

Effect of annealing on the local microstructure and T_c in $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$

M. G. Smith, J. B. Goodenough, and A. Manthiram

Center for Materials Science and Engineering, Engineering Teaching Center 9.104, The University of Texas at Austin, Austin, Texas 78712

R. D. Taylor

Physics Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545

H. Oesterreicher

Department of Chemistry B-017, The University of California, San Diego, La Jolla, California 92093

(Received 19 August 1991)

An investigation of the Co distribution in $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$, $z=0.00$ and 0.05 , for different annealing treatments has been made with ^{57}Co emission Mössbauer spectroscopy. Samples prepared by conventional ceramic techniques were first annealed in oxygen at $650^\circ C$ for 15 h, $800^\circ C$ for 1 h, and $400^\circ C$ for 3 h (treatment [O]); they were next annealed at $700^\circ C$ in N_2 (treatment [N]); they were finally annealed at $350^\circ C$ in O_2 (treatment [NO]). After [O], the Co atoms for $z=0.00$ were distributed nearly 50-50 on Cu(1) and Cu(2) sites with evidence for Co-atom clustering in the Cu(1) O_y planes; for $z=0.05$, over 80% of the Co were on the Cu(1) sites, and, more important, Co-atom clustering was evident. During treatment [N], Co atoms migrated from Cu(2) sites to the cobalt clusters in the Cu(1) O_y planes. After [NO], the Co-atom clusters remained, with some increase in size in the $z=0.00$ sample, and the superconductive onset temperature T_0 increased from its value after [O], but its superconductive transition width ΔT_c also increased. A $^{57}Fe^{4+}$ daughter is observed for Co^{3+} in a fivefold-coordinated Cu(1) site. These observations are discussed in comparison with results of similar experiments by others.

I. INTRODUCTION

The effect of partial substitution of a metal M for Cu in $YBa_2(Cu_{1-x}M_x)O_{6+y}$ ($M=Cr, Mn, Fe, Co, Ni, Zn, Al, Ga$) on the bulk crystal structure, local microstructure, oxygen order-disorder transitions, and the superconductor critical temperature T_c have been extensively studied,¹⁻⁴ and a variety of results have been reported (see Ref. 5 for a comprehensive review). It has become apparent that subtle differences in synthetic procedures and subsequent heat treatments of the samples influence both the M -site selectivity and M -atom clustering, which are correlated with the oxygen content and ordering in the Cu(1) O_y planes of the structure. The local microstructure influences, in turn, the macrostructure and such superconductive properties as T_c , flux pinning, and the critical current density J_c .

The dopants $M=Fe, Co$ preferentially occupy the Cu(1) chain site and stabilize the insertion of oxygen to concentrations in excess of $y=1$, which results in macroscopic tetragonal structures for dopant concentrations $x \gtrsim 0.03$ and a trapping out of holes from the superconductive Cu(2) O_2 sheets at Cu(1) atoms coordinated by more than four oxygen atoms.⁶ A relatively smooth decrease of T_c with increasing x suggests that the effects of local oxygen disorder with consequent hole trapping at Cu(1) sites depress T_c in a way to obscure any influence due to breaking of the superconductive pairs by magnetic M atoms on Cu(2) sites.

In the case of $M=Fe$, orthorhombic $YBa_2(Cu_{1-x}Fe_x)O_{6+y}$ ($0.03 \lesssim x < 0.15$) materials with greater Fe occupancy at the Cu(2) sites can be syn-

thesized by subjecting the samples to reducing conditions (N_2 atm) at $800-850^\circ C$ followed by a low-temperature oxygen anneal.^{7,8} These materials have a higher T_c than similarly doped samples prepared under only oxidizing conditions; they also show relatively ordered twinned microstructures⁹ and an increased critical current density J_c relative to the conventionally prepared materials.¹⁰ These observations suggest that, by a suitable manipulation of the preparative procedures, it is possible to segregate the dopant into Fe-rich regions having a flux-pinning potential. We have also found that partial Ca^{2+} substitution for Y^{3+} increases the relative Fe occupancy of the Cu(2) sites in $Y_{1-z}Ca_z(Cu_{1-x}Fe_x)_3O_{6+y}$.¹¹ These more highly doped materials, unlike the $z=0.00$ samples prepared subject to the same reducing conditions, tend to have a much lower T_c relative to undoped ($x=0.00$) samples, which suggests that beyond a critical Fe occupancy of the Cu(2) sites, the superconductive properties of the Cu(2) planes are severely degraded as anticipated for pair breaking by ions with localized paramagnetic moments. The possibility of iron clusters trapping out normal-state regions without modifying significantly the superconductive properties of the iron-poor regions—whereas a random substitution of magnetic iron atoms at Cu(2) sites suppresses T_c sharply—has implications not only for the processing of practical materials, but also for any mechanistic model of the superconductive phenomenon.

For $M=Co$, evidence for preferential substitution of Co on the Cu(1) chain sites comes from neutron diffraction,⁴ differential anomalous scattering,¹² and x-ray-absorption near-edge spectroscopy¹³ in bulk

$\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$; however the extent of substitution on Cu(1) sites appears to vary sensitively with x and the preparation conditions as for $M=\text{Fe}$. For example, ^{57}Co Mössbauer spectroscopy on $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ doped with ^{57}Co at the parts per million level placed the majority of the dopant in the Cu(1) chain sites in the fully oxygenated system;¹⁴ however, with such light doping the cobalt migrates to either a Cu(2) or an interstitial site during an 800°C N_2 anneal.¹⁵ Recently, Renevier *et al.*¹⁶ have obtained an orthorhombic modification of $\text{YBa}_2(\text{Cu}_{0.94}\text{Co}_{0.06})_3\text{O}_{6+y}$ (which is normally tetragonal for $x \geq 0.03$) with an 800°C N_2 anneal followed by a low-temperature O_2 anneal. The superconductive onset temperature $T_0 \approx 65$ K remained the same as that of the tetragonal starting phase; however, the midpoint of the transition was shifted approximately 10 K lower in the orthorhombic material. Although Renevier *et al.*¹⁶ concluded from TEM and STEM data that the changes in macroscopic structure and the width of the superconductive transition produced by their more complex annealing schedule were a consequence of oxygen reordering rather than Co redistribution between Cu(1) and Cu(2) sites, the influence on T_c of the cobalt distribution in $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$ was not clearly resolved in their study.

We have used an annealing schedule on $\text{YBa}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ similar to that of Renevier *et al.*;¹⁶ however, with $x=0.10$ our samples remain tetragonal even after an 800°C N_2 anneal followed by a 350°C O_2 anneal. In this paper we report data of ^{57}Co emission Mössbauer spectroscopy that show, in tetragonal $\text{YBa}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$, a Co migration—during a 700°C N_2 anneal—from Cu(2) to Cu(1) sites that is not reversed on reoxidation of the sample at 350°C. The reoxidized samples, which have a lower Co concentration on the Cu(2) sites, have a higher T_0 . A larger y on reoxidation than before reduction indicates that the Co on Cu(1) sites may accept a larger oxygen coordination than those on Cu(2) sites, and Mössbauer spectroscopy provides a direct demonstration that this is indeed the case.

