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Electronic behaviour of iron ions at copper sites

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The electronic properties of the ceramic superconductor Y–Ba–Cu–Fe–O system with different amounts of iron cations versus temperature are discussed. The spin fluctuations of copper and its relation to the superconducting state are discussed from the point of view of the mixed valence state of copper ions. The results suggested a spin–glass behaviour at low temperature.

1. Introduction

Since the discovery of the high T_c superconducting ceramic oxide, intensive efforts have been made to understand and characterize both its structure, and composition with the aim of finding the phase responsible for the superconductivity [1–4]. A great effort has also been made to achieve superconductivity at higher temperatures for materials such as $Y_1Ba_2Cu_3O_{3-x}$ with T_c about 92 K, which has become a standard superconducting composition [2, 5], and the research for finding new materials and systems with the same objective has not ceased. Many scientists began doping these systems with different elements, especially iron atoms [6, 7], in order to explain this phenomena.

2. Experimental procedure

The Y–Ba–Cu–Fe–O system with different values of the iron ions/copper ions ratio were prepared from a mixture of high-purity Y_2O_3, $Ba(NO_3)_3$, CuO and Fe_2O_3. Appropriate amounts of the above oxides were mixed, pressed into pellets and heated to 950 °C for about 24 h in an oxygen atmosphere. The samples were cooled at 150 K h^{-1}, and then reground and pressed to 600 kg cm^{-1} and heated again to 950 °C in a flow of oxygen for 5 h, then left to cool at 50 K h^{-1}. Finally, these samples were examined by an X-ray diffraction technique, which showed no deviation from the 123 structure, i.e. the iron atom has participated in the crystal structure. The diamagnetic behaviour of parts of the samples has been checked by observing the Miessner effect, using the levitating magnet technique. The critical temperature, T_c, and the superconducting behaviour at each iron atom concentration was observed by

(1) d.c. electrical conductivity data which were obtained by a four-probe electrical conductivity technique for a temperature range $78 \leqslant T \leqslant 300$ K; and

(2) a.c. magnetic susceptibility in terms of X (real part), measured as a function of temperature.

3. Results and discussion

As shown in Fig. 1, the samples with Fe $\leqslant$ 0.4% showed similar superconducting behaviour and those samples with Fe $\leqslant$ 1% showed superconducting transition temperature above 78 K with zero resistance. On the other hand, a sample doped with a higher amount of iron showed that T_c is well below liquid nitrogen temperature. From the above electrical behaviour of our samples, we can conclude that on increasing the iron atomic concentration there is no change induced in the behaviour of curves up to 0.4% Fe, while above this value the superconducting transition in temperature T_c decreases with increasing iron dopant.

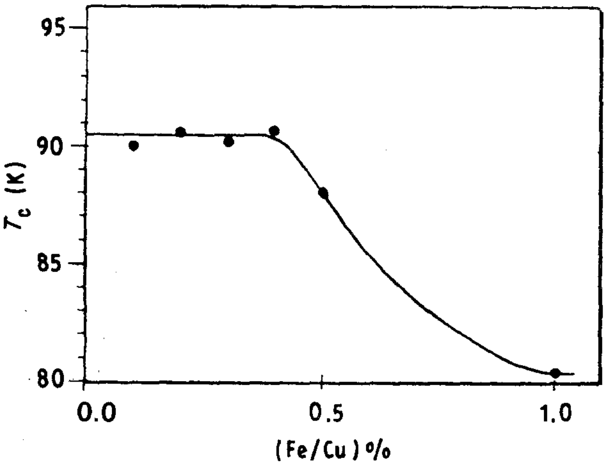

Figure 1 (Fe/Cu)% dependence of T_c determined by resistivity measurements.

