Superconductivity and Magnetism in the High-T_c Superconductor Y-Ba-Cu-O

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The new high-T_c superconductor Y-Ba-Cu-O was prepared and characterized. Measurements were performed to determine the superconducting and magnetic properties of the samples. Onset of superconductivity was found above 90 K. Antiferromagnetism was also observed, probably associated with the nonsuperconducting parts of the samples. Modest critical current density as well as large upper critical fields were inferred from the data.

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Superconductivity in the 90-K range, well above liquid-nitrogen temperatures, has recently been discovered in multiphase Y-Ba-Cu-O,[1] following the earlier discovery of high–transition-temperature superconductivity in the La-Ba-Cu-O system by Bednorz and Müller.[2] The results obtained in our laboratory and reported here confirm high-temperature superconductivity in this system and further elucidate its properties. In particular, we have established a significant Meissner effect, a lower limit on the critical currents of the superconducting portions of our samples, a high extrapolated upper critical field, and an apparent connection between the superconductivity and the magnetism exhibited in this material. Specifically, we observe the existence of ~90-K superconductivity in a variety of compositions, always with the result that as superconductivity weakens, magnetism appears. In addition, we have explored a large region of compositional space of the Y-Ba-Cu-O system. Unlike the extensively studied La-X-Cu-O system (with X = Ca, Ba, or Sr) for which superconductivity has been established to arise in the K_2NiF_4 structure, the superconducting phase of the multiphase Y-Ba-Cu-O system has not been established. However, we do find that large amounts of the perovskite and related structures exist in our bulk samples whenever they are good superconductors. We elaborate on all these points below.

Our Y-Ba-Cu-O samples were prepared from mixtures of high-purity Y_2O_3, $BaCO_3$, and CuO powders. The powders were premixed in methanol or water and subsequently heated to 100 °C to evaporate the solvent. Two thermal heat treatments were then used. In the first, the samples were heated in Pt crucibles for 6 h in air at 850 °C and then for another 6 h at 1000 °C. After the first firing, the samples were a dark-green powder, and after the second firing, they became a very porous, black solid. In the second method, the powders were heated for 8–10 h at 1000 °C, ground and then cold pressed to form disks of ~1-cm diameter and 0.2-cm thickness. The superconducting properties of samples prepared in these two ways were similar. We aimed at two structures: first, the cubic perovskite $Y_{1-x}Ba_xCuO_{3-y}$ (type A) with $x = 0.1$, 0.25, and 0.5; and second, the K_2NiF_4 structure $Y_{2-x}Ba_xCuO_{4-y}$ (type B) with $x = 0.6$, 0.4, and 0.2.

The samples were examined by x-ray diffraction and microprobe to establish their structure and to confirm their composition. The interpretation of the x-ray data is not yet entirely clear. We unambiguously observe the perovskite and the K_2NiF_4 structures. But, in addition, we see substantial $Y_2Cu_2O_5$, CuO, and other as-yet unidentified phases. It is interesting to note that even samples prepared with the composition corresponding exactly to the K_2NiF_4 structure showed very little of this phase at the end of the heat-treatment processes, although the superconductivity was very strong. This behavior contrasts markedly with the behavior of the La-Sr-Cu-O system where it has been argued that the perovskite phase is insulating and that the superconductivity arises in the K_2NiF_4 phase.[3]

Four-terminal dc resistance measurements were performed on these samples. Some typical results are shown in Fig. 1. We clearly see that all the superconducting transitions are very similar with midpoints at about

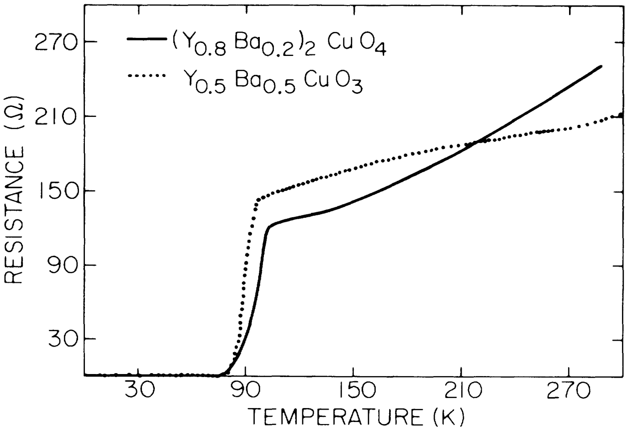

FIG. 1. Resistivity vs temperature for two samples with different nominal compositions.

