Observation of the Reverse ac Josephson Effect in Y-Ba-Cu-O at 240 K

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(Received 30 March 1987; revised manuscript received 16 April 1987)

A two-step resistive transition, one beginning at 240 K and the other at 90 K, has been observed in Y-Ba-Cu-O compounds. The superconductivity, possibly in granular form, at both temperatures has been verified by means of the rf-to-dc conversion associated with the ac Josephson effect.

PACS numbers: 74.10.+v, 74.50.+r, 74.70.Ya

Recently, a furor of activity has been created by the report of superconducting transitions above 100 K in various oxide compounds (e.g., the special session on high-temperature superconductivity at the March 1987 meeting of the American Physical Society). Moreover, Chu[1] has recently announced that there was a possible indication of superconductivity at temperatures as high as 240 K. In several of our yttrium-based oxide compounds, we have also observed resistivity anomalies in the vicinity of 240 K. In one particular sample, the resistive drop starting at 240 K was nearly equal in magnitude to the resistivity drop starting at 90 K. Since the 240-K phase coexists with a lower-temperature superconducting phase in the same material, conventional resistance measurements cannot clearly establish or identify the superconductivity at the higher temperature. Consequently, a different technique is required to verify the superconducting transition or phase when it does not result in a zero-resistance state. Using the reverse ac Josephson effect,[2-7] we have experimentally verified the occurrence of superconductivity not only at the lower transition temperature, but also at the higher transition temperature of 240 K.

A superconductor consisting of grains may be considered to be composed of coupled Josephson junctions. In dc measurements, the zero-resistance state can be observed if the bias current is less than the smallest critical dc Josephson current of all the junctions in the sample. If some of the junctions are in the finite-voltage state, the ac Josephson effect may arise as ac currents are generated in these junctions. To study the nature of the resistive transition at 240 K, we have utilized the reverse of the ac Josephson effect, i.e., use of an alternating current of radio frequency to induce a constant voltage. The behavior of the induced *constant* voltage associated with the ac Josephson effect is distinctly different from a nonvanishing, time-averaged voltage due to rectification effects associated with asymmetrical current-voltage characteristics. Thus, it is possible to distinguish these two effects by careful and thorough examination of the induced voltage as a function of temperature, rf amplitude, rf frequency, and time. For example, the Josephson-effect–related voltage has a constant component versus time which can be verified visually on an oscilloscope.

This reverse ac Josephson effect has been observed in single junctions[2-4] and in arrays[5] with microwave radiation generating induced dc voltages as large as 0.5 mV in a single junction[3] and on the order of volts in multiple junctions.[5] With radio-frequency radiation, similar effects were first observed in granular superconductors by Saxena, Crow, and Strongin,[6] and more recently in granular superconducting films by Sadate-Akhavi *et al.*[7] using an rf current directly. The rf-induced dc voltage in these latter measurements ranged from a few microvolts to millivolts with its polarity changing as a function of temperature, rf amplitude, and rf frequency in a random fashion. We have observed a similar behavior in the multiphased Y-Ba-Cu-O compounds for the transition beginning at 90 K as well as the one at 240 K.

The samples investigated in this Letter had nominal compositions of $Y_{1.8}Ba_{0.2}CuO_{4-y}$ and $Y_1Ba_2Cu_3O_{6+x}$, where the oxygen content is undetermined. These compounds were prepared by the solid-state reaction method with the appropriate mixture of starting powders of Y_2O_3, $BaCO_3$, and CuO. The mixtures were prepared in air under annealing temperatures and conditions previously described in the literature. All of the $Y_{1.8}Ba_{0.2}CuO_{4-y}$ samples were mixed phases as identified by x-ray diffraction analysis. The $Y_1Ba_2Cu_3O_{6+x}$ specimen annealed at 900 °C was a single-phase sample with no additional diffraction peaks.