It must be noted that although the behaviour of the samples with Fe = 0%–0.4% does not change, the resistivity increases at a high rate (i.e. higher dR/dT) with increasing iron dopant. Recorded plots of the a.c. susceptibility are shown in Fig. 2. Complete diamagnetic shielding occurs for samples with iron contents up to 0.4%, at $T = 89$ K, but there is a difference in the transition width for samples over 0.4%. This transition width increases with increasing percentage of iron dopant. The increase in width may be attributed to either the increased iron dopant, which means a different environment about the iron atoms, or the sample's lack of homogeneity.

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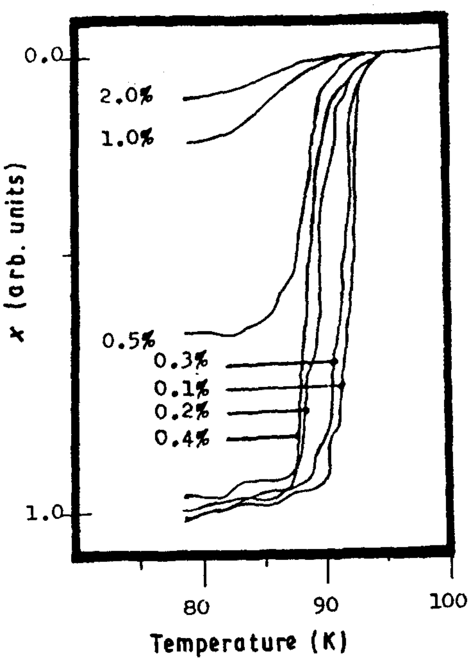

Figure 2 A.c. susceptibility for different (Fe/Cu)% samples at different temperatures.

All the ME spectra at room temperature show the lack of iron atoms in $Y_1Ba_2Cu_3O_{7-y}$ samples, which might demonstrate that the iron atoms are built into the structure of perovskite. Fig. 3 shows the room-temperature Mössbauer spectra for the samples of the $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_{7-y}$ with $x = 0.001$, 0.002, 0.003, 0.004, 0.005, 0.01 and 0.02. One doublet, D1, was required to fit the data for the sample with an iron percentage up to 0.4% and two doublets, D1 and D2, for samples with iron percentages over 0.4%.

The D1 doublet may be attributed to tetragonal pyramidal coordination in the Cu2 plane. Beside the existence of the D1 doublet (the outer one), there also exists a D2 doublet (the inner one) for samples with iron percentages over 0.4%. Probably, this is due to iron replacing copper in the square-planar sites sandwiched between the two barium layers. Whereas the Cu(II) site is located between the yttrium and barium layers is a definite nearest neighbour oxygen coordination, the values of FWHM suggested that iron contributing to D1 occupied crystallographically unique sites, which is the Cu(II) site. The isomer shift calculated from the ME spectra for site D1 might be interpreted as a low-spin Fe(II) state. This may be explained by supposing that the iron ligand field is strong enough to override Hund's rule. A clear broadening was observed for D2 for samples with Fe > 0.4%, which indicates that there is an induced hyperfine field at iron sites for Cu(I) and thus the magnetic moment of the magnetic ions (iron ions) in Cu(I) has a random orientation, as in spin-glass.

From the above discussion we can state generally that the magnetic ions enter Cu(II) in the superconducting matrix without destroying the superconductivity, and they have localized magnetic moment until the iron ions increase and thus begin to enter Cu(I) where the magnetic moment of the magnetic

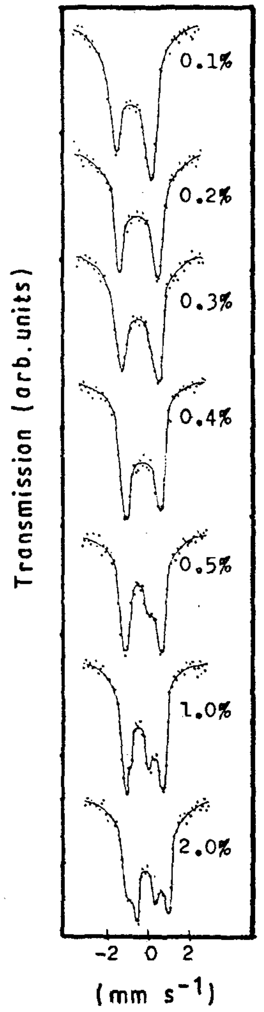

Figure 3 The dependence of the Mössbauer spectra at 300 K on (Fe/Cu)% for the YBaCuFeO system.