We have demonstrated previously¹⁷ that the equilibrium oxidation state of the Cu-O array remains constant on substitution of Ca^{2+} for Y^{3+} in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_{6+y}$, which means that the oxygen concentration decreases as $y=(0.95-0.5z)\pm 0.01$ for samples annealed in 1 atm O_2 .

We report here ^{57}Co -emission Mössbauer spectroscopy on $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ doped with ^{57}Co , which shows a greater Co occupation of the Cu(1) sites than is found in the samples containing no Ca^{2+} ions. Moreover, the Ca-doped materials have a higher T_0 than those without Ca.

Finally, we report the observation of a $^{57}\text{Fe}^{4+}$ daughter state in a fivefold-coordinated Cu(1) site.

II. EXPERIMENTAL

$\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ ($z=0.00$ and 0.05) pellets for ^{57}Co doping were prepared by solid-state reaction. Stoichiometric amounts of dried Y_2O_3 , CaCO_3 , BaCO_3 , CO_3O_4 , and CuO were mixed in a mortar and pestle and fired at 800°C for 12 h. The resulting powders were reground, pressed into pellets, and annealed at 925°C in air for 92 h with three intermediate grindings and pressings. The phase purity of these materials (prior to ^{57}Co doping) was checked by x-ray powder diffraction using $\text{Cu } K\alpha$ radiation. All samples could be indexed to the $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ unit cell. No impurity phases were detected by x-ray diffraction.

The carrier-free ^{57}Co acidic solution was neutralized before doping the samples. Approximately 2 mCi were added to each of two pellets of both samples. The pellets were allowed to air-dry at room temperature; pellets of identical composition were then placed on top of one another with the ^{57}Co -doped sides facing each other. Undoped $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ samples for x-ray diffraction, iodometric titration, and magnetic-susceptibility measurements were treated simultaneously. For the initial diffusion the following protocol, referred to as [O], was used. The pellets were placed in a furnace at room temperature and the temperature was slowly raised to 650°C under flowing oxygen. The pellets were annealed under these conditions for 15 h and then at 800°C in flowing oxygen for 1 h. The pellets were finally slow cooled to 400°C, annealed at this temperature under flowing oxygen for 3 h, and quenched. The samples were subsequently treated by two different techniques. First, the pellets were annealed at 700°C for 9 h and slow cooled to room temperature in flowing N_2 (referred to as [N]). This treatment was then followed by annealing at 350°C for 4 h with slow cooling to room temperature in

TABLE I. Lattice parameters, oxygen stoichiometry ($6+y$), superconducting transition onset temperature (T_0) and 10–90 % transition width (ΔT_c) of $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ prepared by different synthetic methods.

z	Synthesis ^a	$6+y$	a (Å)	c (Å)	T_0 (K)	ΔT_c (K)
0.00	[O]	7.10	3.871(5)	11.66(1)	22	7
	[N]	6.66	3.869(5)	11.75(1)		
	[NO]	7.16	3.873(5)	11.67(1)	37	20
0.05	[O]	7.03	3.870(5)	11.68(1)	35	9
	[N]	6.62	3.866(5)	11.76(1)		
	[NO]	7.15	3.870(5)	11.67(1)	44	14

^aSee text for details of synthesis methods.

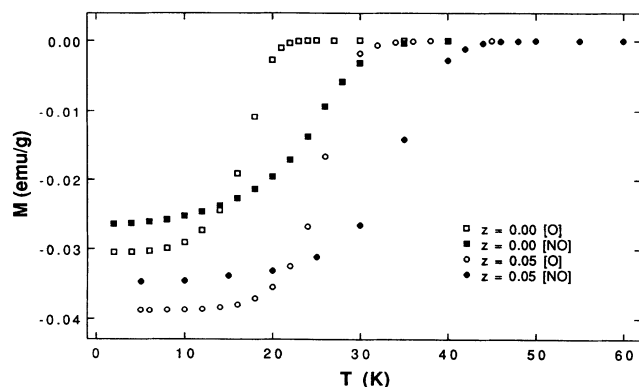


FIG. 1. Field-cooled magnetization M vs temperature in an applied field $H=10$ Oe for $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$ ($z=0.00, 0.05$) prepared by methods [O] and [NO]. See text for details of synthesis.

flowing O_2 (referred to as [NO]). The undoped $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$ samples were characterized after each treatment by x-ray diffraction. Oxygen contents as a function of annealing protocol were determined by iodometric titration.² The oxygen

stoichiometry ($6+y$) has an error limit of ± 0.02 . Magnetic-susceptibility data of the samples prepared by methods [O] and [NO] were obtained on a SQUID magnetometer operating in an applied field of 10 Oe. Room-temperature ^{57}Co -emission Mössbauer spectroscopy with a $K_4Fe(CN)_6 \cdot 3H_2O$ absorber of the ^{57}Co -doped samples was performed after each thermal treatment [O], [N], and [NO].

III. RESULTS

X-ray diffraction showed that all materials obtained after the three annealing procedures ([O], [N], [NO]) were single phase; the powder patterns could be indexed to the $YBa_2Cu_3O_{6+y}$ tetragonal unit cell. The lattice parameters are given in Table I. The lattice parameters of the $z=0.00$ sample prepared by the [O] treatment are similar to those reported by Xu *et al.*¹⁸ for the same level of Co doping. The lattice parameters of the $z=0.05$ sample prepared by the [O] treatment differ little, within experimental error, from the $z=0.00$ sample. The [N] treatment resulted in tetragonal materials with increased c parameter indicative of oxygen loss; however, the [NO] treatment also produced tetragonal materials contrary to

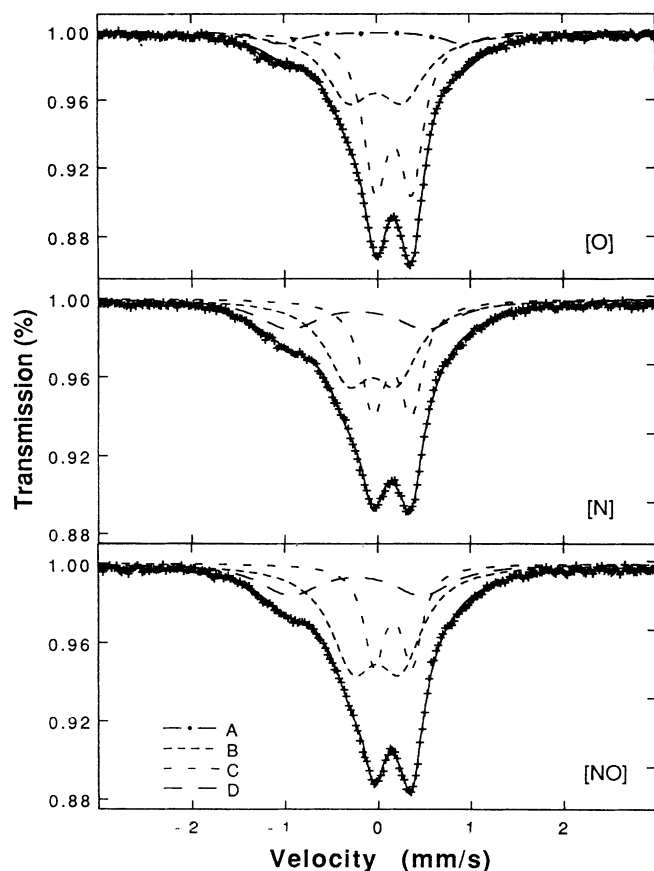


FIG. 2. Room-temperature ^{57}Co emission Mössbauer spectra of $YBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$ (^{57}Co) prepared by methods [O], [N], and [NO]. See text for details of synthesis. The velocity scale has been reversed to coincide with that of an absorption experiment.

