PHYSICAL REVIEW B VOLUME 42, NUMBER 7 1 SEPTEMBER 1990

Mössbauer study of Fe site occupancy and its effect on T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ as a function of thermal treatments

M. G. Smith
Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545
and Department of Chemistry, B-017, University of California, San Diego, La Jolla, California 92093

R. D. Taylor
Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

H. Oesterreicher
Department of Chemistry, B-017, University of California, San Diego, La Jolla, California 92093

(Received 19 March 1990)

Synthesis of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($x=0.06$, 0.10) under relatively reducing conditions (inert atmosphere) and subsequent careful low-temperature annealing in O_2 should produce materials with a lower ratio (r) of Fe in the Cu(1) versus the Cu(2) site compared with conventionally prepared materials. This is expected due to the higher oxygen coordination of 5 in the Cu(2) site [denoted (2)5] under these conditions and is here confirmed by Mössbauer-effect measurements. These low-r materials crystallize in the orthorhombic structure and exhibit an increased superconducting transition temperature T_c compared with conventionally prepared ones. We assume that in conventionally prepared materials Fe at the Cu(1) site is surrounded by clusters of excess O that maintain tetragonal structures and localize charge and depress T_c. The reversal to orthorhombic structure is explained as a result of an increase of Fe in Cu(2) and of oxygen-starvation–Fe clusters in the Cu(1) site (sharing O) due to synthesis involving low-O fugacity at relatively low temperatures. This leaves the rest of the Cu(1) sites in an orthorhombic environment. The increase of Fe occupancy on Cu(2) indicates that Fe on Cu(2) is not detrimental to superconductivity and may actually play a role in charge fluctuations.

I. INTRODUCTION

A large body of work has been concerned with the effects of partial metal (M) substitution for Cu in $YBa_2Cu_3O_{6+y}$. High-temperature sintering followed by a low-temperature anneal in air or O_2 (conventional synthesis) of substituted materials generally results in depressed superconducting transition temperatures and substitution primarily into the chain Cu(1) site with M=Fe, Co, Al, Ga or into the plane Cu(2) site with M=Ni, Zn.[1-4] This site preference can be expressed in terms of a distribution ratio r,

$$r=\frac{M_{\mathrm{Cu}(1)}}{M_{\mathrm{Cu}(2)}}, \tag{1}$$

where $M_{\mathrm{Cu}(1)}$ and $M_{\mathrm{Cu}(2)}$ are the percent site occupancies of the metal M in the Cu(1) and Cu(2) sites, respectively. The effect of Fe substitution is especially intriguing because T_c can remain relatively high for small amounts of substituent ($x<0.02$), and materials with tetragonal structures can be superconducting. Also, Fe is a useful microscopic probe of the structural, electronic, and magnetic properties via Mössbauer spectroscopy. Many studies have appeared using this technique;[5-7] however, spectra vary depending on Fe and O content and synthesis techniques. Generally $r\cong 15$ for Fe-doped $YBa_2Cu_3O_{6+y}$ [i.e., ~6% of the Fe occupies the Cu(2) site]. Synthetic techniques that affect Fe site occupancy, T_c, and structure would be helpful in clarifying the mode of Fe occupancy and the general role of M substitution in $YBa_2Cu_3O_{6+y}$.

In this paper we explore the possibility of creating low-r materials, that is of preferentially forcing Fe into the Cu(2) sites of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($x=0.06, 0.10$). At values near $y=0$ the Cu(1) site is characteristic of Cu^+ in its linear O coordination and should preclude Fe occupation. We therefore treated materials at elevated temperatures under N_2, where $y\sim 0$ in order to force more Fe into the Cu(2) site. Oxygenation to $y\sim 1$ was then effected at low temperatures where metal diffusion is minimized. We used Mössbauer spectroscopy to determine the Fe site occupancy.

