Fermi-surface rearrangement in Bi bicrystals with twisting superconducting crystallite interfaces

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We report an investigation of quantum oscillations of Hall resistance and magnetoresistance in Bi bicrystals with superconducting interface of twisting type. From the observed quantum oscillations, we find a similar Fermi surface consisting at interface of bicrystals and bulk nonsuperconducting rhombohedral Bi. At the same time, clear differences are observed in the normal and superconducting behavior of the small and large crystallite disorientation angle interfaces. It is shown that the Fermi surface for electrons in small angle interfaces is less anisotropic and is much larger in volume than in bulk Bi. The considerable change of the shape, elongation, and volume of hole isoenergetic surface at large angle interfaces is revealed.

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I. INTRODUCTION

Crystallite interface (CI) of bicrystals plays an important and, in some cases, even a dominant role for the physical properties of the material. By degree of perfection, CI can be compared only to a surface cleaved in ultrahigh vacuum and the significance of studying them has become particularly evident for revealing features of properties of nanostructured materials (the grain boundaries of nanocrystals are qualitatively similar to those in macroscopic bicrystals).

The CI of bismuth bicrystals of twisting type exhibits anomalies of various physical behaviors.[1] These anomalies are determined mainly by the changes of the lattice properties and phonon spectra, and by the reconstruction of the energy spectrum on the inner boundary.[2]

Bi is a semimetal with a small energy overlap between the conduction and valence bands, equal number of electrons and holes, highly anisotropic Fermi-surface (FS), low carrier concentrations, small effective carrier masses, etc. The FS of Bi consists of three equivalent electron pockets at the L points of the Brillouin zone and one hole ellipsoid of revolution at the T point.[3,4] The electron part of FS is highly elongated in a direction close to the bisector axes of a crystal, while the hole part is extended along the trigonal axis. One of the principal axes of each electron pocket is parallel to the crystal binary axis and the other two are tilted about 6° from the trigonal and bisector axes.

Remarkable agreement between the calculations of the band structure of Bi and experimental data has been reached. This situation is rather favorable for research of the electronic properties of Bi surface and interfaces. Lately, the band structure of Bi surface has been intensively investigated[5] while insufficient attention is given to the study of the energy spectrum of interfaces.

The present paper describes the results of the investigation of the Fermi-surface rearrangement in CI of Bi bicrystals of twisting type using the quantum oscillations of the Hall resistance $\rho_{ij}(H)$ and magnetoresistance $\rho_{ii}(H)$ in high magnetic fields. Our results show that the small crystallite disorientation angle interfaces with one superconducting transition have n type of conductivity and the charge carriers responsible for oscillations become L electrons. The large angle interfaces containing two superconducting phases exhibit p type of conductivity and their majority carriers are T holes. We observe an essential increase of the volume of the Fermi surface and change of the carrier pocket topology at the crystallite interface of bicrystals. We believe that the differences in the electronic structure between the crystallite interface and crystalline blocks favor the occurrence of a superconducting state.

II. EXPERIMENTAL PROCEDURE

High quality bismuth bicrystals (the Dingle temperature of charge carriers $T_d < 0.8$ K) were obtained by the zone recrystallization method using double seed technique. In bicrystals of twisting type, the crystallites are disoriented relative to each other. In one of them [for example, crystallite A in Fig. 1(a)], the bilayers lie perpendicular to the trigonal axis C_3 ($C_3 \| n_A$), and in the other (crystallite B), the normal to the bilayer plane and direction of the first crystallite axis C_3 make up an angle up to 30°.

The width of CI [about 100 nm, see Figs. 1(b) and 1(c)] was estimated by means of scanning electron microscopy (SEM) and by the magnetic field value when quantum oscillations become observable.[1] Samples for measurements were prepared in the form of parallelepipeds ($1 \times 2 \times 4$ mm^3). Contact electrodes for transport phenomenon measurements were soldered by electrospark welding.

