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ON THE MECHANISM OF OXYGEN DESORPTION IN Fe:Y-Ba-Cu-O SUPERCONDUCTING OXIDES*

by

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"In situ" ^{57}Fe Mössbauer Spectroscopy experiments have been performed on Fe:Y-Ba-Cu-O samples, in vacuum at high temperatures. From the results obtained it has been possible to make evident the kinetics of oxygen loss in doped samples.

Key-words: Superconductivity; Mössbauer spectroscopy; Iron in ceramics; Superconducting oxides.

Since the discovery of the H-T_c superconductor oxides $La_{2-x}Ba_xCuO_4$ and $YBa_2Cu_3O_7$ an intense effort has been made in order to understand their properties as well as the effect of substituent impurity ions in the various lattice sites on the superconducting behavior [1]. The Mössbauer spectroscopy has contributed to these studies mainly in what concerns the substitution of Cu by Fe ions. A relevant conclusion was obtained by combining the local information revealed by this experimental technique with the data from X-ray and neutron diffraction, transmission electron microscopy and the bulk characterization of the superconducting transition for samples with different Fe content [2]. The decrease of T_c, induced by the Fe doping is related to the perturbation in the local structure of Cu(1) site, since the Fe ions increase the oxygen coordination, destroying the chains. Even if these chains are not directly responsible for the supercurrents, they behave as charge reservoir, and their presence in the Y-Ba-Cu-O compound is essential for the establishment of a superconducting state.

The characterization of the iron species in the oxygen reduced phase, $Fe:YBa_2Cu_3O_{6+\delta}$, was performed either by quenching the sample from high temperatures in vacuum [3,4,5] or by annealing them in Ar atmosphere. These experiments established the sensitivity of Fe to the oxygen content in the Y-Ba-Cu-O samples, consistent with the preferential occupation of Cu(1) site by Fe-substituents.

The most interesting experiments are the Mössbauer measurements, performed "in situ", in vacuum at high temperatures. The aim of these experiments is to learn about the kinetics of oxygen desorption in the doped samples. Some studies in air [6] or oxygen atmosphere [7] have been already performed under similar conditions, and relevant information was obtained concerning the relative stability of the different iron species and the possible occurrence of oxygen hopping.

The information obtained from X-ray and neutron diffraction measurements [8] in the undoped $YBa_2Cu_3O_7$, indicated that the oxygen from Cu(1) plane is the one which can be removed by heating the sample above 400°C, in reduced O_2 atmosphere, leading to the tetragonal semiconductor $YBa_2Cu_3O_{6+\delta}$ phase. The analysis of electron diffraction measurements [9] in the doped sample suggested the presence of linear Fe clusters in Cu(1) planes, separated by orthorhombic domains with low Fe concentration with size of 20 to 30 Å. This pattern can play an important role in the desorption of oxygen. Since the Fe-substituent is sensitive to the oxygen occupation in Cu(1) plane, it will be interesting to follow the oxygen loss by the "in situ" measurements.

We report here, to our knowledge, the first "in situ" Mössbauer study on a sample of Fe:Y-Ba-Cu-O in vacuum, at high temperatures.

The Mössbauer hyperfine parameters at RT for the several iron species present in Fe:Y-Ba-Cu-O for different iron and/or oxygen content are listed in Table I. The sample used in this experiment has already 15% of the species (D), characteristic of the tetragonal phase $YBa_2Cu_3O_{6+\delta}$.

Table I - Mössbauer hyperfine parameters at RT of the quadrupole doublets associated to Fe species A,B,C,D,E and F present in Fe:Y-Ba-Cu-O for different oxygen content : IS (Isomer Shift) relative to iron metal; QS(Quadrupole Splitting).

	IRON SPECIES					
	A	B	C	D	E	F
IS(mm s^{-1})	-0.18	0.03	0.19	0.04	0.13	0.30
QS(mm s^{-1})	1.56	1.20	0.30	1.98	0.70	0.55

The sample with 1% Fe was kept in vacuum in

a temperature controlled oven with a boron nitride sample holder and mylar windows.The Co(Rh) source was kept at RT and the typical data collection times were about 12 h at fixed temperatures in the range of 295 K to 640 K. The cooling of the sample was performed in vacuum at a rate of 70°C/h.

The Mössbauer spectra obtained at the indicated temperatures are shown in Fig. 1. They are very similar except for smooth changes of the quadrupole splitting (QS) and the second order Doppler shift (different temperatures of Möss - bauer source and absorber).

More reliable information can be achieved from the analysis of the relative intensities for the several Fe species at different temperatures obtained from the fit of the Mössbauer spectra. Figure 2 shows the variation for species D . Despite the fact that it is known that oxygen under this condition is partially removed in the undoped compound, our results indicated that only a small fraction of the species D, characte - ristic of the oxygen deficient Fe:Y-Ba-Cu-O sample is formed at the first heating up to 763K: the main transformation is only observed when the sample is cooled to RT.