II. EXPERIMENT

The materials, $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($x=0.06, 0.10$), were prepared by the solid-state reaction method. Stoichiometric amounts of dried CuO, Fe_2O_3, Y_2O_3, and $BaCO_3$ were ground with a mortar and pestle and pressed into a pellet. Fe_2O_3 enriched with ^{57}Fe isotope (92.3%) was used for the $x=0.06$ sample to enhance the Mössbauer effect. The initial, conventional (method I) treatment, which produces high-r materials, consisted of sintering in air at 925 °C for 21 h. This process was repeated three more times with intermediate grindings and pressings. The material was then annealed at 850 °C in

©1990 The American Physical Society

flowing O_2 for 2 h with slow cooling to 100 °C over 10 h. Portions of this conventionally treated sample were then treated several different ways. The second method (II) (which produces low-r materials) involved subsequently annealing the sample in flowing N_2 at 770 °C for 48 h and quick quenching to room temperature. This was followed by annealing in flowing O_2 at 350 °C for 1 h with slow cooling to room temperature (3 h). In the third method (III), we annealed the sample in flowing N_2 at 810 °C for 48 h, then cooled it to room temperatures in flowing N_2 over a period of 2 h. Methods II and III both lead to low-r materials. Method III was used to help determine the effects of annealing under N_2 at elevated temperatures and to obtain initial Fe site occupancies. It is known that Mössbauer spectroscopy of oxygen-rich Fe-doped $YBa_2Cu_3O_{6+y}$ is further complicated by several Fe-O coordinations.[6] This method should reduce the number of sites or at least change the intensities of the subspectra as compared to conventionally prepared $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$. Since $y \leq 0.4$ by this method, Fe at the Cu(2) site should be magnetically split due to the antiferromagnetic ordering of the planar Cu sites[8] in this range. X-ray diffraction was performed with Cu $K\alpha$ radiation. Typical errors in reported lattice parameters are 0.007–0.010 Å. Magnetic susceptibility was performed using a superconducting quantum interference device (SQUID) magnetometer in a field of 100 G. Mössbauer spectroscopy was performed with a constant acceleration spectrometer using a ^{57}Co-Rh source. Absorbers were made by grinding the samples into a fine powder, mixing with sugar and enclosing the mixture in a plastic sample holder. Typical absorber thickness was 0.2–0.3 mg $^{57}Fe/cm^2$. Isomer shifts are reported relative to Fe metal at room temperature.

III. RESULTS

X-ray diffraction showed that all materials are single phase. The powder patterns are in accord with the $YBa_2Cu_3O_{6+x}$ unit cell. Structural parameters, r and T_c (determined later) for materials prepared by methods I and II are given in Table I. Conventional synthesis (method I) results in tetragonal structures, whereas treatment in N_2 at 770 °C followed by a relatively short anneal (1 h) at 350 °C in O_2 results in orthorhombic structures. Magnetic susceptibility data for both types of synthesis are shown in Fig. 1. The transition to superconductivity in both types of materials is broader than with conventional undoped $YBa_2Cu_3O_7$, but no signs of phase separation appear. The superconducting transition onset temperatures for the samples prepared by method II are higher than for conventional Fe-doped materials. The superconducting volume fraction of these samples is also greater. For example, $4\pi\chi_s = 0.65(5)$ for the $x = 0.06$ sample prepared by method II, whereas $4\pi\chi_s = 0.45(5)$ for the sample treated by method I.

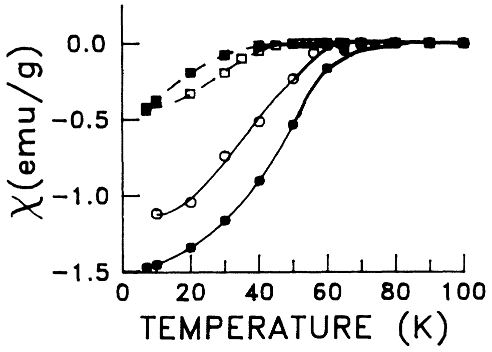

FIG. 1. Magnetic susceptibility of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ [$x = 0.06$ (solid line) and $x = 0.10$ (dashed line)] prepared by methods I (open symbols) and II (solid symbols). See the text for details of synthesis. Lines are guides to the eye.

