Experimental observation of a superconducting phase with $T_c \simeq 8.5$ K in large-angle bismuth bicrystals

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Superconducting inclusions with a transition temperature $T_c \simeq 8.5$ K, an upper critical field $H_{c2}^{\parallel} \simeq 25$ kOe, and a coherence length $\xi \simeq 120$ Å have been observed near the joining surface of large-angle bicrystals ($32° \leqslant \theta \leqslant 62°$) of bismuth.

The physical properties of bicrystals have attracted particular interest because of the suggestion that an "exciton" mechanism for a high-T_c superconductivity might operate in them.[1,2] Although experimental searches for an exciton superconductivity have not been rewarded with positive results, bicrystals remain convenient materials for studying the superconductivity of twin planes in metals,[3] the electronic properties of space-charge layers in semiconductors,[4] etc.

In this letter we are reporting the observation of superconducting regions in large-angle bicrystals ($36° \leqslant \theta \leqslant 62°$) of pure bismuth. These superconducting regions give rise to anomalies on the temperature dependence of the resistance, $R(T)$, the magnetic field dependence of the resistance, $R(H)$, and the current-voltage characteristics. The temperatures at which the anomalies appear on the $R(T)$ curves and the current-voltage characteristics are essentially the same and equal to the transition temperature T_c found through an extrapolation of the temperature dependence of the upper critical field, $H_{c2}^{\parallel}(T)$. To the best of our knowledge, this is the first report of an observation of stable superconducting properties in bismuth samples at temperatures above 6 K without the use of an external pressure.

The bismuth bicrystals were grown by zone recrystallization with a double seed. The angle between the C_3 axes of the crystallites lay in the range $8° \leqslant \theta \leqslant 62°$. The crystallites were unwound an angle $0 \leqslant \varphi \leqslant 9°$ with respect to each other around the normal to the intercrystallite interface, G (Ref. 5). The measurements were carried out with a direct current ($I \perp G$) by the standard four-contact method over the temperature range 4.2–300 K.

On the basis of the value of the angle θ and the shape of the temperature dependence of the resistance (Fig. 1), we classified the samples, somewhat arbitrarily, in two categories. The bicrystals of category A usually had crystallite inclination angles above 30° and a nonmonotonic $R(T)$ curve. The bicrystals of category B ($\theta \leqslant 30°$) exhibited the metallic temperature dependence of the resistance ($dR/dT > 0$) which is characteristic of homogeneous bulk samples of Bi. It follows from Fig. 1 that the ratios $\alpha = R(300\text{ K})/R(10\text{ K}) \simeq 1$–$1.5$ are small for the samples of category A, and the derivative dr/dT changes sign (there is a singularity of the minimum type) at $T = T_{\min} \simeq 150$–180 K.