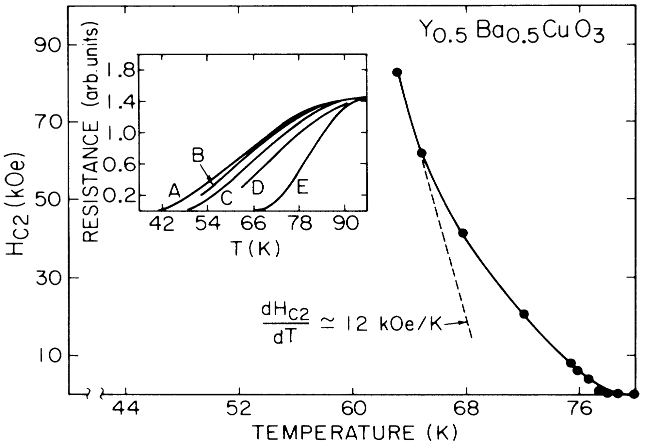

FIG. 2. H_{c2} vs temperature. Inset: Transitions at different applied magnetic fields: curve *a*, 80 kOe; curve *b*, 60 kOe; curve *c*, 40 kOe, curve *d*, 20 kOe; and curve *e*, 0 field.

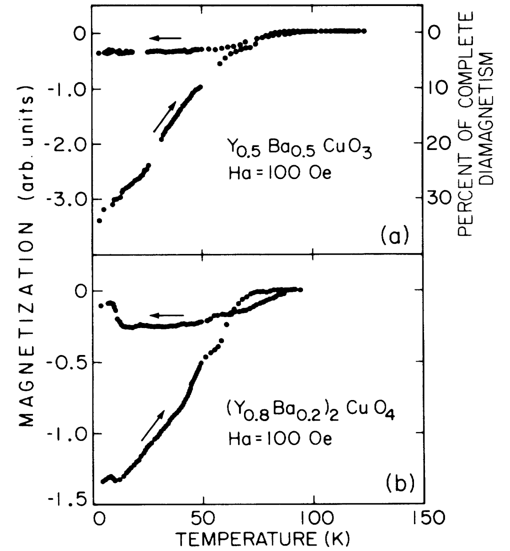

FIG. 3. Shielding and Meissner signals for samples similar to those in Fig. 1.

90–93 K (with onsets as high as 105 K) and widths (10%-90%) of about 8–10 K. The upper critical field H_{c2} in the vicinity of T_c was also determined resistively. $H_{c2}(T)$ rises with positive curvature as the temperature is decreased to the limit of our magnet (85 kOe). Shown in Fig. 2 is H_{c2} versus temperature as well as some superconducting transitions in applied fields. Based on the slope of this curve at the highest field, the extrapolated critical field at zero temperature with use of the standard formulas for the orbital critical field in the dirty limit is 750 kOe.

By use of a vibrating sample magnetometer, magnetic measurements were also made on some samples at temperatures spanning the range from 4.2 K up to the T_c of the sample. In Fig. 3(a) we show a typical magnetization versus temperature plot for a type-A sample with nominal composition $Y_{0.5}Ba_{0.5}CuO_3$. The absolute calibration was established with the use of a similarly shaped sample of Pb to account for the porosity of the samples. Both the dc shielding (increasing temperature) and the Meissner effect (decreasing temperature) traces are shown. The shielding curve in 100 Oe begins at about 30% of complete diamagnetism and decreases continuously as the temperature is increased. The observed Meissner effect is about 3.5% of complete diamagnetism but about 12% of the observed shielding curve, indicating that only a small fraction of the material is a good superconductor. The fact that the Meissner transition is much sharper than that exhibited by the dc shielding response suggests that some of the superconducting phase exists as disconnected regions. Further investigation of the microstructure of these materials will be required to clarify fully these issues. Also, if the superconductivity arises from an interface effect, there still must exist sufficient volumes of well coupled, bulklike material to account for the observation of a detectable Meissner effect.

Figure 3(b) shows similar data for the type-B material with nominal composition $Y_{1.6}Ba_{0.4}CuO_4$. Here, again, we find that the Meissner signal is about 6% of complete diamagnetism. At sufficiently low temperatures, we observe a large loss of the Meissner signal and a corresponding loss in the dc shielding response. We attribute this anomaly to the appearance of spontaneous antiferromagnetic ordering somewhere in the sample, as discussed below.

The fact that the superconductivity is almost independent of overall composition strongly suggests that the superconductivity occurs at a phase boundary in which two phases are in equilibrium with compositions independent of the nominal concentration. The equilibrium could be a metastable one.