Room-temperature Mössbauer spectra of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ prepared by methods I and II are shown in Fig. 2. The spectra could be fit to three symmetric quadrupole-split sites (A,B,C). The isomer shifts (IS), quadrupole splittings (ΔE_Q), and subspectra area (%) of these three subspectra are summarized in Table II. The spectrum of the conventionally prepared material is very similar to that of spectra obtained elsewhere;[5] however, the spectrum of the sample prepared by method II is quite different. The relative intensities of the several quadrupole doublets change with sample treatment. In particular, doublets B and C, increase in spectral area at the expense of doublet A in going from method I to method II. Similar trends are observed in the spectra of the $x = 0.10$ sample; however, small amounts of subspectra D [IS = −0.04 mm/s, $\Delta E_Q = 1.4$ mm/s] are observed in the sample treated by method II. We will show that the change in the relative intensity of doublet C is due to the relatively high occupation of Fe on the Cu(2) site (low r).

In Fig. 3 we show the room-temperature Mössbauer spectrum of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ prepared by method III. This synthesis leads to oxygen-depleted samples that are antiferromagnetic. We fit the spectra to two sites. The major site (E) is a pure quadrupole-split site, and the minor site (C) is a magnetic-quadrupole site,

TABLE I. Lattice constants r and T_c for $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($x = 0.06, 0.10$) for synthesis by methods I and II (see the text).

	Method I				Method II				
x	a_0 (Å)	c_0 (Å)	r	T_c (K)	a_0 (Å)	b_0 (Å)	c_0 (Å)	r	T_c (K)
0.06	3.868	11.69	14.9	69(1)	3.845	3.886	11.67	2.6	81(1)
0.10	3.865	11.67	6.8	55(1)	3.850	3.882	11.67	1.9	63(1)

TABLE II. Isomer shifts (IS), quadrupole splittings (ΔE_Q), and subspectra areas (%) for room-temperature Mössbauer spectra (Fig. 2) of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ prepared by methods I and II (see the text).

	Method I			Method II		
Subspectra	IS (mm/s)	ΔE_Q (mm/s)	%	IS (mm/s)	ΔE_Q (mm/s)	%
A	−0.045(8)	1.97(1)	32.7(1)	−0.001(9)	2.07(4)	3.2(1)
B	−0.025(2)	1.06(1)	61.01(1)	−0.081(2)	1.03(9)	69.2(1)
C	0.371(5)	0.62(2)	6.3(1)	0.304(2)	0.62(1)	27.6(1)

where we assume the magnetic and principal axes of the electric-field gradient to be collinear. The isomer shifts, quadrupole splittings, magnetic hyperfine fields (H_{eff}), and subspectra areas for the two sites are summarized in Table III. In earlier work[9] we showed the subspectrum *C* in oxygen-rich materials ($y \simeq 1.0$) was quadrupole split with parameters similar to those in Table II. Removal of oxygen resulted in further magnetic splitting of this site with parameters similar to those in Table III for a sample with $y \simeq 0.24$. We concluded that this subspectrum was due to Fe substitution at the Cu(2) site. Other researchers have also reached the same conclusion.[10,11] The Mössbauer spectra of the materials prepared under reducing conditions, therefore, show an increase of Fe in the Cu(2) site. For this material $r = 2.6$, whereas $r = 14.9$ for the sample prepared by method I. Changes in site occupancy have been noted before in samples with $x = 0.003$, 0.10, and 0.12.[11–13] Subspectra *A* and *B* are due to Fe substitution at the Cu(1) site in fourfold and fivefold oxygen coordination, respectively. These assignments have previously been made by us and by other groups,[7,9] based among other things, on arguments involving the magnitude of ΔE_Q. Values of ΔE_Q are proportional to the maximum of the electric-field gradient (EFG) tensor V_{zz} component at the *i*th site, which can be written as

$$ {}^{i}V_{zz} = \sum_{i \neq j}^{i} z_j p_j \frac{3 l_{ji} m_{ji} - r_{ji}^2}{r_{ji}^5} \delta_{lm} \tag{2} $$

where z_j is the charge on the *j*th ion, p_j is the occupation factor of the *j*th ion, r_{ji} is the distance of the *j*th ion to the *i*th ion, l_{ji} and m_{ji} are position coordinates of the *j*th and *i*th ions, and δ_{lm} is the δ function. On a straightforward approximation for a lattice sum S_{lat} calculation including the innermost O coordination we find for Cu(1) in threefold coordination [denoted by (1)3] $S_{\text{lat}} = 4/r_c^{-3} - r_b^{-3}$ (where r_c is the bond distance along the *c* direction). For (1)4 $S_{\text{lat}} = -2r_b^{-3} - 2r_c^{-3}$ and (1)5 $S_{\text{lat}} = 2r_a^{-3} - 2r_b^{-3} - 2r_c^{-3}$. In Table IV we show values obtained under the assumption $r_a = r_b = r_c = 1$ and compare these with sums from the literature as well as typical observed sums. We add that the innermost positive ions contribute to these terms an exactly equal amount per