The resistance of these various Y-based compounds was measured by a standard four-probe technique with no attempt to shield the samples from the Earth's magnetic field. The resistances of the single-phase $Y_1Ba_2Cu_3O_{6+x}$ sample and one of the mixed-phase $Y_{1.8}Ba_{0.2}CuO_{4-y}$ samples are shown in Fig. 1. The

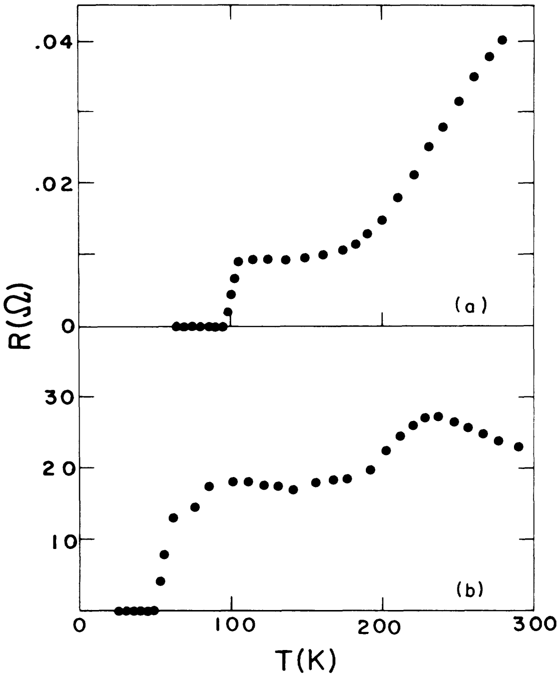

FIG. 1. (a) Resistance vs temperature of a single-phase $Y_1Ba_2Cu_3O_{6+x}$ sample. (b) Resistance vs temperature of a multiphase $Y_{1.8}Ba_{0.2}CuO_{4-y}$ sample.

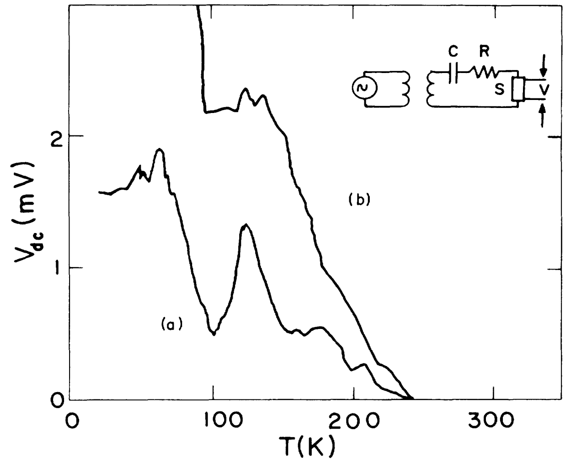

FIG. 2. The rf-current–induced dc voltage V_{dc} across the multiphase sample of Fig. 1(b). The amplitude of the rf current is (curve *a*) 0.2 μA and (curve *b*) 0.4 μA for a 5-MHz frequency. Inset: Experimental arrangement with S denoting sample, $R = 10^2 - 10^3$ Ω, and $C = 47$ pF to 0.0047 μF.

resistance of the single-phase material continuously decreases from room temperature culminating in a fairly sharp transition at 94 K (midpoint value). Also note that the resistance is very small above the transition temperature, which is indicative of a good single-phase material. In contrast, the mixed-phase sample's resistance increases as the temperature is lowered from room temperature and then exhibits an approximately 40% decrease over the temperature range of 240 to 200 K before flatting out at lower temperatures. Finally, at 90 K the resistance begins to drop rapidly with a full zero-state resistance at 60 K. Obviously the resistance measurement is unable to ascertain whether the resistance drop in the 200–240-K range is due to superconductivity or some other type of electronic transition. This is especially true if the two superconducting phases are granular in nature and in some series combination. Thus an alternative technique for identification of the possible superconductivity is required.

Since scanning-electron-microscope pictures show that these oxide materials are rather porous with chains of grains measuring a few microns in size, the possibility of coupled Josephson junctions in the superconducting phases exists. In the pressure of an rf current, individual Josephson junctions in these materials could then develop quantum voltages, given by $V_J = nhf/2e$, on the order of nanovolts, even in an unbiased sample. Because of thermal smearing, individual quantum voltages are not observable. However, dc voltages on the order of a millivolt can result from the summation of thousands of Josephson junctions with values of *n* as large as 100.

