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Microwave absorption in a dc magnetic field up to 12 kG, attributed to nonequilibrium contributions to the ac susceptibility, appears at T_c as the sample is cooled. ESR measurements of Y-Ba-Cu-O show that Cu^{2+} exists only in the fraction of the sample which is not superconducting in a distorted octahedral surrounding.

INTRODUCTION

The recent discovery of high-T_c superconductivity[1,2] has triggered a variety of experimental studies in order to characterize the new compounds and to understand what causes the superconducting state at such high temperatures. Much progress has been made in order to understand this phenomenon and Y-Ba-Cu-O with a $T_c \sim 92.5$ K has been one of the most studied systems. The Cu^{3+} ion is intimately associated with the superconductivity in these compounds.[3] The single-phase compound $YBa_2Cu_3O_{7-\delta}$ ($\delta \sim 0.1$), an oxygen-deficient perovskite, has been identified as the high-T_c bulk superconductor.[4,5] Depending on the sample preparation details, there is a reversible orthorhombic-to-tetragonal phase transition[6] close to 750 °C. The high T_c is associated with the orthorhombic structure, the tetragonal one becoming superconducting at lower temperatures. Mixtures of the two structures can affect the measured values of T_c. The structural phases and the chemical composition of this compound affect the quality of the superconductor as determined from its T_c, its current-carrying capacity, and its Meissner effect. Related information could be determined from ESR measurements since such a technique is a local probe of the sample. We report here ESR and microwave absorption measurements on the Y-Ba-Cu-O system and the effects of structure and chemical composition, in the normal as well as superconducting states.

EXPERIMENTAL DETAILS

Four different samples were prepared. Sample A was a green semiconducting powder (which does not become superconducting) obtained from sample B. Sample B was a superconducting multiphase system prepared according to Ref. 2 and visibly having a mixture of the black and green powder. Sample C was prepared according to the method presented in Refs. 4 and 5. Sample D was a single-phase sample $YBa_2Cu_3O_{7-\delta}$ with tetragonal structure. Figure 1 shows the temperature dependence of the resistance of these samples. The superconducting samples B, C, and D all show an onset of superconductivity about 95 K. Standard dc four-terminal measurements were made with measuring currents of 100 mA. The Meissner effect was measured at 75 and 40 K using a Hewlett-Packard model 428BR flux-gate magnetometer. All samples were examined by x-ray diffraction and their structure was identified from the powder diffraction patterns. Samples B and C had multiple phases; the volume fraction of sample C forming the orthorhombic phase was larger than that of sample B, as determined from the intensity of x-ray peaks. Sample D was almost entirely single phase with tetragonal symmetry at the composition $YBa_2Cu_3O_{7-\delta}$ and the cell parameters were $a = 3.852$ Å, and $c = 11.674$ Å.

ESR measurements were performed in this compound from 293 down to 4 K on a Brüker ER200D-SRC spectrometer operating in the X band (9.4 GHz) with 100-kHz field modulation. The microwave absorption was measured in the ESR cavity from zero to 12 kG.

RESULTS

Above the transition temperatures a paramagnetic resonance signal associated with Cu^{2+} ions in sites with a distorted octahedral symmetry was observed in all four samples. This signal, which is shown in Fig. 2, is strongest for sample A, the orthorhombic semiconducting compound.

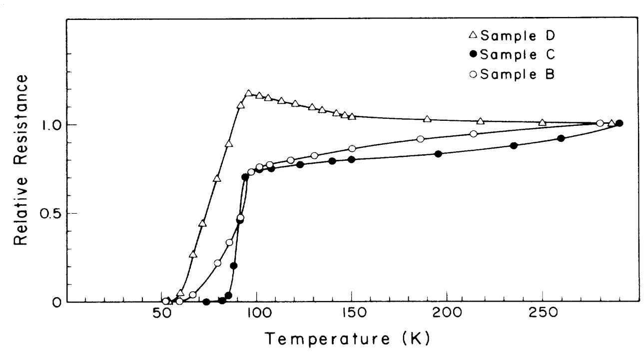

FIG. 1. The temperature dependence of the normalized resistance $R(T)/R(293\text{ K})$. ○: multiphase sample B. ●: multiphase sample C. △: single-phase sample D.