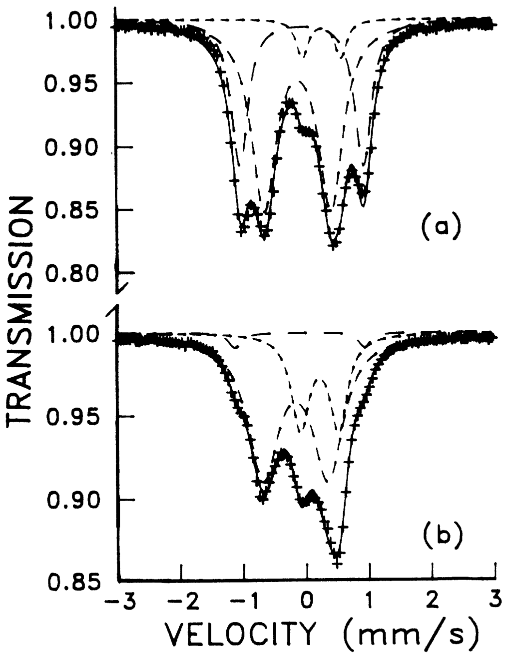

FIG. 2. Room-temperature Mössbauer spectra of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ prepared by methods I [Fig. 2(a)] and II [Fig. 2(b)]. Subspectra are shown by dashed lines: *A* (— — —), *B* (— — —), and *C* (- - -). See the text for details of synthesis.

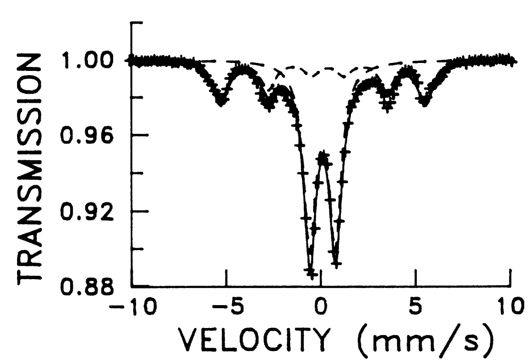

FIG. 3. Room-temperature Mössbauer spectra of $YBa_2(Cu_{0.94}Fe_{0.96})_3O_{6+y}$ prepared by method III. Subspectra are shown by dashed lines: *C* (- - -) and *E* (— — —). See the text for details of synthesis.

TABLE III. Isomer shifts (IS), quadrupole splittings (ΔE_Q), magnetic hyperfine fields (H_{eff}), and subspectra areas (%) for room-temperature Mössbauer spectra (Fig. 3) of $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ prepared by method III (see the text).

Subspectra	IS (mm/s)	ΔE_Q (mm/s)	H_{eff} (kOe)	%
C	0.33(2)	−0.25(6)	337(1)	37.2(1)
E	0.186(4)	1.35(1)	0	62.8(1)

charge (considerations of this type are strictly applicable only to the Fe^{3+} state, which do not have an orbital contribution to the EFG). It is clear that S_{lat} reflects reasonably well the trends in the calculated and observed ΔE_Q, excluding (1)2 as unrealistic for Fe at relatively high y. The largest calculated ΔE_Q is for (1)4 corresponding to subspectrum *A*. As in extremely oxygen-depleted $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$ (Table III) we find subspectra *E* with an intermediate ΔE_Q and relatively high IS, we assign this site to (1)3. More details of assignments are given elsewhere.[9] We note that the Mössbauer spectra do not indicate any traces of impurity phases such as Fe_2O_3 or Fe-doped CuO, $BaCuO_2$, and Y_2BaCuO_5.

