ISSN 0029 - 3865

CBPF-NF-077/88

MÖSSBAUER STUDIES OF ^{57}Fe: $YBa_2Cu_3O_7$ AT HIGH TEMPERATURES*

by

E. BAGGIO SAITOVITCH, I. SOUZA AZEVEDO
and R.B. SCORZELLI

Centro Brasileiro de Pesquisas Físicas - CBPF/CNPq
Rua Dr. Xavier Sigaud, 150
22290 - Rio de Janeiro, RJ - Brasil

*To be published in"Transaction of the Japanese Institute of Metals".

The substitution of Cu by Fe in the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ superconductor induces different effects above and below x = 0.01, as seen by DC magnetization and Mössbauer measurements, despite the fact that the X-ray diffraction still shows the orthorhombic structure. Two iron species associated with doublets D1 and D2 are assigned to the occupation of Cu1 sites with different oxygen coordination, their isomer shift values are consistent with a Fe^{+4} high spin configuration. The Mössbauer spectra obtained, in air, at fixed temperatures from 25 C until 298 C revealed a clear modification of the relative intensity of D1 and D2 before the formation of the iron species related to the oxygen deficient phase.

Key-words: Superconductivity; Mössbauer spectroscopy; Iron in ceramics; Oxides; Magnetic ordering.

1 INTRODUCTION

Since the discovery of H-Tc superconductor oxides $(La_{1-x}Ba_x)_2 CuO_4$ and $YBa_2Cu_3O_7$ an intense effort has been made to understand their properties, particularly the substitution of impurity ions in various lattice sites has been extensively studied[1]. The discovery of $BiBaCaCu_2O_x$ superconductor oxide confirmed the importance of CuO_y clusters for the H-Tc values. Consequently it is of great importance to understand how impurity ions are stabilized in Cu sites to propose mechanisms for the observed deplection of Tc.

The substitution of Cu by Fe in the $YBa_2(Cu_{1-x}Fe_x)_3O_7$ superconductor oxide induces different effects above and below $x=0.01$ as has been already reported by Mössbauer and DC magnetization studies[2]. The results obtained for the substitution of Cu ions by ^{57}Fe has been reported by several authors and the results are not consistent since, in most cases, both the samples and the interpretation of the Mössbauer spectra are different[3]. The most crucial point concerns to the presence of a doublet with 2.0mm/s quadrupole splitting, characteristic of low iron concentration in the $YBaCu_3O_6$ oxygen deficient phase, which has been attributed to iron in Cu2 site.

In our early publication[2] we proposed the preferencial occupation of Cu1 site by iron; this was recently confirmed by neutron and electron diffraction experiments[4].

In order to obtain information about the possible oxygen configuration for the iron species observed at room temperature which can depend on the preparation procedure we studied ^{57}Fe: $YBa_2Cu_3O_7$

samples at high temperatures.

2 EXPERIMENTAL

Several samples of $YBa_2Cu_3O_7$ were prepared with Cu partially substituted by Fe($x \simeq 0.001$, 0.005, 0.01, 0.03 and 0.10). A mixture of appropriate amounts of Y_2O_3, $BaCO_3$, CuO and Fe_2O_3 (94.5% enriched in Fe), were cold pressed, sintered in O_2 atmosphere for 15h at 970 C and cooled down to room temperature at 50 C/h. After crushing and cold pressing, samples were annealed at 500 C in O_2 atmosphere for 12 hours. X-ray studies showed a single orthorhombic structure up to $x \simeq 0.1$ Fe. The absorbers for Mössbauer transmission experiments were prepared from powdered materials.

For the high temperature studies the samples were kept in an Elscint oven with ceramic sample holder. Typical run for a sample with $x = 0.005$ was of 10 hours. Normal air pressure was used in order to avoid the reduction of oxygen content from the sample. The 50mCi $^{57}Co/Rh$ Mössbauer source was kept at room temperature during high temperature measurements.