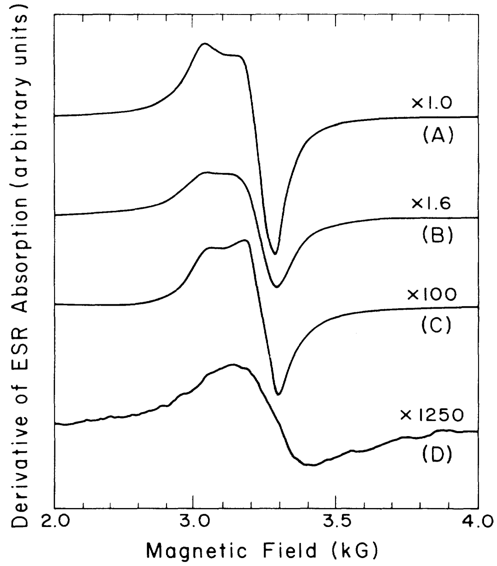

FIG. 2. Room temperature Cu^{2+} ESR lines. (A) green semiconducting compound A, (B) multiphase sample B, (C) multiphase sample C, and (D) single-phase sample D.

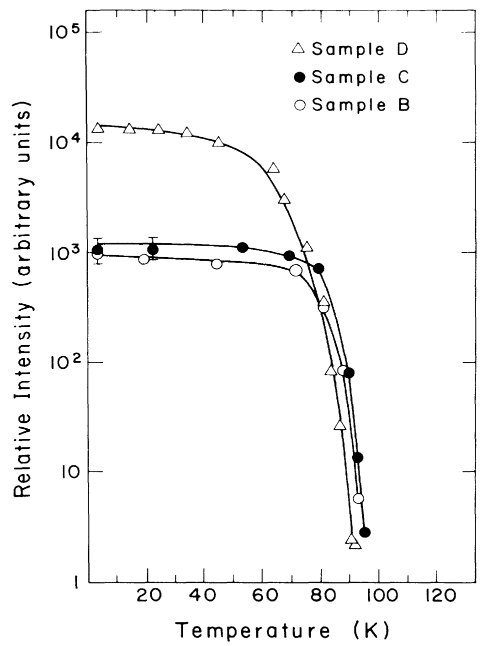

FIG. 3. The temperature dependence of the magnitude of the zero-field absorption. ○: multiphase sample B. ●: multiphase sample C. △: single-phase sample D.

In sample A (top trace in Fig. 2) the ESR intensity corresponds to $\sim 4\times 10^{22}$ spins/cm^3 which represents essentially every Cu atom in the material. It is clear from this result that the valence state for the copper in the semiconducting phase is 2+. In the multiphase samples, B and C, the Cu^{2+} signal is significantly reduced ($\sim 2\times 10^{22}$ and $\sim 5\times 10^{20}$ spins/cm^3, respectively). In the single-phase (or almost single-phase) tetragonal sample (D) the Cu^{2+} signal is further reduced corresponding to $\sim 4\times 10^{19}$ spins/cm^3. The Cu^{2+} signal is proportional to the fraction of the sample which is nonsuperconducting as measured by the Meissner effect and the microwave absorption measurements to be discussed below. We conclude from this trend that the dominant valence state of Cu in the superconducting phases is not Cu^{2+}. In fact, the Cu^{2+} ESR signal is probably indicative of the presence of a nonsuperconducting phase in all our samples. This phase is observed to undergo some form of ordering below about 50 K as has been observed by others[7] and by us in magnetization measurements on the nonsuperconducting phase down to 10 mK, where antiferromagnetic ordering prevails.

As the samples are cooled through the superconducting transition there is no anomalous behavior of the Cu^{2+} ESR line. This fact is a second indication that this line does not originate in the superconducting phase. In addition, we observe a strong microwave absorption as the temperature passes through T_c for fields from 0 G to at least 12 kG. This feature consists of an absorption at zero field with a peak-to-peak derivative width of ~ 20 G and a broad absorption which is only slowly decreasing with increasing dc magnetic field and which extends up to the highest fields measured. These features are not due to spin resonances.

The magnitude of the zero field absorption is plotted as a function of temperature for samples B, C, and D in Fig. 3. Each curve in the figure exhibits two important properties. The first property is the precipitous fall of the signal as the temperature passes through T_c (from below). The second property is the nearly constant magnitude of the signal at low temperatures. We will show that the first property provides a very accurate measure of T_c, while the second may provide an accurate measure of the volume fraction of the sample which is superconducting.

