Anisotropy of the superconducting properties of $YBa_2Cu_3O_{7-x}$ single crystals with reduced oxygen content

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In an investigation of the resistivity anisotropy of $YBa_2Cu_3O_{7-x}$ single crystals with suboptimal oxygen content it is observed that the superconducting transition for the component ρ_c of the resistivity tensor is shifted to lower temperatures with respect to the transition for the component ρ_{ab}. A similar shift is also observed for the transition in the temperature dependence of the dynamic magnetic susceptibility. © *1998 American Institute of Physics.* [S0021-3640(98)01216-X]

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Cuprate high-T_c superconductors are highly anisotropic layered compounds characterized by the presence of CuO_2 planes, which are believed to be responsible for the superconductivity.

In Ref. 1, in a study of the temperature dependences of the resistance and magnetic susceptibility of $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$ single crystals, it was observed that the superconducting transition temperature was approximately 40 K higher in the case of current flow along the CuO_2 layers ($\mathbf{j}\perp\mathbf{c}$, where $\mathbf{c}$ is the direction of the crystallographic axis perpendicular to the layers) than in the case of current flow perpendicular to the layers $(\mathbf{j}\|\mathbf{c})$.

Friedel predicted theoretically a similar behavior of layered superconductors.[2] He proposed a specific mechanism of ''growth'' of ring-shaped Josephson vortices in a certain temperature range $T_f<T<T_c$ below T_c that should suppress superconductivity in this range in the direction perpendicular to the CuO_2 layers. According to Friedel's conjecture, such a temperature interval should exist in any layered superconductor that is described by a model of a stack of superconducting planes between which Josephson links exist. The temperature T_f above which these links are broken is the Friedel transition temperature.

Later, Korshunov and Rodriguez[3] pointed out an error in Friedel's calculations and showed that such a mechanism is not realized in an ideal crystal. However, it was recently shown theoretically in Ref. 4 that a Friedel transition can occur if the layers are not assumed to be ideal and it is assumed that there is a random distribution over superconducting properties of the layers. Specifically, it was assumed that two types of layers with different parameters $J_\|$, characterizing the coupling constant inside a layer in an anisotropic 3D XY model, exist in the crystal. The Friedel transition was obtained only when the distribution of such layers in a crystal was not periodic but random.

The reason for the observed[1] shift of the superconducting transition was not established. In principle, any macroscopic nonuniformity of the sample can lead to a shift of the transition, but the observed phenomenon could have been due to a Friedel transition. In any case, such behavior is a consequence of the layered structure of the single crystals investigated. In this connection, it is of interest to observe the shift of the transition in other layered superconductors.

In the present work, we chose $YBa_2Cu_3O_{7-x}$ single crystals (YBCO) for the investigations. Initially, at optimal doping $x \approx 0.05$ this superconductor possesses a much weaker anisotropy than bismuth or thallium cuprate superconductors, but as the oxygen content decreases, the degree of anisotropy increases rapidly. The behavior of YBCO as a function of oxygen content is reversible and has been rather well studied. For this reason we undertook to observe the shift of the superconducting transition with decreasing oxygen content in high-quality (in the initial state) single crystals for different orientations of the current relative to the CuO_2 layers.

In the experiment, the anisotropy of the electrical resistance and the dynamic magnetic susceptibility was measured on YBCO single crystals in the form of slabs with dimensions of approximately $2 \times 1 \times 0.05$ mm, for which the crystallographic direction **c** was normal to the plane of the slabs.

The $YBa_2Cu_3O_{7-x}$ single crystals were grown in a ZrO_2 crucible by the method described in Ref. 5. The total impurity content in the samples, which was less than 0.005%, was determined by the inductively-coupled plasma method, which consisted of a mass-spectrometric analysis of an argon plasma containing the vaporized sample and ignited by an rf inductor.

After annealing at 500 °C in oxygen, the samples possessed a narrow superconducting transition with $T_c \approx 92$ K and transition width less than 0.5 K. The required reduced oxygen content was achieved by choosing the annealing temperature (up to 820 °C) in air at atmospheric pressure and subsequent quenching in liquid nitrogen in accordance with the data of Refs. 6–8. The samples were annealed in a quartz ampoule and covered with YBCO powder in order to preserve the high quality of the surface. No special measures were taken to detwin the samples.

