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Properties of reduced then reoxidized $YBa_2(Cu_{1-x}Fe_x)_3CuO_{7-\delta}$

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We have investigated $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ (1:2:3) (M =Fe, with preliminary results for Co and Al) prepared using three different heat treatments. Standard samples were prepared using sintering temperatures up to 960 °C, followed by slow cooling in oxygen. Oxygen was removed by heating the standard samples in flowing argon near 830 °C, the resulting specimens being called "reduced." Reoxidized samples, in turn, were prepared from reduced samples that were heated in flowing oxygen near 400 °C. The Fe content of selected standard, reduced, and reoxidized samples was determined by electron microprobe. Transmission electron microscopy and x-ray diffraction for reoxidized 1:2:3 M =Fe are consistent with an orthorhombic phase extending to $x \geq 0.12$. Superconducting transition temperatures as measured magnetically are similar for standard and reoxidized cases (except M =Al). X-ray-absorption measurements were performed on samples M =Fe at the Fe K edge to probe the Fe near-neighbor environment. Our analysis suggests that Fe atoms remain in the chain layer regardless of heat treatment. This result is discussed in terms of proposed models involving migration of Fe, clustering in the Cu-O chain layer, and/or movement of Fe to the CuO_2 plane layer. Preliminary oxygen K-edge studies utilizing fluorescence yield were used to investigate oxygen electronic structure.

I. INTRODUCTION

Substitutions for Cu in $YBa_2(Cu_{1-x}M_x)_3O_7$ (1:2:3) have been studied by many, including ourselves.[1-4] The general behaviors of T_c and lattice parameters are reasonably well established. Substitutions for Cu appear to fall into two distinct categories. Ni and Zn (two valent) remain orthorhombic (with nearly constant b/a) throughout their ranges of homogeneity.[4] Fe, Co, and Al, all apparently three valent, induce an orthorhombic-tetragonal phase boundary near $x=0.03$.[1,4] In particular, the effects of Fe substitution in 1:2:3 (using preparation methods similar to those used for the samples that we call "standard" in this paper) have been extensively studied.[1] Rietveld refinement of neutron-diffraction results suggests that Fe substitutes primarily on the "chain" Cu (1) site.[1,5,6] Estimates of oxygen occupancy are consistent with about $\frac{1}{2}$ additional oxygen atom being introduced into the chain oxygen sites for each Fe substituted into the compound.[1,5] The introduction of Fe into the chain layer and the accompanying changes in the oxygen content and arrangement in the chain layer appear to be related to the observed orthorhombic-tetragonal phase boundary near $x=0.03$. Transmission electron microscopy (TEM),[1,7-9] x-ray absorption,[2,10,11] and Mössbauer spectroscopy,[12-26] as well as other techniques, have been utilized in the study of Fe-substituted 1:2:3.

Removal of oxygen (reduction), followed by reintroduction of oxygen at lower temperatures (reoxidation), in Fe-substituted 1:2:3 was first studied by Takayama-Muromachi, Uchida, and Kato[27] and then by Katsuyama and co-workers.[20,28,29] These investigators showed that, in contrast to the behavior of standard samples, samples reduced in argon, then reoxidized near 400 °C, remain orthorhombic for x up to 0.12. In addition, resistivity measurements indicated that T_c is higher for reoxidized samples, being depressed only a few degrees below 90 K for $x=0.10$.[27,28] Other groups have confirmed the general behavior reported in that study.[21,22]

Our first objective in this investigation was simply to check the possibility that the reduction-reoxidation process causes a precipitation of Fe from the 1:2:3 structure. Such a situation might be anticipated from the T_c's and lattice parameters, since these properties were reported to approach values observed in pure 1:2:3. Multiphase samples might be of practical interest if the hypothesized Fe-rich inclusions were effective flux pinners.

As described below, we satisfied ourselves that the samples do not show evidence of precipitation using a variety of checks. We then attempted to develop an understanding of how reoxidized samples differ from standard specimens. We followed changes in mass through the reduction-reoxidation process and measured T_c inductively. In addition, we studied samples using an electron microprobe and TEM. X-ray-absorption measurements were performed in order to acquire information about the local Fe environment. Extended x-ray-absorption fine structure (EXAFS) can provide local structural information, within about 5 Å of the atom being studied. The interpretation of our results suggests that Fe resides solely on the Cu (1) chain site in standard, reduced, and reoxidized samples. This finding is discussed in light of some analyses of Mössbauer studies, whose models include a migration of Fe from chain to "plane" during the reduction process[21,22] and/or a clustering of Fe in chain layer sites,[20] or movement to an interstitial site.[26] However, the interpretation of at least one Mössbauer study[23] involves neither Fe migration to the plane site nor clustering.

II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURES

Standard samples were prepared from oxide and carbonate starting materials. Stoichiometric quantities of starting powders were ground together by hand in an agate mortar. Pellets were pressed and then placed onto alumina labware. These samples were put into a box furnace set to 900 °C for at least 12 h. After regrinding and repelletizing, the samples were heated again using the same schedule. Following a final grinding and pelletizing, the samples were put into a tube furnace with flowing oxygen. They were heated at 960 °C for 40 h, then at 650 °C for 8 h, and finally furnace cooled to below 100 °C.

