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ABSTRACT

We report on "in situ" high temperature ^{57}Fe Mössbauer measurements on several Fe:YBaCuO samples with different Fe concentrations under controlled oxygen partial pressures. The results are discussed in view of the temperature dependent binding of oxygen in Fe-rich clusters which differs from that in their more Cu-rich surrounding.

I - INTRODUCTION

Studies of the various iron species in the oxygen reduced phase, $Fe:YBa_2Cu_3O_{6+\delta}$, have usually been performed on samples obtained either by annealing under argon flow [1] or quenching from high temperatures in vacuum [2,3,4]. These experiments have demonstrated the sensitivity of Fe to the oxygen content in YBaCuO, consistent with the preferential occupation of the Cu(1) site by iron substituents. Even more informative with respect to the oxygen deloading are Mössbauer measurements performed "in situ" (i.e. taking the measurements during the thermal treatment under a certain oxygen partial pressure (p_{O2}). Such experiments have already been reported for samples of Fe:YBaCuO in oxygen atmosphere [5] or vacuum [6] under controlled heating conditions. They allowed to study the stability of oxygen configurations at high temperatures as well as the mechanism of oxygen loss in more detail.

The Mössbauer hyperfine parameters for the various iron species, present in our samples are listed in Table I for room temperature (RT) and 763 K. Note, that for varying iron and or oxygen content these species are not all observed simultaneously.

The comparison of the Mössbauer spectra obtained at RT before and after heating in vacuum at 763K reveals that the three doublets A, B and C, present in the orthorhombic phase, transform during cooling down mainly into the doublet D characteristic of iron in the reduced phase of Fe:YBaCuO. This indicates an oxygen loss around the Fe positioned in the Cu(1) site in agreement with earlier reported data [2,3,4], for samples quenched from high temperature or annealed in argon atmosphere.

The analysis of the relative intensities (RI) of the various subspectra for the "in situ" studies allows to monitor the oxygen desorption near Fe as a function of temperature and residual pressure. It is known that for undoped YBaCuO oxygen is removed in part at temperatures above 700 K and p_{O2} smaller than 10^{-1} mbar [7]. Our results [6], however, indicate that only a small fraction of the species D is formed at the first heating up to 763 K; the main transformation is only observed when the samples are cooled again to RT. An effect of grain size on the oxygen loss has been observed by repeating these "in situ" experiments for a sample, with the same Fe content, prepared by the citration method [8] and, consequently, consisting of very small grains. In this case Fe looses oxygen already during the heating below 763 K leading to an increase of species D in contrast to the sintered sample.

The present study extends these investigations with the following two aims:
1- To investigate the influence of the Fe concentration on the process of oxygen loss for the condition already described i. e. fixed residual pressure during "in situ" thermal treatment in the temperature range from 295 to 763 K. With increasing Fe concentration one may expect a formation of bigger Fe-rich clusters in which part of the oxygen will be strongly trapped, thus the yield of the species D should be smaller than for low Fe concentration.
2- To follow the influence of p_{O2} on oxygen desorption in Fe:YBaCuO at fixed high temperature. In this case the iron concentration was kept low in order to exclude the influence of Fe clusters (see 1).

We will discuss these new data together with the previous results concerning the influence of the heating conditions and the grain size.

II - EXPERIMENTAL

The samples used for the high temperature Mössbauer studies were labelled as : samples I-1, I-3 and I-10 (1%, 3% and 10% of Cu substituted by Fe, respectively) prepared by the standard sinter procedure. The Mössbauer absorbers were heated in an oven with a boron nitride sample holder. The $^{57}Co/Rh$ source was kept at RT.

For the measurements performed to determine the influence of the iron concentration and of successive thermal cycles, samples I-1, I-3 and I-10 have been used. The Mössbauer spectra for these samples were taken each 12 h under a p_{O_2} of 10 mbar for temperatures in the range of 295 to 763 K, cooling down to RT, and measuring again at high temperatures. For sample I-1 the spectra were collected during the heating up to 763 K and after the cooling to RT; for sample I-3 the spectra were collected during the heating up to 763 K and also during the cooling down to RT, as well as during the successive heatings to 763 K and coolings to RT. Finally, for sample I-10, the spectra were taken mainly to study the saturation of the intensity of doublet D after successive heatings to 763 K.

