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1994 J. Phys.: Condens. Matter 6 1019

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Mössbauer measurements on $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ following progressive oxygen removal by vacuum annealing between 300 and 800 °C

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Received 24 August 1993, in final form 26 October 1993

Abstract. Mössbauer studies are reported on $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ samples with $x = 0.02, 0.05, 0.15,$ and 0.25 . Samples are studied in the untreated, fully oxygenated state, as O is progressively removed by vacuum annealing at 400, 500, 600, 700, and 800 °C, and after vacuum annealed samples are reoxygenated at low temperature. By following the sites as O is progressively removed at increasing annealing temperatures, we conclude that there is no evidence that Fe substitutes on Cu(2) sites. We interpret our results in terms of models based on neutron diffraction and recent EXAFS experiments. The general tendency at high annealing temperatures is to create sites with smaller quadrupole splittings, which are therefore more symmetric with respect to O coordination, at the expense of sites with less symmetric coordinations. We attribute this to clustering of the Fe atoms, and the increased coordination this creates. Observed magnetic sites are also attributed to clustering. Low-temperature reoxygenation of high-temperature-vacuum-annealed samples restores the original doublets, but with a higher population of symmetric sites, as has been reported in other studies. We conclude that this is evidence of the stability of the clusters to low-temperature reoxygenation. The present results and interpretation lead to consistency between Mössbauer and EXAFS. They also eliminate the problem created by the interpretation of previous Mössbauer experiments where thermal treatment resulted in a large population of Fe in Cu(2) sites without a deterioration in the superconducting transition temperature.

1. Introduction

A number of studies have been conducted in which chemical substitutions have been used to probe superconductivity in the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$. Among these, those which examine substitutes for Cu have been most extensive. Cu appears in two sites, a planar site, Cu(2), and a chain site, Cu(1) [1, 2]. The Cu(2)–O(2)/O(3) plane is thought to be primarily responsible for the superconductivity, while the chains of Cu(1)–O(1) supply to the planes carriers that participate in the superconductivity [3]. Substituents in either site at sufficient concentration depress the superconducting transition [4–8].

Substituents with a valence of 2+, such as Ni or Zn, have been found to occupy principally Cu(2) sites, and depress the superconducting transition temperature T_c dramatically, with a few percent of zinc destroying superconductivity [9]. Substituents with a valence of 3+, such as Co or Fe, principally occupy Cu(1) sites and also weaken the superconductivity, but to a much lesser extent; more than 14% Fe is required to destroy superconductivity. These latter substituents also cause an orthorhombic to tetragonal transformation at a doping level of approximately 2.5% as determined in powder x-ray

diffraction [10]. This is thought to occur because these elements attract extra O [6, 8, 15], approximately one additional O atom for every two Co/Fe atoms, and serve as pseudo-twinning centres that rotate the direction of the chains [11, 12]. Thus the material remains orthorhombic on a scale smaller than the correlation length for x-rays [11, 12]. Site locations for these substituents have been determined by neutron diffraction [6, 11–19], EXAFS [20–23], and Raman spectroscopy [24–26].

Various neutron diffraction and EXAFS investigations have led to different conclusions concerning whether Fe and Co can also occupy Cu(2) sites. These elements, and especially Fe, have neutron scattering lengths not very different from Cu. Thus in some neutron diffraction refinements, no Fe/Co is found on Cu(2) [11–13, 17, 18], while in others a small amount has been assigned to the planes, but the improvement of the fit achieved by such an assignment is small. Similarly some EXAFS studies find that Co/Fe occupy only Cu(1) sites [22, 23], while others show very little difference in goodness of fit parameters for 0–20% Co/Fe on planar sites [20, 21].

The evidence used most extensively to establish Cu(2) occupancy comes from Mössbauer studies, where the doublet with the smallest quadrupole splitting (QS) in the Mössbauer spectrum is usually assigned to a Cu(2) site [27–32]. Arguments for this assignment range from the high site symmetry implied by the small QS value (this site is fivefold coordinated), to the fact that when a doped sample is slightly deoxygenated, the relative area of this doublet remains essentially unchanged. Moreover, when a sample is substantially deoxygenated at high temperature, this site disappears, a magnetic site appears with a not very different quadrupole splitting (QS), and the Néel temperature for this site is usually observed to be close to the Néel temperature $T_N = 405$ K of pure $YBa_2Cu_3O_{7-\delta}$. The observed magnetic splitting presumably occurs because of the antiferromagnetic coupling of adjacent Cu(2) atoms in the plane at low O content.

When such deoxygenated samples are reoxygenated at low temperatures, the magnetic site disappears and the symmetric (small- QS) site reappears with a significantly enhanced population. The Mössbauer explanation is that Fe/Co atoms like to be highly coordinated, so that when O is removed from the chains at high temperature, Fe/Co atoms move to Cu(2) sites to achieve this higher coordination. They are then frozen there when the sample is reoxygenated at lower temperature, and the antiferromagnetic coupling of the Cu(2) disappears. However, one Mössbauer investigation using this explanation noted a contradiction when neutron diffraction refinements on the same sample gave no evidence of Fe on Cu(2) sites [42]. Moreover recent EXAFS studies by Moodenbaugh *et al* [23] for Fe and Co, and by Li *et al* [21] for Co and Fe, have found no evidence for a redistribution of Co/Fe to planar sites after a thermal treatment as described above. The latter study has also shown that even in samples vacuum annealed at high temperature, very little change occurs in the O environment of Co or Fe. These results contradict the Mössbauer interpretation, and indicate that the increased population of the high-symmetry Mössbauer site after thermal treatment does not result from migration of Fe/Co to Cu(2) sites, but instead involves a more subtle rearrangement of Fe/Co and O in the Cu(1)–O plane.

The relationship between T_c and the occupancy of Cu(2) sites by Co/Fe is especially important in understanding the superconductivity. Since superconductivity is principally associated with the Cu(2)–O planes, Fe/Co occupancy of sites in this plane would be expected to degrade the superconductivity markedly, as is observed with Zn and Ni substituents. The relationship between superconductivity and the Co/Fe site occupancy has been made more urgent by the experiments of Katsuyama and coworkers [33] which confirmed in more detail earlier work by other investigators [30, 34]. In these experiments Fe doped samples were deoxygenated at a high temperature (800 °C), and then reoxygenated

at a lower temperature (400 °C) with the Mössbauer results just described. Further, samples treated in this way remained orthorhombic to a level of 15% Fe, and, remarkably, a superconducting onset was observed in resistive transitions of heavily doped samples to nearly 90 K. In AC susceptibility measurements, a small tail to the transition was also observed at high temperature [35].

Smith *et al* reproduced these results [36]. Moodenbaugh *et al* [23], measuring AC susceptibility, and Joiner [10] measuring both DC susceptibility and resistivity, saw very little difference in transition temperature between untreated and treated Co and Fe doped samples, although both confirmed that in treated samples the orthorhombicity was extended to large Co/Fe concentrations. If in fact this thermal treatment causes large amounts of Fe and Co to move from chain Cu(1) sites to planar Cu(2) sites and does not significantly change T_c , as was found by Joiner [10] and by Moodenbaugh *et al* [23], or increases T_c , as found by Katsuyama *et al* [33], this has important implications for the superconductivity.

