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Experimental evidence for a *d*-wave pairing state in $YBa_2Cu_3O_{7-y}$ from a study of $YBa_2Cu_3O_{7-y}$/insulator/Pb Josephson tunnel junctions

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Detailed measurements of Josephson tunneling between $YBa_2Cu_3O_{7-y}$ (YBCO) and Pb using YBCO/[MgO (or native barrier)]/Pb junctions with YBCO films either *c*-axis or *a*-axis oriented are presented. In the case of the *c*-axis-oriented films, the dependence of the Josephson critical current on the applied magnetic field exhibits diffraction patterns close to that characteristic of a *d*-wave superconductor. The temperature dependence of the Josephson critical current also shows an anomalous behavior. Incidentally, the diffraction pattern exhibits less-sensitive behavior to magnetic fields at low temperatures. These results suggest the possibility of *d*-wave symmetry for a YBCO superconductor.

Since the discovery of high-T_c superconductors, there has been considerable effort to elucidate the mechanism of high-T_c superconductivity. Some measurements provided data favorable to the BCS theory, while others suggested different mechanisms. From Josephson-effect and flux-quantization measurements, it is now undisputed that the pairing state is formed in the condensed state of high-T_c superconductors. However, the symmetry of the pairing state, whether it be *s*-wave or *d*-wave type, has not been clarified yet. Quite recently, possible direct evidence for a *d*-wave pairing state was presented using phase-sensitive measurements for a Pb/Au/YBCO dc SQUID loop[1] where YBCO is $YBa_2Cu_3O_{7-\delta}$, whose experimental geometry has been proposed recently.[2] There are also several theories predicting *d*-wave symmetry[3–6] and other experimental facts suggest a *d*-wave pairing state.[7–14] On the other hand, we have made a preliminary report of an anomalous temperature dependence for the Josephson critical current between YBCO and Pb,[15] which cannot be interpreted with an assumption of *s*-wave symmetry for a YBCO superconductor; this suggests that another symmetry, such as *d*-wave type might be involved.

In this paper, we present detailed measurements of Josephson tunneling using planar epitaxial YBCO/*I*/Pb tunnel junctions, where *I* is either an artificial MgO or a native insulating barrier. In particular, the dependence of the Josephson critical current on the applied magnetic field was investigated in detail using YBCO films with different crystal orientations and different insulating barrier materials. As a result, it was found that Josephson critical current exhibited diffraction patterns close to that expected for a *d*-wave symmetry when the *c*-axis-oriented YBCO films were used. On the other hand, the temperature dependence of Josephson critical current exhibited an anomalous behavior different from the conventional Ambegaokar-Baratoff theory[16] for several YBCO/*I*/Pb junctions tested irrespective of crystal orientations of YBCO films and barrier materials. The diffraction pattern became almost insensitive to magnetic field at low temperatures. The observed phenomenonon may be interpreted by considering the special situation in Josephson tunneling between *s*-wave and *d*-wave superconductors.[17]

The YBCO/*I*/Pb junctions were fabricated by *in situ* deposition of multilayer films using electron-beam and resistive heater coevaporation techniques using the *in situ* mask-changing system. The thicknesses of YBCO and Pb films were typically 150–200 nm and 300 nm, respectively. The *c*-axis-oriented YBCO films were grown on MgO(100) and $SrTiO_3$(100) substrates, while the *a*-axis-oriented films on $LaSrGaO_4$(100) substrates. The insulating barrier was either an artificial MgO barrier of a few nm thick or a native barrier. The native barrier was formed by *in situ* annealing of a YBCO film at 400 °C for 1 h under oxygen pressure of 200 Torr and then depositing a counterelectrode Pb on it. The surface morphology of films was monitored by an atomic-force microscope (AFM). The junction was of cross type with the effective junction area 0.2×0.2 mm^2 and the four-probe method was used in the measurements. The magnetic field was applied to the junction parallel to the film surface using a small coil. The cryostat was shielded by a μ metal to yield a background noise of less than a few mG. The resistance of the Josephson junction was 0.2–0.3 Ω. The observed Josephson critical current ranged from 20 μA to 0.7 mA at 4.2 K. The suppression of Josephson critical current by external magnetic field yielded almost ideal Pb gap structure.