The experimental arrangement for our experiment is rather simple. An ac current of rf frequency is directly fed into the sample as shown in the inset of Fig. 2 with the dc voltage measured across the potential leads of the four-probe resistance configuration. (A more detailed description of the experimental setup is given in Ref. 8.) The occurrence of the reverse ac Josephson effect in our mixed-phase $Y_{1.8}Ba_{0.2}CuO_{4-y}$ sample is shown in Fig. 2 where the induced dc voltage V_{dc} for two different rf currents is plotted as a function of the temperature. Notice that there is a clear correlation between the initial resistive decrease of this sample from Fig. 1 and the onset of the induced dc voltage at 240 K for both rf currents at 5 MHz. Not only is there a strong correlation, but the nature of the dc voltage below 240 K is drastically different from the background voltage above the onset when viewed with increased sensitivity as seen in Fig. 3. A similar correlation is observed for other rf frequencies as well. The induced dc voltage varies in a random, oscillatory manner as a function of temperature since it is a result of a series combination of a large number of individual junctions whose individual induced voltages also vary in some random, oscillatory manner as a function of frequency and amplitude. A more striking example of this random oscillatory behavior is shown in Fig. 4 for a different multiphased $Y_{1.8}Ba_{0.2}CuO_{4-y}$ sample having a smaller resistive drop at 240 K. Also note that the induced voltage at a fixed temperature varies as a function of the amplitude of the rf current. This dependence is further evidenced by the observation of one and a half oscillations in V_{dc} when the rf current was varied from 0 to 10 μA. Generally there is also a corre-

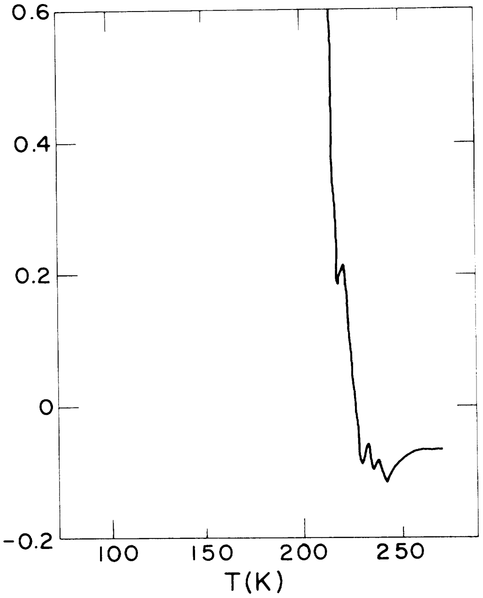

FIG. 3. The rf-current–induced dc voltage near the onset temperature of 240 K on an expanded scale. The amplitude of the rf current is approximately 0.4 μA for a frequency of 5 MHz.

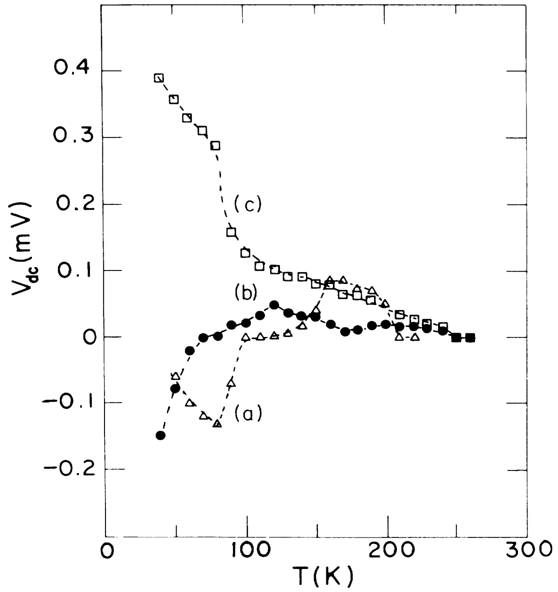

FIG. 4. The rf-current–induced dc voltage for a different multiphase $Y_{1.8}Ba_{0.2}CuO_{4-y}$ sample. The frequency of the rf current is 4 MHz. The amplitudes of the rf current are approximately as follows: curve *a*, 0.2 μA; curve *b*, 0.4 μA; and curve *c*, 0.6 μA. The solid lines are guides for the eye.

