PHYSICAL REVIEW B VOLUME 36, NUMBER 13 1 NOVEMBER 1987

Possible Josephson oscillations spectra and electron paramagnetic resonance of Cu^{2+} in Y-Ba-Cu-O

J. Stankowski,* P. K. Kahol, and N. S. Dalal
Department of Chemistry, West Virginia University, Morgantown, West Virginia 26506-6045

J. S. Moodera
National Magnet Laboratory, Cambridge, Massachusetts 02139

(Received 26 June 1987)

A broad spectrum around 50 G, possibly due to Josephson oscillations, has been observed in the superconductor $Y_1Ba_2Cu_3O_{7+x}$, using standard X-band EPR methodology. The spectrum has its tail extending to high fields and exhibiting complex oscillatory patterns such as expected from Josephson loops of sizes in the range of 0.65–0.81 μ. The EPR method can directly and nonabrasively detect small superconducting domains and Cu^{2+} inclusions in these materials. The detection of numerous Josephson junctions naturally present in such materials open up the possibilities for building new types of superconducting quantum interference devices.

INTRODUCTION

Josephson oscillations have long been observed at helium temperatures in junctions formed by two superconducting metallic pieces separated by a thin layer of a dielectric material.[1] The recently discovered high-temperature superconductors[2-5] A-Ba-Cu-O (with $A = $ Y, La, Eu, . . .) have polycrystalline structure. Due to the presence of grains in such ceramic materials, we expected to observe a large number of Josephson junctions between these grains.

In standard Josephson junctions, the oscillation period measured versus external magnetic field is of the order of a milligauss,[1] due to the large size of the superconducting circuit closed by a weak contact. This periodicity is described by a fundamental equation $B_nS = n\phi_0$, where ϕ_0 is the quantum of flux equal to $\sim 2.07\times10^{-7}$ G cm^2, S is the surface area of the circuit, and B_n is the magnetic field determined by the nth fluxoid locked in the circuit. Since the grain size in Y-Ba-Cu-O ceramic is of the order of a micron, the periodicity of the Josephson oscillations in such material should be several tens of gauss. Due to a wide distribution of the grain sizes in the ceramic superconductors, a significant spread of Josephson periodicities around an average value is expected.

Many authors have speculated that, in these types of materials, copper plays an important role in their superconducting behavior.[6,7] Molecular-orbital calculations even suggest significant changes of the molecular-orbital topology at the Fermi surface (E_F), caused by the possible conversion of Cu^{2+} to Cu^{3+}.[6] EPR should be, therefore, a good method to characterize the superconducting behavior of these materials.

EXPERIMENT

Samples of Y-Ba-Cu-O were made at the National Magnetic Laboratory, MIT, and were found to be completely diamagnetic for $B < 400$ G. Two samples were measured: sample 1 had a more uniform superconducting phase ($T_c = 91.5$ K, $\Delta T_c = 1.1$ K) while sample 2 was more heterogeneous ($T_c = 91$ K, $\Delta T_c \approx 2.5$ K).

EPR measurements in the temperature range 80–300 K were carried out on an IBM-Bruker ER-200D spectrometer at X band ($\sim$9.4 GHz) using microwave power levels up to $\sim$5 mW, and 100-kHz field modulation of amplitude up to 5 G. The temperatures were measured with a calibrated copper-constantan thermocouple with the sample in a nitrogen gas flow cryostat. The magnetic field was calibrated using an NMR gaussmeter for $B > 1500$ G.

