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Co Cluster Formation at Reduced Temperatures in Microdoped $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}(^{57}Co)$

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An investigation of the Co distribution in microdoped ^{57}Co (ppm) $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}$, $z = 0.00$ and $z = 0.05$, for different annealing treatments at reduced temperatures has been made with ^{57}Co-emission Mössbauer spectroscopy. ^{57}Co was first diffused into the lattice in oxygen at 650°C for 9 hr, 800°C for 0.5 hr, and 400°C for 3 hr (treatment [O]). This treatment resulted in Co substitution principally on the Cu(1) site in four-, five-, and sixfold coordination (denoted (1)4, (1)5, and (1)6, respectively). The (1)5 and (1)6 coordinations indicate cobalt atoms can cluster even at the ppm level of doping. Samples were next annealed at 700°C in N_2 (treatment [N]); they were finally annealed at 350°C in O_2 for 4 hr (treatment [NO]). Cobalt atoms migrate to Cu(1) from Cu(2) during treatment [N], and the Co in Cu(1) sites retain at least a (1)4 configuration even though most of the oxygen is lost from the $Cu(1)O_y$ planes. An analysis of the data allows the drawing of a number of conclusions about the oxygen coordination at Co atoms and the Co-atom mobility within the $Cu(1)O_y$ planes as a function of temperature and atmosphere. We conclude that suitable heat treatment should allow the formation of flux-pinning centers at Co-atom clusters without serious degradation of T_c, especially for $z > 0.05$.

Introduction

Subtle differences in synthetic procedures and subsequent heat treatments can modify the site occupancy and intrasite distribution of the metal M (M = Fe or Co) in macrodoped $YBa_2(Cu_{1-x}M_x)_3O_{6+y}$ (*1–3*). In particular, it appears that if a fully oxidized sample is subsequently annealed in N_2 at a temperature T_a, the M atoms tend to form clusters if T_a = 800°C for M = Fe and if T_a = 700°C for M = Co, but they do not for $T_a \geq 920$°C for M = Fe and T_a = 800°C for M = Co; on reoxidation at lower temperatures, T_c is higher than in the original samples where M-atom clusters are formed, but not where clusters are not formed (*3–6*). Moreover, in the reoxidized $YBa_2(Cu_{1-x}$

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$Fe_x)_3O_{6+y}$, $x \leq 0.10$, containing Fe-atom clusters, the microstructure showed relatively ordered twin planes (*7*) and an increase in the critical current density J_c relative to the original material synthesized by conventional methods (*8*). In addition, we (*3, 9*) have shown that the *M*-atom distribution can be modified by a partial substitution of Ca^{2+} for Y^{3+} in $Y_{1-z}Ca_zBa_2(Cu_{1-x}M_x)_3O_{6+y}$.

For technological applications, it is important to retain a high value of T_c and a small ΔT_c while introducing flux-pinning centers. This goal translates into a removal of the *M* atoms from the Cu(2) sites and/or the condensation of all *M* atoms into clusters. It is therefore relevant to ask whether and, if so, under what conditions *M*-atom clustering and migration from Cu(2) to Cu(1) sites occurs in microdoped samples. In the case of M = Fe, the lowest possible doping level observable with ^{57}Fe Mössbauer spectroscopy in a reasonable time is $x \approx 0.001$. However, Bottyán *et al.* (*10*) and Nath *et al.* (*11*) have shown that ^{57}Co doping on the 10–100 ppm level is observable by ^{57}Co-emission Mössbauer spectroscopy, and the data provide a useful probe of the character of the sites occupied by the Co atoms (*11–13*). However, in their studies the samples were treated at a $T_a \geq 800°C$ in an oxidizing atmosphere, and their data showed no evidence for Co clustering.