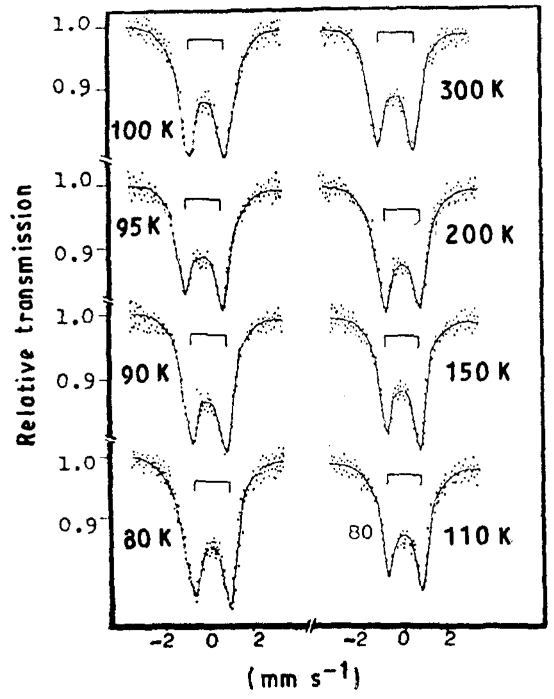

Figure 4 Typical Mössbauer spectra for the sample with (Fe/Cu) = 0.4% at different temperatures.

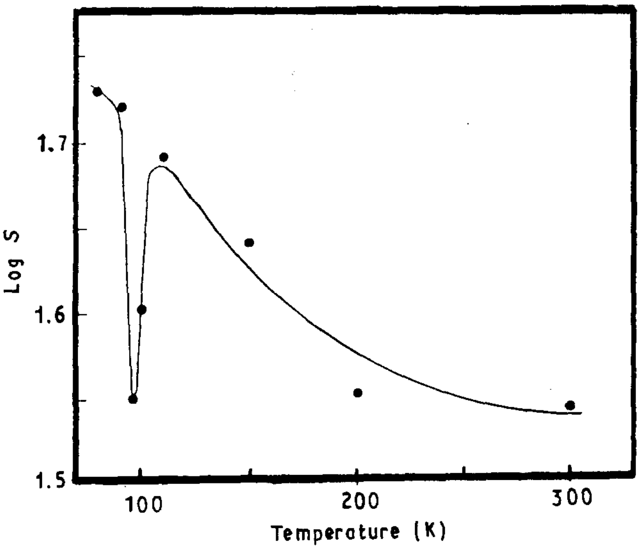

Figure 5 The area under the resonance absorption versus temperature curve for the sample with (Fe/Cu) = 0.4%.

ions interacts with electrons with different spin orientation, thus reducing the superconducting parameters.

Typical Mössbauer spectra for a sample with Fe = 0.4% in the temperature range 80–200 K are shown in Fig. 4, and the area under the curves, S (its value being proportional to a recoilless fraction) were plotted against temperature, Fig. 5. From the figure obtained it can be seen that S shows a sudden drop near T, which implies that lattice softening occurs in this temperature range.

Finally, our samples with low iron dopant show no magnetic order in the temperature range under study, and thus the idea of spin fluctuations of copper are related to the superconductivity phenomenon.

4. Conclusion

The electric, magnetic and Mössbauer effect investigations of (Y–Ba–Cu–Fe–O) superconductor show that iron ions are in the low-spin Fe(II) or Fe(III) state and the drop in both isomer split and recoilless fraction indicates that lattice softening occurs during the metallic– superconductor transformation. The results of FWHM also suggest that iron ions have a random orientation of magnetic moment as in spin–glass.

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