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# Role of bond lengths in the 90-K superconductor: A neutron powder-diffraction study of $YBa_2Cu_{3-x}Co_xO_{7-y}$

P. F. Miceli, J. M. Tarascon, L. H. Greene, and P. Barboux
*Bell Communications Research, Red Bank, New Jersey 07701*

F. J. Rotella and J. D. Jorgensen
*Argonne National Laboratory, Argonne, Illinois 60439*

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We present the results of a neutron powder-diffraction study on $YBa_2Cu_{3-x}Co_xO_{7-y}$. We find that Co preferentially occupies the Cu(1) site, simultaneously attracting extra oxygen into these layers in an amount consistent with Co(III) replacing Cu(II). This compound displays a transition from orthorhombic-to-tetragonal structure for $x$ between 0.05 and 0.1, while $T_c$ decreases continuously and the compound becomes nonsuperconducting for $x = 0.4$. We note several important relationships between bond-length changes, which reflect charge transfer among the ions. Also, we find that $T_c$ changes systematically with the Cu—O bond length.

$YBa_2Cu_3O_{7-y}$ is superconducting[1] above 90 K and has a threefold stacked perovskite structure where the central perovskite unit contains Y while the two remaining units contain Ba. There exist two Cu sites, Cu(1) located between two Ba planes and Cu(2) located between the Y and Ba planes. Diffraction studies show that the structure is slightly orthorhombic with oxygen ordered along "chains" within the Cu(1) planes.[2-5] Vacuum annealing produces oxygen vacancies in the chains, which induce[6-8] an orthorhombic-to-tetragonal transition near $y \sim 0.5$. Neutron powder-diffraction studies on oxygen-deficient $YBa_2Cu_3O_{7-y}$, quenched from high temperatures, reveal that $T_c$ falls continuously as the oxygen transforms from ordered on the chains to disordered, with $T_c$ vanishing for the tetragonal structure, thus providing evidence that the chains may be important for superconductivity.[9] There has been an effort to perturb the structure through isomorphous substitutions[6,10-16] in order to investigate which structural features are relevant to high $T_c$. Magnetic rare-earth ions substituted[10] for Y in $YBa_2Cu_3O_{7-y}$ have essentially no effect on $T_c$, suggesting that superconductivity develops far from the Y site, near the Cu(1) site. Recently, 3$d$ transition-metal substitution[11-13,15,16] for Cu shows a diminution of $T_c$ as the doping concentration is increased. Substitution for Cu should provide the most sensitive information regarding the relationship between structure, chemistry, and high-temperature superconductivity, since, the above results suggest that Cu is involved in the superconducting activity. In this work, we present a neutron powder-diffraction study on $YBa_2Cu_{3-x}Co_xO_{7-y}$ to determine the structural properties of this compound.

As shown in Fig. 1, $T_c$ falls monotonically with increasing Co concentration and vanishes near $x = 0.4$. With the addition of Co, the structure transforms from orthorhombic to tetragonal for $x$ between 0.05 and 0.1. Thus, high-temperature superconductivity persists in a tetragonal structure, in the absence of long-range Cu—O chains, suggesting that these chains might not be essential for high $T_c$. Magnetic susceptibility measurements[15] show that the Co has a paramagnetic moment of $3.5\mu_B$ independent of $x$. However, magnetic interactions may not exclusively cause the diminution of $T_c$, since, we find that nonmagnetic ions such as Zn and Al also reduce $T_c$. In fact, both magnetic Ni and diamagnetic Zn affect $T_c$ in an identical manner. Alternatively, we present evidence that $T_c$ is affected by the nature of the chemical bonds.