Reduced samples were prepared from the standard samples. A portion of a standard sample was weighed and then put into a tube furnace with flowing argon (commercial grade). The sample was heated at 830 °C for 20 h and then furnace cooled. A pure 1:2:3 sample treated using this method decomposed slightly (some liquid formed at high temperature). However, the substituted samples appeared stable. The sample was reweighed. The mass difference, which is assumed to represent the change in oxygen content, could then be determined.

Reoxidized samples, in turn, were prepared from the reduced samples. A portion of the sample was weighed and then put into a furnace with flowing oxygen. The sample was heated to 400 °C for 10 h and then slowly cooled. Again, the sample was reweighed to check the oxygen uptake. We found that additional heat treatments at 400 °C did not affect the properties of reoxidized samples.

X-ray diffraction was performed on many samples to determine lattice parameters (Table I) and to check for additional phases. X-ray diffraction was performed using Cu $K\alpha$ radiation on a setup which includes a diffracted-beam monochromator. Since the reported behavior of these reduced and reoxidized samples could perhaps be explained by a precipitation of Fe from the 1:2:3 phase, we looked carefully for peaks representing additional phases. We could easily discern unobscured peaks with 0.5% of the intensity of the strongest peak in the pattern.

TABLE I. Parameters for (1) standard, (2) reduced, and (3) reoxidized (heat treatments) of $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$. Δ oxygen is the formula change in oxygen of reduced and reoxidized samples relative to standard samples, estimated from mass changes as described in the text. T_c is the midpoint of susceptibility transition, and ΔT_c is the temperature span between 10% and 90% completion of the transition, both in units of K. a, b, and c are lattice parameters determined from x-ray diffraction. Orthorhombicity is $2(b-a)/(b+a)$, determined from x-ray diffraction and, in two cases, TEM.

								Orthorhombicity	
M	x	Heat	Δ oxygen	$T_c(\Delta T_c)$ (K)	a (Å)	b (Å)	c (Å)	x-ray	TEM
	0	1		90(3)	3.821	3.884	11.674	0.0164	
		2	−1.05						
		3	0.00	88(3)	3.820	3.884	11.675	0.0166	
Fe	0.02	1		84(7)	3.838	3.882	11.681	0.0114	
		2	−0.81						
		3	+0.05	83.5(4)	3.827	3.882	11.670	0.148	
Fe	0.03	1		80(10)	3.858	[a]	11.681	0	0
		2	−0.92		3.859	[a]	11.816	0	0
		3	+0.01	77(8)	3.829	3.883	11.668	0.0140	0.0143
Fe	0.08	1		48(12)	3.865	[a]	11.679	0	
		2	−0.76						
		3	+0.02	53(9)	3.839	3.878	11.660	0.0101	
Fe	0.12	1		onset 40	3.863	[a]	11.667	0	0
		2	−0.71		3.869	[a]	11.783	0	0
		3	0.00	onset 20	3.870	[a]	11.653	0	0.056
Fe	0.167	1		<5	3.871	[a]	11.661	0	
		2	−0.76						
		3	+0.04	onset 20	3.870	[a]	11.645	0	
Co	0.04	1		72(16)	3.826	[a]	11.677	0	
		2	−0.90						
		3	−0.01	64(11)	3.826	3.889	11.666	0.0163	
Co	0.10	1		26(20)	3.873	[a]	11.682	0	
		2	−0.60						
		3	+0.13	<5	3.857	3.883	11.654	0.0067	
Al	0.04	1		78(5)	3.861	[a]	11.682	0	
		2	−0.89						
		3	−0.06	87(7)	3.831	3.887	11.677	0.0145	

[a] Pattern was indexed as tetragonal.

In many cases we saw no additional peaks in standard, reduced, or reoxidized samples. In several cases we did observe peaks near 0.5%, but the prominence of these peaks was not enhanced by the reduction or reoxidation. This suggests that the reduction-reoxidation process does not cause decomposition of the 1:2:3 phase in these samples.

In order to provide more direct evidence for the stability of Fe content in the 1:2:3 phase in these samples, compositions of standard, reduced, and reoxidized 1:2:3 ($M=\mathrm{Fe}$, nominal $x=0.08$) were determined using a calibrated electron microprobe equipped with a wavelength dispersive spectrometer. For these samples, the determined Fe contents for standard, reduced, and reoxidized, within an uncertainty in x of ± 0.005, are in agreement with the nominal values.

Superconductivity measurements were performed using a mutual inductance setup. TEM observations were carried out with a JEOL 2000FX microscope. The electron diffuse scattering of the specimens was carefully examined under the second condenser lens in completely overfocused condition.

EXAFS measurements were performed on beam line X-19A of the National Synchrotron Light Source (NSLS) with a Si(111) double-crystal monochromator. The details of the beam-line design have been published.[30] During this run, NSLS was operated at an energy of 2.5 GeV and an electron current of from 200 to 90 mA. The beam size was limited to about 0.1×10 mm^2. We estimate the resolution of the monochromator to be 1.5 eV at the Fe K edge. The monochromator was detuned by reducing the incident photon flux about 20% in order to suppress contamination from harmonics. The fluorescence-type detector was filled with argon gas to monitor $K\alpha$ xrays. The samples used in the EXAFS measurements were ground to fine powders (~ 400 mesh) and then spread uniformly onto Kapton tape. Samples at room temperature were each measured over a 4-h period.