Two groups of Bi bicrystals of twisting type were investigated: small crystallite disorientation angle (SDA) bicrystals with $\theta_1 < 9°$ and large crystallite disorientation angle (LDA) bicrystals with $\theta_1 > 26°$. Distributions of bicrystals into groups were made taking into account the type of conductivity of their interfaces. SDA bicrystals had n-type conductivity and LDA bicrystals had p type. Both groups of

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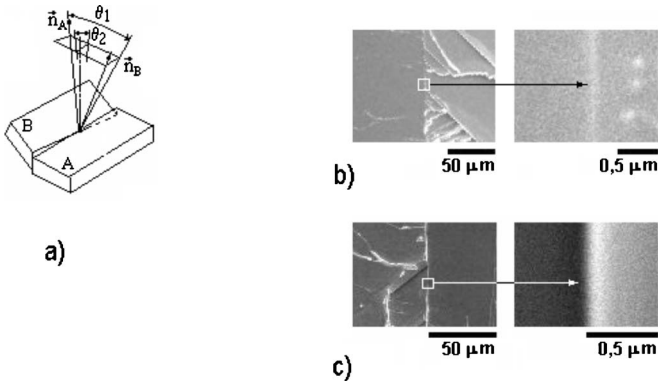

FIG. 1. (a) Schematic representation of bismuth bicrystals with crystallite interfaces of a twisting type. *A* and *B*, crystallites; θ_1, relative CI disorientation angle; θ_2, rotation angle in an interface plane. (b) SEM images of CI of small disorientation angle bicrystals with $\theta_1=5°$ and $\theta_2=5.5°$. (c) SEM images of CI of large disorientation angle bicrystals with $\theta_1=29°$ and $\theta_2=11°$.

bicrystals are of special interest because the CI exhibits superconducting properties (for some samples, $T_{onset}\sim 16$ K and $T_c\sim 10.4$ K,[6] which are much higher than those in ultrathin amorphous or granular Bi films[7,8] and nanoparticles[9]). Two superconducting phases with $T_c\sim 8.4$ K and $T_c\sim 4.3$ K have been observed at CI of LDA bicrystals. Superconducting characteristics of these phases have been described recently in Ref. 1. On the other hand, in SDA bicrystals, only one superconducting phase ($T_c\sim 4.3$ K) is revealed (see Fig. 2) and the superconducting parameters differ from the values of LDA bicrystals. For example, in bicrystal with $\theta_1=5°$ and $\theta_2=5.5°$, the slope of the $H_{c2}(T)$ dependence makes $dH_{c2}/dT\sim 2.97$ kOe/K, upper critical field $H_{c2}(0)\sim 8.8$ kOe, and coherence length $\xi(0)\sim 19$ nm. For comparison,[1] these parameters for LDA bicrystals have the following values: $dH_{c2}/dT\sim 3$ kOe/K, $H_{c2}(0)\sim 25$ kOe, and $\xi(0)\sim 12$ nm (for the first superconducting phase with $T_c\sim 8.4$ K) and $dH_{c2}/dT\sim 5.5$ kOe/K, $H_{c2}(0)\sim 16.6$ kOe, and $\xi(0)\sim 14$ nm (for the second phase with $T_c\sim 4.3$ K).

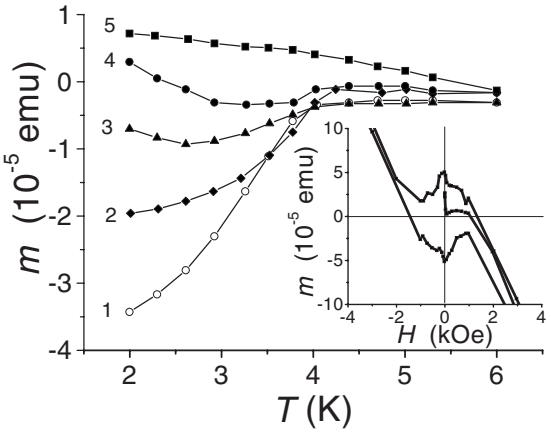

FIG. 2. Temperature dependences of a magnetic moment at different applied magnetic fields in Bi SDA bicrystals with $\theta_1=5°$ and $\theta_2=5.5°$: (1) 50 Oe; (2) 100 Oe; (3) 200 Oe; (4) 400 Oe; (5) 800 Oe Inset: Magnetic hysteresis loop at $T=3$ K.

Similar to LDA bicrystals, the magnetic hysteresis loop of the SDA crystallite interface shows the behavior typical for strong type-II superconductors (see Fig. 2, inset).

The magnetization of Bi bicrystals was studied in the temperature range 1.8–22 K and in fields up to 70 kOe using superconducting quantum interference device magnetometer (Quantum Design) and physical property measurement system. The quantum oscillations of the Hall resistance and magnetoresistance after transition of CI in the normal state (converted by magnetic field and/or a current) were registered in stationary and pulse magnetic fields up to 350 kOe. The measurements were performed in the International Laboratory of High Magnetic Fields and Low Temperatures (Wroclaw, Poland), Institute of Low Temperatures and Structure Research of the Polish Academy of Sciences in Wroclaw (Poland), and Institute for Solid State and Material Research (Dresden, Germany).