In the present work we re-examine the Mössbauer evidence for Fe occupying Cu(2) sites and increasing the population of that site through thermal processing. Previous Mössbauer investigations have looked at fully oxygenated samples, and samples after O has been substantially removed. In this work we measure spectra as O is progressively removed by vacuum annealing at various annealing temperatures up to 800 °C. From these measurements we conclude that Mössbauer data should not be interpreted in terms of Fe occupying planar sites. Instead we reexamine neutron diffraction and EXAFS evidence of Fe/Co-O arrangements and suggest that the most symmetric Mössbauer sites arises naturally from the (110) displacement of Fe/Co in Cu(1) sites found in neutron diffraction [18] and EXAFS [20] experiments, and the clustering of Fe in chains along (110) that this promotes, factors which have not been considered in previous Mössbauer work. We examine the present data relative to these structural considerations and find them entirely consistent.

In the next section we describe our experiment. In section 3 we present our data, and in sections 4 and 5 we discuss our results and summarize our conclusions.

2. Experiment

Ceramic samples were prepared using standard techniques, with four firings for a total of over 50 h at 950 °C, with intermediate grinding. All firings were done in the presence of flowing O_2 at atmospheric pressure. For the final firing, samples were pressed into pellets, and after firing were O annealed for over 75 h, cooling very slowly in the temperature range where maximum uptake of O occurs. The virgin oxygenated samples will be referred to herein as the 'untreated' samples.

O was removed from the samples by placing them in a quartz tube inserted in a tube furnace at the appropriate temperature while pumping on the tube for a period of 2.5 h. At each composition, we prepared 'treated' samples by vacuum annealing 'untreated' samples at 800 °C, again for 2.5 h, removing the quartz tubes containing them from the oven and allowing them to cool rapidly to room temperature, and then reannealing them under flowing O_2 at 400 °C for 24 h, and cooling to 200 °C over another 24 h. We would like to emphasize the quality of our samples, which were prepared similarly to samples used in the EXAFS studies by Li *et al* [21].

O content was measured in two ways, using a gasometric technique and by measuring weight loss using a microbalance. The former technique was used to determine the initial O content of untreated samples, and to compare O content using the two methods in samples with O loss of less than 0.5. We found that the two methods agreed to within ± 0.03 O.

Powder x-ray patterns of the untreated samples and of samples after vacuum annealing at the various temperatures were obtained using a Siemens-500 diffractometer. Peak positions were determined in the range $2\theta = 20\text{--}60^\circ$, and used to determine lattice constants. The x-ray patterns showed no detectable impurity phases. The superconducting transition was measured for the untreated and treated samples using a Quantum Design SQUID magnetometer.

The two low-composition Fe doped samples used in the Mössbauer experiments were made with 95% enriched Fe^{57} , and the two higher-concentration samples were made partially with Fe^{57} and partially with natural Fe. Mössbauer spectra were recorded using a constant-acceleration Mössbauer drive and Co^{57} source in a rhodium matrix. Data were extracted from the 512 channels of a multichannel analyser using a PC, folded, and least-squares fitted. Absorbers were made out of approximately 32 mg of fine powder wrapped in Al foil. Lorentzian lineshapes as doublets and/or sextets were used in combination to fit the various spectra, and the values of isomer shift (IS), quadrupole splitting (QS), relative area A , width Γ , and, where appropriate, hyperfine field H_f , were obtained for each component. The IS was measured with respect to α -Fe metal.

3. Experimental results

The 2%, 5%, and 15% samples were superconducting in both the untreated and reoxygenated circumstances with midpoint transition temperatures in the untreated case of 91.5 K, 82.1 K, and 14.5 K, respectively, and 90.1 K, 75.2 K, and 14.5 K, after reoxygenation. Thus we find, as we [10] and others [23] have previously reported, that the thermal treatment does not significantly increase T_c as was found by Katsuyama *et al* [32, 33]. Lattice constants for the samples are given in table 1, and it can be seen that thermal treatment significantly enhances the orthorhombicity to large Fe concentrations as reported previously [10, 23, 33].

Table 1. Lattice constants of Fe doped samples as prepared and after treating by vacuum annealing at 800°C for 2.5 h followed by reoxygenation at 400°C for 24 h.

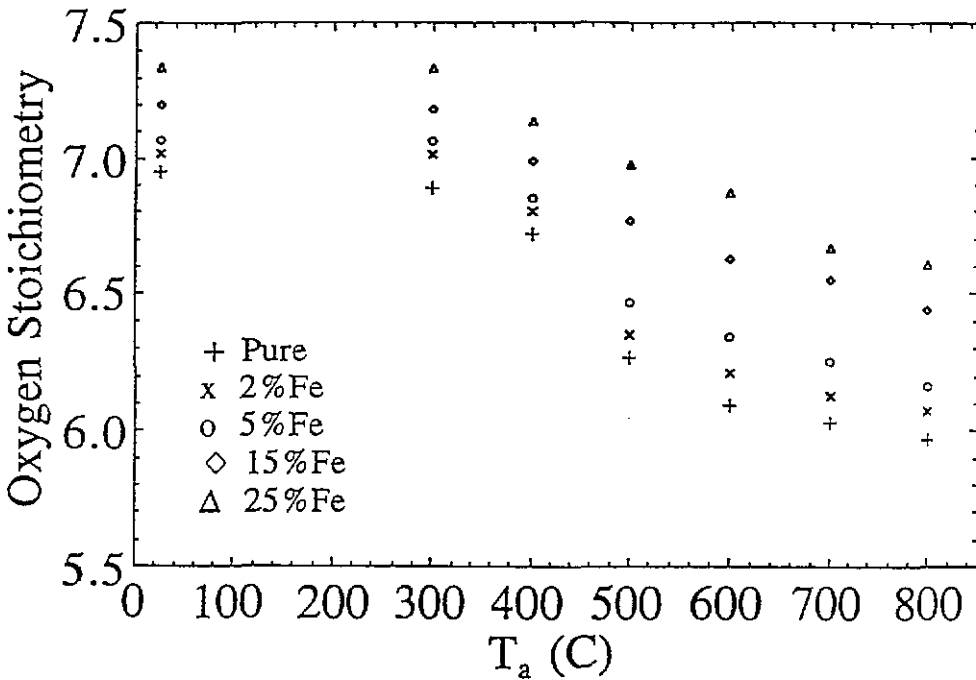
% Fe	Untreated			Treated		
	a (Å)	b (Å)	c (Å)	a (Å)	b (Å)	c (Å)
0	3.818	3.885	11.684	—	—	—
2	3.832	3.880	11.680	3.828	3.884	11.677
5	3.862	3.862	11.677	3.831	3.883	11.673
15	3.872	3.872	11.651	3.870	3.873	11.647
25	3.875	3.875	11.644	3.872	3.872	11.632

In table 2 we list the O stoichiometry of each of the doped samples, as well as that of an undoped sample, after vacuum annealing at various temperatures T_a for 2.5 h. A plot of these data is shown in figure 1.