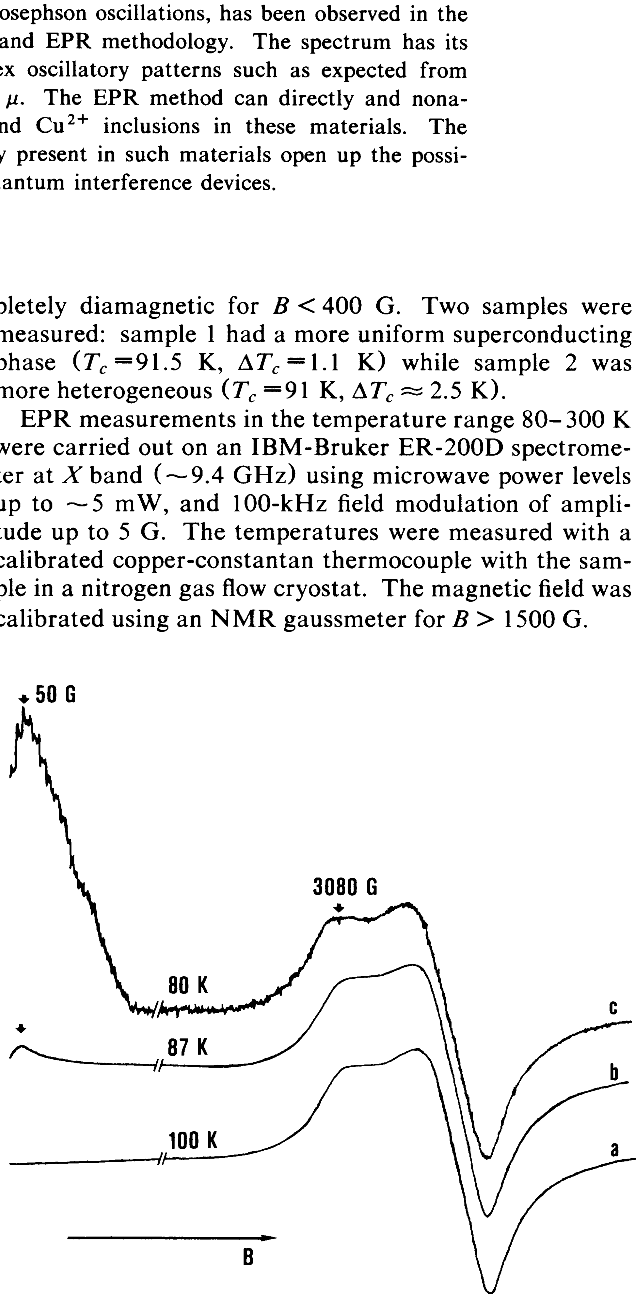

FIG. 1. First derivative EPR spectra showing the 50-G peak and the Cu^{2+} EPR absorption around 3200 G at (a) $T = 100$ K, (b) $T = 87$ K, and (c) $T = 80$ K.

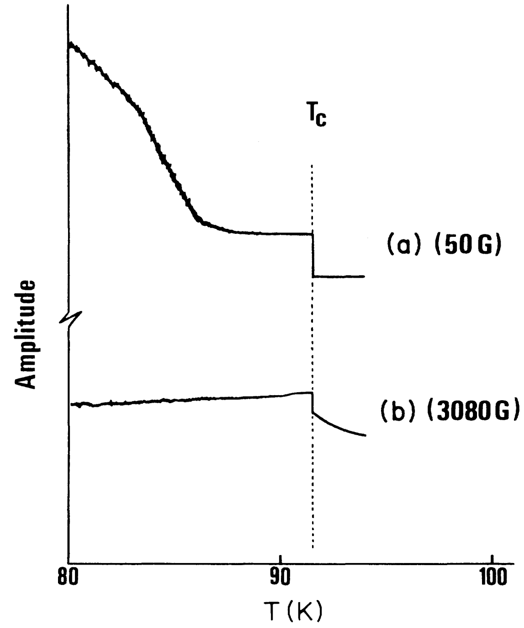

FIG. 2. Temperature dependence of the amplitude of the spectrum at 50 and 3080 G.