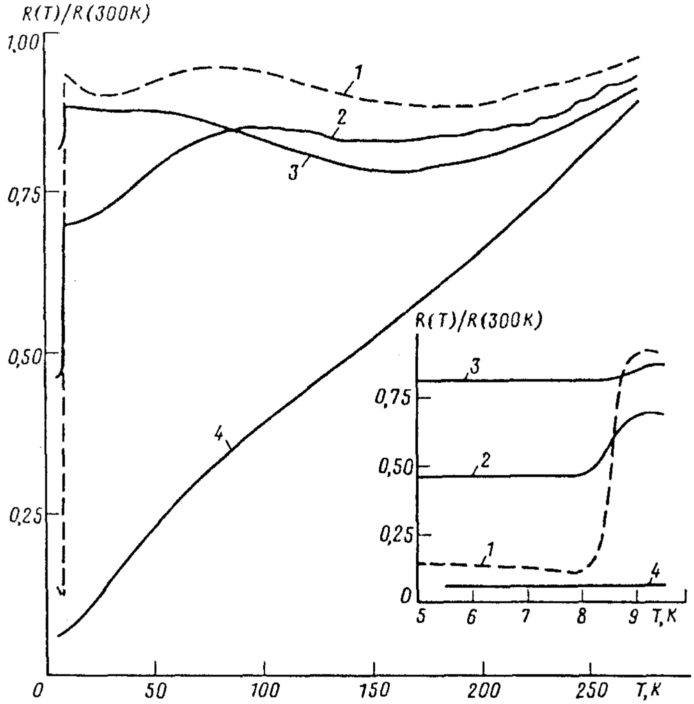

FIG. 1. Temperature dependence of the resistance for three bicrystals of category A (1,2,3) and one of category B (4). These samples have the following properties (θ, φ, α, δ, respectively): 1—For sample Bi-1A, 62°, 2°, 1.08, 6.83; 2—for sample Bi-2A, 33°, 9°, 1.44, 0.51; 3—for Bi-3A, 56°, 6°, 1.14, 0.08; 4—for Bi-4B, 8°, 0°, 12, 9; there is no abrupt change. The inset shows the low-temperature behavior of the resistance for the same samples in larger scale.

For the bicrystals of category A at $T < 9$ K, we observe an abrupt decrease in the resistance in a narrow temperature interval ($\Delta T < 1$ K). The relative size of this decrease, as calculated from the expression $\delta = [R(10\text{ K}) - R(5\text{ K})]/R(5\text{ K})$, can reach 700%. The value of δ increases with increasing $R(T_{\min})/R(300\text{ K})$. Regardless of the crystallite inclination angle, the sharp increase in the conductivity occurs at essentially the same transition temperature $T_c = T(0.9\delta) = 8.5 \pm 0.2$ K. Note that T_c does not depend on whether the $R(T)$ curves are recorded as the sample is being heated or being cooled. For the bicrystals of category B, which typically have ratios $\alpha > 10$, no clearly defined structural features are observed on the $R(T)$ curves.

A possible reason for the anomalous increase in the conductivity of the samples of category A is that a superconducting phase with $T_c = 8.5$ K exists near the large-angle crystallite joining surface (the nonzero resistance at $T < T_c$ reflects an inhomogeneity of the intercrystallite boundary of the Bi bicrystals). This suggestion is supported by other measurements.

Figure 2 shows isotherms of the magnetoresistance, $r(H)|_T = [R(H,T)$

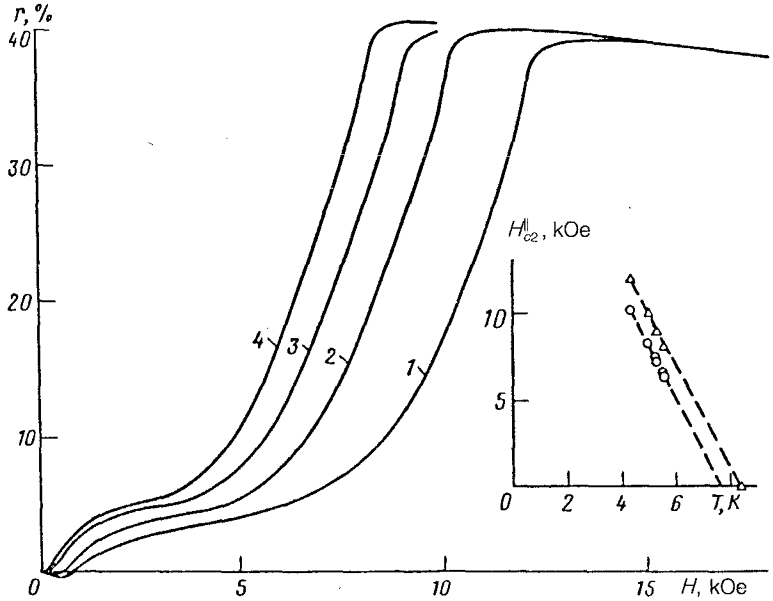

FIG. 2. Isotherms of the relative change in the resistance versus the longitudinal magnetic field $(I\|H\perp G)$ for bicrystal sample Bi-2A at several temperatures. 1—4.32 K; 2—4.97; 3—5.30; 4—5.56 K. The inset shows the temperature dependence of the upper critical field $H^{\|}_{c2}$ as determined at the $0.9r_N$ level (△) and the $0.5r_N$ level (O).