The oxygen K-near-edge studies were performed on the U1 beam line of the NSLS. The average ring current was 250 mA. The beam line is equipped with an extended range grasshopper monochromator with a resolution of about 1.6 eV (full width at half maximum) at the oxygen K edge. A fluorescence yield system (described in Refs. 31–33) facilitates the oxygen K-edge x-ray-absorption spectroscopy (XAS) by allowing rapid sample changes (<15 min). The bulk sensitivity of the fluorescence yield also ensures that signal from the surface region does not contribute disproportionately to the data. This is in contrast to the surface-sensitive character of the electron yield probes often utilized.

III. RESULTS

Our primary observations of these reduced and reoxidized samples are summarized in Table I. The lattice parameters in the case of reoxidized Fe are similar to those published earlier.[21,22,27,28] The x-ray-diffraction pattern for our reoxidized Fe $x=0.12$ sample is indexed tetragonal because an orthorhombic distortion is not resolved. However, the transmission electron microscopy discussed below clearly establishes that the sample is orthorhombic. Our results for $M=\mathrm{Al}$ and Co are similar to those for Fe.

T_c's and transition widths we observe using mutual inductance for standard samples are similar to those reported elsewhere for $M=\mathrm{Fe}$.[1] T_c's of our reoxidized samples are comparable to our T_c's of standard samples, but are significantly lower than T_c's determined resistively by some other investigators.[20,27,28] One must be cautious when comparing T_c from mutual inductance with T_c from resistance measurements: a small higher-T_c region could cause a significantly higher apparent resistance T_c which is not representative of bulk properties. In fact, Mazaki and *et al.*[29] and Qiu and *et al.*[22] report susceptibility measurements on standard and reoxidized samples which are in reasonable agreement with ours, while Smith, Taylor, and Oesterreicher[21] report significantly lower susceptibility T_c's. Susceptibility data do not support the claim of increased T_c's being a characteristic bulk property of reoxidized samples.

Mass changes observed due to the reduction and reoxidation process are also summarized in Table I. These results are consistent with the following picture, assuming that all mass changes are due to oxygen. During reduction, less than one formula oxygen is removed (for these substituted samples less oxygen is lost on reduction than for pure 1:2:3 under similar conditions). During reoxidation of samples with $M=\mathrm{Fe}$, within experimental uncertainty (limited by precision of weighing) of about ± 0.03 oxygen, the same oxygen is taken up. Thus the changes observed in the reoxidized samples are not generally due to an appreciable overall change in the oxygen content. Apparent variations in oxygen content for $M=\mathrm{Al}$ and Co, in our judgement, need to be confirmed by additional measurements.

A. Transmission electron microscopy

Standard, reduced, and reoxidized $M=\mathrm{Fe}$ samples with $x=0.03$ and 0.12 were studied using TEM. Selected-area diffraction was utilized to check for small regions of additional phases, which might be too small to be readily detected in scanning-electron-microscopy (SEM) or x-ray-diffraction studies. No significant level of non-1:2:3 material was observed in any of the samples. The morphology of these samples was studied, with "twin" and "tweed" structures being typical characteristics. Split diffraction spots are characteristic of (orthorhombic) samples with twins, while diffuse-scattering streaks appear in samples with tweed.

The tweed image, typical of standard Fe-substituted 1:2:3, consists of two sets of mutually perpendicular elongated microdomains in [110] and [$\bar{1}$10] directions. Figure 1(a) is an example, observed near the [001] orientation, in a standard preparation $\mathrm{YBa_2(Cu_{0.97}Fe_{0.03})_3O_{7-\delta}}$ sample. This is a consequence of lattice displacive modulation giving rise to the tweed contrast, which corresponds to the streaking (diffuse scattering in diffraction) shown in the inset of Fig. 1(a). Neither diffraction nor morphology shows a visible modulated structure in the reduced sample [Fig. 1b]. After reoxidation the tweed returns and a twin structure appears that had not been observed in the standard sample. Figure 1(c) and 1(d) illustrate this using different diffraction conditions, but of the same area. The corresponding diffraction pattern [inset in Fig. 1(d)] exhibits splitting of spots and weak streaks. The splitting represents twinning, which is characteristic of the orthorhombic structure.

Comparable results were also observed in samples with $x = 0.12$. For a standard sample, $M = \mathrm{Fe}$ and $x = 0.12$, the structure modulation is weak and no longer observed in morphology [Fig. 1(e)]. The existence of the structure modulation can, however, be deduced from streaks observed in electron diffraction [inset of Fig. 1(e)]. After reduction the streaks of the diffuse scattering disappear [Fig. 1(f)]; when oxygen is added back into the sample, twin and tweed reappear. This is shown in Figs. 1(g) and 1(h), which illustrate the same area using different diffraction conditions. This confirms the orthorhombic character of the reoxidized specimen.

