

Magnetic ordering in $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ below the superconducting transition temperature

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(Received 8 June 1987)

A coexistence of magnetic ordering and superconductivity has been found in $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ at 4.2 K. The magnetic ordering is seen in the Fe moments using Mössbauer spectroscopy. The small Fe percentage was chosen to enable us to probe the crystalline and magnetic environment of an isolated Fe ion. Possible mechanisms responsible for the establishment of the magnetic order and its nature are discussed.

Much of the excitement about the new high-temperature superconducting materials concerns efforts to understand the mechanism responsible for the superconductivity. The cuprate perovskites with compositions $\text{YBa}_2\text{Cu}_3\text{O}_{9-\delta}$ ($\delta \approx 2.1$) (referred to as 1-2-3 compounds) are particularly interesting because the superconductivity is not very much affected by replacing the rare-earth yttrium with several other rare-earth elements with large localized moments.¹⁻³ This leads to the view that the superconductivity in this class of materials involves primarily the CuO layers,³ and that the electrons involved in the superconductivity (i.e., the electrons near the Fermi level) have a low density at the rare-earth and barium sites.

In the work reported here, we have substituted Fe for Cu in 6% of the Cu sites. The small percentage of Fe was chosen to provide a good Mössbauer spectrum while keeping the probability low that an Fe ion probe would have an Fe nearest neighbor. In this way the local crystalline and magnetic environment of the Fe ion could be examined. The 6% substitution of Fe for Cu also results in a compound which still shows superconducting behavior albeit at a lower T_c (see below). Larger substitutional percentages lowered T_c even more and broadened the transitions. For the purposes of our work this is undesirable. The $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ compound was prepared through a solid-state reaction of appropriate amounts of Gd_2O_3 , BaCO_3 , CuO , and Fe_2O_3 . The Fe_2O_3 was ^{57}Fe -isotope enriched for the purpose of easier Mössbauer investigation. The actual preparation process consisted of grinding, pressing, and sintering several times under conditions similar to those described elsewhere.¹ Because of the similarity of ionic size and electronic structure we expect that a 3d element such as Fe will occupy the Cu sites. Furthermore, we have produced samples with up to 15% Fe substitution and have obtained high-quality x-ray diffraction patterns which show that the iron-containing samples are single phased with a very similar structure to the undoped 1-2-3 compounds. This substitution of 3d elements in the Cu sites has been successfully carried out before for a wide variety of 3d metals.⁴

Further evidence that Fe substitutes for Cu in our samples comes from the room-temperature Mössbauer spectra as shown in Fig. 1. The spectrum consists of two pairs of quadrupole doublets whose parameters are listed in Table I. The isomer shifts indicate trivalent iron, and the elec-

tric field gradients are quite large. We associate these large field gradients with the oxygen deficiencies associated with these compounds. It is now established that the rare-earth planes of the 1-2-3 compounds are devoid of oxygen and that the Cu-O planes located between two Ba-O planes exhibit ordered oxygen vacancies which result in one-dimensional Cu-O chains along the b axis.^{5,6} A crude calculation shows that the electric field gradient at the center of a square planar arrangement of four oxygens is halved if a fifth oxygen is added on the perpendicular axis at the same distance from the center of the square as the original four. This leads us to conclude that the larger quadrupole splitting in our spectrum (Fig. 1) arises from Fe ions between two Ba-O planes since each has four oxygen nearest neighbors, while the smaller splitting arises from Fe between a Ba-O and a Gd plane, with five oxygen nearest neighbors. The Cu-O planes adjacent to the Gd planes are distorted with the oxygen atoms pulled toward the Gd. As a result the smaller quadrupole splitting is slightly greater than half the larger splitting. The greater intensity of the large splitting feature in turn suggests that the Fe ions favor Cu sites between two Ba-O layers.

Measurements of the temperature dependence of the

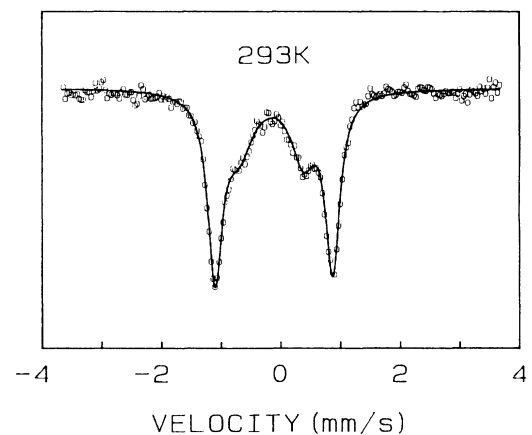


FIG. 1. Mössbauer spectrum of $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ taken at room temperature.

TABLE I. Mössbauer parameters of $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ at room temperature.