Neutron powder diffraction was performed on two Co-doped samples for $x = 0.2$ and 0.8. We also studied these same samples when oxygen deficient after vacuum annealing. The details of sample preparation have been reported elsewhere.[15] $T_c$ (midpoints) were determined[15] resistively as well as by ac and dc susceptibility. The room-temperature, high-resolution, neutron powder-diffraction data were collected on the special environment powder diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The time-of-flight data obtained at a scattering angle of 150° were used for the analysis below. Both the neutron data

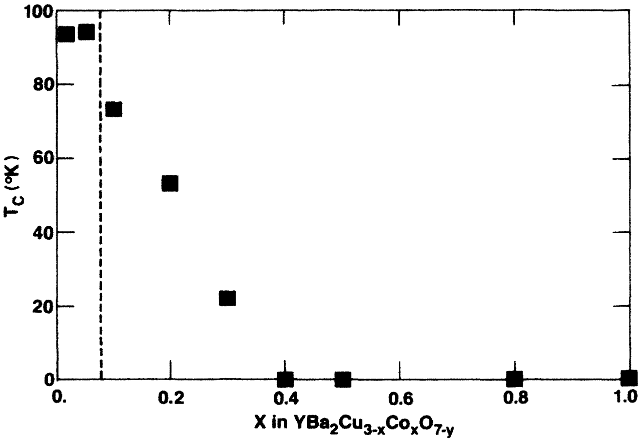

FIG. 1. Superconducting temperature $T_c$ as a function of Co concentration. The dashed line indicates the orthorhombic-to-tetragonal transition.

and previous x-ray diffraction show no evidence for impurity phases.

The powder-diffraction data were analyzed by the Rietveld technique[17] which allows the refinement of structural parameters. For all samples, the reflections could be indexed to the tetragonal *P4/mmm* space group. To include the effects of Co substitution, the occupancies of the Co and Cu were allowed to vary, independently, on both the Cu(1) and Cu(2) sites, subject to the constraint of complete occupancy for these sites. The occupancy of the O(1) site [in the Cu(1) plane] was also allowed to vary in the refinement. For future reference, we define the oxygen O(4) site as located directly above the Cu(1) site along the $c$ axis, and the oxygen O(2) sites lie within the Cu(2) plane. This site notation is given in Ref. 9.

The occupancies obtained from the refinement are shown in Table I. For $x=0.2$, the Co completely occupies the Cu(1) site, while for $x=0.8$ Co predominantly occupies the Cu(1) site with a small amount on the Cu(2) site. The $x$ values are in excellent agreement with the concentration expected from sample preparation and, since no impurity phases were observed, all of the Co is accounted for in the refinement.

Considering the oxygen annealed samples, the O(1) site occupancy increases as Co is substituted, indicating that the Co valence is higher than that of Cu in the Cu(1) sites. Similar behavior is also found for Al substitution[15,16] where the Al is a well-defined trivalent ion, therefore, Co(III) is likely in this case. The number of additional oxygens brought in by the Co may be used to determine the Cu(1) valence, $v_{\mathrm{Cu}(1)}$. The fraction of Co on the Cu(1) site, $f_{\mathrm{Co}(1)}$, times the difference in valence between Co(1) and Cu(1), $\Delta v$, is equal to twice the number of additional oxygen ($O^{2-}$): $\Delta v f_{\mathrm{Co}(1)}=2(y_0-y)$, where $7-y_0$ is the oxygen stoichiometry in the undoped material. From the occupancy data we obtain $7-y_0=6.93\pm0.03$ (i.e., $YBa_2Cu_3O_{7-y_0}$), and using Co(III), $v_{\mathrm{Cu}(1)}=1.98\pm0.14$. The Cu(2) valence, $v_{\mathrm{Cu}(2)}$, may be calculated from $v_{\mathrm{Cu}(1)}+2v_{\mathrm{Cu}(2)}=7-2y_0$ (derived from the chemical formula assuming $Ba^{2+}$, $Y^{3+}$, and $O^{2-}$) to obtain $v_{\mathrm{Cu}(2)}=2.44\pm0.08$. These estimates have neglected charge transfer between the Cu(2) and Cu(1) sites, as Co is added. However, our data show that the Ba moves away from Cu(1) towards Cu(2) with the addition of Co, suggesting a negative charge transfer. This would have the effect of lowering the estimated $v_{\mathrm{Cu}(1)}$. Since $v_{\mathrm{Cu}(1)}\leq 2$ is not likely, due to charge balance arguments, the observed Ba motion is probably a steric response and charge transfer between Cu sites is small.