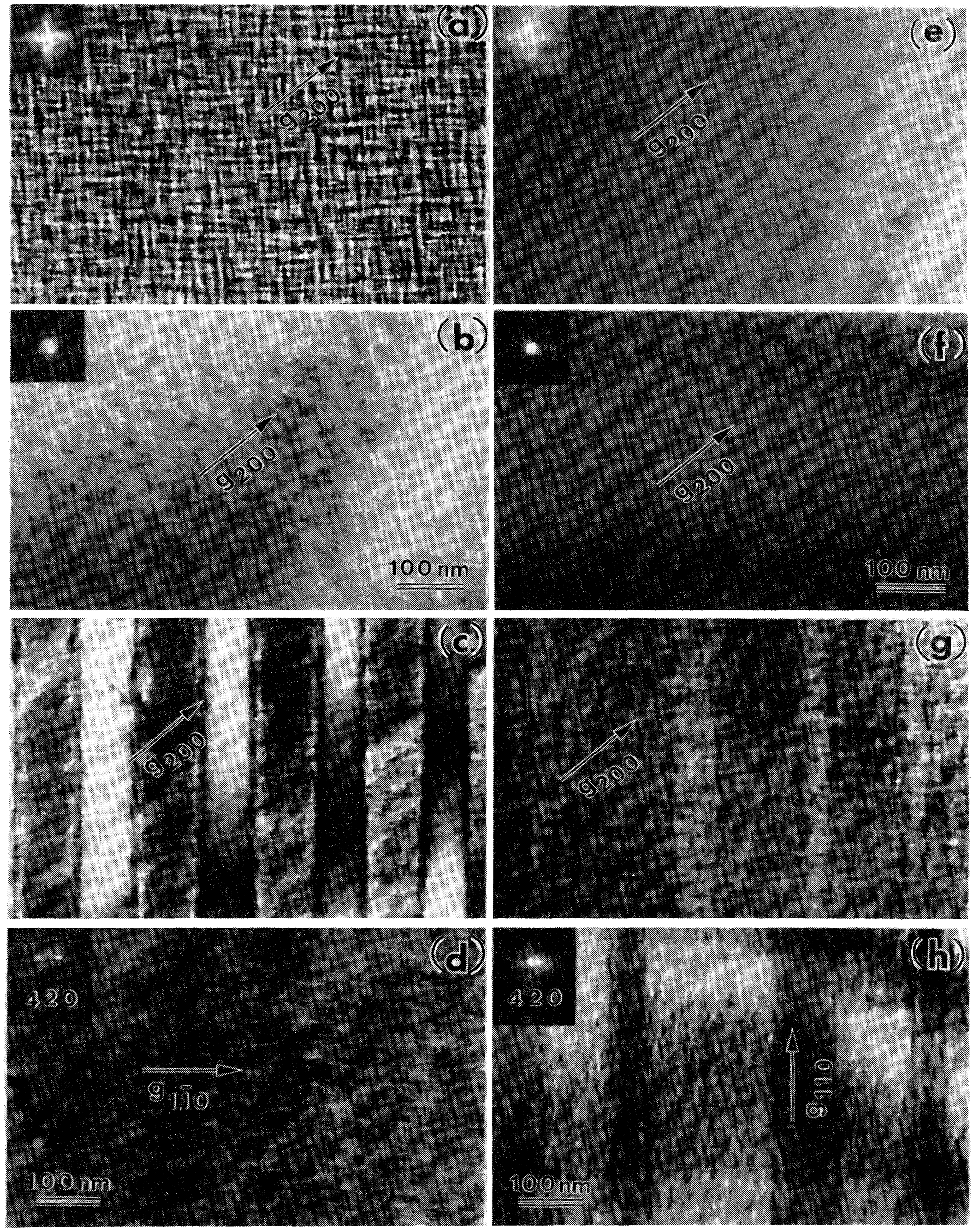

FIG. 1. Transmission electron microscopy of $\mathrm{YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}}$ for standard, reduced, and reoxidized samples; corresponding diffraction spots are shown in insets. (a) Standard $x = 0.03$, (b) reduced $x = 0.03$, (c) and (d) reoxidized $x = 0.03$, (e) standard $x = 0.12$, (f) reduced $x = 0.12$, and (g) and (h) reoxidized $x = 0.12$. Tweed patterns are associated with streaks observed around diffraction spots, while twin patterns are associated with doubled spots.

For reoxidized samples, $M=\text{Fe}$ and $x=0.03$ and 0.12, the microstructure differs from that of the standard samples. The reoxidized sample ($x=0.03$) shows a weak tweed modulation but strong twinning with large orthorhombicity. The reoxidized sample ($x=0.12$) shows strong tweed modulation and very weak twinning, indicating a small but definite orthorhombicity not seen in the standard sample.

B. X-ray absorption studies

We are now left with the problem of identifying the cause of the crystallographic changes in the reoxidized samples, compared with the standard samples. The possibility of a significant change in overall oxygen content appears to have been eliminated by the mass determinations reported above.

Other workers report Mössbauer results[12,21,22] which are interpreted to indicate migration of Fe within 1:2:3, from chain to plane, with perhaps some additional rearrangement of that Fe remaining in the chain layer, during the reduction process (which takes place at a high temperature relative to the reoxidation). It also has been suggested that under reducing conditions Fe migrates within the chain layer to form clusters.[34] Another possibility is that Fe is immobile during reduction and reoxidation, and the structural changes are primarily due to oxygen rearrangement in the chain layer. The observed differences between standard and reoxidized samples would then be attributable to the differences in oxygen chain arrangement due to the different temperatures at which oxygen is introduced: for standard samples, above 500 °C, and for reoxidized samples, near 400 °C.