It is well known that the magnetic-field dependence of Josephson critical current between *s*-wave superconductors exhibits a conventional Fraunhofer pattern. In the case of Josephson tunneling between *s*-wave and *d*-wave superconductors, it exhibits the same Fraunhofer pattern against magnetic field when the phase change in the current path of a *d*-wave superconductor does not occur (i.e., current flows only along the *a* or *b* axis) but it does a signficiantly different pattern when the phase change occurs, as was pointed out by Wollman *et al.*[1] In the former case, Josephson critical current at $\Phi=0$ takes a maximum value, but it becomes zero for the latter. According to the AFM observation, the real YBCO film surface was not flat in an atomic scale and the growth of micrograins of 2–5 nm height was generally observed for the films of 150–200 nm thickness. The size of micrograins ranged from 10 to 100 nm in lateral scale. In the inset of Fig. 1 a schematic model of a YBCO surface in the case of a *c*-axis-oriented film was presented. There are some experimental facts that show Josephson current would not flow along the *c*-axis when the junction was formed on a YBCO film probably due to surface degradation effect. Josephson current will flow between the sides of micrograins and a Pb film. Then it is possible to consider the three different current routes as shown in Fig. 1: *a* axis to Pb, *b* axis to Pb (edge tunneling), and (110) direction to Pb (corner tunneling). As a result, the mixture of these processes is expected to be observable. We consider that because of the microsize of the grains, the contribution of the (110) direction to Pb will be rather large for the *c*-axis-oriented films. In the case of the *a*-axis-oriented films, the current flow from the *a* axis to Pb will be dominant.

In the presence of different current routes, the Josephson critical current may be approximately given by the sum of these contributions:[2]

$$I_c = I_c^{\mathrm{edge}} \left| \frac{\sin(\pi\Phi/\Phi_0)}{\pi\Phi/\Phi_0} \right| + I_c^{\mathrm{corner}} \left| \frac{\sin^2(\pi\Phi/2\Phi_0)}{\pi\Phi/\Phi_0} \right| , \tag{1}$$

where Φ is the magnetic flux and Φ_0 is the flux quantum. I_c^{edge} and I_c^{corner} are the Josephson critical currents between the *a* or *b* axis and Pb, and the (110) direction and Pb, respectively. Figure 1 depicts the calculated Fraunhofer pattern at different values of $\alpha = I_c^{\mathrm{corner}}/I_c^{\mathrm{edge}}$. For small values of α, the diffraction pattern approaches a conventional one, while for large values of α, the contribution of corner tunneling becomes dominant and the dip at $\phi=0$ is enhanced. We point out that the periodic structure is kept in dip positions and the peak positions become nonperiodic in this pattern. The data of Wollman *et al.* show that the observed relative periods for edge and corner junctions are not consistent with the calculated ideal curves, which probably arises from the mixing effect of edge and corner types of Josephson currents (corresponding to certain curves in Fig. 2) since the pure corner effect will be quite difficult to realize by considering the disordered surface morphology of crystal in an atomic scale and the macroscopic junction size.

First, it is shown that the dependence of Josephson critical current on applied magnetic field H or the YBCO/MgO(or native barrier)/Pb junctions with the *c*-axis-oriented YBCO films exhibited minimum behavior instead of maximum behavior around $H=0$. Figure 2 depicts such an enhanced example for the Josephson critical current as a function of magnetic field H for a YBCO/MgO/Au/Pb junction on a MgO(100) substrate at 4.2 K. The thicknesses of the MgO barrier and the Au film were 4 and 3 nm, respectively. The Au film was deposited in order to avoid the formation of Pb oxide material at the tunneling boundary. Josephson critical current was strongly suppressed and took on minimum behavior around $H=0$. The solid line is the calculated curve for $I_c^{\mathrm{corner}}/I_c^{\mathrm{edge}}=6.6$ using Eq. (1). The agreement between the experimental data and theory looks qualitatively good, indicating that the *a*-*b* corner contribution [current: (110) direction] is dominant according to Fig. 1. The result is consistent with the AFM observation on the YBCO surface because there existed the micrograins of lateral size of a few tens of nm which may enable us to carry a greater part of Josephson current at the grain corners. Because of small Josephson current, the self-field effect induced by Josephson current itself is negligible. Note that the diffraction pattern like Fig. 2 cannot be obtained by considering either a nonuniform current flow in the junction[18] or the flux trapping effect. The observed diffraction patterns seem to be dependent on the