In figure 2 we show typical Mössbauer spectra for the 5% Fe sample untreated, and vacuum annealed with $T_a = 400, 500, 600, 700$ and 800°C , and in figure 3 we show spectra for the 25% Fe sample untreated, and vacuum annealed with $T_a = 600$ and 800°C . A large number of Mössbauer studies of untreated Fe doped samples with low-concentration doping levels have been reported and analysed in terms of from two to six doublets, with the use of four doublets most common. We find that three Lorentzian doublets are sufficient to fit

Table 2. Oxygen stoichiometry $7-\delta$ for pure and Fe doped samples vacuum annealed for 2.5 h at the designated annealing temperature T_a .

T_a (°C)	Pure	2% Fe	5% Fe	15% Fe	25% Fe
25	6.95	7.02	7.07	7.20	7.34
300	6.89	7.01	7.06	7.18	7.33
400	6.72	6.80	6.85	6.99	7.14
500	6.27	6.35	6.47	6.77	6.98
600	6.09	6.21	6.34	6.63	6.87
700	6.03	6.13	6.25	6.55	6.67
800	5.97	6.07	6.16	6.44	6.61

**Figure 1.** Oxygen stoichiometry, $7-\delta$, for pure sample and 2%, 5%, 15%, and 25% Fe doped samples after vacuum annealing for 2.5 h at various annealing temperatures T_a .

our untreated sample data for doping levels up to 15% Fe. We have tried adding additional sites, in particular a commonly found one with a quadrupole splitting of approximately 1.60 mm s^{-1} , and found no improvement in the fits, or unphysical values of the parameters.

Several aspects of our using a three-doublet fit are worth pointing out. First, the average widths of the doublets are 0.36 , 0.33 , and 0.34 mm s^{-1} for the 2%, 5%, and 15% Fe samples, respectively. (These widths were obtained by varying the width of each doublet independently during the fitting procedure.) This compares to linewidths of an α -iron calibration spectrum of 0.32 mm s^{-1} obtained using the same Mössbauer spectrometer, and to a natural linewidth of 0.20 mm s^{-1} for Fe^{57} . Second, Swartzendruber *et al* [37], have shown that the need for some workers to use more than three doublets to fit their spectra was a result of an asymmetry in the spectra, which they demonstrated was due to preferential alignment of crystallites in the sample. Our spectra show very little asymmetry. Finally, a

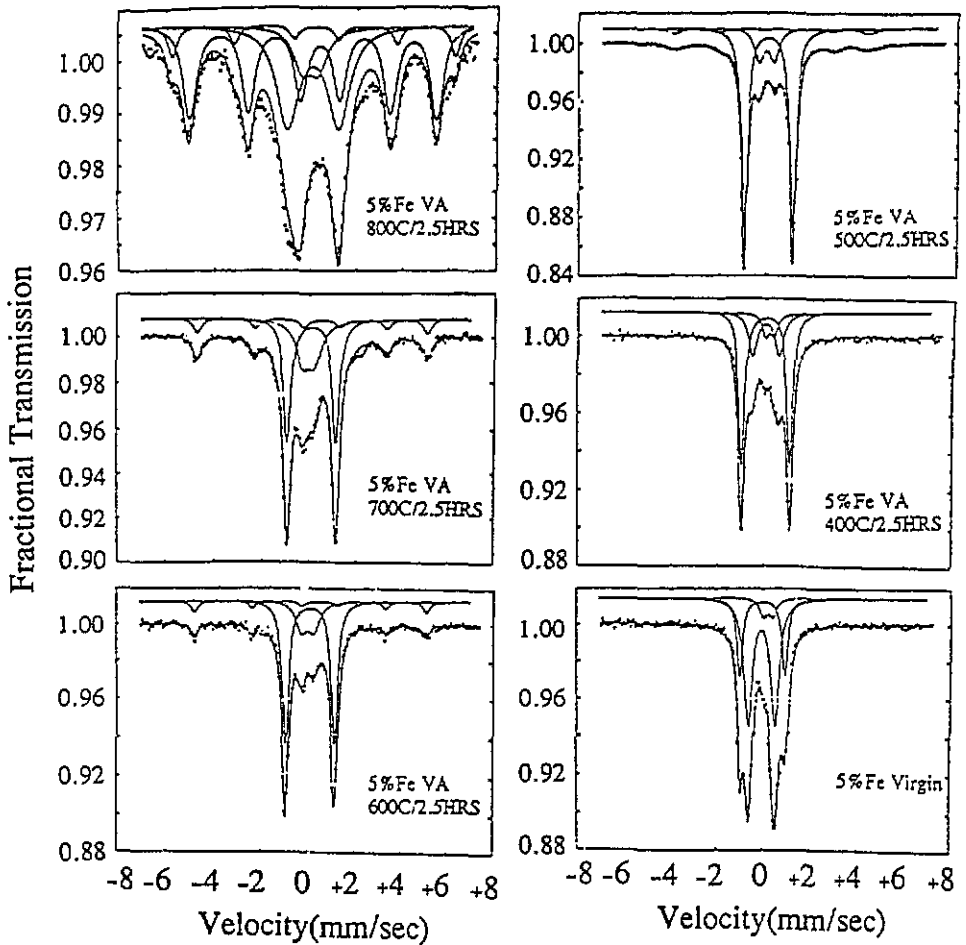


Figure 2. Mössbauer spectra obtained for 5% Fe doped sample, untreated, and then after vacuum annealing for 2.5 h at annealing temperatures T_a of 400 °C, 500 °C, 600 °C, 700 °C, and 800 °C.

number of published spectra do not show structure that is as well defined as that which is present in our spectra, whereas those that do show similar structure, such as were obtained by Smith *et al* [36], are fitted satisfactorily by three doublets. We emphasize this point, because the inclusion of extraneous doublets confuses the already difficult task of making site assignments. Further, since the present work follows the evolution of sites as O is removed, an accurate characterization of the subspectra and a determination of the number of contributing sites is essential.

For 25% Fe doping, the spectrum of the untreated sample becomes much more complex as two magnetic sextets appear. The need for two closely spaced magnetic lines is evident by inspection of the structure in the spectrum. Although the widths of these magnetic lines are considerably larger than the widths of the doublets, trying to fit the magnetic structure with a single sextet, in addition to providing a poor fit, leads to unrealistically large line widths. Also after vacuum annealing this sample, the requirement for two magnetic sextets becomes even more pronounced. Moreover for the 5% and 15% Fe samples, vacuum annealing also results in two magnetic sextets.