In Fig. 2 we present the EXAFS (x-ray-absorption signal χ) extracted from Fe K-edge XAS measurements of $\text{YBa}_2(\text{Cu}_{0.88}\text{Fe}_{0.12})_3O_{7-\delta}$ for (1) standard sample (solid line), (2) reduced sample (dashed line), and (3) reoxidized sample (dotted line). The data are multiplied by k^3 to enhance the amplitude of high-k information. The frequency of the sinusoidal EXAFS signal is determined by the radial distances of the backscattering atoms and their phase-shift functions. These spectra are similar below 8 Å^{-1}, but differ noticeably at higher values of k. We note that oxygen scattering contributions to EXAFS diminish rapidly above $k \cong 10\ \text{Å}^{-1}$. It therefore seems likely that the observable differences in these EXAFS spectra arise mainly from metal backscattering contributions, such as Ba and Cu (or Fe) atoms.

The results of Fourier transforms are shown in Fig. 3. The k^3 transforms were taken over a k-space interval of $2.8-13.2\ \text{Å}^{-1}$. Structural differences among these samples can also be discerned by examining changes of the radial structure relative to the standard sample with $M=\text{Fe}$ and $x=0.12$ (solid line in Fig. 3). For the corresponding reduced sample (dashed line), the first and third peaks are smaller, while the second peak is slightly enhanced. For the reoxidized sample, the first peak is significantly reduced, while the second and third peaks are enhanced. Perhaps the most significant qualitative feature in Fig. 3 is the similarity in position and shape of the first EXAFS peaks, which suggests that the oxygen environment differs only slightly among these three samples.

Bond distances for each Fe—X ($X=\text{O}$, Ba, and Cu or Fe) pair extracted from the EXAFS data are listed in Table II. The bond distances of Fe—O pairs were obtained from a two-shell fit using the empirical Fe—O pairs of a model compound, Fe-glycine.[2] There is no dramatic change of bond distances for the Fe—O pairs for these samples (Table II). The bond distances of Fe—Ba, Fe—Cu(1) (or Fe), and Fe—Cu(2) pairs were obtained from a three-shell fit using a published tabulation of theoretical values.[30,35] Since, with the present data, nonbonding Fe—Fe backscattering cannot be distinguished from nonbonding Fe—Cu(1) backscattering contribu-

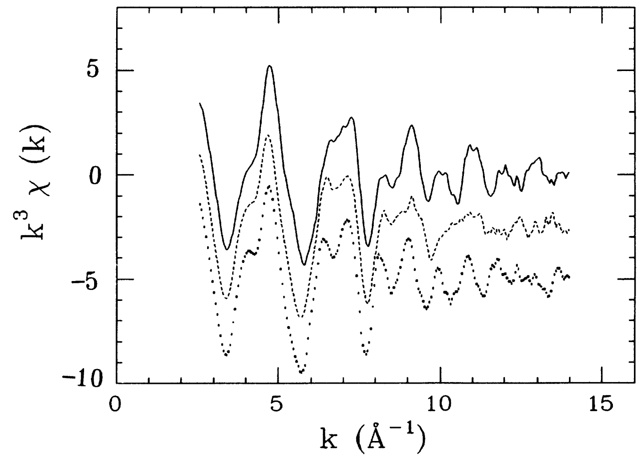

FIG. 2. Plotted are $k^3\chi(k)$ (χ is the x-ray-absorption signal) for standard (solid line), reduced (dashed line), and reoxidized (dotted line) $\text{YBa}_2(\text{Cu}_{0.88}\text{Fe}_{0.12})_3\text{O}_{7-\delta}$.

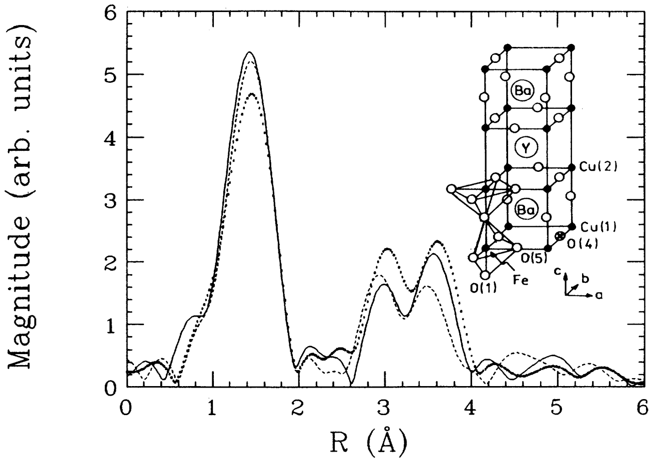

FIG. 3. Fourier transforms of the $k^3\chi(k)$ that are plotted in Fig. 2. The k^3 transforms were taken over a k-space region of $2.8-13.2\ \text{Å}^{-1}$. Standard sample is represented by solid, reduced by dashed, and reoxidized by dotted lines. Superimposed on the figure is a diagram identifying atomic positions in 1:2:3.