III. RESULTS AND DISCUSSION

As mentioned above, the Fermi surface of single crystalline bismuth is highly anisotropic and has a complex structure. So far, as all experimental techniques of the FS study are practically discovered and tested (or can be applied) to Bi, its FS is known in the finest detail.[4] This considerably facilitates research of the electronic band structure of Bi bicrystals.

The main feature of the spectrum of quantum oscillations in the investigated Bi bicrystals is as follows: it either contains, besides oscillation frequencies for crystallites, new harmonics not typical for single crystalline samples or it consists of harmonics specific only for CI when its conductivity is much larger than in single crystalline blocks.

A. Small crystallite disorientation angle interfaces

In SDA bicrystals of bismuth, the quantum oscillations of $\rho_{ij}(H)$ from the FS of crystallites (single crystalline blocks) and FS of interfaces was registered. Examples of such oscillations at the magnetic field parallel to the trigonal axes C_3 of crystallites and at its rotation in the binary plane are given in Fig. 3.

The periods of quantum oscillations for crystallites correspond to well-known[3,4] electron and hole FSs of single crystalline Bi (see Fig. 4, curves 1–3). These data prove that the number of electrons and holes in crystallites of SDA bicrystals, as well as in rhombohedral Bi, is almost equal (n, $p\sim 3\times 10^{23}$ m^{-3}).

Besides the above mentioned oscillation frequencies for crystallites, a number of new harmonics appear in large angular intervals of the magnetic field rotation. For example, two new harmonics in the spectrum of quantum oscillations of $\rho_{ij}(H)$ in SDA bicrystals are revealed at $H\|$CI. The frequencies of these harmonics essentially differ from the values characteristic of single crystalline samples. Hiruma and Miura[10] observed that at the magnetic field orientation close to the trigonal axes ($H\|C_3$), the magnetoresistance of single crystalline bismuth monotonically increases up to 450 kOe and in the magnetic fields $H>100$ kOe, the Shubnikov–de

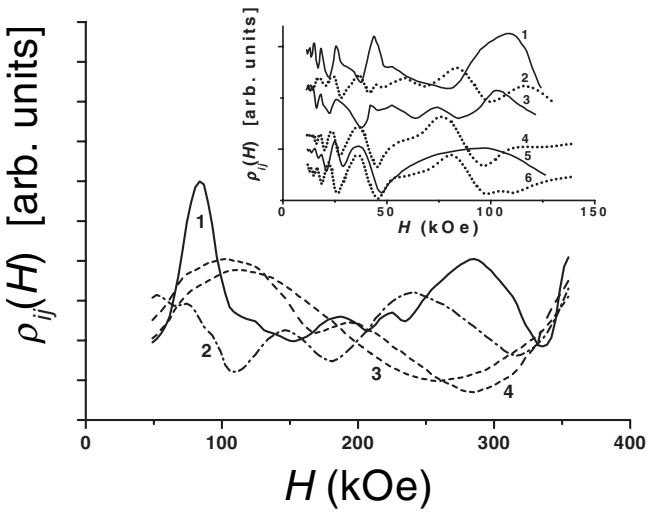

FIG. 3. The quantum oscillations of the Hall resistance in Bi SDA bicrystals with $\theta_1=5°$ and $\theta_2=5.5°$: (1) $H\|C_3$, $T=1.5$ K; (2) $H\|C_1$, $T=4.2$ K; (3) $[H,C_3]\sim 10°$, $T=4.2$ K; (4) $H\|C_2$, $T=4.2$ K (the monotonic part has been subtracted). C_1, C_2, and C_3 are bisectrix, binary, and trigonal axes, respectively. Inset: The quantum oscillations of the Hall resistance in Bi SDA bicrystal with $\theta_1=8.6°$ and $\theta_2=4°$: (1) $H\|C_3$; (2) $[H,C_3]\sim 31°$; (3) $[H,C_3]\sim 20°$; (4) $[H,C_3]\sim 17°$; (5) $[H,C_3]\sim 8°$; (6) $[H,C_3]\sim 11°$ (the monotonic part has been subtracted).