$-R(0,T)]/R(0,T)$, recorded in longitudinal magnetic fields $(I\|H\perp G)$ for one of the bicrystals of category A. With increasing H, the magnetoresistance undergoes a transition to a level $r(H)\simeq r_N$, the same for all temperatures. As in the case of conventional superconductors,[6] the shape of the greater part of the resistive transition $(0.4r_N\leqslant r\leqslant 0.9r_N)$ in a magnetic field does not change as the temperature is raised. This result means that we can find the temperature derivative of the upper critical field, $dH^{\|}_{c2}/dT$, from the standard criteria: from the midpoint of the transition curves or at the $0.9r_N$ level (see the inset in Fig. 2). The values of the derivatives $|dH^{\|}_{c2}/dT|_{0.5r_N}$ and $|dH^{\|}_{c2}/dT|_{0.9r_N}$ are the same, 3 kOe/K. From the $H^{\|}_{c2}(T)$ curve constructed on the basis of the $0.9r_N$ criterion we find $H^{\|}_{c2}(0)\simeq 25$ kOe. This result is very close the the value of $|dH^{\|}_{c2}/dT|T_c$. Using the relation $\xi^2(0)=\Phi_0/2\pi H^{\|}_{c2}(0)$, where $\Phi_0=2.07\times 10^{-7}$ G·cm^2, we estimate the coherence length to be $\xi(0)\simeq 120$ Å.

In a magnetic field oriented perpendicular to the current flow, the resistive transitions are greatly smeared out, because of the masking effect of the magnetoresistance of the nonsuperconducting bismuth. It is thus difficult to correctly determine the anisotropy of the upper critical fields. Nevertheless, at $H>50$ kOe we were able to observe some well-expressed quantum oscillations of the resistance in this case, for both the parallel orientation $(I\perp H\|G)$ and transverse orientation $(I\perp H\perp G)$ of the field with respect to the intercrystallite boundary. It turns out that for the bicrystals of category A, in contrast with the samples of category B, the situation is dominated by

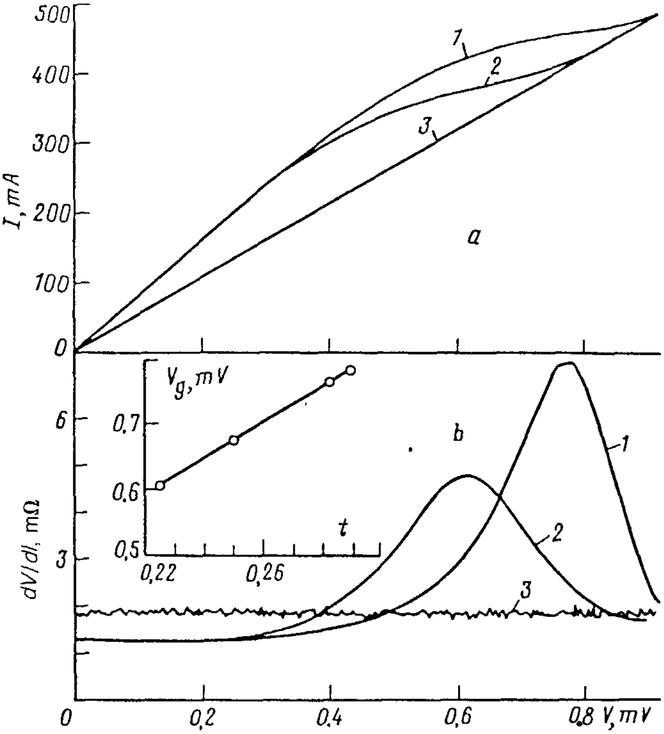

FIG. 3. Current-voltage characteristics (a) and their derivatives (b) for a Bi-2A bicrystal at several temperatures. 1—7.82 K; 2—8.07 K; 3—8.65 K. The inset shows the position of the maximum of the differential resistance as a function of the parameter $t=(1-T/T_c)^{1/2}$.