In order to study the influence of p_{O_2} at fixed temperature on the oxygen desorption, sample I-1 was used. The Mössbauer spectra were taken each 12 h at 763 K and varying p_{O_2} from 20 to 2×10^{-3} mbar. To avoid any deloading of the sample during heating, the temperature was raised fast (in about 20 min) to 763 K at 20 mbar.

III. RESULTS

a) Influence of the iron concentration on the oxygen desorption

Fig. 1 shows the Mössbauer spectra obtained at several temperatures in course of the heating cooling treatment for a sample with 3% of Fe. This figure also demonstrates the data deconvolution which was done in this case with three quadrupole doublets B, D and F. The variation of the quadrupole interactions and isomer shifts turned out to be smooth and reversible with temperature. No anomalous line broadenings were observed up to 700K. Above 700K only the widths of the lines of doublet B broaden from about 0.45 mm/s to 0.60 mm/s. This broadening disappears again on cooling. In principle this may be due to a displacement of Fe by passing-by oxygen. From the present data, however, a distinction between a static or a dynamic origin of the broadening cannot be made.

All significant changes in RI occur between the doublets B and D. We remind that doublet B is supposed to have a fivefold oxygen coordination, whereas the doublet D has a fourfold one. Thus an increase of the relative intensity RI (D) of doublet D reflects directly the oxygen deloading near Fe. No attempt was made to correct for the different f-factors of species B and D (this actually would lead to a slight increase of RI (D)).

In fig. 2 we show the temperature variation of RI (D) at a p_{O2} of $\cong 10$ mbar for three samples with different iron concentrations. Realistic errors in RI (D) are less than $\pm 4\%$. In fig. 2a we give previous data [6] for a sample with 1% of Fe which demonstrate that the oxygen loss around the iron in Cu(1) site mainly occurs in the cooling down process at $\cong 10$ mbar.

The result shown in fig. 2b, for a sample with 3% of Fe confirms that RI (D) remains almost constant up to 763 K, a marked increase is only observed when cooling down. In the first cycle (1-2-3) there is a saturation of the formation of doublet D around 500 K in the cooling down process. When heating the sample again to 763 K, in the second cycle (3-4-5), there occurs a further increase of doublet D, which is continued again when cooling down to RT. Similar behavior is observed in the following thermal cycle (5-6-7). Final saturation seems not yet to be reached at step 7, but this was not further investigated for this sample.

In fig. 2c we show the variation of RI (D) from the measurements performed in a sample with 10% of Fe. In this case, we could follow the saturation for the formation of species D. Successive heatings from RT to 763 K do not induce a detectable further increase of RI (D). Note that this value of RI $\cong 50\%$ is clearly smaller than those for the samples with 1% and 3% Fe for which there was not even yet achieved saturation. This result is similar to those we obtained for samples reduced by heating under Ar flux.

b) Measurements for different p_{O2}

Figure 3a shows the spectrum of sample I-1 obtained at RT and ambient pressure before heating up. Fig. 3b shows the spectra obtained at 763 K and different oxygen partial pressures (upper spectrum $p_{O2} = 20$mbar; lower spectrum po2 $= 2.10^{-3}$ mbar).

At 20 mbar mainly the RI of the iron doublets A, B have changed compared to the initial RT data. This is not caused by an oxygen deloading which is still neglegible for this oxygen partial pressure but is rather a consequence of the different thermal stabilities of the related iron species [6].

In order to be sure that the oxygen content does not change considerably during the measurements, the spectra have been collected in a short time period only, which resulted in not so good counting statistics. However, we can clearly see the enhancement of the absorption lines of doublet D (QS=1.98 mm/s at RT, QS=1.67 mm/s at 763K) with the decrease of the oxygen partial pressure. Figure 3c shows the spectrum at RT after cooling down from 763 K at 2.10^{-3} mbar.

