# NO EVIDENCE OF Fe TRANSFER BETWEEN Cu1 AND Cu2 SITES IN

# $YBa_2(Cu_{1-x}Fe_x)_3O_{7-d}$ (0.02≤ x ≤ 0.04) ANNEALED IN AN INERT ATMOSPHERE

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## Abstract

$YBa_2(Cu_{1-x}Fe_x)_3O_{7-d}$ (0.02≤ x ≤ 0.04) annealed in an Ar atmosphere, then reoxygenated have been characterized (X-ray diffraction, Tc) and studied by Mössbauer spectroscopy at room and low temperatures. The results are interpreted as due to Fe clustering rather than to a significant occupation in the plane.

## 1. Introduction

Substitution of some of the components in high-$T_c$ compounds by other chemical elements is one of the possible means of obtaining new materials with improved superconducting and mechanical properties. Such materials are necessary for practical applications of high-$T_c$ superconductors.

The superconducting, magnetic and structural properties of iron substituted $YBa_2Cu_3O_{7-d}$ have been studied in hundreds of papers during the last six years. However, many important questions remain unanswered, or in some cases, contradictory interpretations of certain effects are given.

Such a problem is the distribution of iron over the chain (Cu1) and plane (Cu2) sites, the effect of this distribution on the superconducting transition temperature $T_c$ and the possibility of a transfer of some Fe ions from Cu1 to Cu2 sites and back at certain thermal treatment. The results of recent Mössbauer studies of samples, annealed in an inert atmosphere then reoxygenated, have been interpreted as an indication of a transfer of Fe from chains to planes [1.2]. On the other hand, EXAFS,

electron microscopy and NQR measurements on similar samples do not show any noticeable redistribution of iron over the plane and chain Cu sites [3,4].

In an attempt to resolve this contradiction, we have investigated several series of samples with different levels of Fe substitution and special thermal treatments.

## 2. Results

Two series of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-d}$ treated in Ar atmosphere were realized. The initial polycrystalline samples were prepared from the respective oxides and carbonates by the well known solid state sintering technique with x=0.02 and 0.04 for the 1st series and x=0.03 and 0.04 for the 2nd. For the 1st series, heating in Ar atmosphere (atm.) at 840°C for 24h followed by heating in $O_2$ atm. at 400°C for 24h, and by heating in $O_2$ atm. at 300°C for 72h with slow cooling between each step were done. These samples are labelled 300/$O_2$. Afterwards, heating in $O_2$ atm. at 500°C or 600°C for 96h was carried out. For the 2nd series, the samples have been heated successively in Ar atm. at 800°C, then in

Table 1. Hyperfine parameters for the different doublets for various samples. Isomer shift $\delta$ (±0.02), quadrupole splitting $\Delta$Eq (±0.03) and population (±0.02)

| Doublet | $\delta$ mm/s | $\Delta$Eq mm/s | Population | | | | |
|---------|------|------|---------|---------|---------|---------|---------|
| | | | Initial | $210/O_2$ | $400/O_2$ | $600/O_2$ | $800/O_2$ |
| D1 | 0.03 | 1.94 | 0.35 | 0.07 | 0.05 | 0.12 | 0.71 |
| D2 | -0.18 | 1.32 | 0.15 | $\cong$ 0 | $\cong$ 0 | 0.10 | 0.03 |
| D3 | -0.01 | 1.10 | 0.37 | 0.38 | 0.33 | 0.23 | 0.10 |
| D3' | -0.01 | 0.66 | 0 | 0.13 | 0.21 | 0.13 | 0.06 |
| D4$_1$ | 0.35 | 0.64 | 0.13 | 0 | 0 | 0 | 0.10 |
| D4$_2$ | 0.31 | 0.51 | 0 | 0.42 | 0.42 | 0.42 | 0 |

$O_2$ atm. at 210°C, 400°C, 600°C and 800°C for 24h for each step with slow cooling (furnace inertia) between. Samples have been taken at each stage and labelled 800/Ar, $210/O_2$, $400/O_2$, $600/O_2$ and $800/O_2$ respectively.

For all the samples, X-ray diffraction shows patterns in agreement with the $YBa_2Cu_3O_7$ structure. However very small non identified additional lines are observed for samples heated in Ar atm. only. This means that the crystallographic structure is not too perturbed. $T_c$ has been determined from a.c. susceptibility and resistivity measurements. Briefly, $T_{onset} \cong$ 88 K and zero resistance $T_{offset} \cong$ 80 K are obtained for the initial samples (x = 0.04, series 2). These values vary very little for the $210/O_2$ and the $400/O_2$ samples while a clear decrease occurs for the $800/O_2$ samples which is in fact a normal sample with lower d value (see below). For all the samples susceptibility measurements reveal a very broad superconducting transition. Detailed results will be published elsewhere.