TABLE I. Site occupancies found from neutron powder diffraction on $YBa_2Cu_{3-x}Co_xO_{6.93-y}$. The estimated standard deviation is given in parentheses.

| | Oxygen-annealed | | Vacuum-annealed | |
|---|---|---|---|---|
| Occupancy | $x=0.2$ | $x=0.8$ | $x=0.2$ | $x=0.8$ |
| $x$ | 0.22 (2) | 0.83 (2) | 0.20 | 0.82 (2) |
| Co(1) | 0.22 (1) | 0.73 (1) | 0.20 | 0.67 (1) |
| Co(2) | 0.00 (2) | 0.10 (2) | 0.00 | 0.15 (2) |
| O(1) | 1.04 (2) | 1.30 (2) | 0.45 (3) | 0.91 (2) |
| $-y$ | 0.11 (2) | 0.37 (2) | −0.48 (3) | −0.02 (2) |

An oxygen concentration of 6.93 is in general agreement with previous[2–4,7,14,15,18] neutron powder-diffraction experiments on oxygen-annealed $YBa_2Cu_3O_{7-y}$ which indicate values slightly less than 7.0, where only half of the available oxygen sites within the Cu(1) planes are filled. Furthermore, the Co-doped materials are tetragonal, yet they exhibit a large number of oxygen vacancies, which, if all were filled, would give an oxygen stoichiometry of 8.0. These facts suggest that the maximum oxygen concentration limit is chemical in origin. Since the Cu(2)–O(4) bond length is very long, leading to a small charge transfer estimated[19] to be less than 0.2 electrons, the O(4) and O(1) sites receive electrons almost entirely from the Ba and Cu(1) ions which can contribute at most 6 electrons [2 $Ba^{2+}$ and $Cu(1)^{2+}$], thereby accommodating 3 oxygen ions [2 $O(4)^{2-}$ and $O(1)^{2-}$]. This configuration corresponds to a limiting oxygen stoichiometry of 7.0. However, dedicating both of the $Ba^{2+}$ electrons to the O(1) and O(4) oxygen atoms will not allow the Ba to bind to the remaining structure; thus, some Ba charge must be shared with the O(2) oxygens in the Cu(2) plane at the expense of a reduced oxygen concentration in the O(1) site, giving a maximum oxygen stoichiometry slightly less than 7.0.

This charge balance may be summarized by considering the structure as consisting of two "Cu layers" separated by a Ba ion. The "Cu(1) layer" contains Cu(1), O(1), and O(4) while the "Cu(2) layer" contains Cu(2), O(2), and Y. Due to the weak Cu(2)–O(4) bond, the Ba ion controls the charge balance between these layers. We identify two predominant bond-length changes: the Cu(1)–O(4) bond length changes to balance charge *within* the Cu(1) layer while the Ba ion moves relative to the Cu(1) and Cu(2) layers in order to balance charge *between* them.

To illustrate the behavior of bond lengths, the Cu(1)–O(1) bond length is plotted versus the Cu(1)–O(4) bond length in Fig. 2(a). The data for $x=0.3$ and the oxygen-deficient, undoped materials have been taken from the literature (Table II). With the addition of Co, the Cu(1)–O(1) bond length increases with decreasing Cu(1)–O(4) bond length, first linearly, then saturating near the value for the long Cu(1)–O(1) bond length along the chains for undoped, orthorhombic $YBa_2Cu_3O_{7-y}$. The similarity of the Co(1)–O(1) and Cu(1)–O(1) bond lengths might account for the large solubility limit for Co while lower solubility limits are observed for other substitutions[15] such as Al, which is also trivalent, but should desire a shorter bond length.

As small amounts of oxygen ($y\leq0.3$) are removed, or as Co is added, the decrease in Cu(1)–O(4) bond length is matched by an increase in the Cu(1)–O(1) bond length [solid line in Fig. 2(a)], while the Cu(1)–O octahedral volume remains approximately constant, as shown in Fig. 2(b). This may indicate that the Cu(1) valence is not changing, while the hybridization of Cu–O bonding orbitals will be affected by the relative changes in Cu(1)–O(1) and Cu(1)–O(4) bond lengths.