The comparison of the Mössbauer spectra obtained at 295 K before (Fig. 3a) and after heating in vacuum up to 763 K (Fig. 3b), indicates that the three iron doublets (A, B and C), present in the orthorhombic phase, transform mainly into a species D characteristic of the reduced phase of Fe:Y-Ba-Cu-O in the cooling down process. From this analysis it is clear that, after cooling the sample to RT, oxygen loss occurs around the Fe positioned in the Cu(1) site. This result is in agreement with what was reported,by us and other groups [3,4,7], for samples quenched from high temperature or annealed in argon atmosphere. In this process another iron species

(IS = 0.30 mm/s; QS = 0.68 mm/s) can be formed , but it will not be discussed here.

To understand our results we need to refer to the information obtained from electron diffraction measurements for Y-Ba-Cu-O doped with Fe [9]. When the sample is heated up to 763 K, the oxygen loss would occur mainly in domains between the iron clusters. The iron clusters themselves seem to keep the same oxygen content. This picture could explain that the relative intensities of the Mössbauer spectra are nearly constant along the whole heat treatment, but it implies that at high temperatures, in our conditions, the oxygen diffusion from the neighborhood of Fe is inhibited. Cooling down under a gradient of oxygen concentration induces an anion diffusion out from the iron clusters. This mechanism promotes the loss of oxygen in these clusters, suggested by the growing of the intensity of iron species D.

Our results can be understood on the basis of the existence of two main regions already proposed for the Fe:Y-Ba-Cu-O samples [9] : annealing in vacuum at high temperatures induces oxygen loss mainly in the iron – free domains . Subsequent cooling to RT promotes the oxygen diffusion from the iron clusters to the iron-free regions. To our knowledge this is the first observation of oxygen rearrangement in the cooling down process in the Fe:Y-Ba-Cu-O samples heated at high temperatures in vacuum.

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Figure Captions:

Fig. 1 - ^{57}Fe Mössbauer spectra of Y-Ba-Cu-O doped with 1% iron, measured in vacuum at the indicated temperatures.

Fig. 2 - Relative intensities of Fe^{3} species D, characteristic of oxygen deficient phase in Y-Ba-Cu-O, as a function of temperature.

Fig. 3 - ^{57}Fe Mössbauer spectra at RT of Y-Ba-Cu-O sample: a) before heating; b) after heating in vacuum up to 763 K.

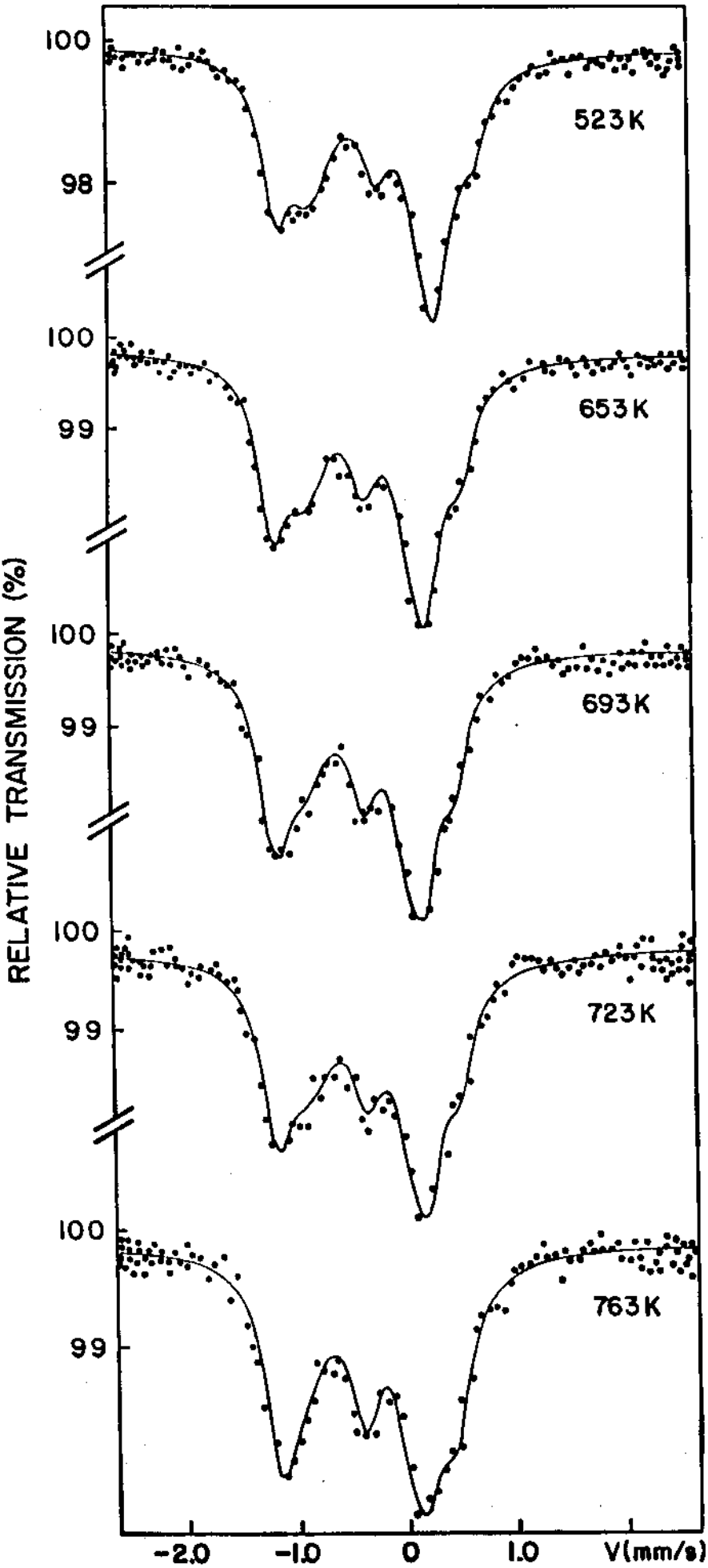
100
98
523K
100
99
653K
100
99
693K
100
99
723K
100
99
763K
RELATIVE TRANSMISSION (%)
-2.0
-1.0
0
1.0
V(mm/s)