Mössbauer spectra were taken at 300 K for all the samples and at low temperature for some samples. The variation of the

spectral shapes shows the same trend for the two series. At 300 K, the shapes (fig.1) and the parameters (table 1) of the initial sample spectra are characteristic of oxygenated samples with d about 0.1. A good fit is obtained from usual parameters (table 1) but also by using for the D4 doublet a smaller isomer shift $\delta$ and quadrupole splitting $\Delta$Eq values as proposed in [5], specially for x=0.02 and 0.03. For samples treated only with Ar (fig. 2a), the spectra consist of superposition of magnetic and paramagnetic patterns. The magnetic part corresponds mainly to sextuplets with $\delta \approx 0.4$ mm/s, $\Delta$Eq$\approx$0 and hyperfine field $H_{hyp} \approx 330$ kOe, with population about 50% and the paramagnetic part corresponds to a mixture of parameters of initial and reoxygenated samples.

Typical spectra of reoxygenated samples are shown in fig. 1 and the parameters are given in table 1. The spectra consist of the superposition of several doublets. Their hyperfine parameters are identical within the error limits for all the samples except for the D4 doublet. For the samples $210/O_2$, $400/O_2$ and $600/O_2$, the $(D4)_2$ parameters are slightly but significantly smaller than those of $(D4)_1$ obtained for the initial and the $800/O_2$ samples. Relative to the initial samples, a new
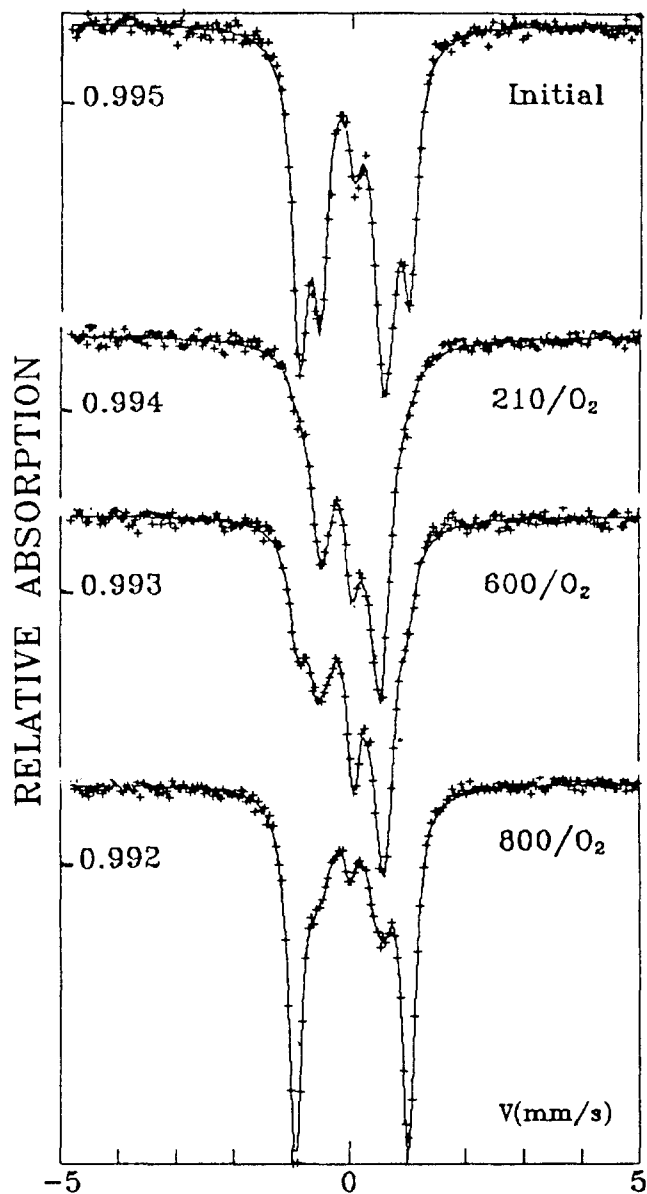
Figure 1. Mössbauer spectra at 300K for various samples. Lines correspond to fitted spectra.

samples, the parameters are again those of the normal oxygenated sample with d about 0.2-0.3. However, the D3' population is not equal to zero. Indeed, a not too bad fit is obtained by suppressing this doublet, similar to those obtained for samples in a traditional treatment when D1 dominates. The introduction of D3' improves the fit of these latter samples appreciably which indicates that the particular Fe species corresponding to D3' also occurs.

The spectra at 4.2K for x=0.04 and $300/O_2$ (1st series) and $210/O_2$ (2nd series)

