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MAGNETIC HYPERFINE INTERACTION IN IRON DOPED SUPERCONDUCTING AND SEMICONDUCTING YBaCuO OXYDES

by

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The information obtained from $^{57}Fe$ Mössbauer spectroscopy about the magnetic ordering of iron moments and its dependence on oxygen content, is reported for $YBa_2(Cu_{1-x}Fe_x)_3O_y$ samples with x=0.05 and 0.10. The data indicate that the magnetic order of Fe at Cu(1) in the semiconducting samples is enhanced by the magnetic order of Cu(2) and a proper order of Fe takes place clearly below the antiferromagnetic order of Cu(2).

Key-words: Mössbauer spectroscopy; Oxide superconductor; Magnetic order; Fe-doping.

## 1 INTRODUCTION

Large efforts in the studies of superconducting copper oxides deal with the partial substitution of Cu by other metals and its effect on the chemical and physical properties. In the case of Fe impurities Mössbauer spectroscopy has been extensively used to study the local structural changes induced by the substitution of Cu as well as the sensitivity of iron to the oxygen content especially for YBaCuO. The observation of a magnetic hyperfine splitting of Fe in these compounds[1] for concentrations above 4.0 at % and temperatures below 30 K motivated us and other authors to study the magnetic order which takes place between the iron moments. This kind of magnetic interaction looked to be most interesting due to its appearance also in the superconducting regime.

Previously[2] we have reported the magnetic hyperfine spectra for fully oxygenated $YBa_2(Cu_{1-x}Fe_x)_3O_y$, x=0.005 and 0.15 at 4.2 K under applied external magnetic field. The ambiguity in fitting and the proposal by other groups[3,4] that this type of spectra may be interpreted by relaxation effects lead us to perform a further study of the temperature dependent magnetic hyperfine field ($B_{hf}$) in these oxides[5,6].

Here we present Mössbauer studies of the magnetic ordering of iron atoms at the Cu(1) site for x=0.05 and 0.10 focusing on its dependence on the oxygen content; these studies may provide information about the influence of the antiferromagnetism of Cu(2) (which occurs for the undoped compound) on the magnetic behavior of the iron moments. Moreover a comparative analysis of the temperature dependent magnetic hyperfine field and its saturation value in the two samples may help to clarify the location and oxygen coordination corresponding to the several iron species.

Although the two samples have different Fe concentrations we assume that this is not relevant for the point we want to analyse connected with the difference of the oxygen content.

The difference in iron concentration for the two studied, samples is of little relevance when we are going to analyse their difference with respect to their oxygen content.

## 2 EXPERIMENTAL

We have studied the magnetic hyperfine interaction for iron in $YBa_2(Cu_{1x}Fe_x)_3O_y$ from 4.2 to 300 K. The samples with (x=0.10, y>7.01) and (x=0.05, y<6.5) named I and II, respectively, were prepared by the sinter method, and the oxygen deloading was performed by heat treatment at 500C under argon flux.

The Mössbauer spectra at various temperatures were taken with the samples under He exchange gas, the 50 mCi $^{57}Co/Rh$ source was kept at room temperature (RT).

## 3 RESULTS AND DISCUSSION

In the superconducting phase no magnetic order is found at 300K. The RT spectra for sample I reveal three Fe species represented by paramagnetic doublets (B with about 60%, C about 10% and D with about 30% of the total spectral weight). D is typical for the oxygen deficient state and there is high agreement that it represents Fe at Cu(1) with 4-fold oxygen coordination, while B represents a 5-fold oxygen coordination which is more probable for Fe ions in oxygen rich YBaCuO samples[6].

In the semiconducting phase (sample II) the Mössbauer spectrum at RT shows two paramagnetic doublets (D with about 60%, E with about 20% of the spectral weight) and one magnetic sextet (F with about 18% of the spectral weight). All these iron doublets reflect distinct oxygen coordinations as is indicated by the hyperfine parameters (TABLE 1). From all these iron species we believe that C, E and F are less defined with respect to location and oxygen coordination.

TABLE 1

| IRON SPECIES | | | | | |
|---|---|---|---|---|---|
| | B | C | D | E | F |
| IS(mm/s) | 0.03 | 0.19 | 0.04 | 0.13 | 0.30 |
| QS(mm/s) | 1.20 | 0.30 | 1.98 | 0.70 | 0.55 |

Mössbauer hyperfine parameters at RT associated to Fe species B,C,D,E and F.