In this paper we explore the influence of a lower-temperature (650°C) oxygen anneal on microdoped $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}$ (^{57}Co); at 650°C in pure O_2, Jorgensen *et al.* (*14*) report a $y \approx 0.6$ with oxygen disordered within the Cu(1)O_y planes of $YBa_2Cu_3O_{6+y}$. A subsequent nitrogen anneal followed by reoxidation was similar to that used in our studies (*3*) of macrodoped $Y_{1-z}Ca_zBa_2(Cu_{1-x}Co_x)_3O_{6+y}$. We use ^{57}Co-emission Mössbauer spectroscopy to show that in microdoped materials (i) Co clusters can form, (ii) Co can be induced to migrate from the Cu(2) to the Cu(1) sites, and (iii) partial substitution of Ca^{2+} for Y^{3+} ($z = 0.05$) reduces Co occupancy of the Cu(2) sites and increases cluster size in the Cu(1)O_y planes. These results indicate that the superconductive properties of lightly doped ($x \leq 0.03$) $YBa_2(Cu_{1-x}Co_x)_3O_{6+y}$ may be favorably modified by suitable annealing procedures and counter-cation substitutions.

Experiment

$Y_{1-z}Ca_zBa_2Cu_3O_{6+y}$ (z = 0.00 and 0.05) pellets for ^{57}Co doping were prepared by conventional solid-state reaction. Stoichiometric amounts of dried Y_2O_3, $CaCO_3$, $BaCO_3$ and CuO were mixed in a mortar and pestle and pressed into pellets. The $z = 0.00$ sample was annealed at 925°C in air for 65 hr with two intermediate grindings and pressings, and the $z = 0.05$ sample was annealed at 925°C in air for 90 hr with three intermediate grindings and pressings. Both samples were then annealed at 400°C in flowing O_2 for 24 hr with slow cooling to room temperature. The phase purity of these samples (prior to ^{57}Co doping) was checked by X-ray powder diffraction with Cu$K\alpha$ radiation. Both samples could be indexed to the $YBa_2Cu_3O_{6+y}$ unit cell. No impurity phases were detected by X-ray diffraction. The superconductor transition temperature T_c of both samples was determined from magnetic-susceptibility data obtained on a SQUID magnetometer operating in an applied field of 100 Oe as a further check of phase formation. For the $x = 0.00$ sample T_c was 93(1) K and for the $x = 0.05$ sample T_c was 89(1) K. Both results are in good agreement with published data.

The carrier-free ^{57}Co acidic solution was neutralized before doping the samples. Approximately 2 mCi were added to the surface of two pellets of both samples. The solution easily diffused into the samples; this is probably due to the porous nature of the pellets. The local concentration of the ^{57}Co dopant of all of the samples was estimated to be

10–100 ppm. 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. 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 9 hr and then, to insure complete substitution, at 800°C for 0.5 hr. The pellets were finally slow cooled (5°C/min) to 400°C, annealed at this temperature under flowing oxygen for 3 hr, and quenched. The pellets were subsequently given two different thermal treatments. First, the pellets were annealed at 700°C in flowing N_2 for 4 hr and slow cooled (5°C/min) to room temperature in flowing N_2 (referred to as [N]). This treatment was then followed by annealing at 350°C for 4 hr with slow cooling ($\approx$ 1°C/min) to room temperature in flowing O_2 (referred to as [NO]). 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].

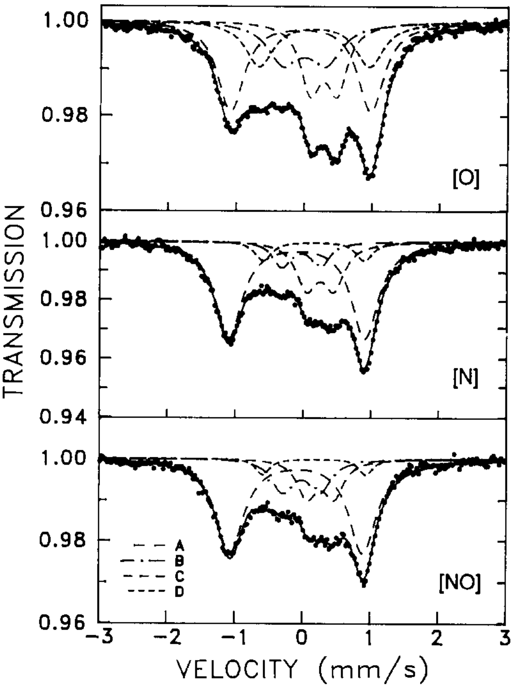

FIG. 1. Room-temperature ^{57}Co-emission Mössbauer spectra of $YBa_2Cu_3O_{6+y}$(^{57}Co) prepared by methods [O], [N], and [NO]. See text for details of synthesis. The velocity scale has been reversed to coincide with that of an absorption experiment.