3 RESULTS AND DISCUSSION

The variation of the transition temperatures Tc induced by iron impurities in $YBa_2Cu_3O_7$ oxides is presented in Fig. 1. From this results it is clear that to study the superconductive phase it is important to analyse samples with Fe content below $x = 0.01$, since above this value the superconductive transition is perturbed

From the Mössbauer spectra obtained at room temperature for $x < 0,01$ (Fig. 2) three doublets can be defined: D1(IS1 = 0.17 mm/s, QS1 = 1.55mm/s), D2(IS2 = 0.3mm/s QS2 = 1.30mm/s and D3(IS3 = 0.20mm/s, QS3 = 0.28mm/s). The doublets D1 and D2 which dominate the Mössbauer spectra, are sensitive to the oxygen content of the samples: they both transform mainly to a doublet D_T(IS_T = 0.06mm/s, QS_T = 2.00mm/s) when the $YBa_2(Cu_{1-x}Fe_x)_3O_6$ phase is prepared either by quenching the sample from 1000C or by annealing in Ar atmosphere[2].

The Fe species associated with doublets D1 and D2 are attributed to the occupation of Cu1 sites with different oxygen coordination, their isomer shift are consistent with a Fe^{+4} high spin configuration, that can be stabilized only if an additional oxygen is fixed by Fe in the Cu1 plane. For a better understanding of the differences between both we determine the behavior of D1 and D2 in air under temperatures of 25C to 300C; the upper limit was taken to avoid the decrease of oxygen content with the consequent formation of D_T.

The Mössbauer spectra obtained for some temperatures are shown in Fig. 3. They were fitted assuming equal intensities and linewidth for each pair of lines which form the three doublets. The analysis of the Mössbauer data at different temperatures indicate a small decrease of the quadrupole interactions for D1 and D2 for higher temperatures, possibly due to a variation of lattice parameters[5].

The most important result is that the relative intensity of the iron species corresponding to D2 increases with temperature at expenses of the species corresponding to D1. This is an extra confirmation of the correlation already observed between this two iron species.

This modification in the intensities is partially reversible when the sample is cooled down in air. The behavior of the species corresponding to D1 which decreases intensity with increasing either Fe concentration or temperature is also observed for twinnings in similar systems[4,6]. Combining these results with the fact that D2 has always broad lines we suggest that it corresponds to iron in Cu1 site with an extra oxygen which has a distribution in position, while the D1 corresponds to iron at Cu1 sites with only 4 oxygen coordination. The assignement for D3 is still not defined.

Further experiments are being performed, now in O_2 atmosphere, to achieve better understanding on these points.

FIGURE CAPTION

Figure 1: The DC magnetization measurements for different iron concentrations in $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples.

Figure 2: Mössbauer spectra $YBa_2(Cu_{1-x}Fe_x)_3O_7$ samples at room temperature for: a) $x = 0.001$, b) $x = 0.005$ and c) $x = 0.01$.

Figure 3: Mössbauer spectra for $YBa_2(Cu_{0.995}Fe_{0.005})_3O_7$ obtained at the indicated temperatures.

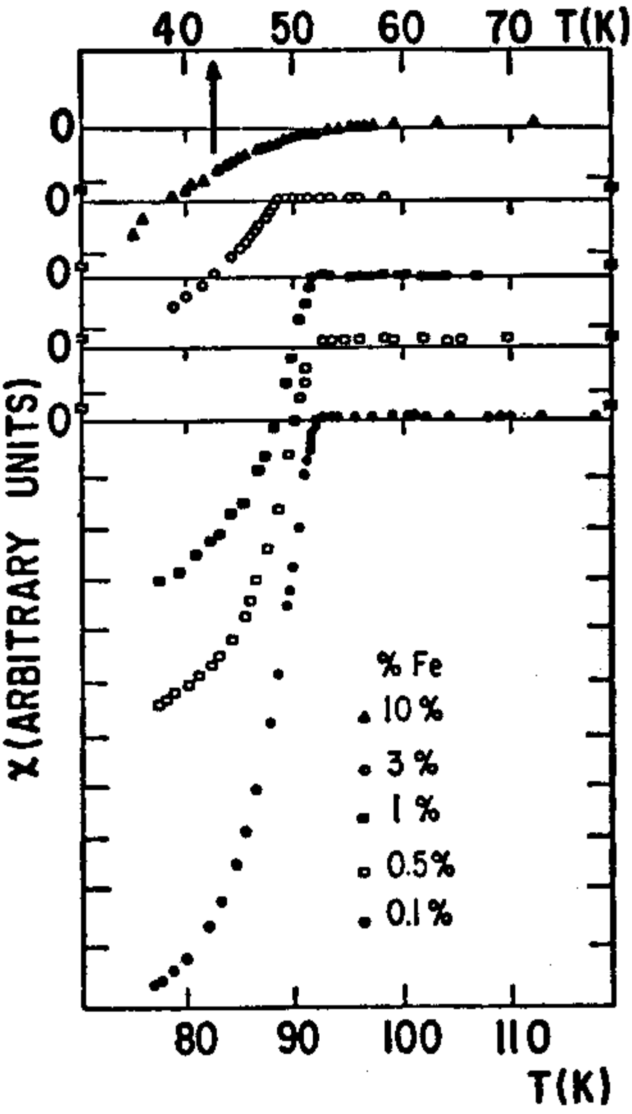
40
50
60
70
T(K)
0
0
0
0
0
χ(ARBITRARY UNITS)
% Fe
10 %
3 %
1 %
0.5%
0.1 %
80
90
100
110
T(K)