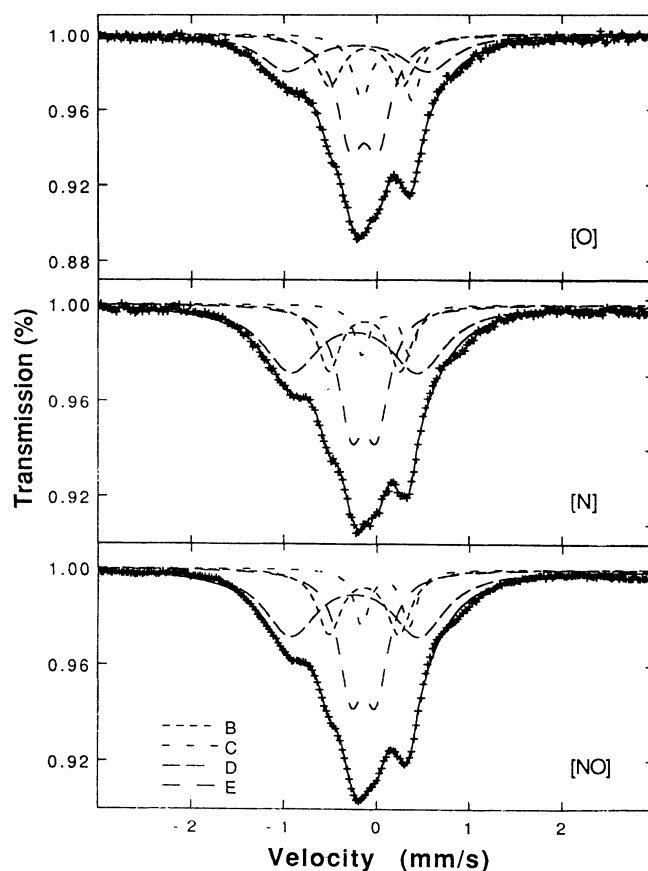


FIG. 3. Room-temperature ^{57}Co emission Mössbauer spectra of $Y_{0.95}Ca_{0.05}Ba_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$ (^{57}Co) prepared by methods [O], [N], and [NO]. See text for details of synthesis. The velocity scale has been reversed to coincide with that of an absorption experiment.

the results obtained by Renevier *et al.*¹⁶ on $\text{YBa}_2(\text{Cu}_{0.94}\text{Co}_{0.06})_3\text{O}_{6+y}$ and results^{7,8} obtained on $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6+y}$.

Iodometric titration of the samples prepared by protocol [O] gave oxygen stoichiometries in excess of $y=1.0$ (Table I), which is consistent with previous reports on $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$.^{2,4} After the 700°C N_2 anneal, protocol [N], the oxygen stoichiometry decreased to $y \approx 0.6$; but on reoxygenation at 350°C, protocol [NO], more oxygen is reintroduced than after treatment [O] with an oxygen concentration reaching $y=1.16$.

Magnetic-susceptibility data for the [O] and [NO] samples are shown in Fig. 1; the [N] samples were not superconductors. The superconductive onset temperature T_0 and the transition width ΔT_c (10–90 %) are also summarized in Table I. A $T_0 \approx 22$ K for an [O] sample of $z=0.00$ is comparable with the literature value.¹ Partial substitution of Ca, $z=0.05$, increases the onset temperature to $T_0 \approx 35$ K for an [O] preparation. These values are increased by the additional treatment [NO], but the width ΔT_c of the transition is also increased. The increase in T_0 that we observe contrasts with the relative independence of T_c reported by Renevier *et al.*¹⁶ for orthorhombic $\text{YBa}_2(\text{Cu}_{0.94}\text{Co}_{0.06})_3\text{O}_{6+y}$ after similar treatment. Moreover, we observe a final T_0 that is higher than previously reported, and we do so for materials nominally higher in Co content.

Figures 2 and 3 show the room-temperature

^{57}Co -emission Mössbauer spectra for $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ ($z=0.00$ and 0.05 , respectively) doped with ^{57}Co and given the various annealing schedules designated by protocols [O], [N], and [NO]. The data extracted by line fitting are summarized in Table II; they include isomer shifts (Δ_{IS}), quadrupole splittings (ΔE_Q), full-width-at-half-maximum line width (FWHM), and percent-spectral area (%) for the several subspectra that were identified. The Δ_{IS} values reported are relative to $\alpha\text{-Fe}$ at room temperature with signs corresponding to absorption measurements. No impurity phases—such as ^{57}Co -doped CoCl_2 , CoCO_3 , or cobalt oxides—were observed in any of the emission spectra.

Subspectra *A*, *C*, and *D* have been reported in numerous places in the literature^{15,19} (and references therein) for $^{57}\text{Co}/^{57}\text{Fe}$ Mössbauer spectroscopy of $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$; however, subspectra *B* and *E* have not, to our knowledge, been reported previously. On the other hand, Hechel *et al.*,²⁰ in a study of $\text{YBa}_2(\text{Cu}_{0.75}\text{Fe}_{0.25})_3\text{O}_{6+y}$, report two subspectra with similar ΔE_Q but different Δ_{IS} . For convenience we denote Co with m -fold oxygen coordination in a $\text{Cu}(n)$ site ($n=1$ or 2) as $(n)m$. With this notation subspectra *A* and *D* have been associated^{15,19} with (1)4 square-coplanar and (1)5 square-pyramidal environments, respectively, and subspectrum *C* with the (2)5 square-pyramidal site. The new subspectra *B* and *E* have a negative Δ_{IS} like those of *A* and *D* consistent with ^{57}Co substitution on a

TABLE II. Isomer shifts (Δ_{IS}), quadrupole splittings (ΔE_Q), full-width-at-half-maximum line widths (FWHM) and percent spectral area (%) of subspectra observed in room-temperature ^{57}Co Mössbauer emission spectra of $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ (^{57}Co) samples prepared by different synthetic methods.