The low T spetra for both samples reveal magnetic hyperfine interactions for all Fe species. The least-square fits were performed with the following conditions: isomer shifts, quadrupole splittings and relative intensities were kept fixed to the values found at temperatures above the onset of magnetic hyperfine splitting. Line positions and intensities were determined from the eigenvalue and eigenvectors of the Hamiltonian comprising magnetic and quadrupolar hyperfine contributions.

The onset of magnetic splitting at 13 K for the superconducting sample (I) is well defined and $B_{hf}(T)$ follows a typical sublattice magnetization curve; a detailed analysis has been already reported[4]. The magnetic behavior can be described by two temperatures $T_a$ (13 K) for the collapse of the magnetic splitting due to species B and D and $T_b$ (25 K) for the collapse of sextet belonging to species C.

For the analysis of the Mössbauer data of sample II it was necessary to allow for non magnetic fractions ($f_m$), therefore the average magnetization curve has a more flat T dependence[5]. In fig. 2 we plot the temperature dependence of the magnetic hyperfine interactions, $B_{hf}(T)$, for the three iron species and the corresponding magnetic fractions.

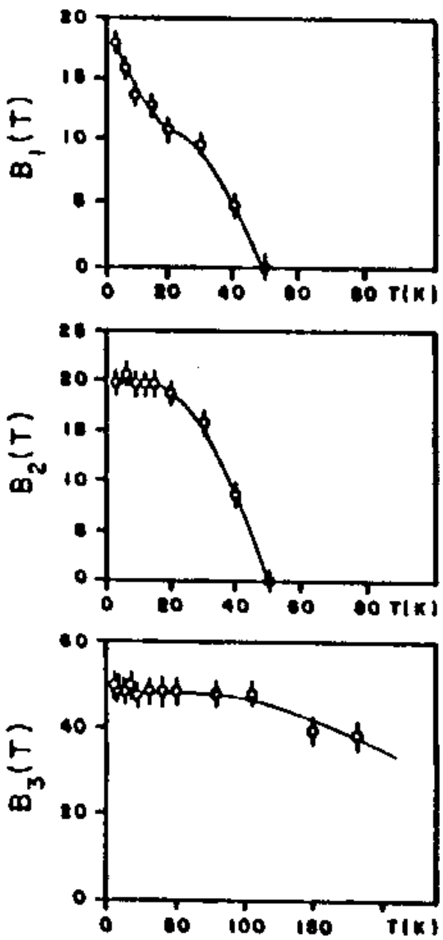


Figure 1a

Temperature dependence of the magnetic hyperfine field for the three Fe species.

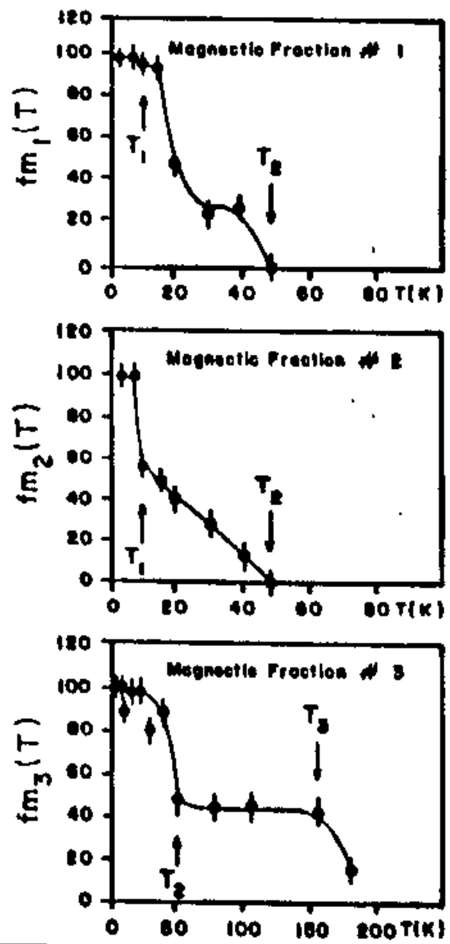


Figure 1b

Temperature dependence of magnetic fraction for the three Fe species.

To describe the magnetic behavior, as seen by Mössbauer spectroscopy, three temperatures $T_1$(10 K), $T_2$(50 K) and $T_3$(150 K) are necessary for this semiconducting sample.

The species D and E have similar behavior: a partial magnetic ordering (with the coexistence of a paramagnetic fraction) between $T_a$ and $T_b$ below which complete order is obtained, with a further increase of magnetic hyperfine field of species E. The saturation values for both species are very similar which lead us to conclude that species E is also due to Fe at Cu(1).