Results

The room-temperature ^{57}Co-emission Mössbauer spectra of $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}$(^{57}Co) prepared by methods [O], [N], and [NO] are shown in Fig. (1) (z = 0.00) and Fig. 2 (z = 0.05). The data extracted by line fitting are summarized in Table I; they include isomer shifts (IS), quadrupole splittings (ΔE_Q), full-width-at-half-maximum linewidth (FWHM), and percent-spectral area (%) for the several subspectra that were identified. The IS values reported are relative to α-Fe at room temperature with signs corresponding to absorption measurments. No impurity phases, such as $^{57}CoCl_2$, $^{57}CoCO_3$, or cobalt (57) oxides, were observed in any of the emission spectra.

Subspectra A, C, and D have been reported in numerous places in the literature (*11, 15*) for ^{57}Co/^{57}Fe Mössbauer spectroscopy of Co-doped $YBa_2Cu_3O_{6+y}$. Subspectrum B was first observed (*3*) in $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$. For convenience, we denote Co with m-fold oxygen coordination in a Cu(n) site (n = 1 or 2) as (n)m. With this notation, subspectra A, B, and D have been assigned (*1–3, 10, 15*) to Co in (1)4 square-coplanar, (1)6 octahedral, and (1)5 square-pyramidal sites, respectively, and subspectrum C to Co in the (2)5 pyramidal site (*15*). (Nath *et al.* (*11*) assigned subspectrum C to Co in an unspecified interstitial site.)

The observation of Co in (1)6 sites, sub-

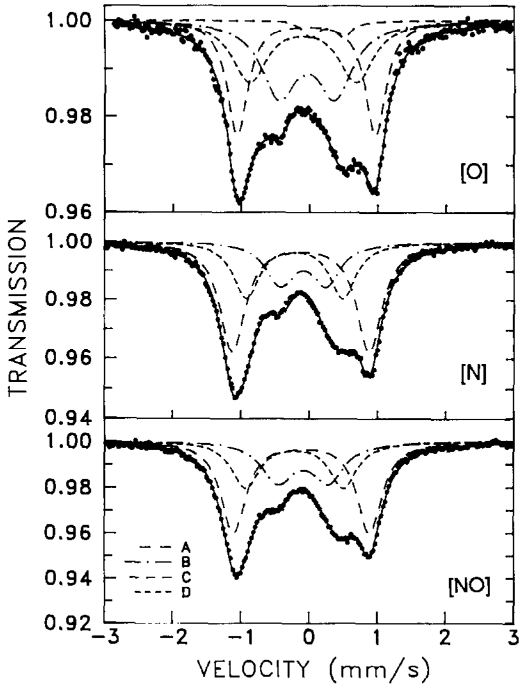

FIG. 2. Room-temperature ^{57}Co-emission Mössbauer spectra of $Y_{0.95}Ca_{0.05}Ba_2Cu_3O_{6+y}(^{57}Co)$ prepared by methods [O], [N], and [NO]. See text for details of synthesis. The velocity scale has been reversed to coincide with that of an absorption experiment.

spectrum B, is taken to signal the presence of Co clusters within a Cu(1)O_y plane. From Table I, it follows that Co clusters are already formed in thermal treatment [O] and that migration of Co from Cu(2) to Cu(1) sites occurs in treatments [N] and [NO]. Moreover, as in the macrodoped case (*3*), the substitution of Ca^{2+} for Y^{3+} sharply reduces the concentration of Co on Cu(2) sites. However, after treatment [NO], the reoxidized samples have a smaller percentage of Co in (1)5 and (1)6 sites, a strikingly larger percentage in (1)4 sites compared to the situation after treatment [O].

Discussion

Table II compares the Co distribution after treatment [O], in which $T_a \leq 800°C$, with that reported by Nath *et al.* (*13*) after annealing in O_2 at $T_a = 900°C$. Samples annealed at 900°C exhibit no (1)6 subspectrum, which means that any clustering is confined to only pairs of cobalt atoms whereas those annealed at 650°C with only a half-hour excursion to 800°C, treatment [O], show clear evidence of cluster formation within the Cu(1)O_y planes.

