.55 \times 10^{-8}$ cm, $G = 1.2 \times 10^{11}$ dyn/cm^2, and $\nu = 0.33$, we obtain $T_{melt} - T_e \approx 30°K$, $r_{0e} \approx 10$ Å. Figure 6 shows the temperature dependence of r_0 and P over the entire range $T \leq T_{melt}$. It is seen that r_0 increases most significantly near the melting temperature $T_e < T < T_{melt}$.

Overlapping of centers, which leads to their merging with formation of liquid layers along the grain boundaries, evidently sets in at angles of disorientation of neighboring grains

$$\theta \geq b/2r_0. \quad (11)$$

Glicksman and Vold[13] have observed that in the case of contact of the crystal with the melt, the appearance of liquid on the grain boundary is accompanied by a change in the dihedral angle of the groove on it from a finite value not less than 68° to zero. At T_e, formation of a continuous liquid layer sets in for grain angles of disorientation $\theta \geq 15°$. An increase in the temperature should, in accord with (5), (7), (11), lead to merging of the centers at smaller θ, thickening of the liquid layers and melting of the crystal as a whole.

Consequently, for formation of the liquid phase along the boundaries, it is necessary that, at the moment of coalescence of the grains, the temperature of the film be close to the melting temperature ($T > T_e$) and that the grains be disoriented at the corresponding angles. Stabilization of the phase occurs, on the one hand, thanks to the significant increase in the amorphous phase—crystal transition temperature for the thin layer[9] (see also Sec. 1) and, on the other hand, as a result of sufficiently fast cooling of the film, when further processes of crystallization are "frozen"[14] due to the substantial increase in the viscosity of the medium and intergrain layers remain amorphous.

The electric explosion is characterized by high temperatures of condensation, so that crystallization from the liquid layer is possible at sufficiently high cooling rates.[1,2] The presence of grooves with small dihedral angles on the grain boundaries in films of type II indicates realization of the above conditions for formation and stabilization of the amorphous layers, which constitute a netlike superconducting structure branched in the plane of the film. The dimension of the cell of this structure is equal to the size of the grain and the thickness of the wall to the thickness of the amorphous layers, which amounts to ~ 20 Å according to the estimate of r_{0e}. The presence of faceted grains without

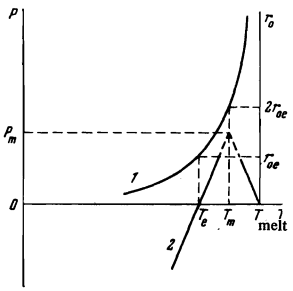

FIG. 6. Temperature curves of radius of dislocation center r_0(1) and of pressure P in center (2).

grooves along the boundaries in the films of type II is due to nonsatisfaction of the condition on the angle of disorientation. Films with such grains are not superconductors. Higher rates of cooling lead to homogeneous crystallization of the liquid film in the diffusion region, with formation of oval grains.[14] In the given case, crystallization takes place at high supercooling ($\Delta T > T_{melt} - T_e$) with high rates of nucleation, and the conditions for formation of amorphous layers at the moment of coalescence of the grains are absent. This explains the fact that nonsuperconducting films of type I are obtained with fine oval grains. Thus the mechanism of formation and stabilization of the superconducting phase of bismuth is very sensitive to the conditions of condensation and crystallization, and can be realized in a narrow range of these conditions. Therefore the formation of a relatively small fraction of films that possess superconductivity is understandable.

Turning to Sec. 2a, we consider the effect of a magnetic field perpendicular and parallel to the plane of the film on the superconducting properties of the netlike structure. As has been noted, the superconducting properties of the films change in $H_\perp$ and do not depend on $H_\parallel$ in the range of fields investigated. This may seem incomprehensible, since $H_\perp$ is directed along the superconducting layers located perpendicular to the plane of the film. It would appear that the critical field in this direction should be significantly greater than $H_\parallel$. Thus, the critical longitudinal field $H_{cF}^{\parallel}$ of a thin continuous film with diffuse boundaries has been calculated by Shapoval[15] near T_c:

$$eH_{cF}^{\parallel}/\hbar c \sim (1 - T/T_c)^{1/2}/(\xi_0 l)^{1/2} l, \quad (12)$$

where l is the thickness of the film and $\xi_0 = 0.18 \times \hbar v_F/kT_c$ is the pair dimension. The transverse field for such a film, $H_{cF}^{\perp}$, can be estimated with the help of the Ginzburg-Landau theory, while the thickness of the film l plays the role of the free path length;

$$eH_{cF}^{\perp}/\hbar c \sim (1 - T/T_c)/\xi_0 l \quad (13)$$

(see, for example,[16]). It then follows that the longitudinal field is much greater than the transverse.

However, for the branched netlike structure formed in the films considered, the situation changes in comparison with an isolated layer. This is seen even in the example of an individual cell, which can be approximated by a thin-walled superconducting cylinder with diffuse boundaries. The critical field along the axis of such a cylinder, near T_c, is equal to

$$eH_1/\hbar c \sim (1 - T/T_c)^{1/2}/(\xi_0 l)^{1/2} R, \quad (14)$$

where l is the thickness of the wall ($l \ll \xi_0$) and R the radius of the cylinder ($R \gg l$). From (12) and (14), we find $H_1 \ll H_{cF}^{\parallel}$. The decrease in the longitudinal critical field in the nonsingly-connected case is a consequence of the additional limitation on the wave function of the Cooper pair, which follows from the requirement of its single-valuedness.

For a netlike superconducting structure with a large number of cells, the critical field is still smaller. Thus, in the limit $\sqrt{\xi_0 l} \gg R$, we can obtain the estimate

$$eH_c^{\perp}/\hbar c \sim (1 - T/T_c)/\xi_0 l, \quad (15)$$

where R is the grain size and l the thickness of the superconducting layer. This expression is the same as that for a superconducting impurity film with free path

l in a transverse magnetic field,[16] i.e., the netlike structure considered behaves, in relation to the magnetic field, as a continuous superconducting film.

The critical field $H_c^{\parallel}$ parallel to the netlike structure can be estimated in the same way as for the continuous impurity film of thickness L (see, for example,[15]):

$$eH_c^{\parallel}/\hbar c \sim (1-T/T_c)^{1/2}/(\xi_0 l)^{1/2}L, \qquad (16)$$

where l is the free path length, $l \ll L$. In our case, l is the thickness of the superconducting layer. It is seen from a comparison of (15) and (16) that $H_c^{\parallel} > H_c^{\perp}$.

In conclusion, we express our gratitude to D. Tess for taking part in the initial stage of the work.

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104