Pair	IS (mm/sec)	QS (mm/sec)
I	-0.12	1.97
II	-0.17	1.05

resistance of the 6% Fe substituted samples were carried out using a standard four-probe technique with a computer-controlled data acquisition system in the temperature range from 3.8–300 K. Figure 2 shows the results. The resistance goes to 0 at 31 K with a transition temperature width (10%–90%) ΔT at 16 K. Using the convention of defining T_c as the temperature midway between the onset of the large resistance change and the zero point, we have a T_c of ~ 42 K. This contrasts with the pure Gd-Ba-Cu 1-2-3 compound which has a T_c of 92 K and a ΔT of 1 K. The 6% substitution of Fe for Cu has a large effect. This comes presumably from the fact that scattering of paired electrons from the large Fe moment tends to suppress the superconductivity.⁷ In addition, the nonuniform distribution of the Fe ions at the Cu sites suggests that a significant inhomogeneity in the superconducting properties of the sample should exist and that a large transition width should be expected. The resistance versus temperature curve shows approximately metallic behavior above 90 K, below which an increase in resistivity with T occurs until the superconducting transition is reached. This suggests a metal-insulator transition induced by the random Fe impurities.

A Mössbauer spectrum of the same sample used for Fig. 1, but with the temperature reduced to 4.2 K is shown in Fig. 3. The spectrum is complex, but shows clear evidence of magnetically split six-line structures, which indicates that the Fe moments are magnetically ordered at 4.2 K. This strongly suggests the coexistence of magnetic or-

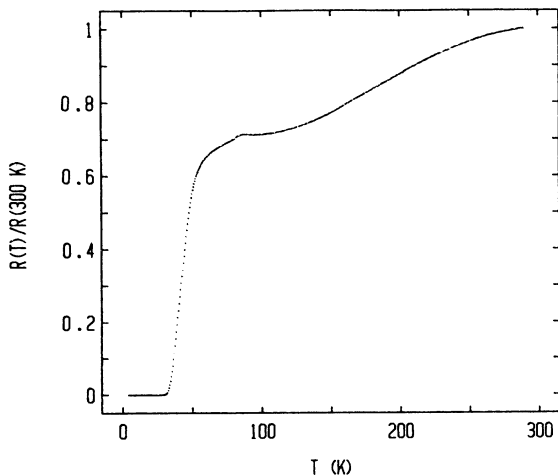


FIG. 2. Temperature dependence of normalized electrical resistance of Gd-Ba-Cu-O with 6% Fe doping.

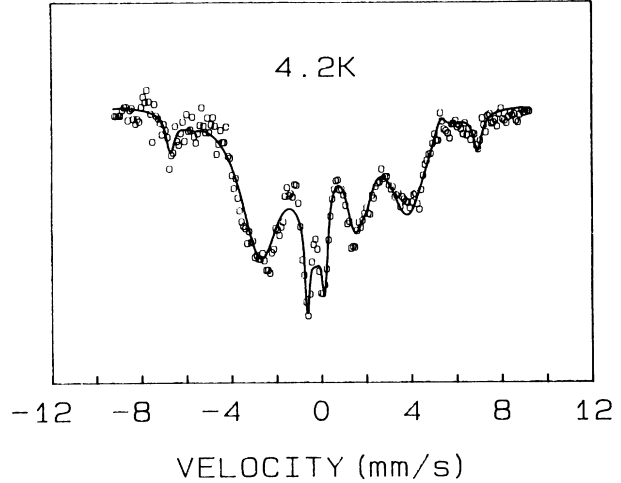


FIG. 3. Mössbauer spectrum of $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ taken at 4.2 K.

dering and superconductivity in the CuO layers or CuO-Ba-CuO structures, contrasting with cases of magnetic ordering where the magnetic ions and the superconducting electrons occupy separate sublattices.

Interestingly, the establishment of magnetic order among the Fe^{3+} moments does not depend on the existence of the magnetic Gd ions as one might think. We have also observed a similar phenomenon in the $\text{YBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ compound in which the trivalent Y ions carry no magnetic moments.⁸ Thus, the interaction responsible for the magnetic order among the Fe moments must be confined to the CuO-Ba-CuO layer assembly or an individual CuO layer. One possible explanation involves a Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction between the localized Fe^{3+} moments mediated by conduction electrons provided that the compound is still sufficiently metallic. Another possibility is a superexchange interaction between neighboring Fe ions. This is quite unlikely since for a 6% Fe doping the Fe-Fe neighboring probability is very small. It is also possible that the Cu ions, which carry a small magnetic moment, join the Fe ions to form the magnetically ordered state through either superexchange or RKKY interaction. In this sense, the Fe ion acts only as a probe to display the magnetic order among the Cu^{2+} moments, which might be antiferromagnetic as reported previously by Sun *et al.*⁹ More work needs to be done to fully understand the mechanism of this ordering.