During a previous study[14] it was found that conventionally prepared $YBa_2(Cu_{0.833}Fe_{0.167})_3O_7$ had an unusually low activation energy for oxygenation of 33.2 kJ compared to 88.2 kJ for $x=0$, presumably due to the rapid exchange of O clusters around Fe in the Cu(1) site. We were therefore interested in the response of T_c of reduced materials to varying exposure time to O_2. Accordingly we took a portion of $YBa_2(Cu_{0.9}Fe_{0.1})_3O_{6+y}$ treated by method III and annealed it in air at 300 °C for several time intervals (10 min, 0.5 h, and 1 h). While method III produces $T_c < 4$ K, the sample is, after only a 10-min anneal, superconducting with an onset temperature of 75 K. Annealing for 0.5 and 1.0 h does not much further influence T_c. These results indicate that oxygen uptake is extremely fast in our samples.

IV. DISCUSSION

We have presented arguments that at low values of y (low-O fugacity) Fe should show an increased relative tendency to occupy the Cu(2) site, where it is fivefold oxygen coordinated relative to the Cu(1) site, where it would be lower coordinated.

Treatment of $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ ($x=0.06, 0.10$) by method II results in such low-r materials ($r=2.6$ for $x=0.06$), which are orthorhombic by comparison with conventionally prepared materials that are tetragonal and have $r \cong 15$. However, while the total Fe concentration in Cu(1) is lower in low-r materials, there exists a slightly larger number of fivefold coordinated Fe in the material prepared by method II compared with method I. Assuming that Cu(1) remains fourfold coordinated in $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$, we calculate $y=1.11$ and 1.12 for synthesis by methods I versus II, respectively. This should, in principle, result in a trend to tetragonal structure for the low-r material contrary to observation. We shall, in the following, offer a consistent explanation for this retrograde behavior in terms of increased Fe clustering in the orthorhombic material.

The major difference in the preparation of the low-r

TABLE IV. Calculated local lattice sums (S_{lat}) and quadrupole splittings (ΔE_Q) for various local configurations compared with typical observed ones.

Coordination[a]	S_{lat}[b]	$\lvert\Delta E_Q\rvert$[c] (calc.) (mm/s)	$\lvert\Delta E_Q\rvert$[d] (obs.) (mm/s)
(1)2	−4	−2.4	
(1)3	−3	−1.8	1.35*E*
(1)4	+4	1.8	1.97*A*
(1)4*t*	−2	−1.2	1.39*D*
(1)5	+2	1.0	1.06*B*
(1)6	0	0.35	

[a] (1)3 stands for Cu(1) environment with threefold local O coordination. The symbol *t* depicts a trend towards tetrahedral coordination with an *a*- and *b*-axis coordination rather than the two *b*-axis ones of (1)4.

[b] S_{lat} is obtained from lattice sum from innermost O coordinations only (as outlined in text) assuming $r_a=r_b=r_c=1$.

[c] Reference 15.

[d] Typical observed ΔE_Q from this paper. The letters correspond to assigned spectra. Spectrum *D* is described in Ref. 9.

material (method II) involves a relatively low-temperature annealing at low-O fugacity. This O starvation induces Fe on Cu(1) sites to scavenge for and share the minute amounts of extra O beyond $y=0$. This leads to an increased tendency for Fe clustering (possibly linear) in low-*r* materials. On subsequent low-temperature oxygenation larger regions of the sample are relatively Fe poor on Cu(1), and the material stays orthorhombic. It should then also have a higher proportion of Fe in (1)5 due to extensive O sharing in the Fe clusters. The high percentage of Fe in (1)5 is brought out in Table II. A schematic representation of Fe-O cluster formation in the Cu(1) plane is shown in Fig. 4. We should mention that there are no obvious signs for phase separation attendant to cluster formation either in Mössbauer or x-ray measurements. Following, we will expand this O-starvation–Fe cluster model to explain trends in T_c.

We assume that a main reason for the relative increase in T_c in low-*r* materials, over conventionally prepared ones, appears to be connected with the change from tetragonal to orthorhombic structure. At the same time, however, the fraction of Fe in the Cu(2) site increases. It is now commonly assumed that the Cu(2) site is mainly responsible for superconductivity in $YBa_2Cu_3O_{6+y}$. Increased substitution in this site, therefore, should more strongly lower T_c. The relatively mild reduction in T_c in low-*r* materials compared to the unsubstituted compound indicates that Fe on Cu(2) has only a mildly detrimental effect on superconductivity as it can probably participate to some extent in the valence fluctuations. Also, the O-starvation–Fe clusters on Cu(1), which should localize charge and be detrimental to superconductivity, are now more spatially confined.