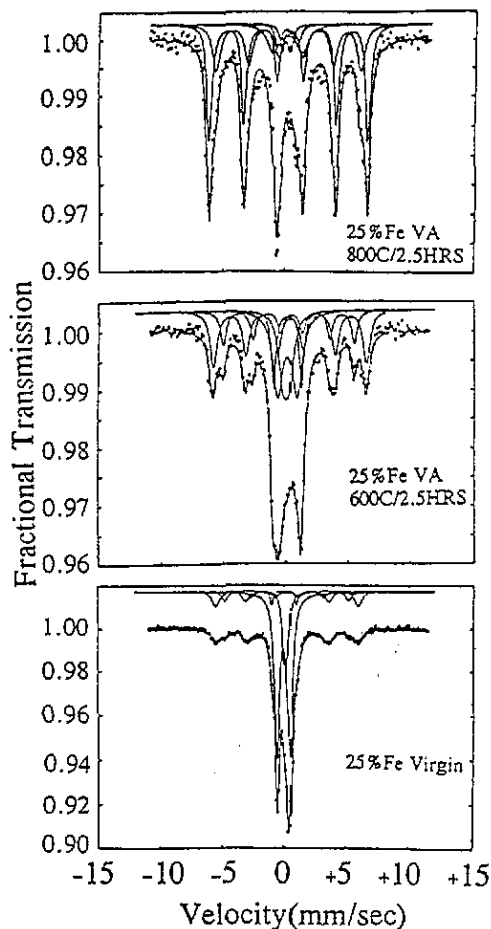


Figure 3. Mössbauer spectra obtained for 25% Fe doped sample, untreated, and then after vacuum annealing for 2.5 h at annealing temperatures T_a of 600°C and 800°C.

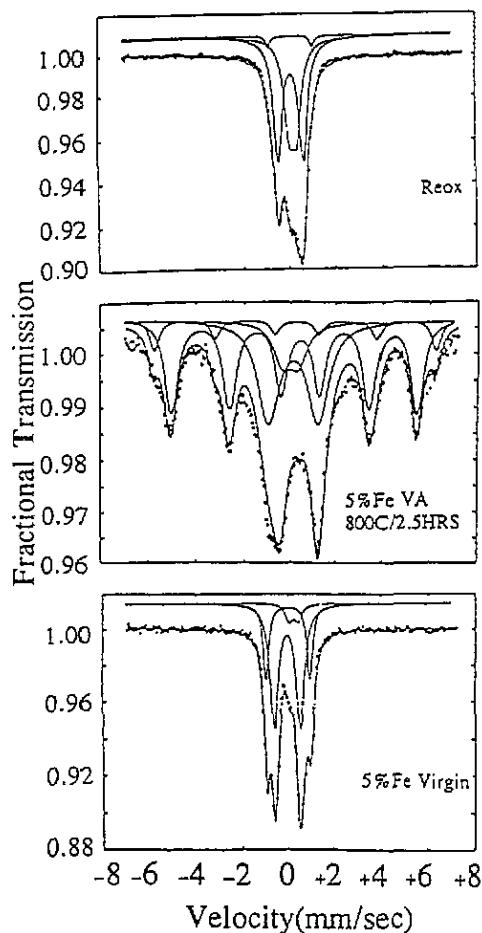


Figure 4. Mössbauer spectra obtained for 5% Fe doped sample, untreated, vacuum annealed for 2.5 h at 800°C, and then after reoxygenating at 400°C.

In figure 4, we show comparisons between the 5% sample untreated, vacuum annealed at 800°C, and then reoxygenated at 400°C, and in figure 5 we show similar data for the 25% sample. In table 3 we show the fitting parameters for the subspectra of all the samples after the various treatments.

4. Discussion

4.1. Comparison with previous Mössbauer results

For our as prepared, oxygenated samples, the isomer shifts (ISs) and quadrupole splittings (QSs) characterizing our three doublets are similar to those of other reports in the literature for Mössbauer spectra taken at room temperature. Thus there is (i) an outer doublet, which we will refer to as D1, with a QS which in the literature ranges from 1.80 to 2.10 mm s^{-1} ,

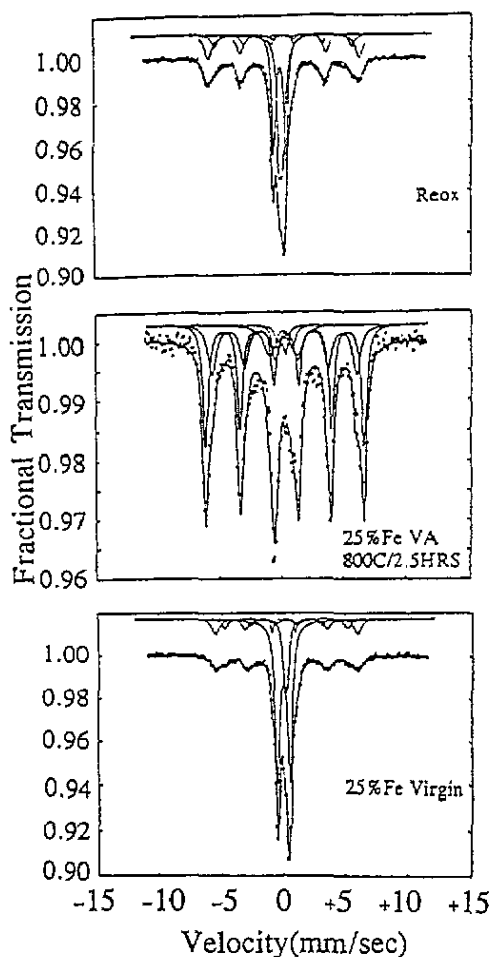


Figure 5. Mössbauer spectra obtained for 25% Fe doped sample, untreated, vacuum annealed for 2.5 h at 800°C, and then after reoxygenating at 400°C.

and with a very small IS, (ii) an intermediate doublet D2 with a QS reported between 0.90 and 1.20 mm s⁻¹, and also with a very small IS, and (iii) an inner doublet D3 with a reported QS ranging from 0.30 to 0.65, and an IS between 0.2 and 0.3. Our values fall within these ranges, and for D1 and D2 are typical of many studies. Our QS for D3 is at the low end of the range; QS values around 0.6 are more common.

Although a number of spectra for deoxygenated samples have been published, very few analyses of these spectra have been included. Katsuyama *et al* [33] gave data for two O deficient 4% Fe samples, one quenched from 930°C into liquid nitrogen, and the other after heating at 800°C in nitrogen gas. Both were analysed in terms of three doublets and one magnetic sextet. The first sample had IS and QS parameters close to those we have identified in our high-temperature vacuum annealed samples as D1, D4, and M1, plus an additional doublet with an intensity of 8% with a QS of 0.73. The second sample had two subspectra with parameters close to our D1 and M1, another doublet with a small IS similar to D4, but has a QS significantly larger at 1.13, and a third doublet, which we do not find, with an area of 21% and a QS of 1.27. Sedykh *et al* [28] also presented data on two 1.67%

Table 3. Mössbauer parameters for samples after vacuum annealing for 2.5 h at various annealing temperatures T_a .