An understanding of the driving force for site changes and/or clustering begins with the oxygen insertion/extraction reactions occurring within the Cu(1)O_y planes of the structure (*3*). In undoped $YBa_2Cu_3O_{6+y}$, oxygen is reversibly inserted/extracted into/from the Cu(1)O_y sheets (*16*, *17*). Annealing treatments [O], [N], and [NO] change the value of y from 0.95 ± 0.01 after [O] to <0.1 after [N] and back to 0.95 ± 0.01 after [NO]. Two possible oxygen sites per Cu(1) atom in the plane make geometrically possible an oxygen content varying over the range $0 \leq y \leq 2$. This range is also possible chemically since Cu can be stabilized in linear, twofold coordination as Cu^{+}, in triangular coordination as Cu^{2+}, in square-coplanar or square-pyramidal coordination as Cu^{2+} or Cu^{3+}, and in octahedral coordination as Cu^{2+} or Cu^{3+}. However, the equilibrium oxygen content in 1 atm O_2 below 400°C appears to be $y = 0.95 \pm 0.01$. With half of the available sites empty, the oxygen atoms order in chains parallel to an orthorhombic *b*-axis; the *a*-axis sites are empty. At 400°C, extraction of oxygen to $y = 0.5$ proceeds by removing oxygen from every other *b*-axis chain (*18*); oxygen diffusion appears to occur within a chain via a rotation about the *a*-axis that interchanges *c*-axis and *b*-axis oxygen atoms (*19*). At higher temperatures, especially in N_2, the oxygen concentration parameter y is reduced and the oxygen atoms become disordered. At 650°C in 1 atm O_2, $y = 0.6$ and the oxygen atoms in the Cu(1)O_y planes are disordered (*14*). The order–disorder

TABLE I

Isomer Shifts (IS), Quadrupole Splittings (ΔE_Q), Full-Width-at-Half-Maximum Linewidths (FWHM) and Relative Spectral Areas (%) of Subspectra Observed in Room-Temperature ^{57}Co-Emission Mössbauer of $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}(^{57}Co)$

z	Treatment	Subspectra[a]	IS (mm/sec)	ΔE_Q (mm/sec)	FWHM (mm/sec)	%
0.00	[O]	A	−0.02(1)	2.07(4)	0.47(1)	39
		B	0.02(1)	0.62(4)	0.53(3)	20
		C	0.317(5)	0.40(2)	0.36(8)	22
		D	0.170(5)	1.6(1)	0.48(3)	19
	[N]	A	−0.068(6)	2.00(2)	0.48(1)	60
		B	−0.01(1)	0.56(4)	0.32(3)	11
		C	0.277(9)	0.40(2)	0.37(1)	21
		D	0.20(2)	1.52(6)	0.31(2)	8
	[NO]	A	−0.055(4)	1.96(1)	0.49(1)	60
		B	0.02(2)	0.55(4)	0.40(3)	16
		C	0.30(1)	0.39(4)	0.34(2)	17
		D	0.20(3)	1.52(9)	0.34(5)	7
0.05	[O]	A	−0.016(3)	2.02(2)	0.36(1)	33
		B	−0.013(1)	0.81(6)	0.60(2)	33
		C	0.29(1)	0.52(7)	0.29(2)	4
		D	−0.07(1)	1.54(9)	0.63(3)	30
	[N]	A	−0.089(2)	2.01(2)	0.45(1)	51
		B	−0.064(6)	0.68(3)	0.50(1)	21
		D	−0.19(4)	1.42(2)	0.47(1)	28
	[NO]	A	−0.075(3)	1.99(1)	0.43(1)	46
		B	−0.060(6)	0.73(3)	0.57(1)	26
		D	−0.181(5)	1.43(2)	0.50(2)	28

Note. Isomer shifts are relative to Fe metal at room temperature. See text for details of synthesis.

[a] A = (1)4, B = (1)6, C = (2)5, D = (1)5.

transition temperature decreases with y; at room temperature the oxygen are disordered for $y < 0.3$ (*16*).