Fig. 1

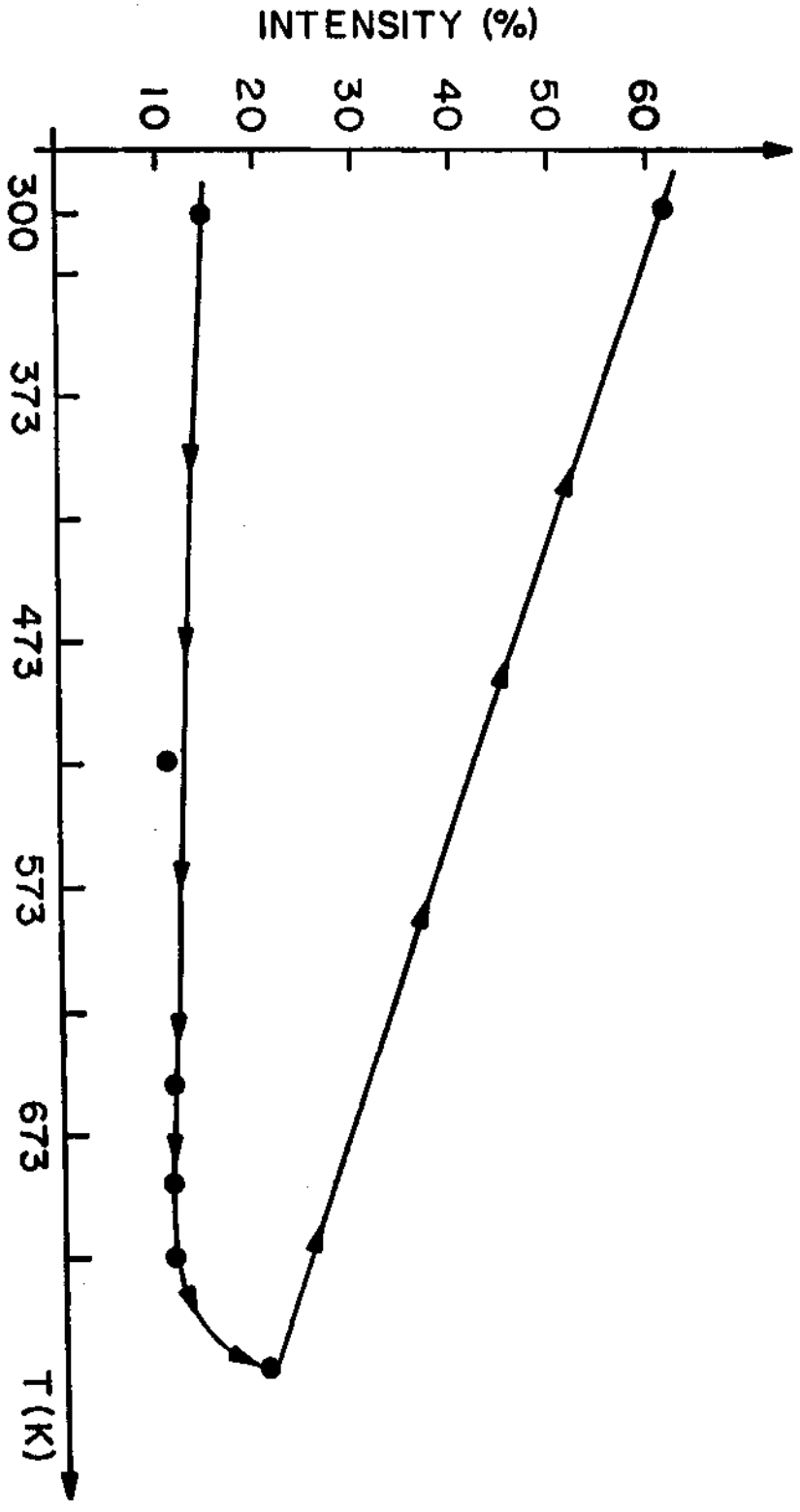

Fig. 2

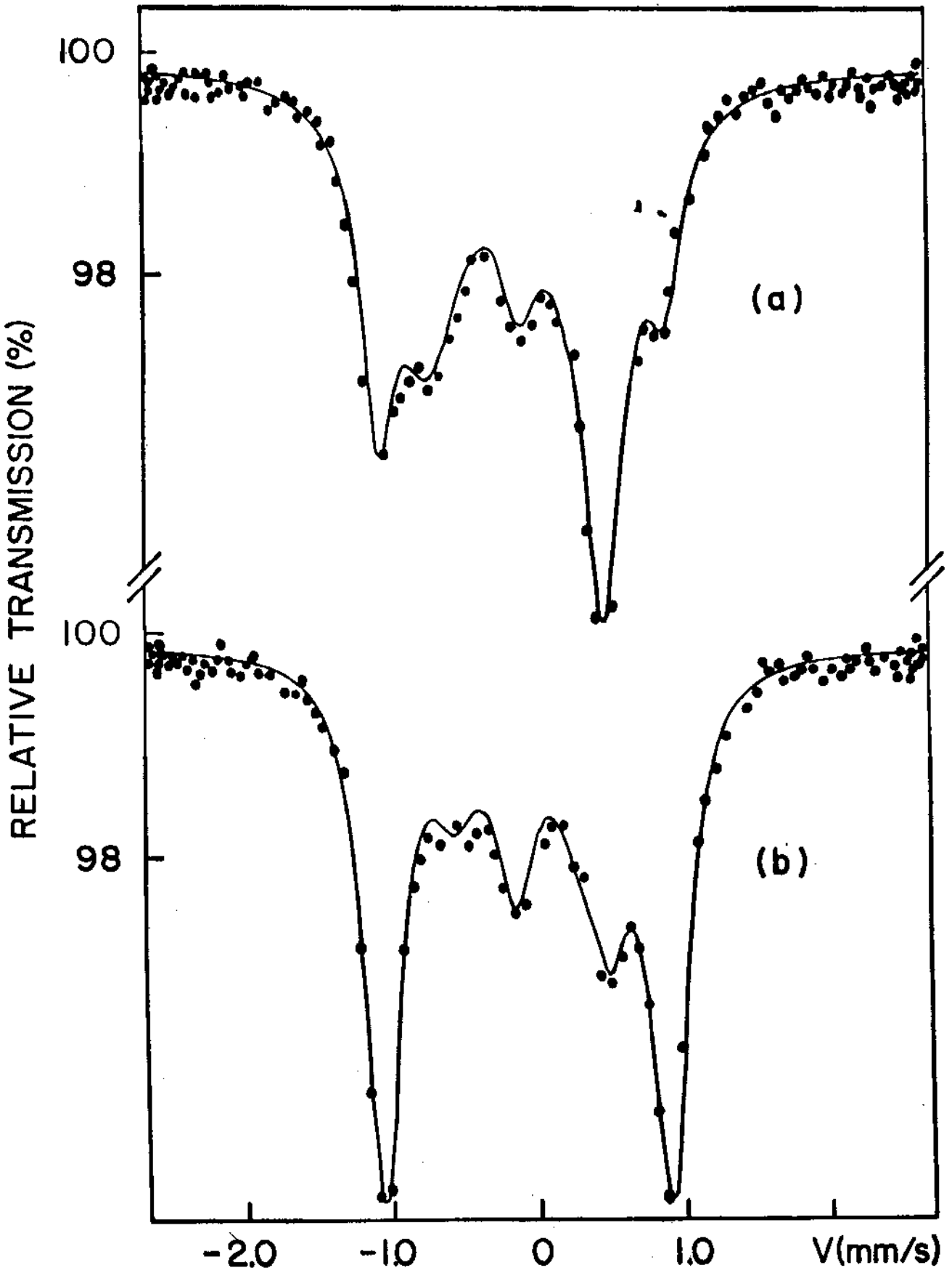

Fig. 3

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