Figure 1

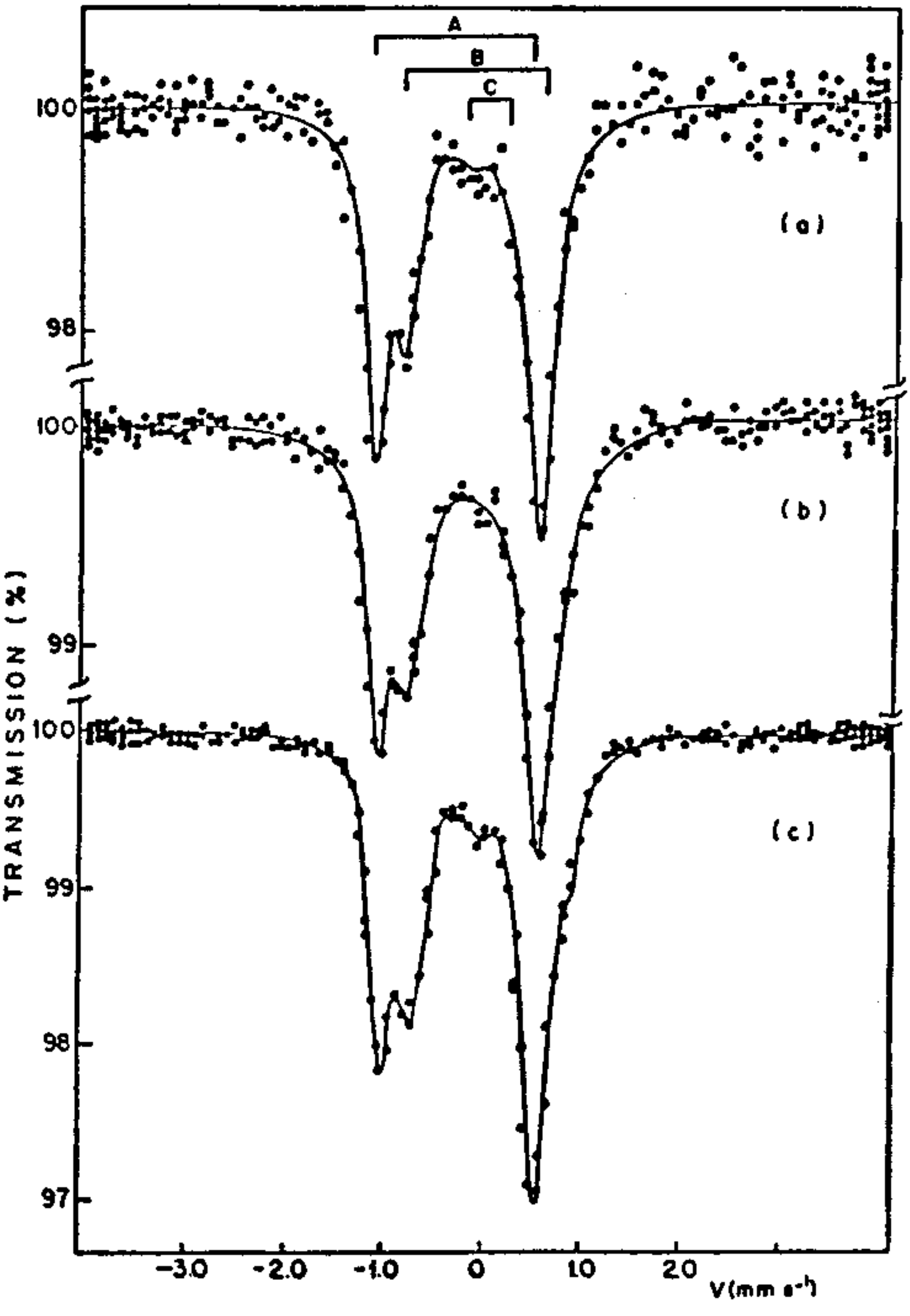
A
B
C
(a)
(b)
(c)
TRANSMISSION (%)
100
98
100
99
100
99
98
97
-3.0
-2.0
-1.0
0
1.0
2.0
V(mm s⁻¹)