Cobalt substitutes for copper in $YBa_2Cu_3O_{6+y}$: Co in the trivalent state (*3*); it is most stable in its low-spin state in sixfold coordination, but it can occupy fivefold or, in an intermediate spin state, square-coplanar coordination. Therefore the cobalt atoms tend to bind extra oxygen in the $Cu(1)O_y$ planes, which makes possible a $y > 1$ in macrodoped samples. In microdoped samples, any Co substituted for Cu(1) atoms hold their oxygen more strongly than do the Cu(1) atoms. We have experimental evidence for this fact. Nath *et al.* (*11*) have reported an increase in subspectrum C after an argon anneal at 800°C. They found no evidence of a (1)3 Co subspectrum. At 800°C in N_2 atmosphere, most of the oxygen atoms in the $Cu(1)O_y$ planes are lost, including the oxygen coordinating Co atoms on Cu(1) sites. Transformation of a (1)4 Co to a (1)3 Co leads to an exchange of the (1)3 Co with a Cu(2) atom since a (2)5 Co is more stable than a (1)3 Co. This exchange leads to an increase in subspectrum C. However, in our thermal treatments, any exchange of Co between Cu(2) and Cu(1) sites is from Cu(2) to Cu(1); subspectrum C decreases. Therefore

TABLE II

COMPARISON OF ROOM-TEMPERATURE Co-SITE OCCUPANCY((n)*m*) AND RELATIVE DISTRIBUTION (%) IN $YBa_2Cu_3O_{6+y}$(^{57}Co) INITIALLY PREPARED BY (A) HEAT TREATMENT [O] OF THIS WORK AND (B) THAT OF NATH *et al.* (*13*)

	Treatment[a]	((n)*m*)[b]	%
(A)	Neutralized $^{57}CoCl_2$ diffused into	(1)4	39
	$YBa_2Cu_3O_{6+y}$ pellets at RT	(1)5 sp	19
	Slow heating to 650°C in O_2	(1)6	20
	650°C in O_2 9 hr	(2)5	22
	800°C in O_2 0.5 hr		
	Slow cooled (5°C/min) to 400°C in O_2		
	Quenched		
(B)	$^{57}CoCl_2$ in ethanol diffused into	(1)4	50
	$YBa_2Cu_3O_{6+y}$ pellets at RT	(1)5 tbp	18
	Heating to 900°C in O_2	(1)5 sp	24
	900°C in O_2 6 hr	(2)5	8
	450°C in O_2 5 hr		
	375°C in O_2 2 hr		

Note. We denote Co with *m*-fold oxygen coordination in a Cu(*n*) site ($n = 1$ or 2) as (*n*)*m*.

[a] Initial diffusion was into pellets with $y \approx 0.95$.

[b] sp = square pyramidal; tbp = trigonal-bipyramidal; The (2)5 site of work B was proposed to be an interstital site by Nath *et al.* (*11*), however, location of this interstitial site was not specified.

the isolated (1)4 Co atoms hold their oxygen even though Jorgensen *et al.* (*14*) have reported a $y = 0.6$ with disordering of the oxygen in the $Cu(1)O_y$ planes at $T_a = 650°C$ in O_2 atmosphere for $YBa_2Cu_3O_{6+y}$. A $y \approx 0.6$ indicates that the mean coordination at a Cu(1) is only about 3 oxygen atoms.

Our data, Table I, further indicate that, in addition, at $T_a = 650°C$ in O_2 atmosphere the Co atoms on Cu(1) sites are mobile; they form clusters. The simplest cluster would be a pair of (1)4 Co bridged by a common oxygen atom in a Co_2O_7 unit. Two (1)5 Co may be bridged by a common "*a*-axis" oxygen to form a Co_2O_9 unit; and indeed formation of an isolated (1)5 Co may attract a (1)4 Co to form such a cluster. We take an "*a*-axis" in a tetragonal space group to be perpendicular to a local square-coplanar configuration. Any oxygen bridging two Co atoms can be expected to be particularly stable, and a driving force for cluster formation may be the stabilization of these bridging oxygen in a $Cu(1)O_y$ plane of mobile oxygen. We presume that any (1)6 cobalt has at least one bridging oxygen and therefore belongs to a cluster. We further assume in the discussion to follow that not only is a square-coplanar configuration stable in our heat treatments, but also an oxygen bridging two Co atoms is more stable than one that bridges a Co on one side and a Cu(1) on the other within a $Cu(1)O_y$ plane.