Site	IS (mm s ⁻¹)	QS (mm s ⁻¹)	H_f (kOe)	Area (%)	Γ (mm s ⁻¹)
$YBa_2(Cu_{0.98}Fe_{0.02})_3O_{7-\delta}$					
Untreated					
D1	-0.02	1.86	—	35.7	0.36
D2	-0.01	1.18	—	56.5	0.38
D3	+0.24	0.39	—	7.7	0.33
$T_a = 400^\circ C$					
D1	+0.05	2.00	—	79.6	0.32
D2	+0.08	1.10	—	8.9	0.44
D3	+0.22	0.47	—	11.5	0.34
$T_a = 500^\circ C$					
D1	+0.06	2.01	—	87.0	0.30
D2	+0.01	1.11	—	0.2	0.44
D4	+0.01	0.59	—	12.6	0.54
$T_a = 600^\circ C$					
D1	+0.07	2.07	—	75.5	0.35
D4	-0.04	0.46	—	18.2	0.60
M1	+0.34	0.37	310	6.3	0.48
$T_a = 700^\circ C$					
D1	+0.09	2.07	—	61.7	0.36
D4	-0.01	0.46	—	26.1	0.60
M1	+0.35	0.32	303	12.2	0.43
$T_a = 800^\circ C$					
D1	+0.13	2.17	—	43.2	0.64
D4	+0.03	0.65	—	17.6	0.69
M1	+0.31	0.28	304	39.2	0.51
Reoxygenated					
D1	+0.05	1.80	—	11.7	0.40
D2	+0.06	1.10	—	41.2	0.40
D3	+0.20	0.42	—	47.1	0.50
$YBa_2(Cu_{0.95}Fe_{0.05})_3O_{7-\delta}$					
Untreated					
D1	+0.02	1.91	—	30.6	0.31
D2	-0.01	1.12	—	62.6	0.42
D3	+0.22	0.30	—	6.6	0.25
$T_a = 400^\circ C$					
D1	+0.05	2.02	—	64.4	0.32
D2	+0.04	1.10	—	25.6	0.45
D3	+0.20	0.35	—	9.9	0.34
$T_a = 500^\circ C$					
D1	+0.06	2.02	—	73.6	0.32
D4	-0.01	0.62	—	16.6	0.47
M1	+0.27	0.28	256	9.8	0.77
$T_a = 600^\circ C$					
D1	+0.08	2.06	—	66.5	0.35
D4	-0.02	0.52	—	22.5	0.58
M1	+0.33	0.32	306	11.0	0.32
$T_a = 700^\circ C$					
D1	+0.10	2.06	—	54.1	0.40
D4	-0.05	0.51	—	30.4	0.72
M1	+0.35	0.32	304	15.4	0.41
$T_a = 800^\circ C$					
D1	+0.10	2.17	—	32.2	1.14
D4	-0.04	0.69	—	10.2	0.93
M1	+0.29	0.21	326	48.5	0.68
M2	+0.24	0.01	374	9.0	0.48
Reoxygenated					
D1	+0.05	1.90	—	26.8	0.24
D2	+0.07	1.09	—	56.2	0.48
D3	+0.17	0.34	—	41.0	0.52

Table 3. (continued)

Site	is (mm s ⁻¹)	qs (mm s ⁻¹)	H _f (kOe)	Area (%)	Γ (mm s ⁻¹)
YBa₂(Cu_{0.85}Fe_{0.15})₃O_{7-δ}					
Untreated					
D1	+0.05	2.00	—	12.6	0.29
D2	+0.01	1.05	—	73.9	0.45
D3	+0.21	0.26	—	13.5	0.28
T _a = 400 °C					
D1	+0.08	2.05	—	44.2	0.37
D4	-0.01	0.80	—	35.6	0.56
M1	+0.27	0.18	282	20.1	0.95
T _a = 500 °C					
D1	+0.09	2.06	—	53.3	0.43
D4	-0.03	0.64	—	31.7	0.72
M1	+0.33	0.27	304	14.9	0.43
T _a = 600 °C					
D1	+0.10	2.12	—	50.5	0.51
D4	-0.03	0.59	—	35.3	0.82
M1	+0.32	0.22	314	14.1	0.51
T _a = 700 °C					
D1	+0.14	2.16	—	43.0	0.76
D4	-0.08	0.65	—	23.4	0.86
M1	+0.25	0.18	355	5.8	0.53
M2	+0.23	0.09	313	27.7	0.74
T _a = 800 °C					
D1	+0.07	2.19	—	12.3	1.17
D4	-0.07	0.88	—	13.1	0.87
M1	+0.27	0.13	392	29.2	0.53
M2	+0.30	0.24	357	45.3	1.05
Reoxygenated					
D1	+0.07	1.99	—	6.5	0.30
D2	+0.06	1.04	—	43.8	0.35
D3	+0.22	0.30	—	49.7	0.41
YBa₂(Cu_{0.75}Fe_{0.25})₃O_{7-δ}					
Untreated					
D1	-0.03	1.93	—	2.8	0.25
D2	-0.01	1.10	—	57.5	0.47
D3	+0.17	0.25	—	15.3	0.36
M1	+0.25	0.01	357	16.9	0.67
M2	+0.24	0.02	309	7.4	0.52
T _a = 600 °C					
D1	+0.04	2.16	—	11.4	0.44
D4	-0.07	0.46	—	16.1	0.81
D5	+0.03	1.49	—	26.1	0.96
M1	+0.27	0.01	384	30.1	0.66
M2	+0.27	0.18	328	15.5	0.55
T _a = 800 °C					
D1	+0.07	2.18	—	11.6	1.17
D4	+0.00	0.61	—	3.9	0.44
D5	+0.10	1.49	—	4.5	0.60
M1	+0.28	0.10	397	48.2	0.51
M2	+0.27	0.18	362	31.7	0.75
Reoxygenated					
D1	+0.03	1.93	—	1.9	0.58
D2	+0.03	1.02	—	32.9	0.42
D3	+0.17	0.30	—	31.7	0.44
M1	+0.26	0.04	379	24.0	0.67
M2	+0.25	0.04	344	9.4	0.52

Fe samples, one quenched from 920 °C, and the other vacuum annealed at 427 °C. In the first sample two doublets and a sextet with parameters corresponding to our D1, D4, and

M1 were found, as well as an additional doublet ($IS = 0.32$, $QS = 0.98$, $area = 12\%$). In the second sample, three doublets with IS and QS values similar to those of D1, D2, and D3 in our 2% Fe sample vacuum annealed at 400°C were obtained, as well as two additional doublets with a combined area of 27%.

Mössbauer data on samples with O removed at high temperature, and then reoxygenated at low temperature, show restoration of D1, D2, and D3, but with changes in relative site population, similar to those reported by other investigators.