Haas oscillations disappear. On the other hand, in SDA bicrystals at the same orientation of the magnetic field, the quantum oscillations of the Hall resistance are observed at the $H>100$ kOe (see Fig. 3), but their frequencies are higher by approximately five and ten times than frequencies typical for extremal cross-sectional areas of the FS of Bi. So, for example, in Bi SDA bicrystal with $\theta_1=5°$ and $\theta_2=5.5°$, these frequencies make ~444.4 kOe and ~884.8 kOe, whereas in bulk Bi, the oscillations frequency according to Ref. 4 is about 85 kOe.[4] Usually, the Hall resistance oscillations of the first frequency appear at $H>25-35$ kOe and those of the second at $H>90$ kOe. Calculated cyclotron orbit diameter corresponding to the appearance of the fields of the first component is ~100–140 nm. This value correlates with the CI width determined by means of SEM. The diameter of cyclotron orbits of charge carriers corresponding to the appearance of the field of the second harmonic is ~60–80 nm. We believe that this value characterizes the thickness of the central layer of the interfacial region. It results from the well-known fact that the CI is a complex system consisting of a solitary central part and two similar adjacent layers on both its sides. Hence, our experimental results on SDA bicrystals of Bi testify that the width of the CI central part makes ~60–80 nm and that of the two adjacent layers takes a value of ~20–30 nm each.

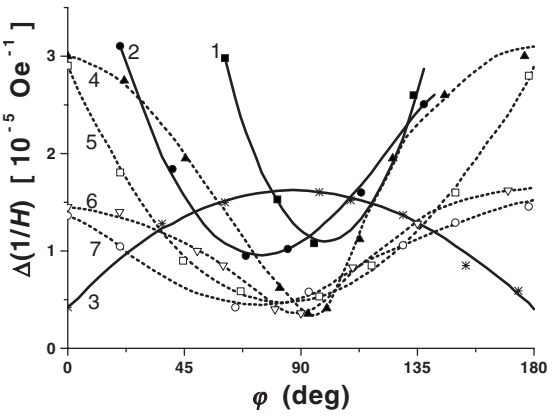

FIG. 4. The angular dependences of oscillation periods in the crystallite binary plane of SDA Bi bicrystals: (1, 2, and 3) crystallites; (4 and 6) CI with $\theta_1=5°$ and $\theta_2=5.5°$; (5 and 7), CI with $\theta_1=8.6°$ and $\theta_2=4°$.

Figure 4 shows examples of the angular dependences of the periods of quantum oscillations of $\rho_{ij}(H)$ for adjacent layers (see curves 4 and 6, and 5 and 7) of CI of SDA bismuth bicrystals.

These data indicate that in adjacent layers, the angular dependences of oscillation periods are typical for Fermi surface of L electrons. The structure of the electron Fermi surface of these layers is the same as in crystallites (three electron pockets located in L points of the Brillouin zone and generated from the principal ones by ±120° rotations around the trigonal axis C_3). The isoenergetic surfaces are less anisotropic and are much larger in volume V_e than the electronic pockets of crystallites. Like that for electronic pockets in the adjacent layers of bicrystal with $\theta_1=5°$ and $\theta_2=5.5°$, $V_e\sim 142\times 10^{-63}$ g^3 cm^3/s^3, while in single crystalline Bi, according to Ref. 4, $V_e\sim 43.98\times 10^{-63}$ g^3 cm^3/s^3. The ratio of the semiaxes of the electron pocket in the adjacent layers considerably differs from that in pure Bi. For example, the ratio of the semiaxes of the electronic quasiellipsoid of the adjacent layers of bicrystal with $\theta_1=5°$ and $\theta_2=5.5°$ is 1:1.34:12.6 while in rhombohedral bismuth, it is 1:1.40:14.8.[4] Hence, in SDA bicrystals of Bi, not only do the electron concentrations increase, as, for instance, in bismuth doped with donor impurity of Te or Se,[11] but the shape of FS also changes. By frequencies of the quantum oscillations, the density of electrons in adjacent layers of SDA bicrystals makes $\sim 0.67\times 10^{20}$ m^{-2}, which is 3 orders higher than in bismuth thin films of similar sizes.[12]

Quantum oscillations of the Hall resistance from the central layer of CI of the Bi bicrystals, connected with electron FS, were clearly observed at the magnetic field orientation along the internal surface plane. At its deviation by an angle >10°, they disappeared. Nevertheless, the obtained data testify that the density of electrons in the CI central part is much higher than in the adjacent layers and makes ~1.5 $\times 10^{20}$ m^{-2}.

