Effect of Fe on the superconductivity of the Ba-Y-Cu oxide system

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We have substituted copper with iron in high-T_c $Ba_2YCu_3O_{7-\delta}$ and formed $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$. It is found that T_c decreases with an increase of the Fe concentration, and the superconductivity is destroyed at $x=0.15$. X-ray diffraction analysis shows that the material has an orthorhombic perovskite structure with larger lattice parameters and smaller $\Delta(a-b)$ than $Ba_2YCu_3O_{7-\delta}$. Magnetic measurements show that the doped samples possess considerable paramagnetism. The effect of Fe on the superconductivity of $Ba_2YCu_3O_{7-\delta}$ is discussed in detail.

Since Bednorz and Müller[1] discovered superconductivity in the Ba-La-Cu-O system at about 35 K, the research activity on high-T_c superconductors has quickly spread to laboratories worldwide. The T_c value exceeded the originally discovered level in a short time, particularly, Chu[2] and Zhao *et al.*[3] finally realized liquid-nitrogen superconductivity by substituting lanthanum in the Ba-La-Cu-O system with yttrium.

Traditionally, the occurrence of high-T_c superconductivity has been based on intermetallic compounds of certain transition metals, such as Nb, V, etc. At present, the object of raising superconducting transition temperature has been achieved with two kinds of metallic oxide superconductors, K_2NiF_4-structure $La_{2-x}Ba(\text{or Sr})_xCuO_{4-\delta}$ (Refs. 4 and 5) and orthorhombic perovskite-structure[6] $A_2BCu_3O_{7-\delta}$. The latter is also called the 1:2:3 phase where, A is one of the alkaline-earth metals, such as Ba, Sr, etc., and B is La, Y, or other rare-earth elements. So far the experimental results show that $La_{2-x}Ba(\text{or Sr})_xCuO_{4-\delta}$ lacks the higher transition temperature of the 1:2:3 phase material. But there is a characteristic in common for both. The Cu-O plane may play a key role in the unexpected high-T_c value[7,8] because it is generally believed that the mechanisms for the occurrence of high-T_c superconductivity are fundamentally understood, based on the electron structure of this kind of basal plane. It is also suggested that the breathing mode in this plane is very important to the strong electron-phonon coupling.

Previous work has been to substitute Y in Ba-Y-Cu-O with the magnetic rare-earth elements Gd and Eu.[9] It is observed that the formed 1:2:3 phase is still a high-T_c superconductor with a zero-resistance temperature of 90 K. Generally, the magnetic ions in superconductors break down the Cooper pair, so the high-T_c of Ba-Gd-Cu-O and Ba-Eu-Cu-O implies unambiguously that the interaction between the rare-earth and the Cu-O plane may not be a primary factor for high-T_c superconductivity. Other experiments substituting Cu by 3*d* elements, such as Co, Ni, Fe, Zn, etc., show that the superconductivity of doped $Ba_2YCu_3O_{7-\delta}$ is remarkably suppressed.[10-12]

In the present report, we concentrate on the influence of Fe in $Ba_2YCu_3O_{7-\delta}$, which has an ionic radius slightly larger than that of Cu. Resistive measurements showed that the superconducting transition temperature of the $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$ system decreases with increasing x, and the superconductivity disappears at $x=0.15$. X-ray diffraction analysis showed that the $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$ has an orthorhombic perovskite structure with a much smaller difference in the lattice parameters $\Delta(a-b)$ and larger lattice parameters than that of Ba-Y-Cu-O. Magnetic measurements showed that the magnetization behavior is like that of a type-II superconductor, despite the fact that the magnetization changes from negative to positive in a rather higher applied field range. At the same time, the diamagnetism decreases with increasing Fe concentration.