In general then, our untreated, high-temperature vacuum annealed, and reoxygenated samples all show subspectra generally consistent with those reported previously, but we find it unnecessary to include additional lines sometimes used to analyse these previous spectra.

4.2. Structural considerations from neutron diffraction and EXAFS

As noted, structural data is available for Co/Fe doping that has not previously been taken into account in interpreting Mössbauer data and in making site assignments. Thus, for example, both neutron diffraction [18] and EXAFS [20] studies have shown that Co/Fe doping of Cu(1) sites results in a displacement of the dopant atom from the Cu(1) position along (110), creating both short and long Co/Fe–O bonds. This displacement encourages the formation of impurity chains along (110), resulting in the (110) streaking observed in electron diffraction [11–14]. For a 1.7% Co untreated sample, it was shown [20] that this leads to an average O coordination of 3.2 atoms at 1.75 \AA , and 1.4 atoms at 2.39 \AA . As the Co concentration increases, the number of short bonds increases and the number of long bonds decreases. Thus for a 30% untreated Co sample, there is an average of 3.8 O atoms at 1.87 \AA and 1.0 at 2.39 \AA . These coordinations compare with an undoped, fully oxygenated sample where Cu(1) has two O(4) bonds at 1.85 \AA and two O(1) bonds at 1.93 \AA . The displacement of Co/Fe along (110) therefore creates short and long O bonds; the average number of each will depend upon the detailed way in which the Co/Fe atoms are arranged with respect to each other. The change in coordination, and the increase in the ratio of short to long bonds with increasing Co/Fe concentration, suggest that clustering plays a role, with the Co/Fe chains, aligned roughly along (110), becoming longer or wider. Clustering permits the sharing of O by dopant atoms, increasing the number of multiple Co/Fe–O bonds and the ratio of short to long bonds. Interpretation of Mössbauer data ought to be consistent with these observations, but previous work has not addressed these considerations.

More recent and detailed EXAFS studies on Co doped samples at various doping levels, and on a 7.5% Fe doped sample, not only found no evidence for a change in the dopant site population on Cu(2) after thermal treatment, but also showed that the local environment of Co and Fe is changed very little with thermal treatment [21]. However it was found that the second-shell EXAFS peaks associated with the dopant environments were reduced and broader after thermal treatment, indicating disorder in dopant–other atom distances. In untreated samples the O peak was largest for the lowest-concentration sample, and monotonically decreased with Co concentration. Again this suggests increasing disorder with Co concentration. Moreover this study showed that even for samples vacuum annealed at high temperature, the Co/Fe–O environment was not drastically different, and the relative O coordination of Co/Fe was relatively unchanged. We emphasize that the samples used in the EXAFS study were prepared in our laboratory, with the untreated samples undergoing very similar treatment to those used here; thus we expect very similar structural properties.

Neutron diffraction and EXAFS studies suggest major considerations in describing sites, and the way these sites are likely to change with dopant concentration and thermal treatment.

Bridges *et al* [20] have suggested models of how impurity chains may exist (figure 9 of [20]). Although noting that many other models might also exist, a double Co/Fe chain as they describe fits their EXAFS data well. It should also be noted that the arrangements required of a proposed model are not arbitrary. One must be able (i) to satisfy the long- and short-bond criteria, (ii) accommodate (110) distortions within the lattice structure, (iii) explain the streaking along (110) probably by having clusters which form along this direction, (iv) explain the fact that these impurities cause the structure to be tetragonal by interchanging the direction of ordering along the *a* and *b* axes, and (v) accommodate the additional O. One must also be able to account for the fact that the coordination of the substituent changes very little on vacuum annealing. Ideally one should be able to account quantitatively for the average number of nearest neighbour O atoms and their distribution with respect to the short and long bond lengths, as the double-chain model does at low Co concentrations. Thus although there may be alternative structures, and although these must be more complex as more complex clusters are required to accommodate more Fe/Co atoms, the environments surrounding Co/Fe atoms are likely to be not very different from those found in the chain models.

Likely sites based on these chain models [20] are therefore (i) square planar with four short bonds, (ii) pseudotetrahedral with four short bonds (this can be achieved either by removing two of the long O bonds in the single or double chain, or adding another Co/Fe at a Cu(1) site where two long bonds terminate. This additional Co/Fe will displace, shortening the O bonds, and forming the tetrahedral site), (iii) octahedral with four short and two long bonds, and (iv) octahedral with six short bonds. Upon vacuum annealing under conditions such that all Fe/Co–O bonds that are not at least double bonds (i.e., one O shared between two Fe/Co atoms) are removed, there will remain square planar and pseudotetrahedral sites with four short bonds, and octahedral sites with six short bonds. In all configurations two of the short bonds are always formed with the O(4) atoms located in the Ba–O plane.

Clustering must take place as dopant concentration increases, if for no other reason than to accommodate all the impurities. It is also likely that clustering occurs when sufficient energy is present to allow dopants to become mobile in the Cu(1)–O plane. Theoretical studies have indicated that large clusters develop when mobility occurs under O deficient conditions. Clustering permits O to occupy positions with multiple Fe bonds, creating very stable configurations. Conversely, clustering allows sharing of O between two or more Fe atoms, thus increasing the coordination of the Fe despite the fact that the material overall is losing O. If, for example, we make the assumption that vacuum annealing at high temperatures depletes the O first from around Cu(1) atoms, then using the data from table 1, we calculate that after vacuum annealing at 800 °C, the average number of O atoms in the Cu(1)–O plane per Fe atom is 1.17, 1.07, 0.98, and 0.81 for the 2, 5, 15, and 25% samples respectively. To achieve the high O coordination for vacuum annealed samples determined by EXAFS [20] (between 2.2 and 2.7 in the Cu(1)–O plane) strong clustering is clearly required.

Clustering also explains the increase in the ratio of short to long bonds in fully oxygenated samples. Using the chain models, sites internal to the chains have short bonds, while sites on the boundary have short and long bonds. Thus as clusters grow thicker, the ratio of short to long bonds will increase as observed. Clustering is also the most logical way of interpreting the extended orthorhombicity that exists in high-concentration Fe and Co doped samples after thermal treatment [33, 36]. That is, clustering of impurities permits the development of impurity free orthorhombic regions of size larger than the x-ray correlation length.

4.3. Mössbauer data and EXAFS models

We now discuss our Mössbauer data in terms of the sites likely to exist using the various chain models proposed by Bridges *et al* [20], recognizing that these are likely to be altered and made more complex with clustering. With that caveat, and with the general site choices that appear to be available for virgin samples, as listed above, we tentatively assign the largest QS site, D1, to square planar or pseudotetrahedrally coordinated Fe, with four short O bonds. We assign D2, the site with intermediate QS, to an octahedral coordination with four short and two long bonds. Finally, we assign the site with the smallest QS, D3, to an octahedral coordination with six short bonds. Having made this tentative assignment, we emphasize the general expectations rather than the specific site descriptions. That is, at low annealing temperatures we expect to see the effects of removing O weakly bound, and, we suggest, singly bonded, to Fe. At higher temperatures, we expect to see the effects of clustering in the form of the growth of sites with increased O coordination, and an increase in sites having short bonds relative to those with short and long bonds. This tendency should be made evident by the growth in sites of greater symmetry and smaller QS at the expense of sites with larger QS. We now review the specific features of our results with these trends in mind.