The spectrum shown in Fig. 3 was not satisfactorily fit by assuming just two different values of the magnetic hyperfine field. For this reason the solid line in Fig. 3 should be considered only as a visual guide. One result that can be safely extracted is that there is a large distribution in the magnitude of the hyperfine field with its upper bound around 510 kOe. This large upper bound is characteristic of many iron oxides, which in turn may imply that the magnetic ordering is antiferromagnetic to a certain extent. The structure of the spectrum indicates that the magnetic order is quite complicated and a spin-

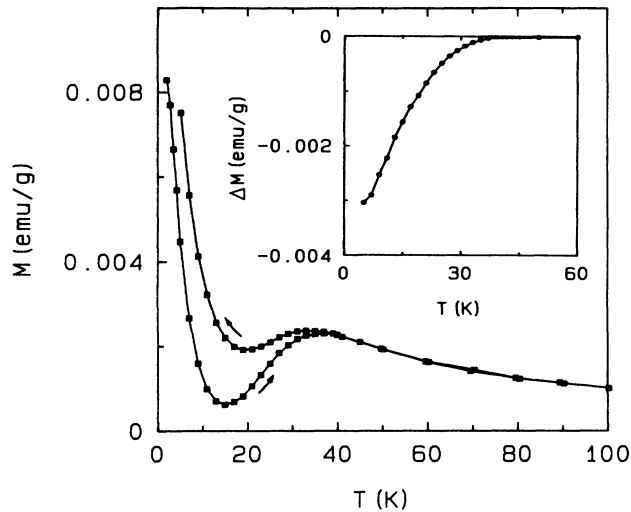


FIG. 4. Temperature dependence of magnetization of $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ (taken at 9.5 Oe) for zero-field cooled and field cooled processes. The inset shows the difference of the magnetizations for the two processes.

glass type of ordering is a strong possibility. In addition to the large distribution in hyperfine field, the large linewidths may result from a random distribution in the angle between the hyperfine field and the electric field gradient. A more quantitative study of the Mössbauer spectra of samples with Fe doping between 0.3% and 6% is underway.

The result of the measurement of the magnetization of the sample is shown in Fig. 4. These results are quite different from the pure 1-2-3 compounds [or even from the $\text{YBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ compound]. Here we have no diamagnetism associated with the superconducting state. Nevertheless, it can be seen that both the zero-field cooled and the field cooled susceptibility curves start to deviate from a paramagnetic form when the temperature reaches about 39 K. At this point the curves actually begin to deviate significantly from each other. This superconducting transition temperature from the susceptibility measurements approximately agrees with the midpoint T_c determined from the resistance versus temperature mea-

surement. At 39 K superconductivity sets in and contributes a Meissner effect, which is superimposed on a paramagnetic effect arising primarily from the large Gd^{3+} moments. The unusual dip we interpret as a result of the competition between these two effects. At lower temperature the paramagnetic effect dominates the Meissner effect. The observed hysteresis must be a manifestation of the Meissner effect so that the difference between the zero-field cooled and field cooled magnetizations, which is shown in the inset of Fig. 4, gives a measure of the strength of the Meissner effect. This weak Meissner effect is characteristic of Fe-doped 1-2-3 compounds.⁴

Unfortunately, the magnetization curve provides no information about the onset of magnetic order of the Fe moments. We feel that the Gd moments dominate the paramagnetic effects and completely mask the order in the Fe moments. The small Meissner effect of this compound may suggest that superconductivity is destroyed in the vicinity of Fe ions, when magnetic order develops at low temperature. Gd ions in this region may interact weakly with the Fe ions, but in any case are not fully shielded from an external field by the perfect Meissner effect, which obtains for pure $\text{GdBa}_2\text{Cu}_3\text{O}_{9-\delta}$. We have evidence that interactions between Fe and Gd ions may occur because an equivalent amount of Fe substitution for Cu in the Y- and Gd-based 1-2-3 compounds produces very different suppression of T_c . A substitution of 6% in $\text{GdBa}_2\text{Cu}_3\text{O}_{9-\delta}$ not only tends to suppress the superconductivity itself but also provides a means for the Gd to interact, perhaps indirectly, with the superconducting electron pairs.

In conclusion, we have observed the coexistence of superconductivity and magnetic order in $\text{GdBa}_2(\text{Cu}_{0.94}\text{Fe}_{0.06})_3\text{O}_{9-\delta}$ at 4.2 K. The new thing about this result is that both the magnetic ordering and the superconductivity seem to involve the CuO-Ba-CuO layers. The nature of the magnetic order is not clear but a spin-glass state or weak antiferromagnetic state is possible.

The authors wish to thank Dr. K. Moorjani for his helpful discussions. This work has been supported in part by the National Science Foundation, Grant No. DMR-8500889.

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