To measure the real part of the dynamic magnetic susceptibility χ, the sample was placed inside a pair of coaxial coils 6 mm in diameter, one of which served to excite an ac magnetic field, while the other was for measuring. An identical pair of coils, which was used to compensate the signal in the absence of the sample, was placed next to it. Using the standard synchronous detection scheme, we measured the component of the imbalance signal proportional to the real part of the induced magnetic moment M of the sample in an ac magnetic field of frequency 10^5 Hz: $M = \chi h V$. Here h is the amplitude of the magnetic field in the coil and V is the volume of the sample. The amplitude h of the field was chosen to be small, so that the signal was linear in h, and equal to 0.1 Oe. The sample in the coil was placed either perpendicular ($\mathbf{c} \parallel \mathbf{h}$) or parallel to ($\mathbf{c} \perp \mathbf{h}$) to the magnetic field. For this, the sample was glued to different faces of a sapphire rod, shaped in the form of a rectangular parallelepiped. We denote by χ_{ab} the susceptibility component measured in the first case, since ring currents flow only in the plane of the CuO_2

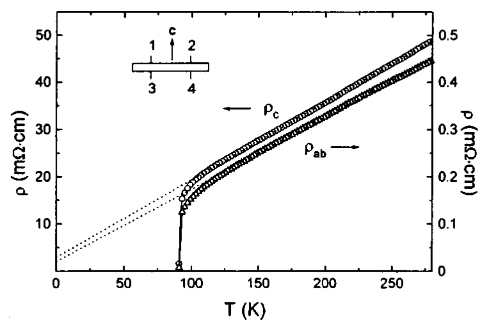

FIG. 1. Temperature dependence of the resistivity components ρ_{ab} and ρ_c of the initial YBCO single crystal. Dotted lines — extrapolations of the linear parts of the temperature dependences of the resistivity to zero temperature. Inset: Geometry of the contacts.

layers, and we denote by χ_c the susceptibility component in the second case, since in this case a portion of the path which the currents must follow to closure is perpendicular to the layers.

The sample together with a thermometer and a heater arranged alongside were placed inside a glass Dewar, which was immersed, upside down, in liquid helium. The measuring coils were wound on the outer surface of the Dewar and were always at liquid helium temperature during the measurements. To prevent a temperature gradient, the sample was placed in a sapphire container.

A four-contact method was used to investigate the electrical resistance of anisotropic single crystals.[9] In this method, two pairs of contacts were placed opposite one another on opposite sides of the sample (see inset in Fig. 1). The contacts were prepared by depositing drops of silver paste on the surface of the sample. The drops were then ''burned in'' by heating the sample in air at 400 °C. The subsequent manipulations of the sample (annealing, remounting) did not change the properties of the contacts. The characteristic size of the contacts did not exceed 0.3 mm, and the accuracy of the placement of the contacts opposite one another on the opposite sides of the sample was not worse than 0.05 mm.

The components of the resistivity tensor ρ_{ab} in the plane of the layers and ρ_c normal to the layers could be calculated numerically, using the formulas of Ref. 9, from the results of two measurements $R_{ab}=V_{12}/J_{34}$ and $R_c=V_{13}/J_{24}$, assuming an infinite sample. This condition limited the applicability of this method to a large anisotropy $\eta=\rho_c/\rho_{ab}$. In our experiments, the calculations of ρ_{ab} and ρ_z were performed only for the initial sample with optimal oxygen content, for which η was of the order of 10^2. For samples with reduced oxygen content, where the anisotropy was much higher, we present only the values of R_{ab} and R_c.

In the present work we investigated two samples in detail. Their behavior was similar overall but different in detail. For the sample whose data are reported in the present letter the resistivities in the state with optimal oxygen concentration were $\rho_{ab}=460\ \mu\Omega\cdot$ cm and $\rho_c=48\ \mathrm{m}\Omega\cdot$ cm at $T=300$ K, and the values decreased linearly with decreasing temperature (but not too close to $T_c\simeq 92$ K; Fig. 1).

Next, the sample was annealed at a fixed temperature, resulting in a lower oxygen

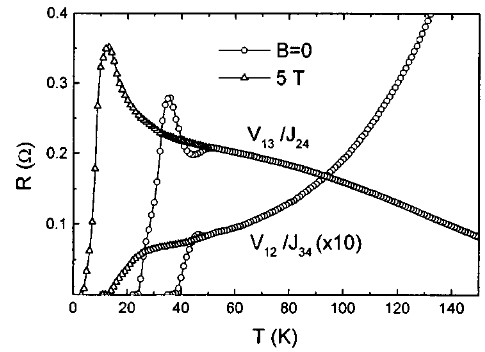

FIG. 2. Temperature dependences $R_{ab}(T)$ ($\mathbf{j}\perp\mathbf{c}$) and $R_c(T)$ ($\mathbf{j}\parallel\mathbf{c}$) in the absence of a magnetic field (○) and in a 5 T field (△).

concentration, after which the temperature dependences of the resistances R_{ab} and R_c and the susceptibilities χ_{ab} and χ_c were measured. Then the procedure was repeated at a higher annealing temperature, all the way up to the temperature ~820 °C at which the sample was no longer a superconductor.[8]

