Josephson Effects in the Ba-Y-Cu-O Compounds

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A point-contact Josephson junction between a bulk Ba-Y-Cu-O compound ($T_c \sim 90$ K) and a Nb needle has been made. The *I-V* characteristics under microwave radiation show Shapiro steps, confirming the Josephson nature of the formed contact. Spin-singlet superconductivity in the Ba-Y-Cu-O system is implied from the voltage of the steps. The temperature dependence of the critical currents suggests that the Josephson junction if formed between Nb and another material with much higher T_c. Internal Josephson structure within the bulk ceramics is not found in the Ba-Y-Cu-O system.

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Recently a series of high-T_c ceramic superconductors have been discovered,[1] triggered initially by the historic finding in the Ba-La-Cu-O system.[2] Among those superconducting oxides, the Ba-Y-Cu-O compound emerged as the first material to show a reproducible T_c higher than liquid-nitrogen temperature, a technological, as well as psychological, milestone temperature. As for the origin of the superconductivity in these high-T_c superconductors, which are categorized as ceramic superconductors, several exotic mechanisms have been suggested such as interfacial superconductivity,[3] resonating-valence-bond theory,[4] and also phonon-mediated superconductivity.[5] Experimentally, the superconductivity in these ceramics has been confirmed through resistance measurements and ac and dc diamagnetism measurements. The only known physical mechanism which can produce the large dc diamagnetism is superconductivity. Alongside the zero-resistance state and the Meissner effect, the existence of macroscopic quantum phenomena signifies the central ideas of the superconductivity. The Josephson junction is the celebrated quantum-phase–sensitive detector capable of proving the wave nature of superconductive system. For instance, the difference in the macroscopic quantum phases of the electron pairs across the Josephson junction (phase difference ϕ) is related to the amount of the supercurrent flowing through the junction, and the rate of change in the phase difference, $d\phi/dt$, is related to the voltage across the junction. The Josephson effect seems to be a universal effect associated with superconductivity, but one might at least innocently ask the following question: "Can BCS electron pairs at one side of the Josephson junction cross to the other side of the junction where non-BCS superconductivity is present (if such superconductivity exists at all), and effortlessly rearrange themselves through a different pairing mechanism?" Assuming such a circumstance, and without clear theoretical guidance, we have set out to construct a point-contact Josephson junction with the Ba-Y-Cu-O compound as at least one of the electrodes.

The preparation processes and the crystal phase of the Ba-Y-Cu-O compound are briefly discussed. The Ba-Y-Cu-O samples were prepared from the appropriate mixtures of Y_2O_3, $BaCO_3$, and CuO powders, heated in air and then pressed into disk shape. Such disks were finally sintered in an oxygen-background crucible to adjust their final oxygen concentration. The occurrence of superconductivity in Ba-Y-Cu-O material is very sensitive to the sintering conditions. Samples were sintered in the temperature range between 950 °C and 1100 °C. The fabrication details of the Ba-Y-Cu-O samples will be given elsewhere.[6] The chemical compositions of the Ba-Y-Cu-O compounds were found to be rather insensitive to the superconducting critical temperature. In most of the samples with rather random initial proportions of Y, Ba, and Cu, superconductivity onsets at around 90 K were still observed. Recently it has been pointed out that $(Y,Ba)_3Cu_3O_{8-x}$ is the composition contributing to the high-T_c superconductivity.[7] We have found similar results from ac diamagnetism measurements.[6] The Ba-Y-Cu-O sample used had a 28% diamagnetic shift at 77 K and a 65% diamagnetic shift at 4.2 K, both compared to that of a Pb sample having the same geometric size. The same sample, in resistance measurements, had a T_c of 90 K with a spread of $\Delta T_c \approx 2$ K.

Nb as well as the Ba-Y-Cu-O compound was used as the needle material for the point contact, where the other electrode was always Ba-Y-Cu-O. Nb and Ba-Y-Cu-O points were hand sharpened with sandpaper and needle points with radii of about 1–2 μm were obtained. The bulk Ba-Y-Cu-O electrode had dimensions of $10\times2\times1$ mm^3. 30-μm-thick gold wires were attached to the bulk Ba-Y-Cu-O sample as the current and the voltage leads. The contacts between the Ba-Y-Cu-O and the gold wires