Figure 2

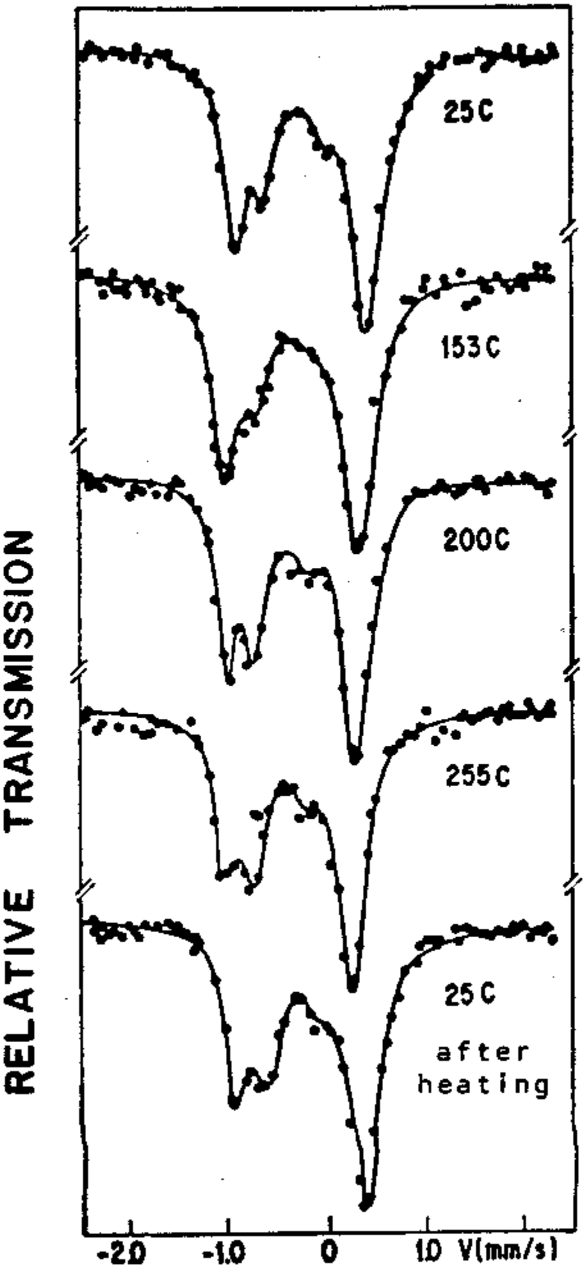
RELATIVE TRANSMISSION
25C
153C
200C
255C
25C
after
heating
-2.0
-1.0
0
1.0
V(mm/s)

Figure 3

REFERENCES

[1] Y. Maeno, T. Tomita, M. Kayo Goku, S. Awagi, Y. Aoki, K. Hoshino, A. Minami and T. Fujika, Nature 328, 512/1987;

[2] E. Baggio Saitovitch, I. Souza Azevedo, R.B. Scorzelli, H. Saitovitch, S.F. da Cunha, A.P. Guimarães, P.R. Silva and A.Y. Takeuchi, ICAME, Melbourne, August 1987, and Phys, Rev. B. 37, 10, 1988;

[3] B.D. Dunlap, J.D. Jorgensen, W.K. Kwork, C.W. Kimba II, J. L. Matykiewicz, H. Lee and C.U. Segre and references there in M2HTSC - Interlaken 1988;

[4] G. Roth, G. Heger, B. Renker, J. Pannetier, V. Caignaert, M. Hervieu, and B. Raveau, submitted to Z. Phys. B.;

[5] Y. Maeno and T. Fujita. M2HTSC - Interlaken 1988.

[6] N. Yamamoto et al., JIMIS-5, Kyoto, March 1988.