z	Synthesis ^a	Subspectra	Δ_{IS} (mm/s)	ΔE_Q (mm/s)	FWHM (mm/s)	%
0.00	[O]	<i>A</i>	−0.02(1)	1.95(8)	0.55(3)	8
		<i>B</i>	0.01(1)	0.58(2)	0.57(2)	38
		<i>C</i>	0.21(1)	0.39(8)	0.32(3)	54
	[N]	<i>B</i>	−0.03(1)	0.52(2)	0.58(5)	42
		<i>C</i>	0.19(1)	0.42(6)	0.31(4)	34
		<i>D</i>	−0.18(1)	1.48(7)	0.81(2)	24
	[NO]	<i>B</i>	0.02(1)	0.51(1)	0.58(5)	51
		<i>C</i>	0.20(1)	0.41(1)	0.27(1)	26
		<i>D</i>	−0.20(1)	1.42(7)	0.79(2)	23
0.05	[O]	<i>B</i>	−0.09(1)	0.79(4)	0.30(2)	17
		<i>C</i>	0.14(1)	0.55(1)	0.24(1)	17
		<i>D</i>	−0.18(1)	1.51(6)	0.68(2)	28
		<i>E</i>	−0.11(1)	0.30(2)	0.34(1)	38
	[N]	<i>B</i>	−0.10(1)	0.77(3)	0.29(1)	16
		<i>C</i>	0.13(1)	0.52(2)	0.20(1)	9
		<i>D</i>	−0.21(1)	1.36(5)	0.73(1)	42
		<i>E</i>	−0.10(1)	0.27(2)	0.33(1)	33
	[NO]	<i>B</i>	−0.10(1)	0.76(3)	0.30(2)	17
		<i>C</i>	0.13(1)	0.52(1)	0.20(1)	9
		<i>D</i>	−0.21(1)	1.37(4)	0.70(1)	41
		<i>E</i>	−0.11(1)	0.27(2)	0.33(1)	33

^aSee text for details of synthesis methods.

Cu(1) site. Furthermore, the small quadrupole splittings indicate a relatively symmetric environment. Therefore, we assign subspectra *B* and *E* to an octahedral (1)6 environment. Subspectrum *E* only appears in the Ca-doped ($z=0.05$) samples and has a much smaller quadrupole splitting than even that of subspectrum *B* ($\Delta E_Q=0.27$ mm/s versus $\Delta E_Q=0.5-0.8$ mm/s).

The FWHM of each of the spectra reported in Table II remain relatively independent of protocol [O], [N], and [NO]; however, they differ from one subspectrum to another and with the introduction of Ca.

The most important result from the ^{57}Co -Mössbauer spectroscopy data is the demonstration that Co migrates from the Cu(2) site of the superconductive CuO_2 sheets to the Cu(1) sites in the Cu(1)O_y planes during the reduction step of protocol [N]. Moreover, in the $z=0.00$ sample, a further migration occurs during the following oxidation step [NO]. In addition, the percentage of Co in (1)5 and (1)6 environments is seen to be increased by protocols [N] and [NO]. These trends are correlated with an increase in T_0 and ΔT_c after the final [NO] treatment, Table I.

IV. DISCUSSION

A. The variable oxygen in undoped samples

We represent the $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ structure in terms of successive (001) planes on traversing the *c* axis:



where the vertical lines represent interfaces between superconductive $\text{CuO}_2\text{—Y—CuO}_2$ layers of fixed oxygen content and nonsuperconductive $\text{BaO—CuO}_y\text{—BaO}$ layers of variable oxygen content. The Cu(2) sites of the superconductive CuO_2 planes have square-pyramidal coordination; they remain relatively unperturbed by changes in the oxygen concentration of the Cu(1)O_y planes within the nonsuperconductive layers. The substitution of Ca for Y to give $\text{Y}_{1-z}\text{Ca}_z$ planes within the superconductive layers does not change this situation; however, the smaller positive charge on a Ca^{2+} ion tends to stabilize the retention of mobile holes on the fivefold-coordinated Cu(2) atoms against trapping by fivefold-coordinated copper in Cu(1) sites.²¹

Oxygen is reversibly inserted (extracted) into (from) the CuO_y sheets of undoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$.^{22,23} With the annealing protocols [O], [N], and [NO], the value of *y* changes from 0.95 ± 0.01 after [O] to $\lesssim 0.1$ after [N] and back to 0.95 ± 0.01 after [NO]. Moreover, ordering of the oxygen in the Cu(1)O_y planes for $y \gtrsim 0.45$ transforms the crystal symmetry from tetragonal to orthorhombic. There are two possible oxygen sites per Cu(1) in the plane, which makes $0 \leq y \leq 2$ geometrically possible. At $y=0.95$, the oxygen atoms order on sites aligned along a unique axis; the structure is distorted from tetragonal to orthorhombic with the oxygen on the orthorhombic *b*-axis sites.²⁴ At $y=0.5$, the oxygen atoms order on every other chain of *b*-axis sites.²⁵ Oxidation of the CuO_2 sheets to induce superconductivity occurs on oxygen ordering in the interval $y > 0.45$; the interval

$0.27 < y < 0.45$ is marked by a transition from the tetragonal, antiferromagnetic semiconductive phase occurring in the interval $0.00 \lesssim y \lesssim 0.27$ to the orthorhombic, superconductive phase found for $0.45 \leq y \leq 0.95$.²³ Ordering of the oxygen on *b*-axis sites of alternate chains at $y=0.5$ yields Cu^+ at half the Cu(1) sites (those with only twofold oxygen coordination) and Cu^{2+} at the other half of the Cu(1) site (those with square-coplanar coordination); sufficient oxidizing power remains to oxidize the superconductive sheets up to 0.25 holes per Cu(2) atoms in fivefold oxygen coordination.²⁶ This level of oxidation of the CuO_2 sheets gives a superconductive critical temperature of $T_c \approx 60$ K. Full oxidation to $y=0.95$ gives a $T_c \approx 90$ K, which appears to be close to the saturation value for this structure.

Low-temperature preparation yielded a tetragonal sample with $y=0.7$ that was a semiconductor; all of the mobile holes of the CuO_2 sheets were trapped out at the Cu(1) sites neighboring *a*-axis oxygen. Removal of the *a*-axis oxygen required an 800°C N_2 anneal; only after such an anneal did reoxidation result in an orthorhombic superconductor.²⁷

Experiments on the system $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_{2-\eta}\text{La}_\eta\text{Cu}_3\text{O}_{6+y}$ have shown, for $z=0.00$, that an $\eta > 0$ can stabilize a $y > 1$ and that each oxygen that occupies an *a*-axis site not only reduces the orthorhombic distortion, but also traps out two holes from the CuO_2 sheets to the Cu(1)O_y planes, thus lowering T_c (Ref. 28)—which appears to vary with the hole concentration in the CuO_2 sheets.²⁹ In the absence of Ca^{2+} in the $\text{Y}_{1-z}\text{Ca}_z$ planes, any fivefold-coordinated Cu(1) copper competes successfully with the Cu(2) copper for oxidation beyond Cu^{2+} ; however, the introduction of Ca^{2+} modulates this competition.²¹ With or without Ca, macroscopically tetragonal phases containing *a*-site oxygen are obtained that retain superconductivity, but with a reduced T_c , for compositions with $y > 1.0$. It is this general situation that is modified by the substitution of *M* atoms for copper in this structure.