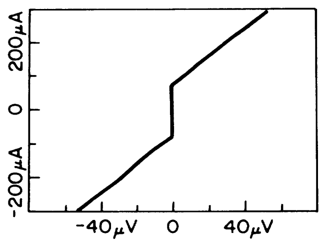

FIG. 1. I-V characteristics of Nb/Ba-Y-Cu-O point-contact junction.

were made by silver paint. The resistance of such contacts was rather high (~ 1 kΩ). A vacuum-sputtered thin coat (~ 200 Å) of gold applied on the surface of the Ba-Y-Cu-O improved the contact resistance greatly. A contact resistance of about a few ohms per 0.01 mm^2 was obtained. All the electrical measurements were done in four-probe fashion. The temperature was monitored by a silicon-diode thermometer. For the point-contact experiments the temperature was controlled simply by our elevating the sample above the liquid-helium surface without any can or feedback mechanism. For the T_c and diamagnetism measurements, the temperature was controlled much more carefully, with double vacuum cans. The junction was formed in the cryogenic environment and controlled by a screw-driven rod connecting the needle-pointed electrode to the room-temperature controller. Microwave radiation was coupled to the samples with the aid of a nondirectional antenna formed by the center conductor of the coaxial semirigid cable.

Figure 1 shows the I-V characteristics of a Nb/Ba-Y-Cu-O junction at 4.2 K. A Josephson supercurrent of about 80 μA can be seen. The characteristic voltage was about 15 μV, much lower than the ideal tunnel value. With the microwave irradiation, distinctive voltage steps appeared in the junction I-V characteristics. Figure 2 shows the I-V characteristics with 8-GHz microwave biasing. The frequency characteristics of the voltages where steps appeared are shown in Fig. 3. In Fig. 3, the

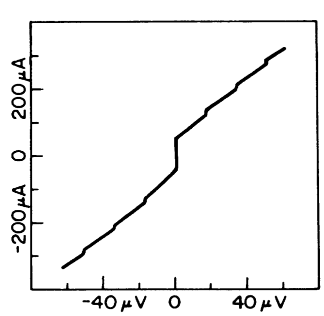

FIG. 2. I-V characteristics of Nb/Ba-Y-Cu-O point-contact junction with the application of 8-GHz microwave radiation. Voltage steps can be clearly seen.

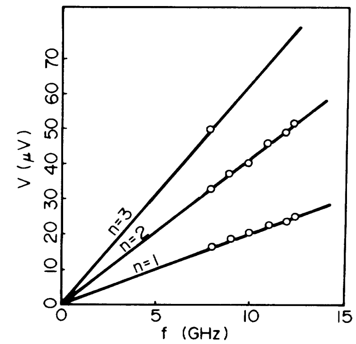

FIG. 3. Frequency dependence of the voltage steps. The lines give the slope $n\Phi_0$.

circles are the measured values and the lines have the slopes of $n\Phi_0$, where n is the order of the steps and Φ_0 is the flux quantum. The observed steps were undoubtedly Shaprio steps, thus confirming the existence of a Josephson junction in the measured system. Moreover, no evidence of $n\Phi_0/2$-dependent voltage steps of a nonsubharmonic nature was observed at any microwave power. Thus it is implied that the superconductive state of the Ba-Y-Cu-O compound has electron pairs in a spin-singlet state.[8] The tip of the Nb point after the formation of the junction was deformed by the pressure applied. The sharpened tip was flattened out to form an "area contact" to the Ba-Y-Cu-O material with an area of about 120×120 μm^2. A nontunneling Josephson junction of such large dimensions is quite inconceivable. The current density of 0.5 A/cm^2, averaged over the whole contact area, also seems unrealistically low for a point-contact junction. Perhaps the distribution of the superconducting crystal phase was rather sparse on the surface of the Ba-Y-Cu-O ceramic sample, so that only a tiny fraction of the seemingly large contact area was actually contributing to the formation of the Josephson junction. Possibly the surface of the Ba-Y-Cu-O is

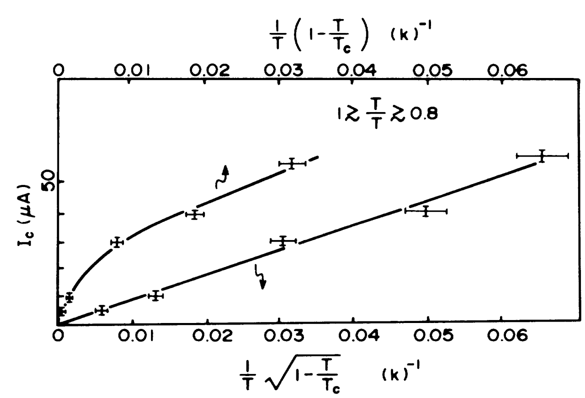

FIG. 4. Temperature dependence of the I_c of Nb/Ba-Y-Cu-O point-contact junction. I_c depends linearly on $T^{-1}(1-T/T_c)^{1/2}$, where T_c is that of Nb.