In microdoped samples, any clusters are restricted to small size, and it is possible to envisage a relatively large concentration of simple pairs of fivefold-coordinated Co as well as of isolated Co in (1)4 and (1)5 coordination. We can then account for the quite dramatic decrease in subspectrum D after treatment [N] for the $z = 0.00$ sample, Table I, if at $T_a = 700°C$ in N_2 the oxygen bridging two Co atoms are retained, but any "*a* – axis" oxygen bridging a Co and a Cu(1) atom in the $Cu(1)O_y$ plane is lost. In the $z = 0.05$ sample, a smaller decrease in subspectrum D after treatment [N] would appear to signal a much greater concentration of "*a*-axis" oxygen sharing two Co atoms within a cluster; and indeed the greater percentage of (1)6 species indicates a more developed cluster formation in the $z = 0.05$ sample.

The difference in the isomer shift of subspectrum D of the $z = 0.00$ and $z = 0.05$ samples indicates a subtle difference in the local coordination geometry of the (1)5 environment of the two samples. The greater Co occupancy of the $Cu(1)O_y$ sheets in the $z = 0.05$ sample implies a high concentration of shared "*a*-axis" oxygen between two cobalt atoms, whereas we can expect isolated (1)5 Co and shared "*a*-axis" oxygen with Cu in the $z = 0.00$ sample. The isomer shift in the $z = 0.00$ sample is typical of Fe^{3+} whereas the isomer shift in the $z = 0.05$ sample is typical of Fe^{4+}. The latter isomer shift was observed[3] in macrodoped $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$ ($z = 0.00$, 0.05) where "*a*-axis" oxygen is primarily shared between two Co atoms. We argued that a $^{57}Fe^{4+}$ daughter of the $^{57}Co^{3+}$ probe was made possible by the distorted symmetry of the (1)5 environment, which drives the highest energy state of the $^{57}Fe^{4+}$ daughter above any band in the Cu–O array. In this situation the daughter cannot recapture an electron to become Fe^{3+}, and an isomer shift corresponding to Fe^{4+} is observed. In the microdoped $z = 0.00$ case Cu antibonding electrons lengthen the Cu–O bond and shorten the Co–O bond in a Co–O–Cu "*a*-axis" bond. This shift of the bridging O atom would decrease the tetragonal component of the crystal field splitting and lower the level of the highest state below the highest occupied level of the Cu–O array. In this situation, the $^{57}Fe^{4+}$ daughter can recapture an electron to become $^{57}Fe^{3+}$, which would account for an observed isomer shift corresponding to Fe^{3+}.

In principle, one would expect to observe Co in (1)5 environments bridged by "*a*-axis" oxygen to Co and Cu in both the $z = 0.00$ and 0.05 samples. This was not observed. This implies that after treatment [O] the $z = 0.00$ sample contains a high concentration of isolated (1)5 Co and, hence, primarily "*a*-axis" oxygen bridging Co and Cu atoms. In contrast, the $z = 0.05$ sample contains a large concentration of paired (1)5 Co where the "*a*-axis" oxygen bridges two Co atoms. This deduction is consistent with a higher Co concentration on Cu(1) sites and a greater Co-atom clustering in the $z = 0.05$ sample. We do not speculate on why the Ca^{2+} substitution for Y^{3+} should drive the Co from the Cu(2) sites.

The preceding discussion suggests why the (1)5 environments and clusters of the $z = 0.05$ sample are more stable in the [N] treatment than those of the $z = 0.00$ sample. In the former case two cobalt atoms compete equally for the "*a*-axis" oxygen and increase its stability relative to "*a*-axis" oxygen bridged by a Co and Cu atom.