TABLE II. Interatomic distances R for Fe—X (X=O, Ba, and Cu or Fe) pairs in standard, reduced, and reoxidized $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ as determined from EXAFS (for $x=0.12$) compared with distances for standard samples ($x=0.10$) and 0.167) as determined from Rietveld refinement of neutron-diffraction data. Notation for atoms is that of Fig. 3 inset. Oxygen content for the $x=0.12$ standard sample was estimated by interpolating results determined for the neutron-diffraction samples. Oxygen contents for reduced and reoxidized $x=0.12$ samples were estimated by combining the standard sample estimate with Δ oxygen values from Table I.

	Neutron		EXAFS		
	std	std	std	reduced	reoxidized
Fe x	0.10	0.167	0.12	0.12	0.12
Oxygen	7.15	7.20	7.17	6.46	7.18
Fe—O(1) (Å)	1.84	1.84	1.82(5)	1.83(5)	1.83(5)
Fe—O(4)/O(5) (Å)	1.94	1.93	1.93(5)	1.94(5)	1.95(5)
Fe—Ba (Å)	3.49	3.47	3.48(10)	3.45(10)	3.48(10)
Fe—Cu(1) (Å)	3.87	3.86	3.86(10)	3.86(10)	3.86(10)
Fe—Cu(2) (Å)	4.16	4.13	4.15(10)	4.13(10)	4.17(10)

tions, the scattering function of Fe was assumed to be identical with that of Cu. Thus the contributions from Fe—Fe pairs were included in those for Fe—Cu(1) pairs. We also assumed no large variation of distance for each pair and no change of metal coordination numbers, which were derived from published Rietveld refinement of neutron-diffraction data.[1] Because the radial structures are so complex, the differences among Fe—X pairs are not significant compared with estimated uncertainties. There is, perhaps, for the reduced sample relative to the standard one a small contraction of Fe—Ba and Fe—Cu(2) bond distances. For the reoxidized relative to the standard sample, the Fe—Cu(2) bond distance may increase slightly.

Normalized fluorescence yield spectra of the oxygen K edge for Fe-substituted ($x=0.08$) samples (standard, reduced, and reoxidized) are shown in Fig. 4. The reduction in edge jump for the reduced sample compared with the standard sample can be interpreted qualitatively as a loss of oxygen. However, the observed 6.5% reduction in edge jump is not in quantitative agreement with the 11% change in total oxygen estimated using mass changes from Table I. After reoxidation the edge jump again increases as expected, but not quite back to the level of the standard sample. The near-edge spectrum for the reduced sample shows a large decrease in the first peak. This is attributable to the reduction in oxygen $2p$ states near the Fermi level.[36–39] However, after reoxidation we find that the oxygen near-edge spectrum resembles that of the original standard sample. This suggests that the number of hole states has returned to the value of the standard sample. This is consistent with the fact that the superconducting properties differ little between standard and reoxidized samples.

Our previous EXAFS studies[2,3] identified major structural characteristics of standard Fe-substituted samples: (1) Fe substitutes primarily into the Cu(1) chain site and (2) extra oxygen is introduced into the chain layer to maintain charge balance. We use a schematic drawing of the structure (inset of Fig. 3), which is derived from neutron-diffraction studies of standard Fe-substituted samples,[1,6] as a basis for discussion of the structural modification of reduced and reoxidized samples. In pure 1:2:3 the O(4) site is essentially fully occupied, while the O(5) site is empty. In an idealized tetragonal phase, these are indistinguishable O(4) sites randomly occupied by the available oxygen.

In reduced samples we find a decrease in the magnitude of the first peak relative to the standard sample. This reduction we associate with a relatively large Debye-Waller factor for the Fe—O(1) pair (shown in the inset of Fig. 2). Little or no change is found for the Fe—O(4)/O(5) pairs in the chain layer. It is well known[40,41] that a tetragonal structure for unsubstituted oxygen-reduced 1:2:3 is obtained when oxygen atoms are distributed randomly among (or removed completely from) sites identified in the orthorhombic structure as O(4) and O(5). However, in the case of reduced Fe-substituted 1:2:3 with $x=0.12$, there is little change in the intensity or position of the first peak, indicating little change in length or number of Fe—O bonds. It is possible that ox-

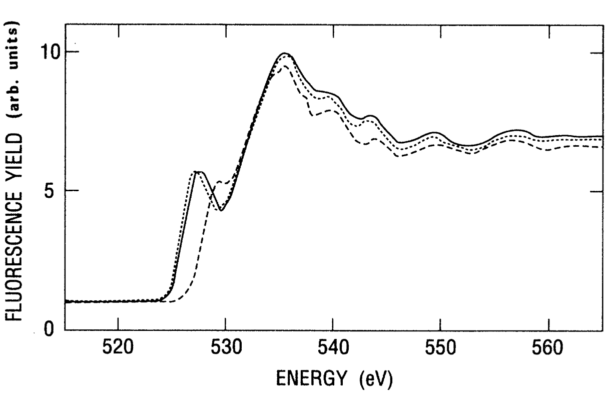

FIG. 4. Oxygen K-edge fluorescence yield of $YBa_2(Cu_{0.92}Fe_{0.08})_3O_{7-\delta}$ for standard (solid line), reduced (dashed line), and reoxidized (dotted line) samples.

ygen is strongly bound to Fe even after reduction. There is no evidence (such as a change in observed bond lengths or significant change in the number of oxygen near neighbors) that an appreciable percentage of Fe now occupies the Cu(2) plane site.