The temperature dependence of the magnetic interaction of F is typical for superparamagnetic clusters of iron oxides with a mean blocking temperature of $T_3$=150 K. Above this temperature practically all the Fe ions of species F reveal a paramagnetic pattern. Below $T_c$ about half of the ions display the full magnetic hyperfine field but only below $T_2$=50 K all ions reach the saturation hyperfine field. The identification of the paramagnetic spectrum corresponding to this species has been already reported in a study of reduced Fe:YBaCuO samples[7] and several assignments have been proposed for it.

From the analysis of the Mössbauer spectra for samples I and II we may derive some conclusions about the location of the iron species B, D and E in YBaCuO. In the superconducting phase B and D show a normal magnetization curve with the same onset temperature of hyperfine field and also the same saturation value. In the semiconducting sample (II) species D and E show an intermediate stage with partial magnetic ordering between 10 and 50 K and again very similar saturation values of the magnetic hyperfine interaction. Thus we conclude that B, D and E are all due to iron in Cu(1), however, with different oxygen coordination.

In contrast, one can not give a simple interpretation for species C (sample I) and F (sample II). They become completely or partially ordered at higher T with higher saturation values for $B_{hf}$ compared with the other species. This may be an indication of strong iron clustering in the YBaCuO system or in a different phase.

To study the effect of oxygen content on the magnetic order for Fe at Cu(1) we need to analyse the $B_{hf}(T)$ for a Fe species which is found in both samples and is known to be at Cu(1): this is species D.

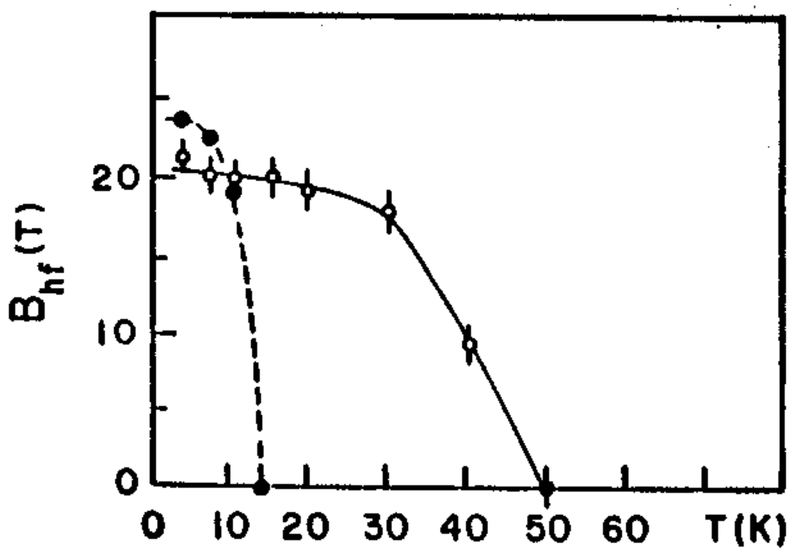


Figure 2

Temperature dependence of the magnetic hyperfine field for the Fe species D in sample I and II.

In fig. 2 we compare the temperature dependence of $B_{hf}$ for species D from samples I and II. Two main informations can be drawn from this figure:

1. The saturation value for $B_{hf}$ is bigger for sample I. This can be explained by its higher iron concentration.
2. The magnetic ordering temperature $T_a$ (sample I) is lower than $T_1$ (sample II), this fact can be attributed to the difference in oxygen content of the two samples since the iron concentration should induce an opposite effect as known from neutron diffraction[10] and Mössbauer[11] data. The lack of oxygen in the Cu(1) plane and the oxygen disorder should not enhance the magnetic order between the Fe ions at Cu(1). We relate this result with the establishment of the known antiferromagnetic order of Cu(2) ions induced by the reduction of the oxygen content.

The data give a qualitative trend for the magnetic of Fe at Cu(1) for the semiconducting sample which is enhanced by the magnetic order of Cu(2). Proper ordering of Fe at Cu(1) sites takes place clearly below $T_N$ of Cu(2).

Systematic work based on the Mössbauer and μSR studies on highly homogenized sintered sample with controlled oxygen content is under progress to get a wider understanding about the interplay of magnetic order and oxygen content for all the Fe species in this material. Preliminary results for the same Fe concentrations reveal a systematic increase of $T_1$ upon further oxygen deloading in agreement with the tendency derived from the present data.

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