The results presented here raise some critical questions regarding the relevant phase for superconductivity, the relevant phase for antiferromagnetism, and their relation. Magnetic-moment measurements during heating and cooling of the samples show magnetic ordering near 10 K as illustrated by Fig. 4. Note the close resemblance between the insulating sample (lower curve) and the superconducting sample (upper curve). The insulating sample was seen to be dark green. Dispersed green regions were also seen in the superconducting sample, which was primarily black in appearance. The magnetic ordering at about 10 K is also evident in the data of Fig. 3(b), where the signal is seen to show a paramagnetic component at low temperatures. This component adds identically to both the shielding and the Meissner signals. Moreover, reentrant superconductivity was not seen in the resistive transition. Thus, we conclude that the magnetism exits in different regions of the material

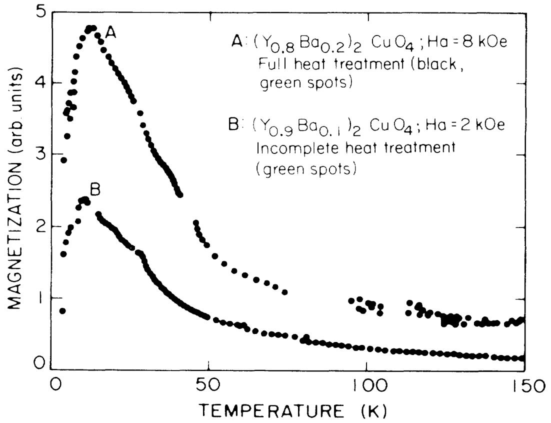

FIG. 4. Comparison of magnetization for samples with different final heat treatments.

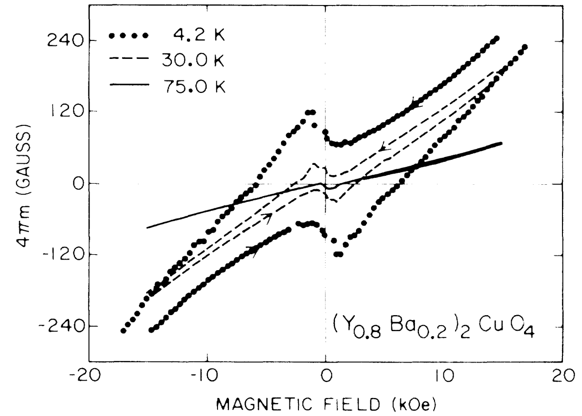

FIG. 5. Magnetic hysteresis loops at different temperatures for the sample shown in Fig. 3(b).

than does the superconductivity. This does not necessarily mean that the magnetic phase is a different structure, or even contains a significantly different composition of Y, Ba, or Cu. The existence of magnetism or superconductivity could depend upon the concentration and/or ordering of oxygen vacancies. A direct connection between oxygen concentration and superconductivity has already been demonstrated in $(La\text{-}Sr)_2CuO_4$.[4]

Since the magnetization decreases to a finite value below the ordering temperature and is linear in H, we suggest that the magnetic phase is antiferromagnetic. The only other possibility for an ordered magnetic phase is a spin-glass. This is ruled out because we did not observe any field-cooling- and/or time-dependent effects for any fields up to 18 kOe. To study the interplay between the superconductivity and antiferromagnetism further, we measured magnetization loops of one of our samples at various temperatures as shown in Fig. 5. As seen in the figure, the magnetization loop shows the superposition of a superconducting and an antiferromagnetic response. These magnetization loops clearly show behavior typical of a strongly type-II superconductor, modified by a constant background slope resulting from the antiferromagnetism. Note that this constant background slope decreases with increasing temperature, consistent with the susceptibility data shown in Fig. 4.

From the width of the hysteresis loop, it is possible to obtain an estimate of the critical current density in the superconducting portions of the sample. With the use of the result that $J_c(H) = (10/4\pi)(m^+ - m^-)/w$, where w is the thickness of the sample[5] and m^+ and m^- denote the negative and positive parts of the magnetization, we obtain critical current densities (at 6 kOe) of 1000, 350, and 15 A/cm^2 at 4.2, 30, and 75 K, respectively. Since in estimating J_c from $m(H)$ we have used the full width of the sample, whereas the superconductivity is localized in small portions of the sample, our estimates are a conservative lower limit. Note also that the value quoted is less than that observed by Panson *et al.* for $(La\text{-}Sr)_2CuO_4$.[6]

In conclusion, we have confirmed the existence of a very-high-T_c superconducting phase in the Y-Ba-Cu-O system. The composition independence of the transition temperature suggests that the high-T_c material exists at a phase boundary. We have estimated a lower bound on $H_{c2}(T=0\text{ K})$ of 750 kOe and a lower bound on $J_c(T=4.2\text{ K})$ of 1000 A/cm^2. In addition we note an interplay between superconductivity and antiferromagnetism in these materials.

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