The original materials of the sample were Y_2O_3 (99.999% pure), $BaCO_3$ (99.9% pure), CuO (99.9% pure), and the added Fe_2O_3 (99.5% pure). The mixture material was ground and presintered at 900 °C for 6 h, ground twice more for through mixing, then pressed into a 14 mm disk 2 mm thick and heated at 920 °C for 14 h, followed by cooling to room temperature within the furnace. This process has been described elsewhere.[13]

The dc four-terminal method was used for the transition-temperature measurement. Pt and Ge resistor thermometers were used in the temperature ranges of 60–300 K and 4.2–60 K, respectively. The phase structure was determined by x-ray diffraction. The magnetic properties were measured using an extracting sample magnetometer. The applied field was continuously adjustable within the range of 0–7 T. The homogeneity of the field over 60 mm of radial range was better than 10^{-4} Oe. The controlled temperature range was 1.5–300 K with an accuracy ± 0.01 K. The resolution of the magnetization was better than 5×10^{-4} emu.

The x-ray diffraction results for $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$ are shown in Fig. 1. Compared with $Ba_2YCu_3O_{7-\delta}$, the diffraction peaks for Fe-doped samples of $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$ are more similar to the tetragonal structure as shown in Fig. 1(a). The difference between a and b, $\Delta(a-b)$, is smaller compared with $Ba_2YCu_3O_{7-\delta}$, as shown in Fig. 1(b).

Figure 2 shows the correlation between resistive T_c and Fe concentration in Ba-Y-Cu-Fe-O. It is found that T_c decreases with increasing Fe concentration, and a large transition width (15–25 K) can be seen for all the samples. This means that the doped samples are more complex than the $Ba_2YCu_3O_{7-\delta}$. The resistivity of this kind

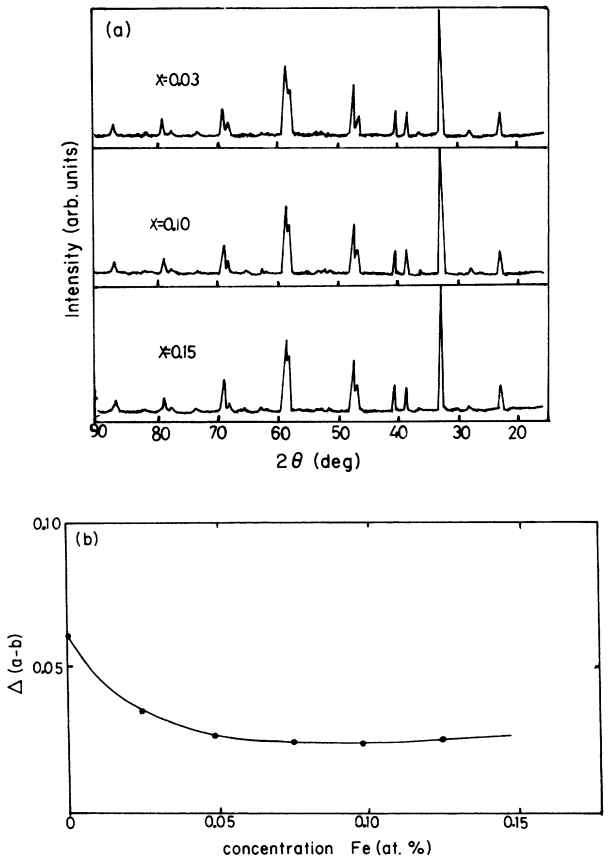

FIG. 1. (a) X-ray diffraction spectrum of $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$. (b) The difference between a and b in $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$.

of sample shows a negative temperature coefficient within the temperature range from T_c (onset) to 300 K, namely they are semiconducting before the normal-superconducting transition.

The correlation between diamagnetization and temperature is shown in Fig. 3. The applied field is $H=200$ Oe. Both the resistive T_c and the temperature of occurrence of the Meissner effect are the same. When the concentration of Fe increases the diamagnetism becomes weak while the highest Meissner-effect temperature and the maximum magnitude of diamagnetism were observed for $x=0.00$. For $T<10$ K, the M-T curve shows that the diamagnetism of doped samples becomes weak. This behavior can be explained as the enhancement of the paramagnetism which is mainly due to the large local paramagnetic moments in the iron site. So, it can be seen that below the superconducting transition temperature the M-T curve will include contributions from both diamagnetism and paramagnetic moments in the matrix of the doped samples.