An interesting difference between the microdoped and macrodoped samples is the failure to regain the same level of (1)5 Co after treatment [NO] as was obtained with [O]; in the macrodoped case, the clusters were more developed (*3*). A $T_a = 350°C$ appears to be too low for Co diffusion, but at 700°C in N_2, treatment [N], a few "*a*-axis" oxygen bridging isolated pairs of Co atoms are lost with a subsequent dissociation of the pair. However, it would appear that at 350°C the oxygen in the $Cu(1)O_y$ planes are ordered with oxygen diffusion occurring within a chain so that displacement to "*a*-axis" positions does not occur.

The smaller size of the clusters in the microdoped samples is also manifest in the decrease in subspectrum B after treatment [NO]. Smaller clusters mean a larger concentration of Co on a cluster surface; loss of a nonbridging "*a*-axis" oxygen from a (1)6, (1)5 Co pair, for example, transforms a (1)6 Co to a (1)5 species. Similarly, loss of a nonbridging "*a*-axis" oxygen from a isolated (1)5 Co transforms it to a (1)4 Co. With our assumption that preferentially the "*a*-axis" oxygen not bridging two Co atoms are lost from the Co at 700°C in N_2, treatment [N], we conclude that the $z = 0.05$ samples contain a relatively high concentration of nonbridging *a*-axis oxygen at (1)6 Co located at cluster surfaces.

Conclusions

From ^{57}Co emission Mössbauer spectroscopy on microdoped $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}(^{57}Co)$ with $z = 0.00$ or 0.05, we can deduce the following:

1. The Co atoms may occupy (2)5, (1)4, (1)5, or (1)6 sites, but not (1)3 or (1)2 positions. The subspectra reported by Nath *et al.* (*13*) and interpreted by them to be (1)5 trigonal prismatic cobalt, Table II, were not observed by us; whether they represent Co at twin planes or some other defect remains undetermined.

2. In heat treatments with $T_a \leq 800°C$ in O_2 or $T_a \leq 700°C$ in N_2, the Co atoms on Cu(1) sites hold a square-coplanar coordination of oxygen atoms even though most of the oxygen of a Cu(1)O_y plane may be lost; and reoxidation by slow cooling in O_2 atmosphere to 400°C may result in the introduction of "*a*-axis" oxygen so as to create (1)5 Co species and some Co-atom clustering. Given disordered orientations of isolated (1)4 Co configurations in the tetragonal phase, ordering of the oxygen atom of a Cu(1)O_y plane in an orthorhombic reoxidized phase, treatment [O], would create some (1)5 Co while leaving more (1)4 Co species.

3. Oxygen atoms bridging two Co atoms within a Co-atom cluster within the Cu(1)O_y planes are particularly stable; essentially they are not lost in the heat treatments of this paper. The stability of such a bridging oxygen could be a driving force for the formation of Co-atom clusters.

4. At 700°C in N_2 atmosphere, treatment [N], the "*a*-axis" oxygen bridging a Co and a Cu(1) atom is lost, which transforms isolated (1)5 Co to (1)4 Co and (1)6 Co at the surface of a cluster to (1)5 Co. At 800°C in argon atmosphere, Nath *et al.* (*11*), oxygens tend to be lost from (1)4 Co, which forces them to migrate to Cu(2) sites as (2)5 Co species rather than isolated (1)3 Co. However, (1)3 Co sharing a common oxygen, Katsuyama *et al.* (*20*), are stable at 800°C in N_2. At 350°C, reoxidation occurs via *b*-axis diffusion, and "*a*-axis" oxygen are not reintroduced to form a Co–O–Cu bridge.

5. At 650°C in O_2 atmosphere, there is an equilibrium distribution between isolated (2)5 and (1)4 Co, but cluster formation among Co within the Cu(1)O_y planes favors migration of Co from Cu(2) to Cu(1) sites. Moreover, at this temperature there is sufficient Co-atom mobility for Co-atom clustering, but, as in the macrodoped case (*3*), cluster formation is more developed in samples where Ca^{2+} is substituted for Y^{3+}

6. At 350°C in O_2 atmosphere, the oxygen in the Cu(1)O_y planes are mobile, but not the Co atoms.

7. Segregation of cobalt in $Y_{1-z}Ca_zBa_2(Cu_{1-x}Co_x)_3O_{6+y}$ to form flux-pinning Co-atom clusters without serious degradation of T_c should be feasible, especially in samples with $z \geq 0.05$.