We have previously[9] given arguements that Fe in (2)5 is 3+ and in (1)4 and (1)5, it is 4+ (low spin) based on IS and hyperfine splitting [the 4+ state for (1)4 by comparison with 3+ for the higher coordinated (2)5 has to do with the smaller bond distance in (1)4]. In addition, we find here in severely O-depleted materials subspectrum *E* with an IS that is between that of 3+ and 4+. This site has a lower O coordination of 3 corroborating a valency of 3+. Comparing in Table IV observed values of ΔE_Q with values of S_{lat} we note that the relatively low ΔE_Q is probably connected with the low valency of Fe, which would reduce ΔE_Q.

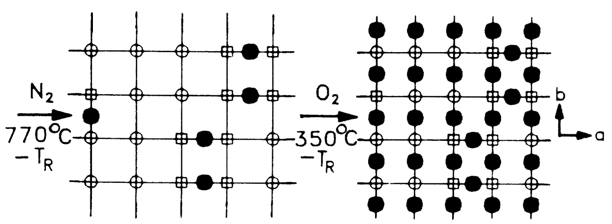

FIG. 4. Schematic representation of Fe-O cluster formation in the *a-b* Cu(1) plane after synthesis by method II (see text for details of synthesis). The notation 770 °C–T_R denotes cooling from 770 °C to room temperature. Open circles and squares represent Cu and Fe atoms, respectively. Large solid circles represent oxygen.

We can now generalize and suggest that a large number of *M* substituents, where *M* have the potential for valences ≥ 2, will at lower O_2 annealing temperatures prefer the Cu(1) and at higher tempertures increasingly populate the Cu(2) site. In the Cu(2) site, these substituents may participate in superconductivity. Much of the conflicting data in the literature about the magnitude of T_c depressions accordingly can be attributed to different thermal treatments. In the case[1] where $M=\text{Zn}$ the catastrophic decay of T_c with *x* appears to reflect the fixed valence of 2+, which now reduces superconductivity on the important Cu(2) site. This phenomenon suggests that Fe in Cu(2) may be mixed valent and is participating in some way in the superconductivity (the low ΔE_Q of this site indicates near spherical charge distribution, which may be important for superconductivity). The situation would appear to be different with $M=\text{Ga}$ or Al. In this case, we expect that substitution should occur on the Cu(1) site at high values of *y* and be severely limited altogether at low values of *y*.

We became aware recently of another work on $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$ in which remarkably stable T_c with *x* (measured resistively) were obtained in orthorhombic materials prepared in a manner similar to ours.[16] In fact, their data with $x=0.1$ with $T_c \sim 89$ K probably has to do with a better optimization of preferential site selection during the preparation. In the latter work no determination of site preference is given, although an opposite trend in site selection compared to ours is discussed. Further optimization of site selection and attendant T_c appears possible at this point. The most crucial point of this discussion would appear to be the one of reoxidation of the reduced superconductor. Low temperatures during this step are important in order to avoid Fe diffusion into Cu(1). Special methods, such as electrochemical O charging, may produce the best material.

This work indicates why rather different Mössbauer spectra can be obtained for identical *x* in $YBa_2(Cu_{1-x}Fe_x)_3O_{6+y}$. Variations in oxygen partial pressure, annealing temperatures and times, and cooling rates influence relative site occupancy and Fe-O coordination with low-temperature annealing in O_2 or air resulting in materials with Fe primarily on the Cu(1) site in multifold O coordination.