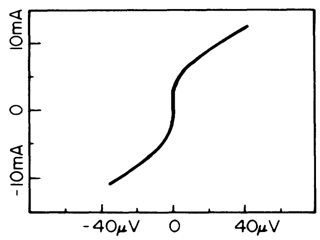

FIG. 5. I-V characteristics of Ba-Y-Cu-O bulk sample just below its T_c.

covered by a rather robust nonsuperconductive oxide layer.

The Josephson supercurrent in the Nb/Ba-Y-Cu-O point contact remained finite up to 9.2 K, the T_c of the Nb electrode. The temperature dependence of the maximum Josephson current I_c near the T_c of Nb ($T/T_c < 0.8$) is plotted in Fig. 4. We assume that the temperature dependence of I_c near T_c has the form $I_c \propto T^{-1}\Delta_1(T)\Delta_2(T)$, as shown by Ambegaokar and Baratoff for the tunneling junction.[9] $\Delta_1(T)$ and $\Delta_2(T)$ are the temperature-dependent superconducting gap energies for each electrode of the junction. Near T_c, $\Delta(T) \simeq \Delta(0) \times (1-T/T_c)^{1/2}$, where $\Delta(0)$ is the energy gap at $T=0$. Thus I_c should be proportional to $T^{-1}(1-T/T_c)^{1/2}$ near the T_c of Nb, on the assumption that $\Delta(T)$ of the Ba-Y-Cu-O is constant in this temperature range. Such an assumption is justified at least under the BCS formalism considering that $T_c(\mathrm{Nb}) \ll T_c(\text{Ba-Y-Cu-O})$. The bottom temperature scale in Fig. 4 is scaled as $T^{-1}(1-T/T_c)^{1/2}$ with $T_c = 9.2$ K, and the measured points form a straight line as shown in Fig. 4. The top temperature scale in Fig. 4 is given in units of $T^{-1}(1-T/T_c)$, reflecting the case where both $\Delta_1(T)$ and $\Delta_2(T)$ are that of Nb. The measured data points do not form a straight line on this scale. Thus, the observed Josephson effects should be attributed to the Josephson junction formed between the Nb electrode and another material with much higher T_c. Point contacts between Ba-Y-Cu-O needles and Ba-Y-Cu-O bulk electrodes were also tried out. But no superconducting current through them was ever observed, let alone the Josephson effects, even at 4.2 K where the ac diamagnetism of the samples was rather large. Such results may also be attributed to the postulated existence of a nonsuperconductive layer on the surface of the Ba-Y-Cu-O ceramics.

Figure 5 gives the I-V characteristics of the bulk Ba-Y-Cu-O sample just after the superconductive percolation path between voltage leads was completed ($T \approx 89.4$ K). Microwave radiation with power all the way up to about 1 W was applied to such a state. But no voltage step was observed. This suggests that the coupling between the superconducting regions along the percolative path are non-Josephson. In another type of ceramic superconductor, the La-Sr-Cu-O compound, such internal Josephson structures were also searched for. In a La-Sr-Cu-O sample where the T_c was suppressed from 40 K to 5.5 K as a result of some still unclear processes (perhaps a water-vapor–mediated process), the ac Josephson effect was confirmed.

In conclusion, we have made a Nb/Ba-Y-Cu-O point-contact Josephson junction. The Shapiro steps produced by the applied microwave radiation confirmed that the coupling mechanism between electrodes was Josephson type. Spin-singlet superconductivity of the Ba-Y-Cu-O system can be inferred from the observed Shapiro steps. Internal Josephson-type structures in the ceramic superconductors were sought. Such structure was found in a degraded La-Sr-Cu-O sample, while no evidence of such structure exists in the Ba-Y-Cu-O samples prepared in our laboratory. The amount of superconducting crystal phase exposed on the surface of the ceramic superconductor seems quite scarce, even for the sample having large diamagnetism. The existence of nonsuperconducting oxide on the surface of Ba-Y-Cu-O ceramics was postulated.

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