B. Large crystallite disorientation angle interfaces

A typical feature of superconducting LDA bicrystals is observation of the quantum oscillation of $\rho_{ij}(H)$, connected with the hole FS of the crystallite interface. Oscillations from the electron FS of the CI and FS of the single crystalline blocks were not detected.

Similar to the case of SDA bicrystals, at the magnetic

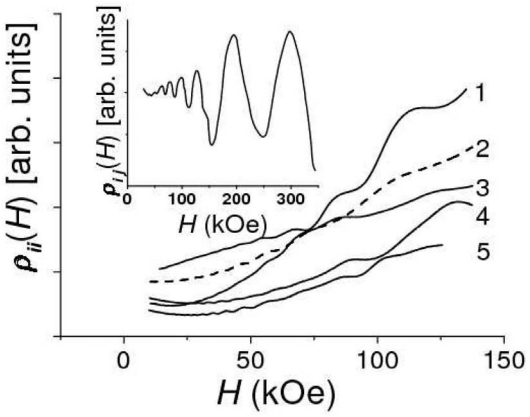

FIG. 5. The quantum oscillations of the magnetoresistance in LDA Bi bicrystals with $\theta_1=62°$ and $\theta_2=2°$ at 4.2 K. The magnetic field rotation in the binary plane: (1) $[H,C_3]\sim 60°$; (2) $[H,C_3]\sim 120°$; (3) $[H,C_3]\sim 140°$; (4) $[H,C_3]\sim 40°$; (5) $[H,C_3]\sim 20°$. Inset: The quantum oscillations of the Hall resistance at the magnetic field directed along the inner boundary plane (the monotonic part has been subtracted).

field orientation along the CI plane, the spectrum of the quantum oscillations of $\rho_{ij}(H)$ of LDA bicrystals contains two new harmonics (see Fig. 5, inset), which start at magnetic fields $H>20-25$ kOe (first frequency) and $H>100$ kOe (second frequency). This suggests that the widths of the central part and of the adjacent layers of the CI in SDA and LDA bicrystals are close in values.

From the frequencies of the quantum oscillations of $\rho_{ij}(H)$, we have found that the hole concentration in the central part of the CI of LDA bicrystals makes $\sim 2.5\times 10^{20}$ m^{-2} and that in the adjacent layers $\sim 1.2\times 10^{20}$ m^{-2}, which are considerably higher than those in SDA bicrystals. Probably due to the low carrier concentration in SDA bicrystals, only one superconducting phase is shown. Evidently, in another phase, the attractive interaction between electrons does not dominate electron repulsions. This situation most likely happens in the CI adjacent layers of SDA bicrystals (the carrier concentration is lower, the proximity effect influences, etc.). In this connection, we believe that the superconducting phase with $T_c\sim 4.3$ K in SDA bicrystals is located in the central part of the CI.

The quantum oscillations of $\rho_{ii}(H)$ in the adjacent layers of the CI (see Fig. 5) of LDA bicrystals were registered in large angular intervals of the magnetic field rotation. At the same time, quantum oscillations from the CI central part were detected in the limited angular intervals ($\pm 40°$ near $H\| C_3$). The angular dependences of the oscillation periods of $\rho_{ii}(H)$ at the magnetic field rotation in the binary plane of crystallites are given in Fig. 6.

As is apparent from the figure, the hole FS of the central and adjacent layers of the CI of LDA bicrystals consists of one pocket, the shape of which is essentially different from the hole FS of single crystalline Bi (the ellipsoid of revolution at the T point of the Brillouin zone extended along the trigonal axis C_3; ratio of cross-sectional area $S_1/S_3=3.327$;[4] see also Fig. 4, curve 3).

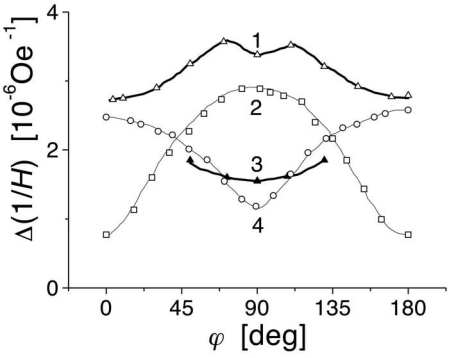

FIG. 6. The angular dependences of hole oscillation periods in the crystallite binary plane of LDA Bi bicrystals: (1 and 3) CI with $\theta_1=62°$ and $\theta_2=2°$; (2) CI with $\theta_1=33°$ and $\theta_2=9°$; (4) CI with $\theta_1=27°$ and $\theta_2=9°$; (1, 2, and 4) adjacent layers; (3) central part of bicrystals.