Figure 2 shows the temperature dependences $R_{ab}(T)$ and $R_c(T)$ for a sample annealed at 790 °C for 35 h. As one can see from the figure, the resistances $R_{ab}(T)$ and $R_c(T)$ do not vanish simultaneously as temperature decreases: first R_{ab} vanishes at $T_1\simeq 40$ K; in the process, $R_c(T)$ increases, reaches a maximum approximately at the point where $R_{ab}(T)$ vanishes, and then decreases and vanishes at $T_2\simeq 30$ K, i.e., at an approximately 10 K lower temperature. This nonsimultaneous vanishing of R_{ab} and R_c started only when T_c of the sample dropped below ≈60 °C, and it was observed for both experimental samples, though the temperature interval ΔT where $R_{ab}=0$ while $R_c>0$ was different.

The same effect was also observed in the temperature dependences of the dynamic magnetic susceptibility, which were measured for two different orientations of the ac magnetic field h — parallel (χ_{ab}) and perpendicular (χ_c) to the **c** axis (Fig. 3). We note

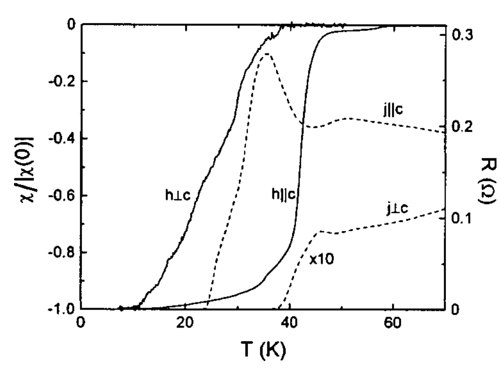

FIG. 3. Comparison of the temperature dependence of the normalized dynamic susceptibility (solid curves) and the resistance (dashed curves) near a superconducting transition.

that Fig. 3 shows the temperature dependences normalized to the susceptibility at zero temperature. In the experiment the ratio $\chi_{ab}(0)/\chi_c(0)=29$, which reflects the anisotropy of the demagnetizing factor of the sample.

As one can see from Fig. 2, applying a magnetic field $\mathbf{B}\parallel\mathbf{c}$ decreases the values of the characteristic temperatures at which each of the measured quantities $R_{ab}(T)$ and $R_c(T)$ vanishes, but the difference between them remains approximately the same as for $B=0$.

The experimentally observed shift of the superconducting transition means that there exists a temperature interval below T_c where the superconducting current exists only in the plane of the CuO_2 layers and equals zero in the perpendicular direction. As we have said, such behavior could be a manifestation of a Friedel transition but it could also be due to the nonuniformity of the sample. There are two types of nonuniformities which can lead to the effect that we observe:

1) the presence of layers with a higher value of T_c which are separated by layers with a lower value of T_c;

2) the presence of planar defects, playing the role of weak links between layers, where a supercurrent arises (on account of thermal fluctuations) at temperatures less than T_c of the layers (a similar mechanism is realized in granular superconductors[10]).

The effect which we observed cannot be due to defects of the second type. This follows from the experiment in a magnetic field. Actually an external magnetic field should destroy the weak links and therefore shift the transition in $R_c(T)$ more strongly than in $R_{ab}(T)$.

An additional argument supporting the fact that the observed defect is not due to defects of the second type follows from the behavior of the dynamic magnetic susceptibility. The point is that in the geometry $\mathbf{h}\perp\mathbf{c}$, i.e., when the field is parallel to the layers, planar nonsuperconducting defects make virtually no contribution to the susceptibility (provided that their total volume is small compared with that of the sample). For this reason, even though the presence of defects can lead to the phenomenon that we observed in the resistance, it cannot explain the behavior of the susceptibility. For this reason, the nonuniformities of the first type can lead to the observed phenomenon only in the case that the fraction of the higher-temperature layers is small compared with that of the low-temperature layers. In the limiting case, one narrow high-T_c layer can exist in the sample. Although we cannot rule out this variant, it seems unlikely. It would be more natural to infer that the distribution of T_c over the layers is smooth. However, in this case the superconducting transitions should start at the same temperature for different orientations of the current, in contradiction to experiment.

The magnitude of the temperature shift ΔT observed in the experiment depended on the stage of annealing of the sample, and for different samples differed appreciably for approximately equal values of T_c. This shows that the nonuniformity of the sample is still considerable. But, at the present stage of the investigations, it could not be determined unequivocally whether we are dealing with a Friedel transition (with allowance for the fact that the CuO_2 layers are not all identical) or whether the phenomenon is due to a macroscopic nonuniformity of the sample.

In summary, in the present work a shift of the superconducting transition to low temperatures was observed in oxygen-deficient YBCO single crystals in the case of current flow perpendicular to the CuO_2 layers. This phenomenon could be due to a Friedel transition in a nonuniform layered superconductor.

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