Figure 4 shows the magnetization of $Ba_2YCu_{2.7}Fe_{0.3}O_{7-\delta}$ (zero-resistance temperature about 22 K) at various temperatures. It is obvious that for a given measuring temperature, the magnetization is like a type-II superconductor as the applied field is lower than a critical value H'_{c2}, but the magnetization changes from negative to positive as the applied field is larger than H'_{c2} and increases linearly with applied field. It is obvious from the experimental result that H'_{c2} decreases monotonical as the measuring temperature increases. For $T=1.5$ to 15 K, the corresponding H'_{c2} decreases from 4800 Oe to 2000 Oe. It can be understood that the contribution of diamagnetism to magnetization decreases faster than that of paramagnetism with increases of temperature. For $Ba_2YCu_3O_{7-\delta}$, from Ref. 14, $\chi=\chi_0+C/T$, $\chi_0=7.78\times10^{-7}$ (cgs), $C=2.19\times10^{-4}$ (K cgs) then $\chi=2\times10^{-6}$ (cgs) at 200 K. Hence, the susceptibility of $Ba_2YCu_{2.7}Fe_{0.3}O_{7-\delta}$ can be presented as a Curie-Weiss relation $\chi=\chi_0+C/T-\theta$, where θ is the Curie temperature and C comes from $P^2_{\rm eff}=0.9P^2_{\rm eff}(\mathrm{Cu})+0.1P^2_{\rm eff}(\mathrm{Fe})$ as discussed in Ref. 12. From the experimental results, we obtain the susceptibility of $Ba_2YCu_{2.7}Fe_{0.3}O_{7-\delta}$ as 4×10^{-6} (cgs). So, the susceptibility of $Ba_2YCu_{2.7}Fe_{0.3}O_{7-\delta}$ is two times larger than that of $Ba_2YCu_3O_{7-\delta}$. This result should be reasonable; in $Ba_2YCu_3O_{7-\delta}$ the paramagnetism is produced mainly by Cu^{2+} (or Cu^{3+}), but in $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$, due to the existence of Fe^{2+} and Fe^{3+}, the C of $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$ is larger than that

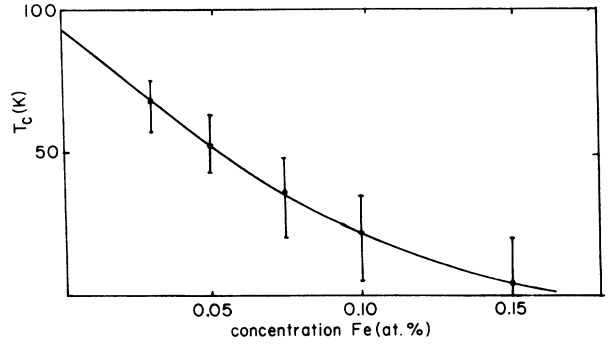

FIG. 2. The correlation of resistive T_c and concentration of Fe in $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$.

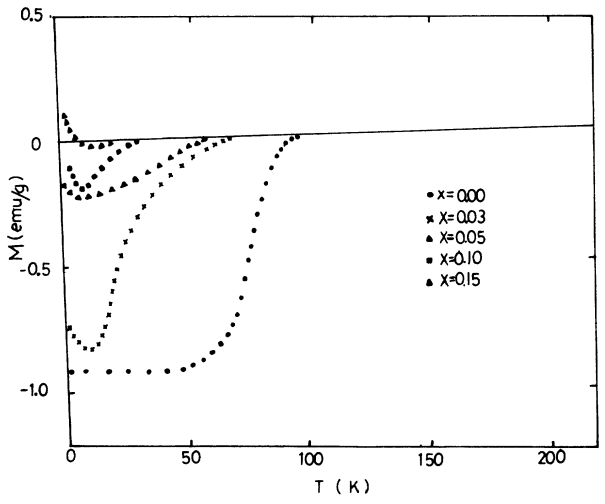

FIG. 3. The correlation between diamagnetization and temperature for $Ba_2YCu_{3(1-x)}Fe_{3x}O_{7-\delta}$.