B. Cobalt valence and spin state

In oxides, cobalt is found as high-spin Co^{2+} or Co^{3+} and as low-spin Co^{III} or Co^{IV} . In the presence of Cu^{2+} we should normally anticipate Co^{3+} or Co^{III} ; and a low-spin Co^{III} may be stabilized in sixfold oxygen coordination, but not in fivefold oxygen coordination. An intermediate spin state is probable on trivalent cobalt in square-coplanar coordination. In the presence of Cu^{III} , a low-spin Co^{IV} may be stabilized in sixfold oxygen coordination. With this background knowledge of cobalt in oxides, we are in a position to interpret our results given the assumption that—as in the parent oxides $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2\text{Cu}_3\text{O}_{6+y}$ —among the oxygen atoms only those of the Cu(1)O_y planes are variable in position and concentration at room temperature in an annealed sample. Of course, the *c*-axis positions of the apical oxygen bridging the Cu(1) and Cu(2) positions are also variable;³⁰ but we assume these positions do not drive the properties observed, they respond to them.

The spread of reported magnetic moments for cobalt

and the deviations in Curie-Weiss behavior found for $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$ indicate that the susceptibility data above T_c is very sensitive to cobalt distribution and oxygen coordination as well as to possible low-spin to high-spin transitions on trivalent cobalt. Reported effective magnetic moments of 3.4 to $3.8\mu_B$ per cobalt atom^{2,4} are intermediate between low-spin ($0\mu_B$) and high-spin ($\sim 4.8\mu_B$) values for trivalent cobalt. Our ^{57}Co Mössbauer data show that the site occupancy and the oxygen coordination at a Cu(1) site can be modified by different heat treatments, so the observed variations in μ_{eff} per cobalt ion in $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$ are not surprising, especially in view of difficulties associated with subtraction of the copper-ion contribution.

C. Superconductive pair breaking by Co^{3+}

The Δ_{IS} and magnetic hyperfine field (H_{eff}) of subspectrum *C* (Ref. 31) correspond to a high-spin Fe^{3+} daughter and have been assigned to a high-spin Co^{3+} at a Cu(2) site. A high-spin Co^{3+} ion at a Cu(2) site can be expected to suppress superconductivity via breaking of the superconductive pairs. In Tables I and II we report data that show an increase in T_0 in tetragonal $\text{YBa}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ upon Co migration—from the distribution after treatment [O] to that after [NO]—from Cu(2) to Cu(1) sites. Although it can be argued that the appearance of fivefold-coordinated Co at the surface of the Co clusters after treatment [NO]—subspectrum *D*—is removing fivefold-coordinated Cu(1) at which mobile holes are trapped, these results would seem to provide unambiguous evidence for the suppression of T_c by Co^{3+} ions on Cu(2) sites. The increase in the superconductive transition width ΔT_c (Table I) of samples treated by method [NO] relative to those treated by method [O] is indicative of an increased inhomogeneity of the Co distribution on the Cu(2) sites. We note that the increase in T_c with Ca substitution in $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ is opposite to that observed in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6+y}$ (Ref. 11) prepared by a treatment similar to our method [O]; however, in the latter system T_c decreases with further increased occupancy of the Cu(2) sites, which is promoted by a reduction protocol (method [NO]), by high-spin Fe^{3+} cations.

D. Observation of a $^{57}\text{Fe}^{4+}$ daughter

The isomer shifts of the ^{57}Fe in (1)4 and (1)6 environments (subspectra *A*, *B*, and *E*) follow the general systematics³² of intermediate-spin and low-spin Fe^{III} , respectively, and thus correspond to an intermediate-spin and low-spin Co^{III} parent, as was anticipated for Co in square-coplanar and sixfold oxygen coordinations. However, the isomer shift of the ^{57}Fe daughter in the (1)5 environment (subspectrum *D*) is not intermediate between that of (1)4 and (1)6 environments, as might be expected, but is much less. From isomer shift systematics, this observation implies that the ^{57}Fe daughter is in a more positive valence state in (1)5 than in (1)4 or (1)6 coordination. Therefore we need to argue how a $^{57}\text{Co}^{3+}$ parent can

yield a $^{57}\text{Fe}^{4+}$ daughter at a (1)5 site in preference to any other site.

Capture of an inner-shell electron by a $^{57}\text{Co}^{m+}$ nucleus transforms the $^{57}\text{Co}^{m+}$ species into a $^{57}\text{Fe}^{m+}$ ion having an inner-shell hole in its electronic structure. This event is followed by an electron-vacancy cascade that generates an Auger-electron cascade, which leaves the probe atom in an ionized $^{57}\text{Fe}^{(m+n)+}$ state. If the ejected Auger electrons are not recaptured within the ca. 10^{-7} s before the emission of a 14.4-keV- γ ray, the event monitored in the present experiment, the probe exhibits the spectrum of a more positive ionic state. $^{57}\text{Fe}^{3+}$ and $^{57}\text{Fe}^{2+}$ daughter ions of $^{57}\text{Co}^{2+}$ -ion probes have been observed in emission studies of ^{57}CoO (Ref. 33) and the $^{57}\text{Fe}^{4+}$ daughter of a $^{57}\text{Co}^{3+}$ -ion probe has been observed in the emission spectrum of $\text{La}_2\text{Li}_{0.5}\text{Co}_{0.5}\text{O}_4$.³⁴ In the present case, the distorted symmetry of the high-spin $^{57}\text{Co}^{3+}$ probe in fivefold oxygen coordination can drive the highest energy level of the $^{57}\text{Fe}^{4+}$ daughter above any band in the Cu-O array provided the shortest Cu-O distances are short enough. In this situation, the $^{57}\text{Fe}^{4+}$ daughter cannot recapture an electron to become Fe^{3+} within 10^{-7} s, and an isomer shift corresponding to high-spin Fe^{4+} is observed. At a (1)5 site, the highest energy state is a linear combination of the $d_{z^2-y^2}$ and d_{z^2} orbitals (x, y, z axes parallel to crystallographic a, b, c axes), and the Cu(1)-O(4) bond length along the c axis is particularly short. The highest energy state at a (2)5 site is the $d_{x^2-y^2}$ orbital, which is associated with a somewhat longer mean Cu-O bond length. It would appear that the difference in mean Cu-O bond length and also the Madelung energy discriminates between (1)5 and (2)5 sites; the (2)5 Co^{3+} yields a high-spin $^{57}\text{Fe}^{3+}$ daughter. The observation of an intermediate-spin Fe^{3+} daughter, instead of a Fe^{4+} daughter for a $^{57}\text{Co}^{3+}$ parent, in the unsymmetrical (1)4 site appears to be due to the lower Madelung potential and covalency of fourfold coordination. These two factors lower the energy of the antibonding state of the (1)4 site relative to that in the (1)5 environment making possible an intermediate-spin Fe^{3+} daughter.

E. Evolution of the Co microstructure in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$

The Mössbauer data show that the microstructural arrangements of Co in $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$ are different in a microdoped (parts per million level) sample than in the sample with $x=0.10$. In the microdoped samples, the Co are randomly distributed; in the $x=0.10$ samples there is evidence of Co clustering.