Shubnikov oscillations with a period $P^{\|,\perp}(1/H)$ smaller than the smallest possible periods associated with the electron part (0.53×10^{-5} Oe^{-1}) or the hole part (0.45×10^{-5} Oe^{-1}) of the Fermi surface of a homogeneous bismuth single crystal.[7] For example, for samples Bi-1*A*, Bi-2*A*, and Bi-3*A* (Fig. 1) we have $p^{\|}(1/H)=0.23\times10^{-5}$, 0.34×10^{-5}, and 0.39×10^{-5} Oe^{-1}. We also have $p^{\perp}(1/H)=(0.20\text{–}0.24)\times10^{-5}$ Oe^{-1}. According to these results, the large-angle Bi bicrystals contain regions in which the carrier density n is higher by a factor of 50–100 than that in the host material, with $n=3\times10^{17}$ cm^{-3}.

We also measured the current-voltage characteristics of Bi bicrystals in a given-current regime for currents in the range $I=1\text{–}500$ mA. Figure 3a shows some representative characteristics, recorded at three temperatures near T_c. We see that at $T<T_c$ there is a clearly defined maximum in the differential resistance dV/dI on the I-V characteristics (Fig. 3b). The position of this maximum along the voltage scale, V_g, has a temperature dependence $V_g\propto(1-T/T_c)^{1/2}$ as $T\to T_c$ (see the inset in Fig. 3b).

We should stress that the current-voltage characteristics obtained for the bicrystals of category *A* are similar to those which have been observed for Bi–Bi point contacts[8] and Sb–Sb point contacts.[9] A comparison of the $V_g(T)$ curves with the temperature dependence for the energy gap, $\Delta(T)$, in the BCS model led Shklyarevskii *et al.*[8] to conclude that bismuth point contacts contain superconducting clusters with $T_c \simeq 3.9$ K and 5.9 K.

According to Ref. 6, the temperature dependence of the gap parameter near T_c can be described approximately by

$$\Delta(T) \simeq (7/4)\Delta(0)(1 - T/T_c)^{1/2}, \quad T \to T_c. \tag{1}$$

Working from the square-root $V_g(T)$ dependence which we found, and assuming that expression (1) applies to it, we can estimate a possible value of $2\Delta(0)$: $\simeq 3.3$ meV. This value seems completely reasonable for a strong-coupling superconductor.

The fact that stable superconducting characteristics are observed for crystalline Bi samples at atmospheric pressure is by no means a trivial matter (ordinary rhombohedral Bi is not a superconductor). The Cooper pairing of charge carriers in bicrystal samples seems to result from a structural change in the bismuth lattice (the change occurs in regions directly adjacent to the large-angle intercrystallite boundary) caused by a relative intergrowth of crystallites or by strong elastic deformation fields. In the latter case we might expect that one of the high-pressure phases, BiII–BiVI, would be responsible for the superconductivity of the bicrystals.[10] Judging from the value of T_c, this phase might be BiIV ($T_c = 8.7$ K at $p = 4.3$ GPa) or BiVI ($T_c = 8.55$ K at $p = 9.0$ GPa).

However, we do not rule out the possibility that the superconductivity occurs because a residual lead impurity (on the order of 10^4 at. %) concentrates at the intercrystallite boundary of the bismuth bicrystals, and inclusions of the ϵ phase of bismuth-lead alloys form.

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