doublet D3' appears for the $210/O_2$, $400/O_2$ and $600/O_2$ samples with $\delta \approx 0$ mm/s, as for the D1 and D3 doublets. These doublets are usually attributed to Fe in the chains. But the $\Delta$Eq value of the D3' doublet is very near to the D4 one, usually attributed to Fe in the planes. In addition the D4 population increases strongly in agreement with previous results [1,2]. For the $800/O_2$
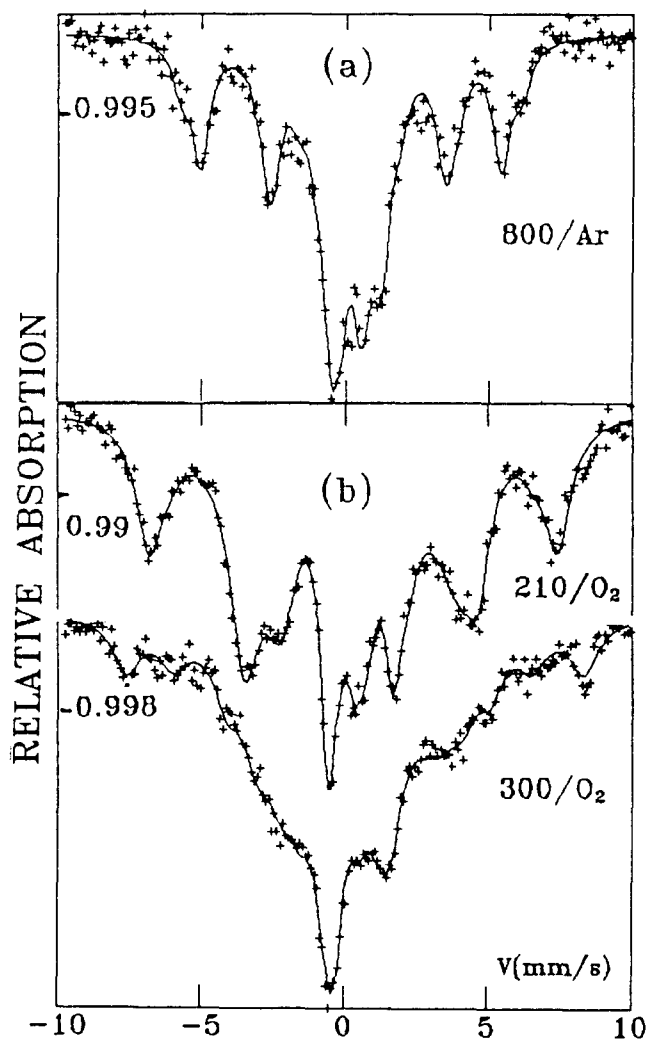


Figure 2. Mössbauer spectra (a) at 300K for Ar annealed sample (b) at 4.2k for reoxygenated samples. Lines correspond to fitted spctra

are shown in fig. 2b. the hyperfine magnetic patterns spread out but the transition temperature is different though x values are the same and the site populations at 300K are not too different (the degree of reoxygenation is slightly higher for the 1$^{st}$ series samples). On the other hand, it is clear from the temperature variation of the parameters that there is a transition temperature distribution. For example, full magnetic spectrum is obtained within 2 K for the 210/O$_2$ samples where the transition begins at about 10 K.

## 3. Discussion

Ar treatment leads to a strong desoxygenation of the samples. As the temperature is sufficiently high, Fe move in order to keep the highest coordination. There are two ways of reaching such an objective (i) Fe occupies planes with pyramidal coordination or (ii) Fe forms clusters in chains at least partially with octahedral coordination. After Ar treatment, only small disturbances occur in the crystallographic structure, as shown by X-ray diffraction. However a strong magnetic component (fig. 2a) is detected at 300 K, which is replaced by a paramagnetic one (D4 doublet) after reoxygenation at 210°C (fig. 1). At this temperature Fe cannot move and reoxygenation does not concern a priori the planes. Therefore, the magnetic to paramagnetic change is difficult to understand if these Fe are in the planes. However the D4 parameter values (table 1) are very close to those generally accepted for Fe in the planes. This is the main reason for the previous interpretation [1,2]. The question is to be sure that only Fe in the plane has these parameters. Calculations have shown that almost the same values are obtained for octahedrally coordinated Fe in the chains. Further, the D3' δ value is characteristic of Fe in the chains and can be attributed to this site occupation, but with a Fe arrangement different from those corresponding to D1 and D3 because the D3' ΔEq value is lower and similar to the D4 ΔEq value. In our opinion, D3' and at least partially D4 correspond likely to Fe clusters in the

chains. Increasing the heating temperature, Fe moves and return to the usual coordination (800/O$_2$). Finally any magnetic order of Cu in the planes is detected though the oxygen concentration is probably low, specially for the 210/O$_2$ sample. This is in agreement with the observed superconducting properties with T$_c$ close to the values of the pure compound. In fact, the existence of these latter properties is a strong argument against a significant Fe plane occupation as established by very numerous studies.

The low temperature spectra reveal a transition temperature distribution, as we have pointed out above. This distribution depends strongly on the treatment. In our opinion, Fe clusters of different sizes are the only way of explaining these features. Desoxygenation does not change the coordination in the plane and cannot favour Fe clustering on this site. Therefore, the clusters occur probably in the chains. However, a small Fe population of about 10% is present in the planes. This is confirmed by the results the 300/O$_2$ samples for which a sextet with this population is clearly detected at 4.2 K (fig. 2b).

In conclusion, too unsolved questions and some contradictions result from the hypothesis of a strong plane Fe occupation after Ar treatment. Fe clustering in the chains is clearly a better explanation of the results but further work is necessary to conclude.

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