The p_{O_2} dependence of the oxygen desorption around iron at 763 K has been monitored via the change of the RI. Figure 4a shows RI (D) for sample I-1 annealed at 763 K under different p_{O_2}. The increase of RI (D) is again mainly due to a decrease of RI (B). Below about 2.10^{-2} mbar RI (D) tends to saturate.

IV. DISCUSSION

From electron diffraction measurements [11] on YBaCuO doped with Fe it has been concluded that linear Fe-rich clusters are formed in Cu(1) planes, separated by orthorhombic domains of low iron concentration with sizes of 20 to 30A. The oxygen affinity becoming stronger to Fe than to Cu with increasing temperature allows to explain why in this microstructure of the Fe doped samples the oxygen desorption mainly occurs in the cooling down process:

We propose that oxygen is first removed from Cu rich parts of the sample, and only during the cooling down process it is sucked from Fe rich clusters to the yet oxygen depleted parts in their neighborhood. This is caused by a temperature dependent entropy contribution to the free energy. This process is asymmetrical for reheating: the expected uptake of oxygen to the Fe rich clusters at temperatures where the oxygen affinity to Fe exceeds again that to Cu is apparently impeded, e.g., by a barrier for oxygen diffusion on the surface of the more Fe rich clusters. When cooling again more oxygen is transferred from these clusters to their surrounding, and so forth, leading to a gradual saturation after several cycles. Our data show that saturation is reached more rapidly for higher iron concentrations (i.e. with larger sizes of the Fe rich clusters), yet the saturation value of RI (D) reached after a certain time is lower. Deloading of larger clusters is apparently less effective due to a less favourable surface to volume ratio and in addition the bonding of oxygen seems to be stronger. This is also supported by differential scanning calorimetry (DSC) studies [9] for Fe:YBaCuO which indicate an increasing tendency towards stronger bonding of oxygen with increasing Fe-doping.

It is to be expected that oxygen deloading may be influenced by grain size. The above given description how the oxygen desorption from Fe-rich clusters occurs is valid only for not too small grain size. If the grain size is reduced an oxygen loss is detected already during the heating up process due to a much faster oxygen diffusion out of the Cu-rich parts of the sample. As a consequence the gradient of oxygen content between Cu-rich and Fe-rich parts of the sample increases and finally oxygen will also diffuse out of the not yet depleted Fe-rich parts even during the heating up process.

In fig. 4 we compare the formation of doublet D (i.e. the effect of oxygen deloading near Fe) with the oxygen desorption (fig. 4b) of the undoped samples (YBaCuO) at the same temperature [10] as a function of p_{O_2}. Despite the shapes of both curves in figs. 4a and 4b are different, the formation of doublet D has the same tendency as the overall oxygen desorption. The transformation into doublet D is steep down to 1 mbar, but tends to saturate for lower pressures, the overall oxygen desorption, however, is still increasing in this range. This again points to a stronger bonding of oxygen to Fe than to Cu at high temperatures.

In conclusion, our results are in agreement with the picture that Fe:YBaCuO contains Fe-rich and Fe-depleted regions [11]. Annealing in vacuum at high temperatures induces oxygen loss mainly from Fe-free domains, subsequent cooling to RT promotes the oxygen diffusion from the Fe-rich clusters to the Fe-free regions. Effective oxygen deloading of the Fe-rich clusters can only be achieved after subsequent thermal cycling under vacuum.

At a fixed temperature of 763 K a lowering of pressure leads initially to an oxygen depletion around Fe going parallel to the net oxygen deloading of the sample. For low oxygen partial pressure a saturation is reached due to the stronger bonding of oxygen to Fe compared to Cu.

FIGURE CAPTIONS

Fig. 1 - Mössbauer spectra of sample I-3 (3% Fe) at various temperatures during the thermal cycling. RT_i corresponds to measurements taken at stage RT1, RT3 and RT7 (see also fig 2b).

Fig. 2 - Relative intensity of doublet D as a function of temperature for various temperature cycles. The arrows indicate the direction of temperature increase (decrease). The full line is only a guide for the eye.
(a) sample I-1 (1% Fe); (b) sample I-3 (3% Fe); (c) sample I-10 (10% Fe).