Subspectra *A*, *C*, and *D* are predominantly observed in the fully oxygenated microdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ (^{57}Co) samples.³⁵ These spectra correspond, respectively, to (1)4 square-coplanar and (2)5, (1)5 square-pyramidal environments. The Co^{3+} ions are more stable in fivefold than in fourfold coordination, and it appears that even the microdoped samples trap some oxygen in a -site positions to accommodate Co^{3+} ions in Cu(1) sites in a higher oxygen coordination. However, it should be noted that an a -site oxygen that bridges a (1)5 cobalt on one side and a Cu(1) atom on the other creates a fivefold-coordinated Cu(1)

that can compete for a hole in the CuO_2 sheets, thereby lowering T_c . It is therefore difficult with microdoped samples to distinguish the influence on T_c of hole trapping in the Cu(1)O_y planes from any pair breaking by Co in Cu(2) sites.

On the other hand, in $\text{YBa}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ (^{57}Co) treated by method [O], we observe Co in (1)6 as well as (1)4 and (2)5 environments. The relatively few Co in a (1)4 environment are probably isolated as in the microdoped case; the appearance of (1)6 in place of (1)5 Co implies the introduction of Co clustering in which excess oxygen on a -axis sites bridge two (1)5 Co to create two (1)6 cobalt instead. A schematic representation of a possible cluster is shown in Fig. 4(a).

Treatment by protocol [O] of $\text{Y}_{0.95}\text{Ca}_{0.05}\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ gives a smaller oxygen concentration y than in the case $z = 0.00$. Nevertheless it appears to eliminate Co from the (1)4 configuration—subspectrum A is missing—and to reduce the (2)5 population—subspectrum C ; the increased concentration of cobalt on Cu(1) sites apparently resides in larger Co clusters containing two (1)6 configurations—subspectra B and E —as well as some (1)5 configurations. The new (1)6 subspectrum E has a smaller quadrupole splitting (~ 0.30 mm/s) than that of subspectrum B (~ 0.55 mm/s), which implies a more symmetric (1)6 environment. The appearance of the (1)5 subspectrum D indicates that the morphology of at least some of the clusters has changed from one containing only (1)6 cobalt—as in Fig. 4(a)—to one containing (1)5 cobalt at the surface of a cluster. This situation is illustrated in Fig. 4(b). The (1)6 cobalt in the center of the cluster of Fig. 4(b) has a more symmetric environment than the (1)6 cobalt in the cluster of Fig. 4(a). This change in morphology, which is accompanied by a stripping of a -axis oxygen away from the cobalt at the surface of a cluster, is compatible with the constraint¹⁷ of a smaller value of y in the Ca-substituted samples.

The observation that reduction via a nitrogen

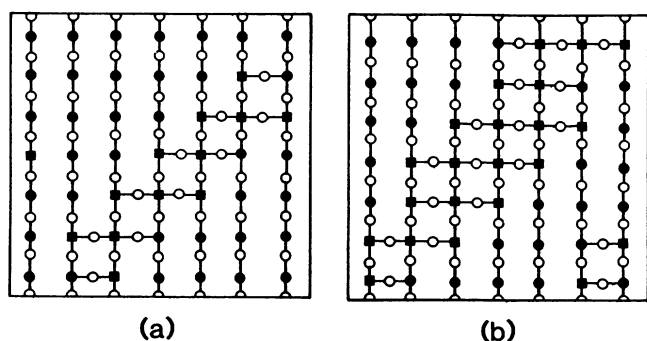


FIG. 4. Schematic representation of Co clusters in the Cu(1)O_y sheets of $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ for (a) $z = 0.00$ and (b) $z = 0.05$. The solid circles, open circles, and solid squares represent the copper, oxygen, and cobalt ions, respectively. The figure is one example of many possible Co morphologies. Note the isolated (1)4 environment in (a), the qualitatively different (1)6 environments in (b), and the fivefold-coordinated copper atoms.

anneal—treatment [N]—induces a migration of cobalt from Cu(2) to Cu(1) sites would seem to be at odds with the known preference of trivalent cobalt for sixfold oxygen coordination. However, although treatment [N] reduces the oxygen concentration y , nevertheless the Mössbauer data confirm that all the Co atoms have only fivefold or sixfold coordination after treatment [N]. Retention of a $y \approx 0.62$ – 0.66 (Table I) shows that the Co atoms on Cu(1) sites bind oxygen. Clearly the anneal has increased the size, if not the number, of Co-atom clusters in the Cu(1)O_y planes. Given the evidence for some Co-atom clusters after treatment [O] in our samples and the apparent lack of mobility²⁷ of a -axis oxygen at $T < 800^\circ\text{C}$ in disordered $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$, the stability of the Co-atom clusters in a 700°C N_2 anneal is not surprising; however, the observation of a growth of these clusters by transfer of Co from Cu(2) to Cu(1) sites is noteworthy.

The involvement of the c -axis oxygen O(4) in the insertion (extraction) of oxygen into (from) the Cu(1)O_y planes has been confirmed by oxygen isotope exchange.³⁶ More direct confirmation comes from neutron diffraction³⁷ on disordered $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$ samples²⁷ that show the presence of a considerable concentration of O(4) vacancies. Removal of an apical O(4) from a Co^{3+} ion at a Cu(2) site would place the Co^{3+} ion in an unfavorable square-coplanar coordination; exchange with a Cu(1) at the surface of a Co-atom cluster would place the Co in a more favorable oxygen coordination. For $z = 0.00$, reduction seems to add a cobalt to the surface of a cluster of the type shown in Fig. 4(a) so as to create (1)5 species; in the $z = 0.05$ sample, reduction also increases the percentage of (1)5 species and decreases only slightly the concentration of (1)6 cobalt atoms in the more symmetric environments. The fairly broad linewidth of subspectrum D ($\text{FWHM} = 0.80$ mm/s) is indicative of the multiple near-neighbor environments possible for a (1)5 site.

Subsequent oxidation, treatment [NO], further decreases the percentage of Co on Cu(2) sites in the $z = 0.00$ sample; it does not change the small percentage occupancy in the $z = 0.05$ sample. A modest increase in the (1)6 percentage in the $z = 0.00$ sample contrasts with little change in the $z = 0.05$ sample; these data indicate not only a further growth of cluster size with cobalt transfer from Cu(2) to Cu(1) sites, but also that the majority of oxygen reintroduced in the last step contribute primarily to a reoxidation of copper without any significant increase in the mean oxygen coordination at a cobalt atom. The final oxygen contents of both materials ($z = 0.00, 0.05$) are nearly identical ($y \approx 1.15$) even though the initial stoichiometries (see Table I) and final Co-cluster morphologies are different. This result is probably fortuitous; however, the larger increase in T_0 for the $z = 0.00$ sample despite a smaller increase in y on going from [O] to [NO] would seem to reflect the greater decrease in Co concentration on Cu(2) sites. This observation is consistent with a more important suppression of T_c by Co on the Cu(2) sites than by Co on the Cu(1) sites.