For a reoxidized 1:2:3 sample $M=\mathrm{Fe}$, $x=0.12$, we again find no evidence for the occupancy by Fe of the Cu(2) plane site. If Fe were to occupy the Cu(2) plane site, we would expect an increase of oxygen coordination about Fe [the Cu (2) site has five oxygen near neighbors, which we assume would remain relatively undisturbed] and a contribution from one longer Fe(2)—O(2) pair (2.3 Å). Surprisingly, we find a further decrease of oxygen coordination number near the Fe site (suggested by the decrease in intensity of the first peak in Fig. 3) and no evidence for a longer bond distance. Therefore, our interpretation of the EXAFS results suggests that Fe remains at Fe(1). This picture is at odds with several interpretations of Mössbauer results for similar samples, where a migration of Fe from the Cu(1) to Cu(2) site[13,21,22] and clustering,[20] or perhaps a migration to an interstitial site,[26] have been proposed. The cause of the decrease in oxygen coordination in the reoxidized (relative to standard) samples cannot be firmly established. We propose that the change of crystal symmetry is primarily associated with a redistribution of O(4)/O(5) atoms. We have previously suggested[2,3] that the introduction of extra oxygen into the chain layer sites allows at least three coordination geometries for Fe in the chain layer (fourfold, fivefold, and sixfold) and leads to the tetragonal structure observed above $x=0.03$. In order for these reoxidized samples to revert to orthorhombic symmetry, some of the oxygen in the chain layer must be redistributed into a configuration where a majority occupy the orthorhombic O(4) site. It is reasonable to speculate that, after reoxidation, the percentage of higher coordination Fe sites (fivefold and sixfold) is reduced, since oxygen atoms previously occupying one or two of the (four available) Fe near-neighbor tetragonal O(4) sites were redeployed to fill nonadjacent orthorhombic O(4) sites (i.e., near a Cu atom). In this picture the migration to orthorhombic O(4) sites fills the chains and promotes the orthorhombic structure.

IV. DISCUSSION

The basic properties of the reduced and reoxidized Fe-substituted 1:2:3 samples have been established. TEM shows that the orthorhombic region extends to at least Fe $x=0.12$. Extensions of the orthorhombic phase region are also observed for $M=\mathrm{Co}$ and Al. TEM studies confirm the expected twin structure for reoxidized orthorhombic $M=\mathrm{Fe}$ samples. Bulk superconducting transition temperatures of the reoxidized samples as measured by ac susceptibility are similar to those of the standard samples. The oxygen contents of reoxidized samples with $M=\mathrm{Fe}$ are, within our measurement precision, the same as standard samples. Electron microprobe study confirms that the Fe contents of reduced and reoxidized samples do not differ measurably from those of standard samples.

Certainly the Fe-substituted 1:2:3 system is extremely complex, and a complete understanding of these materials has not yet been achieved. Electron-diffraction work on pure and Fe-substituted 1:2:3, standard, reduced, and reoxidized, confirms the importance of the chain oxygen organization. The chain oxygen configuration, rather than the three-valent substituent Fe, may be the direct cause of the tweed structures observed by TEM. This is suggested by the existence of tweed in oxygen-reduced pure 1:2:3 as well as in Fe-substituted samples.

The detailed structures which cause the tweed observed in samples containing three-valent substitutions are not yet understood. It has been suggested that tweed consists of orthorhombic domains in a tetragonal matrix.[9] Based on results of diffuse electron scattering, calculations predicted that tweed acts as a microtwin, and the size of the twin domain decreases with increasing x (as is observed for $M=\mathrm{Fe}$ and Co). However, we do know that tweed indicates a structural modulation with wave vector k along the two equivalent 110 tetragonal directions. The twin and tweed structures coexist after reoxidation.

It appears that tweed cannot be interpreted directly as a small twin. However, it is likely that the oxygen distribution in the chain layer is responsible for both twinning and tweed.[40,41] The contrast of the modulation under two-beam conditions can be treated as a variation of the deviation parameter s from the Bragg reflection. Such variation is expected to exist in both tweed and twin domains. For tweed structure the change in s is relatively small and gradual; for twin structure it remains constant within the twin domain, but changes abruptly across the twin boundary. For reoxidized samples the structure can be thought of as a superposition of two modulations with different values of s, one associated with twin and one with tweed structure.

The EXAFS results presented here provide a starting point for understanding the mechanism which underlines the change of symmetry from tetragonal (standard samples) to orthorhombic (reoxidized). These results suggest that Fe does not appreciably migrate from the chain to plane site. The possibility that Fe does migrate within the chain layer[34] is not excluded, however. Under certain conditions large clusters of Fe might be observable using TEM, but no microstructure indicative of clustering was observed. However, small clusters (15–20 Å typical dimension) might not be visible. We cannot exclude the possibility that Fe clusters form within the 1:2:3 structure.