V. CONCLUSION

We conclude that under inert atmospheres at high temperatures transition metals with a preference for higher oxidation states than 2+ (e.g., Fe) will migrate from the Cu(1) site to the Cu(2) site in $YBa_2Cu_3O_{6+y}$. Careful synthesis involving oxygenation at lower temperatures, where Fe atoms cannot readily relocate, can produce orthorhombic materials that have a greater percentage of Fe on the Cu(2) site (low *r*) with higher T_c than that for conventionally prepared materials. The relatively high

T_c in these low-r materials suggests that Fe at the Cu(2) site is either not overly detrimental or may in some sense be participating in superconductivity. The orthorhombic structure of low-r materials is explained by O-starvation–Fe clusters, induced by the relatively low-O fugacity treatment at relatively low temperatures. This concentrates Fe into special regions but does not influence so much the bulk of the material. Fe ion states are 3+ for (2)5 coordination and 4+ for (1)4 and (1)5 (low spin), but a new state near 3+ has been found in severely O-depleted materials with (1)3.

We have become aware of a recently published paper[17] that reported similar results to ours. The authors of the latter paper also note the formation of Fe clusters in the Cu(1) plane.

ACKNOWLEDGMENTS

We would like to thank Dr. J. D. Thompson for assistance with magnetic susceptibility measurements and Dr. F. T. Parker for useful discussions and suggestions. This work was supported by the U.S. Department of Energy. One of us (M.G.S.) would like to thank Los Alamos National Laboratory for financial assistance under the UC-LANL INCOR program.

---

[1] G. Xiao, F. H. Streitz, A. Gavrin, Y. W. Du, and C. L. Chien, Phys. Rev. B **35**, 8782 (1987).

[2] J. M. Tarascon, P. Barboux, P. F. Miceli, L. H. Greene, G. W. Hull, M. Eibschutz, and S. A. Sunshine, Phys. Rev. B **37**, 7458 (1988).

[3] J. Jung, J. P. Franck, W. A. Miner, and M. A.-K. Mohamed, Phys. Rev. B **37**, 7510 (1988).

[4] M. Hangyo, S. Nakashima, M. Nishiuchi, K. Nii, and A. Mitsuishi, Solid State Commun. **67**, 1171 (1988).

[5] Z. Q. Qiu, Y. W. Du, H. Tang, J. C. Walker, W. A. Bryden, and K. Moorjani, J. Magn. Magn. Mater. **69**, L221 (1987).

[6] C. Blue, K. Elgaid, I. Zitkovsky, P. Boolchand, D. McDaniel, W. C. H. Joiner, J. Oostens, and W. Huff, Phys. Rev. B **37**, 2896 (1988).

[7] M. Eibschutz, M. E. Lines, J. M. Tarascon, and P. Barboux, Phys. Rev. B **38**, 2896 (1988).

[8] J. M. Tranquada, A. H. Moudden, A. I. Goldman, P. Zolliker, D. E. Cox, G. Shirane, S. K. Vinha, D. Vaknin, D. C. Johnston, M. S. Alvarez, A. J. Jacobson, J. T. Lewandowski, and J. M. Newsam, Phys. Rev. B **38**, 2477 (1988).

[9] M. G. Smith, R. D. Taylor, F. T. Parker, and H. Oesterreicher (unpublished).

[10] T. Shinjo and S. Nasu, in *Mechanisms of High Temperature Superconductivity*, edited by H. Kaminura and A. Oshiyama (Springer-Verlag, Berlin, 1989), p. 166.

[11] Z. Q. Qiu, Y. W. Du, H. Tang, and J. C. Walker, J. Magn. Magn. Mater. **78**, 359 (1989).

[12] M. Takano and Y. Takeda, Jpn. J. Appl. Phys. **26**, L1862 (1987).

[13] Z. Q. Qiu, Y. W. Du, H. Tang, J. C. Walker, J. S. Morgan, and W. A. Bryden, J. Appl. Phys. **64**, 5947 (1988).

[14] B. Higgins and H. Oesterreicher, Mater. Res. Bull. **24**, 739 (1989).

[15] C. W. Kimball, J. L. Matykiewicz, H. Lee, J. Grapintzakis, A. E. Dwight, B. D. Dunlap, J. Jorgensen, B. W. Veal, and F. Y. Fradin, Physica C **156**, 547 (1988).

[16] S. Katsuyama, Y. Ueda, and K. Kosuge, Mater. Res. Bull. **24**, 603 (1989).

[17] S. Katsuyama, Y. Ueda, and K. Kosuge, Physica C **165**, 404 (1990).