RESULTS AND DISCUSSION

An EPR spectrum, typical for Cu^{2+} ions in a polycrystalline sample, was observed at room temperature [Fig. 1(a)]. Additional features start to develop sharply at T_c (91.5 K), as shown in Fig. 1(b), and these features dominate the EPR spectra below about 85 K. For $T \leq 85$ K, a strong peak develops at about 50 G, and a broad background appears over the entire magnetic field range. The averaged level of the 50 G signal increases with decreasing magnetic field [Fig. 1(c)]. The temperature dependence of the peak's amplitude at 50 G [cf. Fig. 1(c)] is shown in Fig. 2(a). At low temperatures, the amplitude undergoes large fluctuations, and these are thought to be associated with a size distribution of Josephson circuits. With increasing temperature, these fluctuations decrease and show a discontinuous drop at T_c. Above T_c, only microwave absorption from paramagnetic Cu^{2+} centers remains. A similar experiment was performed at a field (3080 G) corresponding to $g_{\parallel}$ of the Cu^{2+} spectrum; the results are shown in Fig. 2(b). At T_c the EPR amplitude again shows a drop caused by the disappearance of the oscillations.

The 50-G peak assigned to Josephson oscillations is shown in Fig. 3 in an expanded field scale (from 20 to 180 G). Oscillations seen in the figure are thought to result from the superposition of signals from a large number of Josephson circuits characterized by their own periodicity. The maximum in the Josephson spectrum (~ 50 G) corresponds to the maximum in the distribution of the loop sizes. Then from the fundamental relation

$$B_{ni}S_i = \frac{nhc}{2e}\,[\mathrm{G\,cm^2}]\ , \qquad (1)$$

and using $S_i = \pi r_i^2$, it follows that

$$r_i = \left[\frac{2.07\times10^{-7}}{\pi B_{li}}\right]^{1/2} . \qquad (2)$$

In Eq. (2), r_i is the radius of the ith circuit and B_{ni} is the field corresponding to the nth peak of the ith loop (i.e., $B_{ni} = nB_i$, $n = 1, 2, \ldots$). Equation (2) can thus be used to calculate the radius of the most common circuits present in the system. With $(B_{li})_{\max} = 50$ G, one obtains $(r_i)_{\max} = 0.36 \times 10^{-4}$ cm, which is a reasonable estimate. Several series of peaks with periodicity from 40–60 G were found in each spectrum. Each series contains some-

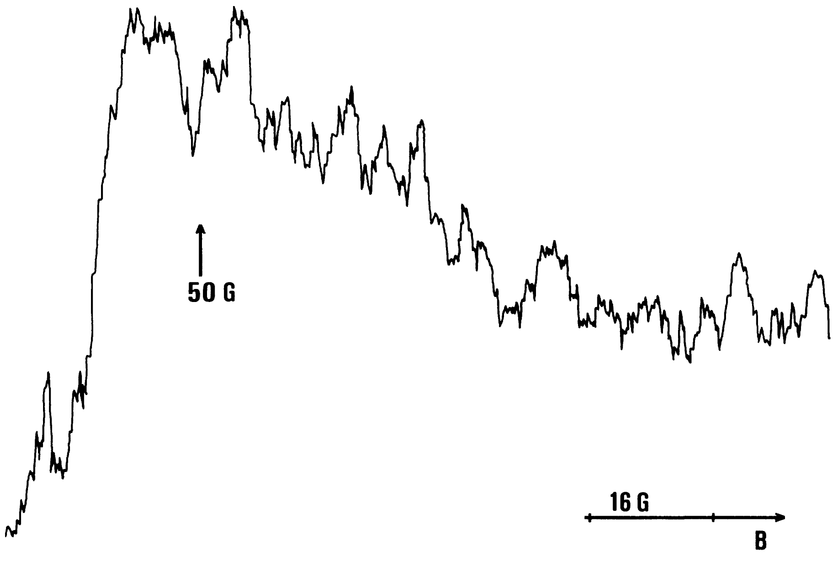

FIG. 3. An expanded view of the "50-G" peak in the field range of 20–180 G.