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Note Added in Proof. After submission of this paper, we received a preprint of independent ^{57}Co-emission Mössbauer spectroscopy studies of microdoped $YBa_2Cu_3O_{6+y}(^{57}Co)$ and macrodoped $YBa_2(Cu_{1-x}Co_x)_3O_{6+y}$ by Katsuyama *et al.* (*20*) They investigated materials treated in a similar manner as ours, but at higher temperatures. Their microdoped $YBa_2Cu_3O_{6+y}(^{57}Co)$ sample was initially prepared at 900°C and slow cooled (14 hr) to room temperature in flowing oxygen. The sample was then annealed at 800°C and slow cooled (rate not specified) to room temperature in flowing nitrogen. They report a tetrahedral (1)4 site (IS = 0.05 mm/s, ΔE_Q = 1.94 mm/sec) with 7% occupancy, an unidentified (D7 in their notation) site (IS = 0.27 mm/sec, ΔE_Q = 0.96 mm/sec) with 13% occupancy, and a magnetically split (2)5 site with 80% occupancy. Nasu *et al.* (*21*) report the spectra of the original O_2-treated sample, however, they do not give details of site occupancies. The spectra reported by Nasu *et al.* (*21*) is similar to that of Nath *et al.* (*13*) To compare the data of Katsuyama *et al.* (*20*) with ours we assume that the initial Co distribution is similar to that of Nath *et al.* (*13*) (Table II) and that their site D7 corresponds to (1)3 Co in a Co–O–Co cluster. We (*2*) previously reported a (1)3 site (IS = 0.186(4) mm/sec, ΔE_Q = 1.35(1) mm/sec) in oxygen depleted ($y \sim 0.1$) $YBa_2(Cu_{0.94}Fe_{0.06})_3O_{6+y}$; and their anneal at 800°C in flowing N_2 should give a similar oxygen depeletion. Moreover, we identify the (1)4 Co as intermediate-spin Co^{3+} in a square-coplaner site rather than Co of unidentified valence in a tetrahedral site.

According to Nath *et al.* (*13*), an initial treatment at 900°C in O_2 with slow cooling to room temperature results in (1)5 Co sites that appear to be isolated—an *a*-axis oxygen bridging two Co atoms in adjacent chains. The absence of (1)6 sites signals that larger Co clustering does not occur in microdoped samples at 900°C; most of the Co are in isolated (1)4 or (2)5 sites

(Table II). At 800°C in N_2 oxygen atoms of a Co–O–Cu bridge—but not those of a Co–O–Co bridge—are lost, which results in an increase of (1)4 Co and the appearance of paired (1)3 Co sites. However, the isolated (1)3 Co sites are unstable, so the depletion of oxygen causes a migration of Co from Cu(1) to Cu(2) sites; this migration is manifest in a dramatic increase in the concentration of (2)5 Co. In contrast, our initial low-temperature (650°C) anneal in O_2 results in cluster formation with an a-axis oxygen bridging Co atoms of neighboring chains. Within the clusters (1)6 Co are present. A subsequent anneal in N_2 at 700°C leaves Co–O–Co bridges, so (1)5 Co are retained at the cluster surface.

Katsuyama *et al.* (*20*) also report Co clusters in macrodoped $YBa_2(Cu_{0.96}Co_{0.04})_3O_{6+y}$, as we (*3*) do in $Y_{1-z}Ca_zBa_2(Cu_{0.90}Co_{0.10})_3O_{6+y}$. Their samples, which were prepared at higher temperature (900°C in O_2 and 800°C in N_2, followed by a low-temperature O_2 anneal), have 40% occupancy of Co on the Cu(2) site (versus 26 and 9% for $z = 0.00$, and 0.05, respectively (*3*)) and 27% occupancy of Co in (1)6 coordination (versus 51 and 50% for $z = 0.00$, and 0.05, respectively (*3*)). These results, even though for different Co concentrations, show that low-temperature anneals in O_2 favor Co cluster formation in the $Cu(1)O_y$ sheets, which is consistent with the results reported in this paper on microdoped $Y_{1-z}Ca_zBa_2Cu_3O_{6+y}(^{57}Co)$.

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