The evolution of the bulk microstructure in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$ (^{57}Co) with preparation conditions [O], [N], and [NO] is quite different

from that reported by Nath *et al.*¹⁵ for microdoped $\text{YBa}_2\text{Cu}_3\text{O}_{6+y}$ (^{57}Co). No evidence for Co clustering was found for the latter system; the dominant species observed in oxygenated ($y=0.87$) and depleted ($y=0.00$) samples were (1)4—subspectrum *A*—and an interstitial site denoted as *M'* with room-temperature parameters $\Delta_{\text{IS}}=0.3$ mm/s and $\Delta E_Q=0.56$ mm/s. We do not observe subspectrum *M'*; Nath *et al.*¹⁵ have indicated that this site forms under fast cooling ($\geq 20^\circ\text{C}/\text{min}$) from high temperatures ($\sim 950^\circ\text{C}$). Our cooling rate was much slower ($\sim 5^\circ\text{C}/\text{min}$) from a lower temperature (700°C); these are more favorable conditions for cluster formation—especially with a higher cobalt concentration. Renevier *et al.*,¹⁶ in their study of nominal $\text{YBa}_2(\text{Cu}_{0.94}\text{Co}_{0.06})_3\text{O}_{6+y}$, did not specify the cooling rate from their N_2 anneals. However, their observation of orthorhombic—versus tetragonal—symmetry, a similar $T_c \approx 65$ K before and after an [NO] treatment and a transition midpoint ~ 10 K lower after treatment [NO] are all consistent with little Co clustering, smaller Co concentrations on the Cu(2) sites, and fewer fivefold-coordinated sites.

We note that the $z=0.00$ sample under preparation [O] has a higher Co occupancy of the Cu(2) site than previously reported^{12,13} for bulk Co-doped samples. This unusual phenomenology may be a result of our preparation technique or may represent a nonequilibrium condition. However, this observation does not detract from the trend of increasing Co occupancy of the Cu(1) site and further cluster formation in bulk samples under reducing conditions evident in our experiments. Further experiments involving different amounts of cobalt doping (x) and anneal protocols would help clarify the extent, if any, of nonequilibrium conditions on Co site occupancy and its effects on superconducting properties in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$.

F. Comparison of *M* (*M*=Fe, Co) site occupancy in $\text{YBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{6+y}$

In contrast to the $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$ system reported here, the $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{6+y}$ system reported previously^{2,7,8} behaved quite differently. Reduction in N_2 at 800°C of samples with $0.03 \leq x \leq 0.15$ resulted in a smaller value of y ; the Fe atoms apparently did not cluster in the original treatment [O] and the oxygen atoms in the Cu(1) O_y planes, including any *a*-axis oxygen, were mobile at 800°C . As a result, Fe atoms were transferred from Cu(1) to Cu(2) sites in treatment [N] at 800°C , and the Fe atoms remaining on Cu(1) sites formed clusters of (1)3 Fe^{3+} sharing either a *b*-axis or *a*-axis oxygen in an oxygen-depleted Cu(1) O_y layer. The relative instability of a (1)3 environment for Fe^{3+} versus Cu^{2+} favors displacement of the Fe^{3+} ions from Cu(1) to Cu(2) sites. Upon reoxygenation in treatment [NO], orthorhombic materials with clusters of (1)5 atoms are formed; an increase in T_c and a narrower ΔT_c with increased occupancy of the Cu(2) planes appears to be a consequence of the formation of Fe-rich regions containing Fe clusters and Fe-poor regions. The former regions appear to be normal—flux-pinning¹⁰—regions within superconducting

Fe-poor regions. Such a segregation is compatible with a metastability of compositions transitional between localized-electron states with antiferromagnetic order (or spin fluctuations) and itinerant-electron states capable of forming Cooper pairs at lowest temperatures.³⁸

V. CONCLUSIONS

Use of ^{57}Co emission Mössbauer spectroscopy as a microprobe of the cobalt distribution in $\text{Y}_{1-z}\text{Ca}_z\text{Ba}_2(\text{Cu}_{0.90}\text{Co}_{0.10})_3\text{O}_{6+y}$, $z=0.00$ and 0.05 , has permitted identification of the variation in Co distribution on Cu(2) versus Cu(1) sites after three different annealing procedures: [O], [N], and [NO]. The following observations were made.

(1) Treatment [O] results in the formation of Co-atom clusters within the Cu(1) O_y planes; these clusters are larger—contain a greater fraction of subspectrum *E*—the larger the concentration of Co atoms in the Cu(1) sites. [Note that 30% of the Cu(1) sites would be occupied by Co were all the Co in the Cu(1) O_y planes.]

(2) Removal of some oxygen from the Cu(1) O_y planes either by introducing Ca^{2+} for Y^{3+} ($z=0.05$) or by reduction (treatment [N]) results in transfer of Co from the Cu(2) sheets to the Cu(1) O_y planes and increases the size of the Co-atom clusters.

(3) At temperatures $T \leq 800^\circ\text{C}$, the Co-atom clusters bind oxygen within the Cu(1) O_y planes, so every Co atom within a cluster has sixfold oxygen coordination and those at the surface have fivefold or sixfold oxygen coordination.

(4) A cobalt in sixfold coordination at the surface of a cluster creates a fivefold-coordinated Cu(1) atom that may trap a mobile hole from the CuO_2 sheets. This situation introduces an ambiguity as to the effectiveness of superconductive pair breaking by Co atoms.

(5) An increase in both the onset temperature T_0 and ΔT_c with transfer of Co atoms from Cu(2) to Cu(1) sites after [NO] is interpreted to indicate that Co^{3+} ions at Cu(2) sites suppress T_c and that the transfer of Co from Cu(2) to Cu(1) sites is inhomogeneous.

(6) Observation of a high-spin $^{57}\text{Fe}^{4+}$ daughter for high-spin Co^{3+} at a (1)5 site—but not for high-spin Co^{3+} at a (2)5 site—is attributed to a short mean Cu-O bond length for the least stable antibonding orbital in the fivefold-coordinated site and to a lower symmetry at fivefold versus sixfold coordination that allows formation of a shorter mean Cu-O bond length for one orbital.

Finally, we also speculate that the mobility of the *c*-axis O(4) oxygen atoms contributes, under reducing conditions, to the migration of Co from the Cu(2) to the Cu(1) sites.

Note added in proof. Katsuyama *et al.*³⁹ report on the effects of an 800°C nitrogen anneal followed by a low-temperature oxygen anneal on the Co site occupancy, crystal symmetry, and T_c of $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_{6+y}$ ($0 \leq x \leq 0.33$). They find materials with orthorhombic symmetry ($x \leq 0.12$), higher Co occupancy of the Cu(2) site, lower superconducting transition midpoints, and

broader transition widths ΔT_c (10–90 %) relative to the parent materials. These results are consistent with ours and Renevier *et al.*¹⁶ The broader ΔT_c are consistent with a larger random distribution of Co on the Cu(2) sites. Also, we have recently shown that Co clusters form in the Cu(1)O_y plane of ⁵⁷Co microdoped (ppm) Y_{1-z}Ca_zBa₂Cu₃O_{6+y} when prepared at lower temperatures.⁴⁰ These results extend the range of Co clustering to lightly doped samples. Segregation of Co in Y_{1-z}Ca_zBa₂(Cu_{1-x}Co_x)₃O_{6+y} to form flux-pinning Co-

atom clusters without serious depression of T_c should be feasible.