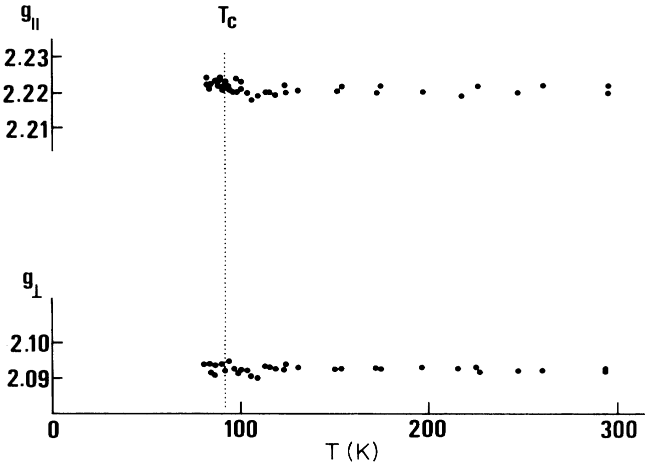

FIG. 4. Temperature dependence of $g_{\parallel}$ and $g_{\perp}$ for Cu^{2+} inclusions in Y-Ba-Cu-O.

times up to five peaks before disappearing into the incoherent fluctuations region. The power absorbed by individual Josephson junctions and the whole sample can be also estimated. The resistivity of a typical junction is 1 kΩ. The microwave frequency used in the experiment (9.45 GHz) would generate a voltage of 19.5 μV at each Josephson junction. Thus the power absorbed by one junction was 3.8×10^{-13} W. Assuming that each junction takes up the sphere of a radius $(r_i)_{\max}=0.36\times10^{-4}$ cm, the minimum number of junctions per cubic centimeter is 5.1×10^{12}. This leads to power absorption of about 2 W cm^{-3} by the whole sample.

EPR spectra show the shape typical of powder Cu^{2+} over the entire temperature range 80–300 K with no discernible change. The temperature dependence of the parameters $g_{\parallel}$ and $g_{\perp}$ is shown in Fig. 4 and, within experimental errors, these values do not show any change even at T_c. It is thus apparent that the observed Cu^{2+} ions exist only in some nonsuperconducting grains. This conclusion is supported by our observation that the narrower the width (ΔT_c) of the superconducting transition for a given sample, the weaker the Cu^{2+} EPR signal was.

CONCLUSIONS

Standard methods can detect superconducting behavior which occurs in bulk material, but this EPR method is specific enough to detect small superconducting regions in isolated domains.

While the current interpretation of the 50-G peak is only tentative, and there might well be other explanations, further confirmation of Josephson oscillations in Y-Ba-Cu-O ceramic can lead to a new type of superconducting quantum interference device with a very small sensor which will be able to operate at nitrogen temperature.

ACKNOWLEDGMENTS

J.S. thanks the Chemistry Department, West Virginia University, for hospitality during his stay when this work was carried out. We all would also like to thank Dr. R. Blinc, Dr. W. Sobol, Dr. B. Cooper, and Dr. S. Osoroff for many helpful discussions.

---

[*] Permanent address: Institute of Molecular Physics, Polish Academy of Sciences, Poznan, Poland.

[1] L. Solymor, *Superconductive Tunneling and Applications* (Chapman and Hall, London, 1972).

[2] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[3] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[4] P. H. Hor, R. L. Meng, Y. Q. Wang, L. Gao, Z. J. Huang, J. Bechtold, K. Forster, and C. W. Chu, Phys. Rev. Lett. **58**, 1891 (1987).

[5] R. M. Hazen, L. W. Finger, F. J. Angel, C. T. Prewitt, N. L. Ross, H. K. Mao, C. G. Hadidiacos, P. H. Hor, R. L. Meng, and C. W. Chu, Phys. Rev. B **35**, 7238 (1987).

[6] M. E. McHenry, A. Collins, M. M. Donovan, C. Counterman, K. H. Johnson, R. C. O'Handley, and G. Kolonji (unpublished).

[7] L. F. Mattheiss, Phys. Rev. Lett. **58**, 1028 (1987).