Moreover, in some bicrystals, the elongation of FS in adjacent layers changes and the hole ellipsoid of revolution in pure Bi turns to a deformed pocket with all three main cross-sectional areas different in size. For example, in adjacent layers of LDA bicrystal with $\theta_1=27°$ and $\theta_2=9°$, where T_{onset} corresponding to that in Ref. 6 achieved 16 K, FS is rotated at $\sim 90°$, in comparison with the ones in crystallites. It is established also that the hole FS of the central part and adjacent layers of LDA bicrystals considerably surpass in volume the hole isoenergetic surface of single crystalline Bi, which, according to Ref. 4, has value $V_h\sim 43.99\times 10^{-63}$ g^3 cm^3/s^3 (for comparison, the volume of the hole pocket in the adjacent layers of LDA bicrystal with $\theta_1=62°$ and $\theta_2=2°$ is $V_h\sim 164\times 10^{-63}$ g^3 cm^3/s^3).

So, we found the significant differences in FS characteristics of twisting superconducting crystallite interfaces and ordinary bismuth.

As noted above, the rhombohedral Bi at atmospheric pressure is not a superconductor. However, weak growth of the carrier densities in Bi, when it is doped with small amounts of tin or tellurium, results in occurrence of the superconducting state with transition temperature $T_c<0.1$ K.[13] The mechanism causing the superconductivity in lightly doped Bi, according to Ref. 13, is most likely the electron-phonon interaction, with resonances[14] probably playing a determining role at characteristic frequencies in phonon and Coulomb interaction. Lightly doped Bi (in limits of the "rigid band model," according to Ref. 11) and pure crystalline bismuth have identical $A7$ crystal structure and similar topology of the Fermi surface. On the other hand, in comparison with the lightly doped Bi, the interfaces of SDA and LDA bicrystals have the modified shape of the isoenergetic surfaces and higher carrier densities, which are beneficial for superconductivity as these favor[15] electron pairing and enhance the transition temperature in one of the CI phases up to 10.4 K. The topological features of FS in SDA and LDA bicrystal interfaces indirectly reflect changes in displacement of atoms from the equilibrium positions characteristic for crystalline Bi. Also, intensification of the bonding of electrons with the lattice takes place. Based on superconducting transition temperature $T_c\approx 10.4$ K and bulk Debye energy[5] of 10 meV us-

ing the approximate McMillan formula,[16] we extract a coupling constant of 0.71. This value shows that the electron-phonon interaction in CI of Bi bicrystals is strong enough. The magnetic hysteresis loops and the current-voltage characteristics[17] of Bi superconducting interfaces confirm this statement and clearly testify the behavior typical for strong type-II superconductors with the possible value[17] of energy gap $2\Delta(0) \approx 3.3$ meV.

Thus, we state that our results clearly reveal features of the Fermi surface at CI of SDA and LDA bicrystals, nonspecific to ordinary rhombohedral Bi. Being dependent on the intensity of local fields and torsion deformations, they do not reflect sharp deviations in structural stability of interfaces. Observation of identical Fermi surfaces consisting of bicrystal components (interface and crystallites) confirms this assertion. At the same time, in comparison with the bulk Bi (crystallites), the significant deformations of FS and the appreciable increase of its volume at superconducting CI of bicrystals are found. We think that both these factors play an obvious role in the manifestation of superconductivity in the interfaces of our bicrystals.

IV. CONCLUSION

In the present work, the quantum oscillations of the Hall resistance and magnetoresistance were investigated in Bi bicrystals of twisting type. These researches are caused especially by unique properties of bismuth (not a superconductor), which are perfectly combined with the unusual characteristics of its crystallite interfaces, having superconducting critical temperatures reaching 8.4 K. In spite of the fact that the electron band structure of the surface differs from that of the bulk,[5] we found a Fermi surface consisting of layer components of bicrystal interfaces similar to those in single crystalline Bi. However, the shape, elongation, and volume of isoenergetic surfaces at CI undergo essential changes that eventually (together with the changes in the phonon spectra) stimulate electron pair correlation.

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