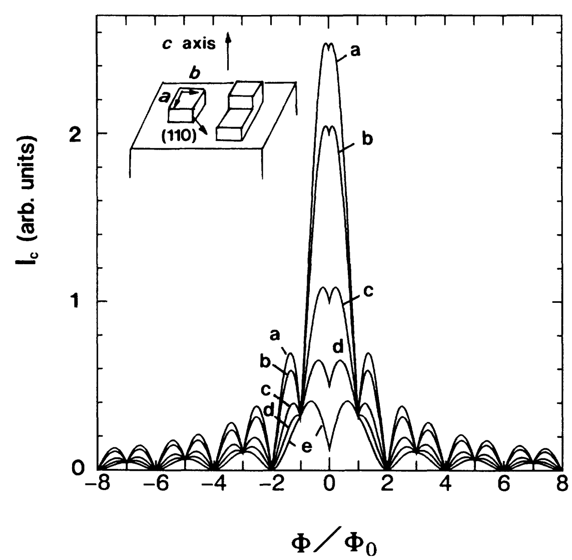

FIG. 1. Calculated Josephson critical current I_c as a function of the normalized magnetic flux Φ/Φ_0 at different ratios of $\alpha = I_c^{\mathrm{corner}}/I_c^{\mathrm{edge}}$. a: $\alpha=0.4$; b: $\alpha=0.5$; c: $\alpha=1.0$; d: $\alpha=2.0$; e: $\alpha=8.0$. The inset shows a schematic drawing of the YBCO film surface in an atomic scale in a real situation.

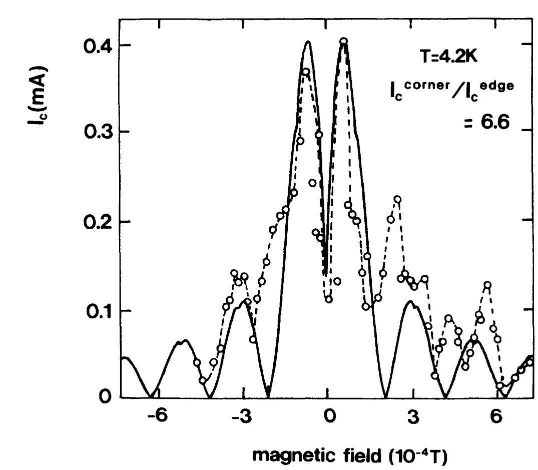

FIG. 2. Dependence of Josephson critical current I_c on applied magnetic field at 4.2 K for a YBCO/MgO/Pb tunnel junction on a $SrTiO_3(100)$ substrate. The YBCO film was *c*-axis oriented. The solid line is the calculated curve by assuming $I_c^{\mathrm{corner}}/I_c^{\mathrm{edge}}=6.6$.

detailed YBCO crystal structure on the film surface. On the other hand, the use of *a*-axis-oriented YBCO films yielded a diffraction pattern similar to the conventional one. In this case, Josephson current is dominated by tunneling from the *a* axis to Pb.

We note that the Josephson penetration depth λ_J is estimated to be 0.51 mm for $I_c = 0.5$ mA and 0.73 mm for $I_c = 100\ \mu$A. Since the size of tunneling junctions is $L = 0.2$ mm ($L/\lambda_J < 1$), the Josephson current is expected to flow almost uniformly in a junction and the cross-type geometry does not affect the observed results significantly. The calculated magnetic period by assuming that London penetration depth of YBCO and Pb were 150 and 50 nm, respectively, was 0.7 G, rather close to the experimental value of 1 G, although the geometry for flux entry would be complicated according to Fig. 1.

It is very remarkable to point out that the temperature dependence of Josephson critical current I_c was quite anomalous. Figure 3 depicts the recent measurements on several samples. The data were normalized by the value of I_c at 4.2 K. Below T_c of Pb, I_c first increased rapidly, then decreased nearly linearly with further reduction of temperature, forming maximum behavior at around $T/T_c = 0.7$ ($T \sim 5$ K). This phenomenon was observed irrespective of the crystal directions (*c* axis or *a* axis) of YBCO films and barrier materials (native or artificial MgO). According to the Ambegaokar-Baratoff theory,[16] in the case where the superconductor is *s*-wave originated, I_c monotonically increases with reducing temperature. The results suggest that a YBCO superconductor is in the different pairing state from an *s*-wave one, maybe in a *d*-wave pairing state. Some explanations have already been given by considering the Josephson tunneling between *s*-wave and *d*-wave superconductors. Tanaka proposed the following model:[17] just below T_c of Pb, the strong superconductivity of YBCO induces the *d*-wave pairing state in the Pb side, but as bath temperature is reduced, the *s*-wave pairing state develops. Then, by considering a rather ill-defined surface morphology in an atomic scale in the junction area, it is shown that Josephson currents from Pb to *a* axis and *b* axis flow in an opposite direction to each other, causing the canceling effect which contributes to the reduction of Josephson current. We note that the temperature dependence of Josephson critical current for a YBCO grain boundary junction on a $SrTiO_3(100)$ bicrystal substrate exhibited monotonically increasing behavior with reducing bath temperature, similar to the work of Dimos, Chaudhali, and Mannhart.[19] This result is naturally expected for Josephson tunneling between *d*-wave superconductors.