ACKNOWLEDGMENTS

We thank the NSF, Texas Advanced Research Program, and the R. A. Welch Foundation, Houston, Texas, for financial support. Work performed at Los Alamos National Laboratory was done under the auspices of the U.S. Department of Energy.

- ¹G. Xiao, M. Z. Cieplak, A. Gavrin, F. H. Streitz, A. Bakhshai, and C. L. Chien, *Phys. Rev. Lett.* **60**, 1446 (1988).
- ²Y. K. Tao, J. S. Swinnea, A. Manthiram, J. S. Kim, J. B. Goodenough, and H. Steinfink, *J. Mater. Res.* **3**, 248 (1988).
- ³M. G. Smith, J. Zhang, and H. Oesterreicher, *Mat. Res. Bull.* **23**, 563 (1988).
- ⁴J. 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).
- ⁵T. J. Kistenmacher, *Phys. Rev. B* **38**, 8862 (1988).
- ⁶N. Okazaki, S. Kambe, A. Kishi, N. Kanazawa, A. Ohtomo, A. Fukuoka, T. Hasegawa, K. Kishio, K. Kitazawa, and K. Fueki, in *Proceedings of the 1988 Materials Research Society International Meeting on Advanced Materials*, Tokyo, 1988 (Materials Research Society, Pittsburgh, 1988), p. 737.
- ⁷S. Katsuyama, Y. Ueda, and K. Kosuge, *Physica C* **165**, 404 (1990).
- ⁸M. G. Smith, R. D. Taylor, and H. Oesterreicher, *Phys. Rev. B* **42**, 4202 (1990); H. Oesterreicher, M. G. Smith, and R. D. Taylor, *Proceedings of the ICM Conference*, Garmisch-Partenkirchen (1990) (unpublished).
- ⁹L. T. Romano, M. G. Smith, H. Oesterreicher, and R. D. Taylor, *Phys. Rev. B* **45**, 8012 (1992).
- ¹⁰M. G. Smith, H. Oesterreicher, M. P. Maley, and R. D. Taylor (unpublished).
- ¹¹M. G. Smith, R. D. Taylor, and H. Oesterreicher, *J. Appl. Phys.* **69**, 4894 (1991).
- ¹²R. S. Howland, T. H. Geballe, S. S. Laderman, A. Fischer-Colbrie, M. Scott, J. M. Tarascon, and P. Barboux, *Phys. Rev. B* **39**, 9017 (1989).
- ¹³C. Y. Young, A. R. Moodenbaugh, Y. L. Wang, Y. Xu, S. M. Heald, D. O. Welch, M. Suenaga, D. A. Fischer, and J. E. Penner-Hahn, *Phys. Rev. B* **42**, 2231 (1990).
- ¹⁴A. Nath, S. Nagy, M. Barsoum, S. D. Tyagi, and Y. Wei, *Solid State Commun.* **68**, 181 (1988).
- ¹⁵A. Nath, Z. Hommonay, S. D. Tyagi, Y. Wei, G. Jang, and C. C. Chan, *Physica C* **171**, 406 (1990).
- ¹⁶H. Renevier, J. L. Hodeau, T. Fournier, P. Strobel, M. Marezio, J. C. Martinez, and J. J. Prejean, *J. Less-Common Met.* **164&165**, 907 (1990).
- ¹⁷A. Manthiram, S. J. Lee, and J. B. Goodenough, *J. Solid State Chem.* **73**, 278 (1988).
- ¹⁸Y. Xu, R. L. Sabatini, A. R. Moodenbaugh, Y. Zhu, S.-G. Shyu, M. Suenaga, K. W. Dennis, and R. W. McCallum, *Physica C* **169**, 205 (1990).
- ¹⁹P. Boolchand and D. McDaniel, in *Studies of High Temperature Superconductors*, edited by A. V. Narlikar (Nova Science, New York, 1990), Vol. 4, p. 143.
- ²⁰D. Hechel, I. Nowik, E. R. Bauminger, and I. Felner, *Phys. Rev. B* **42**, 2166 (1990).
- ²¹A. Manthiram and J. B. Goodenough, *Physica C* **159**, 760 (1989).
- ²²A. Manthiram, J. S. Swinnea, Z. T. Sui, H. Steinfink, and J. B. Goodenough, *J. Am. Chem. Soc.* **109**, 6667 (1987).
- ²³R. J. Cava, B. Batlogg, C. H. Chien, E. A. Rietman, S. M. Zahurak, and D. Weider, *Nature (London)* **329**, 423 (1987); *Phys. Rev. B* **36**, 5719 (1987).
- ²⁴J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **36**, 3608 (1987).
- ²⁵C. Chaillout, M. B. Alario-Franco, J. J. Capponi, J. Chénavas, P. Strobel, and M. Marezio, *Solid State Commun.* **65**, 283 (1988).
- ²⁶J. B. Goodenough, in *Workshop on the Materials Science of High-T_c Superconductors—Magnetic Interactions* [*J. Mater. Ed.* **9**, 618 (1988)].
- ²⁷A. Manthiram and J. B. Goodenough, *Nature (London)* **329**, 701 (1987).
- ²⁸A. Manthiram, X. X. Tang, and J. B. Goodenough, *Phys. Rev. B* **37**, 3734 (1988).
- ²⁹Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzari, *Phys. Rev. B* **38**, 7156 (1988).
- ³⁰R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. S. Peck, Jr., and L. W. Rupp, Jr., *Physica C* **165**, 419 (1990).
- ³¹L. Bottyán, B. Molnár, D. L. Nagy, I. S. Szűcs, J. Tóth, J. Dengler, G. Ritter, and J. Schöber, *Phys. Rev. B* **38**, 11 373 (1988).
- ³²N. N. Greenwood and T. C. Gibb, *Mössbauer Spectroscopy* (Chapman & Hall, London, 1971).
- ³³Ch. Song and J. G. Mullen, *Phys. Rev. B* **14**, 2761 (1976).
- ³⁴J. Fontcuberta, A. Fernandez, and J. B. Goodenough, *Phys. Rev. Lett.* **57**, 1931 (1986).
- ³⁵A. Nath and Z. Hommonay, *Physica C* **161**, 205 (1989).
- ³⁶W. K. Ham, S. W. Keller, J. N. Michaels, A. M. Stacy, D. Krillov, D. T. Hodul, and R. H. Fleming, *J. Mater. Res.* **4**, 504 (1989).
- ³⁷J. D. Jorgensen, A. Manthiram, and J. B. Goodenough (unpublished).
- ³⁸J. D. Jorgensen, B. Dabrowski, S. Pei, D. G. Hinks, and L. Soderholm, *Phys. Rev. B* **38**, 11 337 (1988).
- ³⁹S. Katsuyama, S. Nasu, Y. Ueda, and K. Kosuge, *J. Solid State Chem.* **97**, 466 (1992).
- ⁴⁰M. G. Smith, J. B. Goodenough, A. Manthiram, R. D. Taylor, and H. Oesterreicher, *J. Solid State Chem.* **99**, 140 (1992).