The apparent reduction in the oxygen coordination of Fe upon reoxidation points to a rearrangement of oxygen within the chain layer to promote the orthorhombic distortion. We conclude that oxygen rearrangement in the chain layer is the primary cause of the shift from tetragonal (standard samples) to orthorhombic (reoxidized). This differs from interpretation of Mössbauer studies published for similar samples.[20–22,26] Investigators often attribute some differences in Mössbauer spectra of standard and reduced samples to a migration of some Fe from the Cu(1) to Cu(2) site during the reduction process,[12] sometimes accompanied by clustering[20] (and assume further that Fe does not move during reoxidation). However, these conclusions are not unanimous. Other workers analyze their results using a model with all Fe on Cu(1) sites,[23] propose migration to an interstitial,[26] or do not explicitly consider the possibility of Fe migration.[24] Certainly the interpretation of EXAFS data as well as of Mössbauer spectra requires assumptions that may not be perfectly valid. Moreover, both Mössbauer spectroscopy and EXAFS are local probes. Interpretations, especially for these complicated materials, should be supported by additional evidence. Neutron diffraction and Rietveld refinement of data would be a desirable addition for the general (as opposed to local) structural information they provide.

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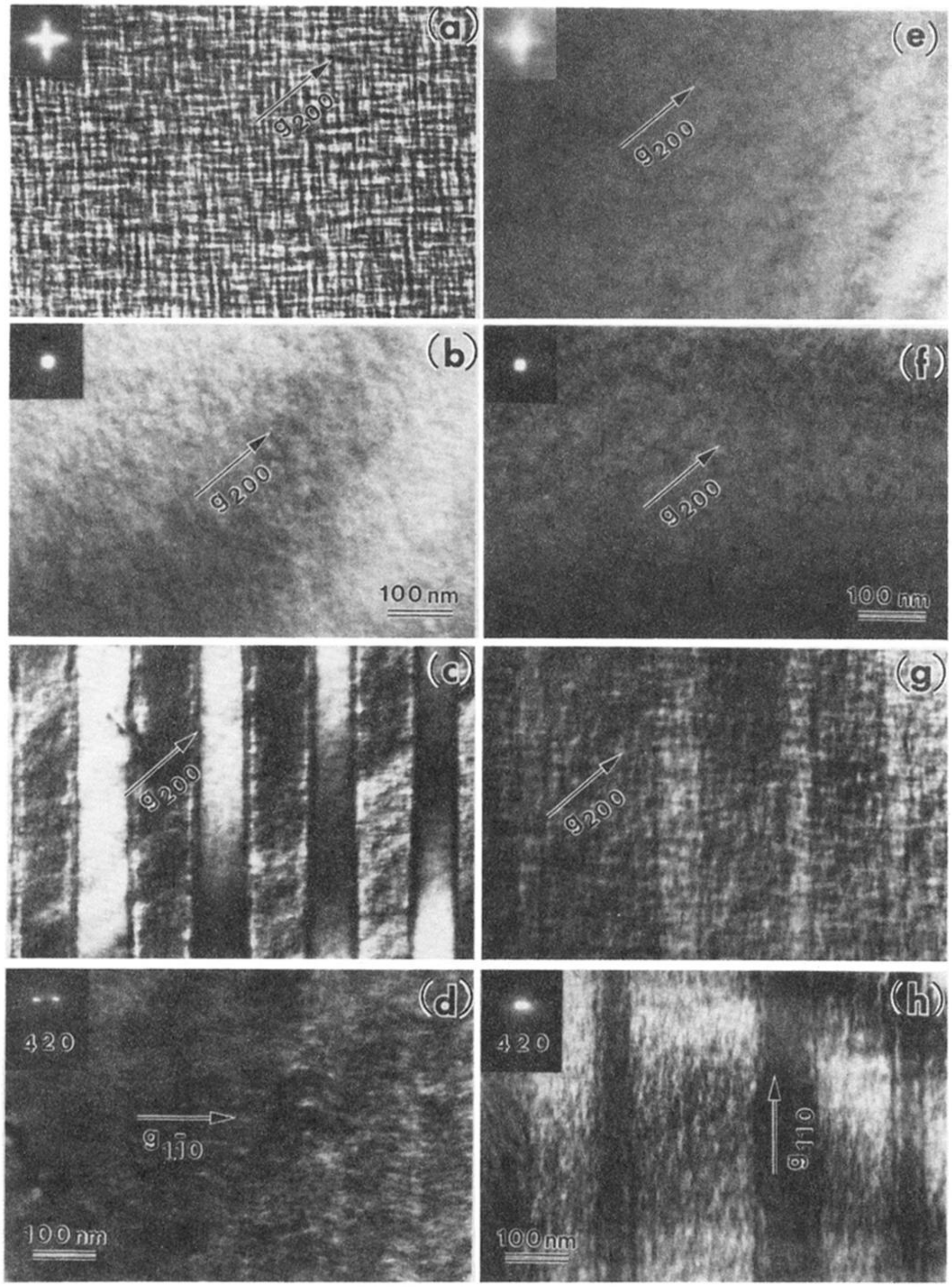

FIG. 1. Transmission electron microscopy of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ for standard, reduced, and reoxidized samples; corresponding diffraction spots are shown in insets. (a) Standard $x=0.03$, (b) reduced $x=0.03$, (c) and (d) reoxidized $x=0.03$, (e) standard $x=0.12$, (f) reduced $x=0.12$, and (g) and (h) reoxidized $x=0.12$. Tweed patterns are associated with streaks observed around diffraction spots, while twin patterns are associated with doubled spots.