Next, the dependence of Josephson critical current on magnetic field at different temperatures for the YBCO/*I*/Pb junctions was recorded, which revealed very interesting behavior. With reducing bath temperature, the diffraction pattern itself was also weakened as well as the reduction of Josephson critical current and became almost insensitive to magnetic field at low temperatures. Figure 4 compares the result at 4.2 K with the one at 2.1 K for a YBCO/native barrier/Pb junction (YBCO: *a*-axis oriented) on a $LaSrGaO_4(100)$ substrate. The Josephson critical current at $H = 0$ at 2.1 K was asymmetric against the polarity of current direction ($I_c^+ = 28\ \mu$A, $I_c^- = 40\ \mu$A). The positive-current axis corresponds to the case when Josephson current flows from YBCO to Pb. In this case, the electron pairs in Pb are converted to hole pairs in YBCO. The Fraunhofer patterns look different between positive- and negative-current axes, indicating that the pair conversion process will be apparently different, although we do not expect a significant difference between the positive and negative pair-tunneling processes in the conventional concept. For

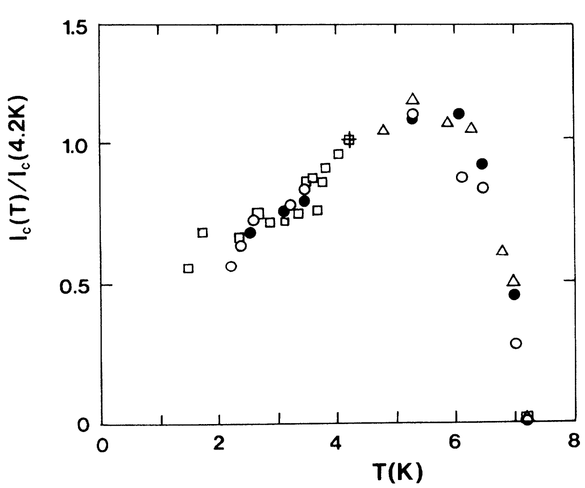

FIG. 3. Temperature dependence of Josephson critical current I_c normalized at the value at 4.2 K. The values of I_c (4.2 K) are 58 μA (○), 46 μA (●), 2.1 mA (△), and 1.0 mA (□).

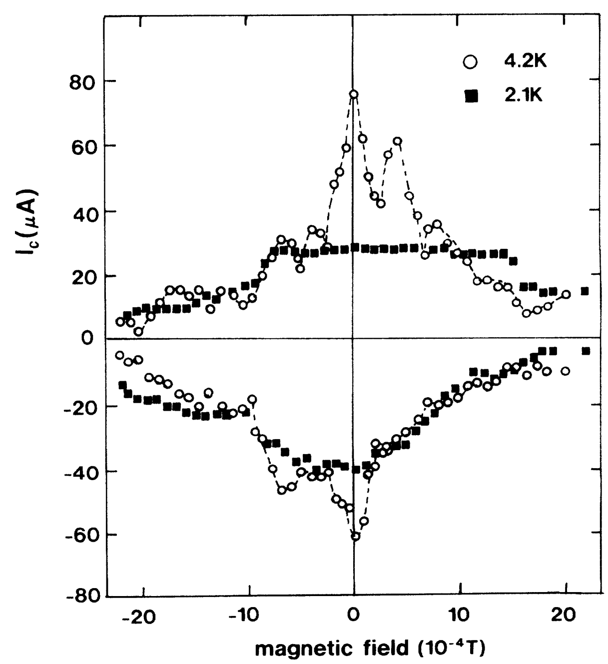

FIG. 4. Dependence of Josephson critical current I_c on applied magnetic field at 4.2 K and 2.1 K for a YBCO/native barrier/Pb tunnel junction on a $LaSrGaO_4(100)$ substrate. The YBCO film was *a*-axis oriented.

positive-current flow, the diffraction pattern became almost flat at 2 K. A similar phenomenon was also observed for the junction with higher Josephson current about 0.7 mA. The flat response against magnetic field may be also related to the contributions of different phase current flows in the junction region where some cancellation effect is expected due to the imperfect interface morphology as described above,[17] which will perturb the current diffraction phenomenon considerably.

We have reported detailed measurements on the Josephson tunneling between YBCO and Pb. The dependence of Josephson critical current on magnetic field did not exhibit a conventional Fraunhofer pattern especially for the junction with the *c*-axis-oriented YBCO films. The main features of observed patterns were interpreted by the model calculation of Josephson tunneling between *s*-wave and *d*-wave superconductors. The temperature dependence of Josephson critical current was also quite anomalous, which cannot also be interpreted by Josephson tunneling between *s*-wave superconductors. The results suggest a possible *d*-wave pairing state in a YBCO superconductor.

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