First, we note that with the long oxygenation times received by our untreated samples, these are likely to have the addition of one O atom for each two Fe atoms, as found in neutron diffraction studies on untreated samples. As noted previously, this result is consistent with maintaining charge balance, assuming Fe exists as a substituent as Fe^{4+} . In our untreated samples the major doublets in terms of intensity are D1 and D2. Together they represent 92.2%, 93.2%, and 86.5% of the area in the untreated 2%, 5%, and 15% samples. For D1 the IS ranges from -0.03 to $+0.05$ $mm\ s^{-1}$, and for D2 it ranges from -0.01 to $+0.01$ $mm\ s^{-1}$, and both ranges of IS values are indicative of Fe in a 4+ state.

Our Mössbauer results show that the relative intensity of D1 increases dramatically with the initial removal of O, and this is compensated for by an almost equal decrease in the relative intensity of D2. This suggests that D2 is a site from which O is relatively easily removed, and that its removal converts the site into D1. Also the relative intensity of D1 decreases with increasing Fe concentration, whereas the intensity of D2 increases. The sum of the intensities of sites D1 and D2 does not change drastically with Fe concentration up to 15% Fe. Both of these observations concerning the dependence of the two site intensities on O stoichiometry or Fe concentration have been made previously.

In this regard, the data of table 2 show that on vacuum annealing from room temperature to 400 °C, all samples show essentially the same O loss, independent of Fe content. Thus the pure sample loses 0.23 O and the 25% sample loses 0.20 O. This is a somewhat surprising result in that in the pure sample the Cu(1)–O plane has 100% of the O sites from which to lose O, but in the 25% Fe sample only 25% of the sites are Cu. We conclude from these results that at these low annealing temperatures, there is some O that is nearly as weakly bound to Fe as to Cu, and that this is reflected in the conversion of D2 to D1.

Furthermore, the QS of D1 is larger than that of D2, indicating that D1 has lower symmetry, and therefore this conversion represents a loss of O coordination. We suggest that the O weakly bound to Fe is that O that has a single Fe bond and a long bond length. Moreover in the chain models, two such O atoms exist for Fe that is not interior to the chain, and removal of this O converts an octahedral, four short–two long bond site into a pseudotetrahedral site with four short bonds. This forms the rationale for identifying D1 as a square planar or pseudotetrahedral site with four short bonds, and D2 as an octahedral site with four short and two long bonds.

For the two lowest-concentration samples, the intensity of D1 increases at the expense of D2 for vacuum annealing up to 500°C, but for annealing from 600°C to 800°C, the intensity of D1 progressively decreases. The same dependence of the intensity of D1 on T_a is found in the 15% sample, but D2 has already disappeared after annealing at 400°C. We attribute the decrease of D1 at 500°C and above to the increased mobility of the Fe in the Cu(1)-O plane, which, in an O deficient environment, produces increased clustering.

Clustering, as we have noted, should increase the ratio of short to long bonds, and increase the average coordination of Fe atoms. In terms of Mössbauer spectra this suggests that for untreated samples, as the Fe concentration increases, an increase in the symmetry of sites should be observed. That is, sites representing smaller QS should occupy a larger fraction of the spectral area. Clearly that is what is observed, as can be verified by inspection of table 3. D1, with the largest QS, decreases from 36% of the spectral area in the 2% sample to just 13% of the area in the 15% sample and 3% of the area in the 25% sample, while D2 increases from 57% in the 2% sample to 73.9% in the 15% sample, thus keeping the total fraction of D1 plus D2 approximately constant. The area of D3, with the smallest QS, increases somewhat in going from 2% to 15%, but in the 25% sample, in addition to the area D3 increasing further, M1 and M2, both with very small QS, also appear, adding about 24% of a new symmetric site at the expense of D1 and D2.

Similarly we observe this expected increase in site symmetry with vacuum annealing above 500°C. We suggest that at this or higher temperatures Fe or Fe-O complexes become mobile within the Cu(1)-O plane and increased clustering begins to occur. This causes a decrease in D1 in favour of higher-coordination bonds. Thus the more symmetric site D4 grows, but, more importantly, the low-QS, more symmetrically coordinated magnetic site(s) appear, and occupy an increasing fraction of the spectral area as T_a increases.

We also observe that D3, the site previously interpreted as converting to a magnetic site after high-temperature O removal, and therefore attributed to Fe on a Cu(2) site, disappears for T_a between 400 and 500°C for the 2% sample. Coincident with the disappearance of D3, a new doublet D4 appears. The magnetic splitting M1 does not appear until further annealing at 600°C. At this and higher annealing temperatures D4 and M1 coexist. Clearly if D3 were a planar Fe that increased in intensity and became magnetically split after O was substantially removed at high temperatures, it should continue to exist, and perhaps increase in intensity, and then become magnetically split as T_a is progressively increased. By observing the disappearance of D3, the appearance of D4, and independently the appearance of magnetic splitting at higher T_a , we have demonstrated that M1 is not the conversion of D3, and therefore that D3 and the magnetic line cannot both be Fe in a Cu(2) site. D4 and the magnetic sextet M1 simultaneously appear at 500°C in the 5% sample, and D4 and M1 both appear at 400°C in the 15% sample. The QS of D4 is slightly larger than that of D3, and, significantly, the IS is considerably smaller, clearly differentiating the two sites' characteristics. Since D3 disappears at the point D4 appears, and since the intensity of D4 when it appears is about the same as D3, taking into account the increase in intensity of both with increasing T_a , it would be logical to conclude that D3 is converted into D4.

From these results we conclude that the enhancement of the population of D3 after thermal treatment does not represent Fe migration to Cu(2) sites, that D3 is not a site that is magnetically split on the removal of O, and that, in fact, D3 is not a Cu(2) site. Since we will argue that D1 and D2 are also not Cu(2) sites, then we must further conclude that there is no Mössbauer evidence that any Fe in Fe doped $YBa_2Cu_3O_{7-\delta}$ occupies Cu(2) sites. Our evidence for this conclusion is the following: (i) We have clearly shown that on O removal at progressively higher T_a , D3 does not convert directly into the magnetic site, M1/M2, but that D3 disappears, a new subspectrum, D4, with an entirely different IS and QS appears,

and then at higher T_a ; the magnetically split site(s) appears and coexists with D4. (ii) In the virgin, fully oxygenated 25% Fe sample D3 coexists with the magnetic sites, and is therefore clearly distinct from the magnetically split site(s). (iii) In the 15% Fe sample D3 exists in the virgin sample, but disappears on vacuum annealing at just 400°C, and D4 and M1 both appear at that temperature, each with a population in excess of the population of D3 in the virgin sample. If D3 were to be Fe in a Cu(2) site, which becomes the magnetically split site with O removal, or becomes the magnetically split site after passing through an intermediate site configuration, D4, that means that vacuum annealing at this relatively low temperature would be sufficient to allow Fe to move from chain Cu(1) sites to Cu(2) sites in the plane. This seems extremely unlikely, and contradicts the premise of previous experiments where reoxygenation at 400°C supposedly occurred while Fe remained frozen in Cu(2) sites [33, 36]. If Fe were mobile from Cu(2) to Cu(1) at 400°C, then presumably in the presence of O the original equilibrium between the sites would be restored.