lation between the onset of the resistive decrease and the change in V_{dc} for the lower-temperature superconducting phase at approximately 90 K, although this correlation is not always as definitive because of the overlap of the induced dc voltages from both phases. For the single-phase $Y_1Ba_2Cu_3O_{6+x}$ sample, the induced dc voltage was only observable in the vicinity of the superconducting region of 90 K and was substantially smaller. This is a result of the single-phase material's having a much larger critical current and correspondingly the rf current's being unable to switch a sizable number of the junctions to the finite-voltage state. Overall, the behavior of the observed rf-induced dc voltage is consistent with that expected of Josephson-coupled granular superconductors. Thus, we conclude that the superconductivity in granular form exists at 240 K.

Experimental notes.—Care should be taken to allow samples to reach thermal equilibrium at all temperatures since thermal emf's of 10 μV or more can easily develop in these materials. Typically, one trace of temperature dependence was taken over a period of 3 h or longer. In addition, a small rf amplitude is preferred to avoid other rectification effects. Examination of the voltage versus time on an oscilloscope is especially helpful in separating the constant voltage associated with the ac Josephson effect from the time-averaged voltages arising from rectification.

We wish to thank C. W. Chu, H. V. Bohm, Y. W. Kim, S. R. Ovshinsky, and R. Young for discussions of various aspects of the high-temperature superconductivity in oxide materials. The work at Wayne State University is supported in part by the Institute for Manufacturing Research and the Industrial Productivity and Projects Research Institute at Wayne State University, and

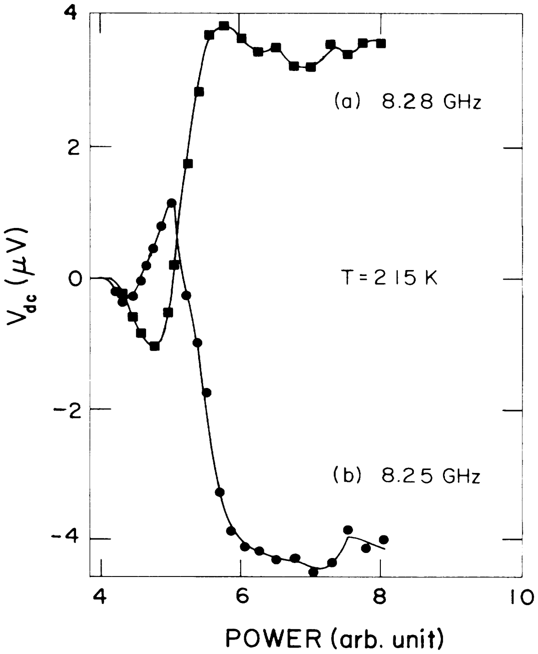

FIG. 5. Microwave-induced dc voltage as a function of microwave power at two different frequencies.

the National Science Foundation through Grant No. DMR-8400711.

Note added.—One further test that can distinguish the reverse ac Josephson effect from the more commonly known rectification effect is its polarity reversibility. Figure 5 clearly shows two examples of this property. In this measurement, the sample was exposed to microwave radiation through a coil not physically connected to the sample. As can be seen in the figure, the polarity of the induced dc voltage is not only reversed as a function of the power, but also the polarities are opposite for two slightly different frequencies.

[1] C. W. Chu, in *New York Times,* 10 March 1987.

[2] D. N. Langenberg, D. J. Scalapino, B. N. Taylor, and R. R. Eck, Phys. Lett. **20**, 563 (1966).

[3] J. T. Chen, R. J. Todd, and Y. W. Kim, Phys. Rev. B **5**, 1843 (1972).

[4] K. Hamasaki, K. Enpuku, F. Irie, and K. Yoshida, J. Appl. Phys. **52**, 6816 (1981).

[5] R. L. Kautz, Appl. Phys. Lett. **36**, 386 (1980).

[6] A. M. Saxena, J. E. Crow, and M. Strongin, Solid State Commun. **14**, 799 (1974).

[7] H. Sadate-Akhavi, J. T. Chen, A. M. Kadin, J. E. Keem, and S. R. Ovshinsky, Solid State Commun. **50**, 975 (1984).