Estimates of the magnitude of the broad microwave absorption feature show, although these numbers are less accurate than those of Fig. 3 because of the broad range of magnetic fields over which they occur, that the precipitous drop of this feature near T_c is still very apparent. Also, the relative sharpness of the drop for the three superconducting samples is very similar to that shown in Fig. 3. The green semiconducting sample A showed neither the low- or high-field microwave absorption features.

DISCUSSION

The microwave absorption at 9.4 GHz in these superconducting samples can be explained by the granular nature of these ceramics. In superconducting composites of this type, which consist of clusters of superconducting grains each of the order of the penetration depth, the superconducting properties are controlled by the effects of percolation and frustration[8] in analogy with the well-known behavior of spin glasses. The superconducting grains are weakly coupled together either by the proximity effect for a metallic host or by Josephson tunneling for an insulating host. Since the macroscopic behavior, and in particular the ac diamagnetic susceptibility, is essentially identical in the two cases, we shall make no attempt in this paper to distinguish between the two possibilities.

In superconducting systems of this type the dc diamagnetic susceptibility is indeed an equilibrium property, but the ac diamagnetic susceptibility is greatly enhanced and, in fact, it can be interpreted as measuring the nonequilibrium (lossy) response of the system for those clusters of superconducting grains where the characteristic relaxation frequency (for decay into a different metastable configuration) is less than that of the applied ac magnetic field.[9] Ebner and Stroud[10] argued that the characteristic relaxation rates for the clusters extend over a very wide range corresponding to frequencies as low as 1 Hz and as high as 100 GHz at low temperatures. If these estimates are correct, our experiments at 9.4 GHz are probing the losses due to most of the nonequilibrium configurations which are possible. Although another mechanism for this absorption could be due to the skin effect,[11] we rule this out because of the lack of normal-state absorption and the observed temperature dependence.

At low frequencies (~ 100 Hz), Razavi, Koffyberg, and Mitrovič[9] have shown that superconducting composites in the system Ba-La-Cu-O exhibit an enhanced ac susceptibility which fits the expected behavior for percolation superconductivity which we have just described. We believe our experiments also show a greatly enhanced ac susceptibility from the microwave absorption at zero field at 9.4 GHz, which was not present in a control sample of superconducting Nb powder, and which appears here abruptly at T_c. In fact, because these measurements (Fig. 3) can be made with sensitivities which extend over many orders of magnitude, the microwave absorption may be a very good way to characterize T_c in these composites. It may also be a better indication of the bulk transition than resistivity or Meissner measurements.

A comparison of Figs. 1 and 3 shows that the superconducting transition is broader in the tetragonal material (sample D) and that the onset of percolation zero resistance occurs at a lower temperature (~ 50 K). The sharpest superconducting transition, which occurs in sample C (filled circles), is demonstrated clearly in both the resistivity measurements of Fig. 1 and the microwave absorptions measurements of Fig. 3. Measurements of the Meissner effect on these samples also correlate well with the relative sharpness of the superconducting transitions in these three samples.

The magnitude of the zero-field microwave absorption at low temperatures (Fig. 3) may also be an important experimental parameter for high-T_c superconductors, because it appears to scale accurately with the volume fraction of superconducting material in the sample. Comparisons with measurements of the Meissner effect at low temperatures, for example, indicate that the ratio of superconducting volume fractions in the two best samples—the tetragonal phase sample D (triangles) and the best mixed orthorhombic and tetragonal phase sample C (filled circles)—are in qualitative agreement. This ratio for the two mixed phase samples, B and C, is ~ 2 by the Meissner effect and ~ 1.5 by the microwave absorption technique at 75 K.

In summary, we have shown that the valence state of the copper in the orthorhombic $Y_1Ba_2Cu_3O_{7-\delta}$ superconducting phase is probably diamagnetic (Cu^{1+} or Cu^{3+}) and that Cu^{2+} exists only as an impurity or in a second semiconducting phase in these ceramics. The utility of microwave absorption measurements for probing metastable effects in these materials has also been demonstrated. The data are qualitatively explained by a description of the superconducting behavior in these ceramics which involves percolation between superconducting grains for which the penetration depth is on the order of the characteristic grain size.

ACKNOWLEDGMENTS

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