We would also argue that D1 and D2 do not result from Fe in Cu(2) sites since D2 is converted into D1 at very low temperatures, whereas the O occupancy in the Cu(2)-O plane is very stable. Thus, based on the present work, there is no Mössbauer evidence that Fe exists in the planes.

Nath and coworkers [38-41] have also used Mössbauer results to argue that Fe does not migrate to planar sites. Their interpretation is that Fe enters an unspecified interstitial site closer to one CuO₂ plane than to the other. They argue that since Cu(2) in O deficient samples is antiferromagnetically coupled along the *c* axis, Fe in a planar site will see no net field, and that it must therefore migrate to an interstitial site closer to one plane than to the other in order to become magnetically ordered. However, EXAFS results in particular show no evidence that the disorder observed in Co/Fe nearest-neighbour distances results from displacements of Co from Cu(1) positions along the *c* axis [20, 21].

The site D4 has a slightly larger QS than D3, but its IS is much smaller, indicating a change from a 3+ to a 4+ charge state. Simultaneously with the conversion of D3 to D4, or at a slightly higher temperature, the magnetic line(s) M1/M2 appear. As noted, both D4 and M1/M2 have small QS, indicating that they are relatively symmetric sites. Moreover their intensity grows upon annealing at even higher temperatures, fulfilling our expectation that symmetric sites increase in population with increased clustering. At 500°C in the 2%, 5%, and 15% samples, the O loss measured from the fully oxygenated state is 0.60 O; the amount of O loss that in the pure sample causes the disappearance of superconductivity and the onset of long-range order in the Cu(2)-O planes. We therefore suggest that both the conversion of D3 to D4 and the appearance of magnetic sites occur not because of the development of new site structures, but because of electronic or valence changes related to the overall loss of O.

If there are substantial regions essentially free of Fe, then with this overall loss of O, many Cu(1) should be in the 1+ charge state, which is believed to be a requirement for antiferromagnetic ordering in the Cu(2)-O planes. We have measured Néel temperatures for the observed magnetic lines in samples vacuum annealed at 800°C, as we will discuss later. We find that in the 2% Fe sample T_N is about 412 K, not very different from the Néel temperature, 405 K, of pure materials with nearly all the chain O depleted. This correspondence strongly suggests that the observed magnetic lines are associated with the Cu(2) ordering, but not, as has been suggested previously, because Fe occupies Cu(2) sites. Rather we suggest that the interaction of ordered Cu(2) and Fe induces order in the Fe sitting in the clusters. Thus the magnetic sites are likely to be symmetric sites of very similar structure to D3/D4, but are differentiated by the configuration of next-nearest Fe atoms in the clusters. One effect of the (110) displacement of Fe at Cu(1) sites creating

short O bonds is that it also brings some Fe atoms into closer proximity with other Fe atoms, creating possible differences between sites that may otherwise have similar O symmetry.

The magnetic sextet M1 appears at $T_a = 600^\circ\text{C}$ in the 2% sample, at 500°C in the 5%, at 400°C in the 15%, and in the untreated 25% sample. The second sextet, M2, does not appear in the 2% sample; it appears at $T_a = 800^\circ\text{C}$ in the 5% sample, at 700°C in the 15%, and in the untreated 25% sample. In all cases the intensities of the magnetic sextet(s) increase with T_a . The values of T_N are 412 ± 7 K, 422 ± 154 K, 434 ± 15 K, and 456 ± 15 K for the 2, 5, 15, and 25% Fe samples, respectively, after vacuum annealing at 800°C . T_N for the 25% untreated sample was 382 ± 10 K. It thus appears that magnetic ordering of the Fe is induced by a combination of O removal and Fe concentration such that samples with a higher concentration of Fe require less O removal, with the 25% Fe sample displaying ordering at room temperature at full oxygenation. Hechel *et al* have also reported a magnetic spectrum in a fully oxygenated 25% Fe sample [31]. However the relative intensities of the magnetic lines were less than we observed, suggesting that the specific details of a sample's history, as well as its stoichiometry, may be important in producing magnetic ordering. In any case it is clear that the same circumstances that lead to increased clustering favour magnetic ordering, and increase the number of sites that are ordered.

Upon low-temperature reoxygenation of the 2%, 5%, and 15% samples, the spectra can be analysed in terms of the original three doublets, although the spectra look very different from those of the virgin samples. This is because there has been a significant shift in the respective site populations, as has been observed by others [33,36]. In particular, D3, which had the smallest population in the virgin samples, becomes the major species, while the populations of D1 and D2 are reduced. This is consistent with the creation of a larger number of symmetric sites, D3/D4 and M1/M2 with clustering. Reoxygenation should not affect these sites, since they are interior to the clusters, and reoxygenation at 410°C should not have a substantial effect in breaking up or otherwise reducing the cluster size. Thus we have the conversion of D4 and M1/M2 to D3 without structural changes, supporting our suggestion that the conversion of D3 to D4 and the appearance of the magnetic splitting were not due to changes in site structure, but were due to an overall decrease in holes due to O removal. In the 25% sample, reoxygenation results in the three doublets D1, D2, D3 as in the other samples, as well as the persistence of M1 and M2. In this case the symmetric site populations of D3 as well as M1/M2 were enhanced with respect to the virgin sample through clustering.

5. Conclusions

Mössbauer measurements on untreated samples, samples vacuum annealed at intermediate temperatures up to 800°C , and samples reoxygenated at low temperature after having been vacuum annealed at 800°C , along with measurements of O loss on vacuum annealing, present a picture of changes in Fe environments on O removal consistent with structural studies, and in particular with recent EXAFS studies of Co and Fe doped samples [20, 21, 23]. In agreement with those studies, we find no evidence that high-temperature vacuum annealing increases the population of Fe in Cu(2) sites. Moreover we conclude that there is no Mössbauer evidence of Fe occupying Cu(2) sites.

From the perspective of the superconductivity, this is an important result. The standard Mössbauer interpretation of thermal treatment leading to significant Fe occupation of Cu(2) sites was difficult to reconcile with the observations that thermal treatment also led to an enhancement [33, 35], or very little change [10, 23] in T_c .

Acknowledgments

We would like to thank Professor Darl McDaniel for his help with the gasometric oxygen analysis of our samples and Mr J P Wang for his assistance with various aspects of the experiments.

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