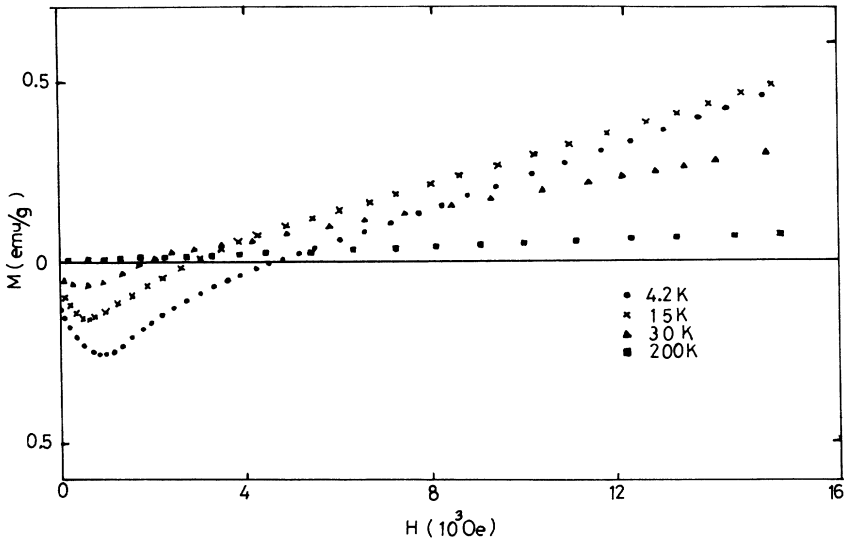

FIG. 4. The magnetization of $Ba_2YCu_{2.7}Fe_{0.3}O_{7-\delta}$ at various temperatures.

of $Ba_2YCuO_{7-\delta}$ (for Fe^{2+} and Fe^{3+}, the effective Bohr magneton is 5.4 and 5.9, respectively). In the same way, we can explain that when the applied field is large enough, the magnetization in the M-H curve could change sign due to larger local paramagnetic moments.

It is well known that for the $Ba_2YCu_3O_{7-\delta}$ system, the high T_c is mainly determined by the vacancies of oxygen and their ordered arrangement in the Cu-O plane, which determines the parameters a, b, and $\Delta(a-b)$. For high-T_c samples the $\Delta(a-b)$ is about 0.07 Å, in general. For the substitution of Cu with Fe in $Ba_2Y_1Cu_3O_{7-\delta}$, T_c and $\Delta(a-b)$ change as shown in Figs. 1(b) and 2. This is consistent with the result of reference.[10-12] It is obvious that the superconducting transition temperature is strongly depressed by dopant Fe. This is very different from the behavior of substitution of Y by rare-earth elements such as Gd, Eu, etc.[9] These results show that due to the substitution of Cu with Fe in the $a-b$ plane the magnetic scattering may cause considerable Cooper-pair breaking[12-15] since it is generally believed that high-temperature superconductivity in $Ba_2YCu_3O_{7-\delta}$ is mainly determined by Cu $3d$ and O $2p$ electrons which originate from the Cu-O basal plane. Of course the dopant Fe may act on other aspects; it may introduce defects in the $a-b$ plane, change the oxygen vacancies, and break the arrangement of them as discussed in Refs. 10 and 11. It may also induce a different oxidation state in the copper. This kind of disorder in the $a-b$ plane could decrease the difference in a and b, finally causing the orthorhombic structure to tend to the tetragonal phase and weaken the superconductivity. From Figs. 1(b) and 2 it can be seen that when the concentration of Fe increases from 0.05 to 0.15, $\Delta(a-b)$ is almost constant, but T_c decreases monotonously. This can also be explained as in the discussion above, i.e., the Cooper pair may be broken by local magnetic-moment scattering, and disorder within the lattice could be caused by substitution of Cu with Fe. So, the higher the concentration of Fe, the stronger the Cooper-pair scattering and the more T_c is decreased by lattice disorder. On the other hand, the change of $\Delta(a-b)$ caused by lattice disorder during the substitution of Cu with Fe would have a limiting value.

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