Fig. 3 - Mössbauer spectra of sample I-1 at various conditions: (a) room temperature at ambient pressure; (b) T=763 K and oxygen partial pressure 20 mbar and 2.10^{-3} mbar, upper and lower spectrum, respectively; (c) room temperature after heating at 763 K at $p_{O2} = 2.10^{-3}$ mbar. Notice the temperature dependence of the hf parameters of doublet. D.

Fig. 4 - a) Relative intensity of doublet D as a function of oxygen partial pressure for Fe:YBaCuO; b) Oxygen desorption as a function of oxygen partial pressure for undoped YBaCuO.
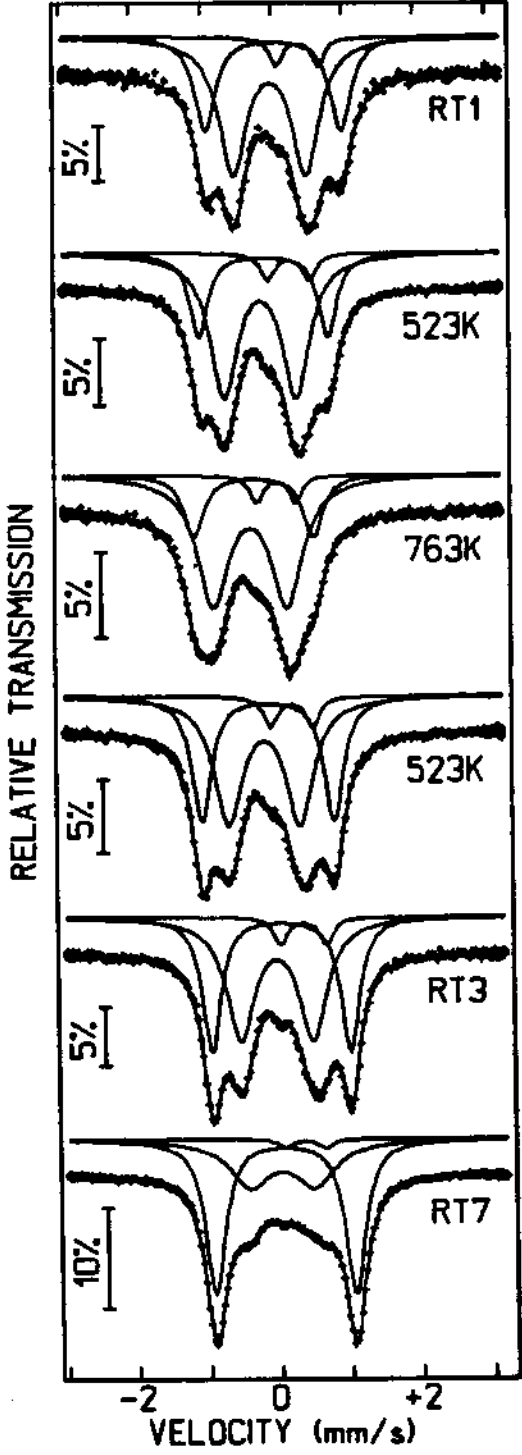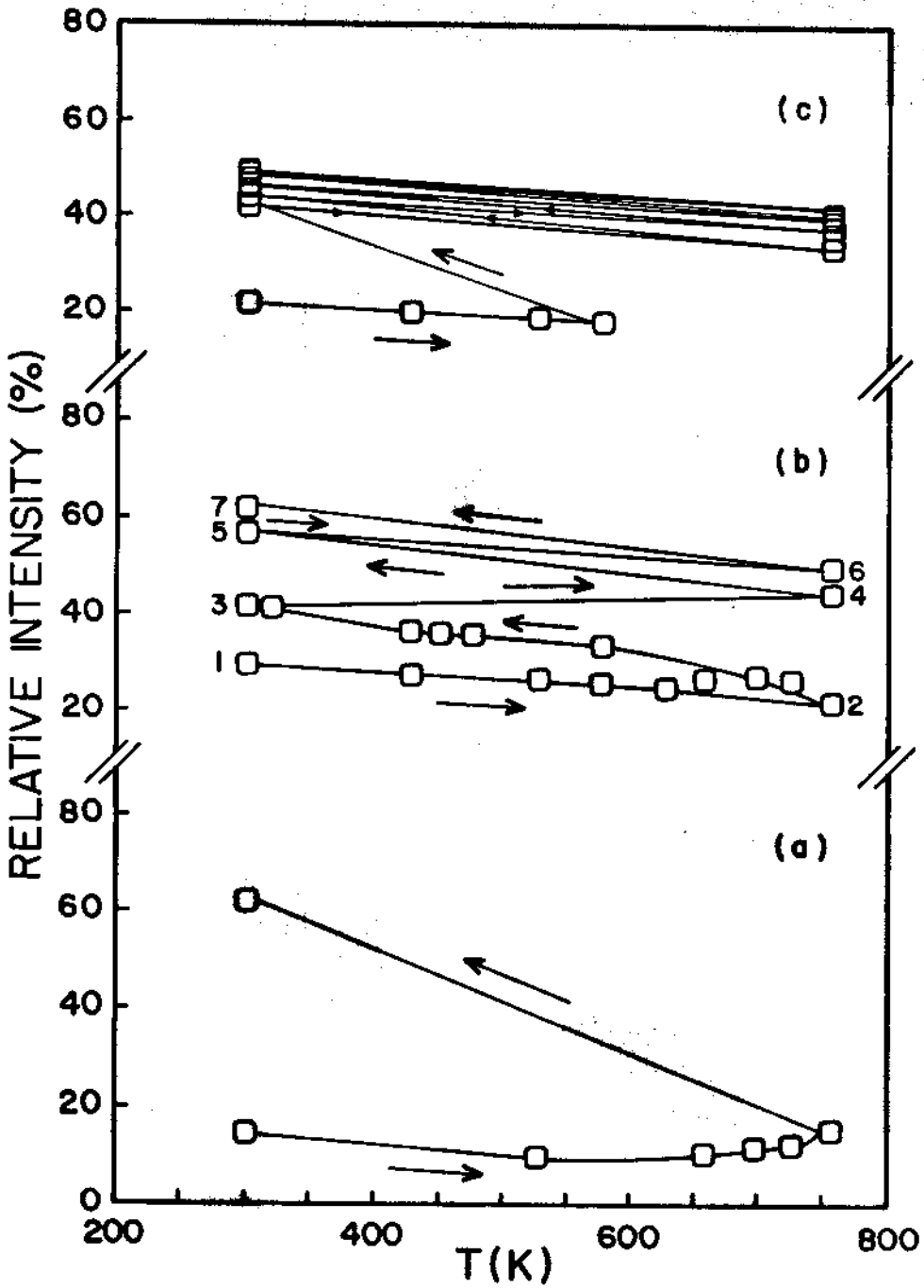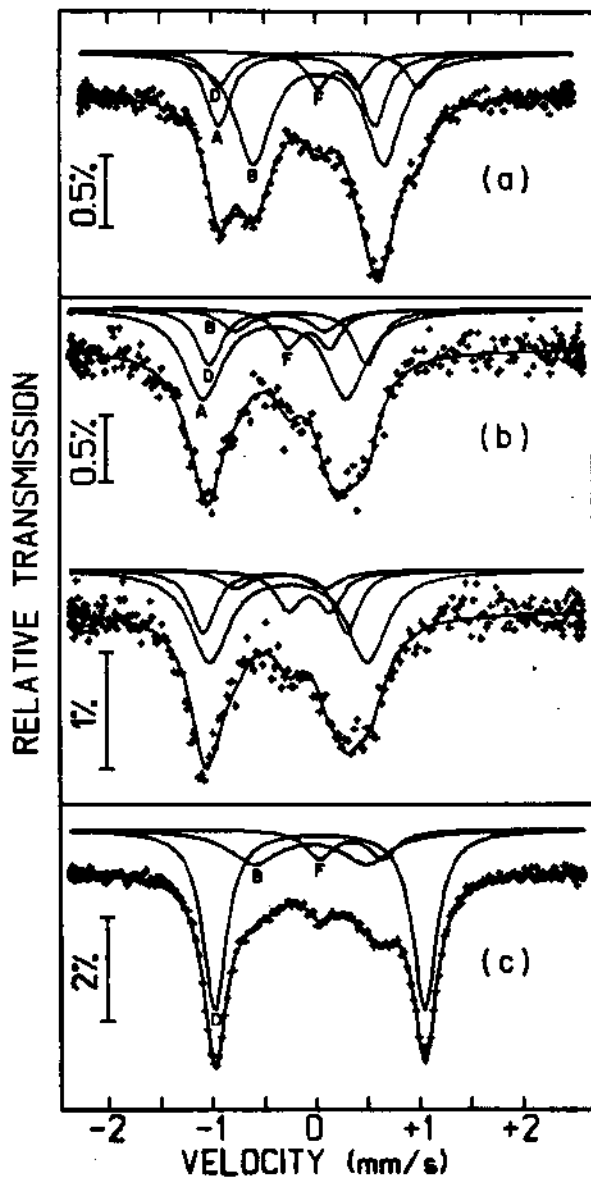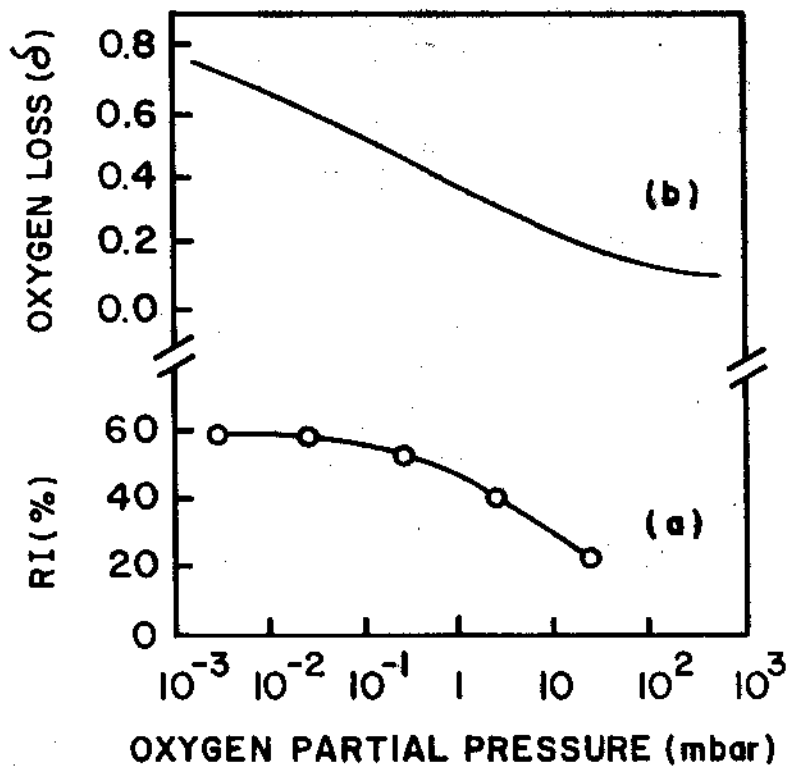
FIG. 1

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FIG. 2

FIG. 3

FIG. 4

		IRON SPECIES					
		A	B	C	D	E	F
300 K	IS (mm/s)	-0.18	0.02	0.20	0.03	0.05	0.30
	QS (mm/s)	1.55	1.20	0.36	1.98	0.70	0.55
763 K	IS (mm/s)	-0.39	-0.34/-0.39	-0.05	-0.28	----	0.03
	QS (mm/s)	1.38	0.70/0.95	0.35	1.67	----	0.50

TABLE I

Mössbauer hyperfine parameters of the iron species present in $Yba_2Cu_3O_y$ samples for different oxygen contents at 300 K and 763 K: IS (isomer shift) relative to iron metal; QS (quadrupole splitting).

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