When large amounts of oxygen are removed, the

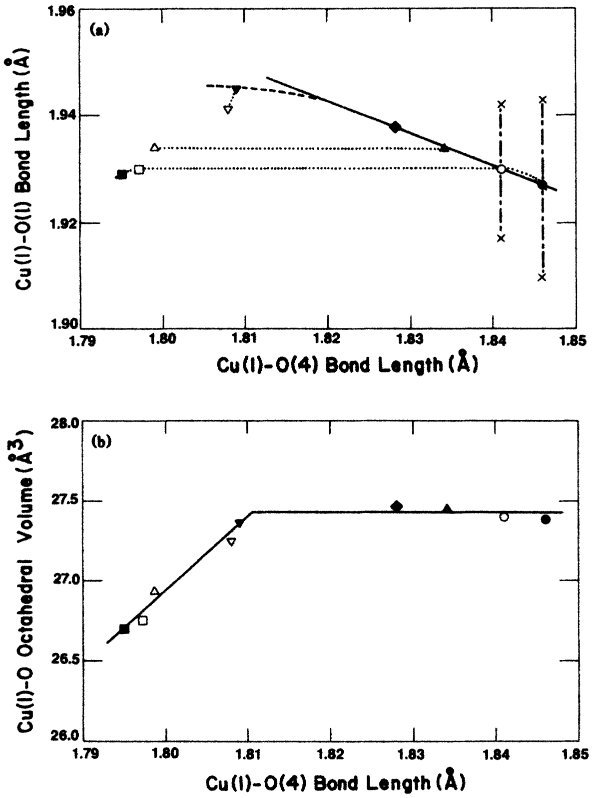

FIG. 2. The local Cu(1)–O environment is an octahedral volume given by the nearest neighbor Cu(1)–O coordination. (a) shows that the coordination becomes increasingly asymmetric as Co is added or as O is removed. The dot-dashed lines are for the orthorhombic samples where both the *a* and *b* axes have been plotted (x) while the circles are their average. (b) demonstrates that the Cu(1)–O octahedral volume is approximately constant for a Cu(1)–O(4) bond length > 1.81. The symbols are defined in Table II.

Cu(1)–O(4) bond length decreases considerably, while the Cu(1)–O(1) bond length remains relatively constant, as indicated by the dotted lines in Fig. 2(a). An exception is the Co $x = 0.8$ sample, which appears to retain much of its oxygen after vacuum annealing. The decrease in the Cu(1)–O(4) bond length is evidently an effort to compensate for lost $O^{2-}$ in the Cu(1) layer. However, we have also noticed that the Ba ion exhibits a marked shift towards the Cu(2) layer, indicating a charge transfer between Cu layers. Therefore, unlike the case of small oxygen removal, large oxygen deficiency cannot be compensated locally within the Cu(1) layer and requires a charge transfer between the Cu layers. From Fig. 2(b) we see that, concurrently, the Cu(1)–O octahedral volume decreases, which may be due to a smaller electronic contribution from Ba, although at low O(1) occupancy, this may also result from a reduced Cu(1)–O(1) average coordination.

TABLE II. Symbols used in Figs. 2 and 3.

| Sample | Symbol | Reference |
|---|---|---|
| $YBa_2Cu_{2.8}Co_{0.2}O_{7.04}$ | ▲ | This work |
| $YBa_2Cu_{2.8}Co_{0.2}O_{6.45}$ | △ | This work |
| $YBa_2Cu_{2.2}Co_{0.8}O_{7.30}$ | ▼ | This work |
| $YBa_2Cu_{2.2}Co_{0.8}O_{6.91}$ | ▽ | This work |
| $YBa_2Cu_{2.7}Co_{0.3}O_{6.81}$ | ◆ | Ref. 20 |
| $YBa_2Cu_3O_{6.90}$ | ● | Ref. 18 |
| $YBa_2Cu_3O_{6.73}$ | ○ | Ref. 18 |
| $YBa_2Cu_3O_{6.39}$ | □ | Ref. 18 |
| $YBa_2Cu_3O_{6.13}$ | ■ | Ref. 18 |

The presence of one extra oxygen for every two Co in the Cu(1) plane provokes some thought as to the configuration of these atoms. At low Co concentrations, the Co ions would be far separated, making this compositional relation between Co and oxygen difficult to satisfy without long-range correlations. A possible remedy would be to introduce pairs of Co, forming Co–O–Co, where the additional oxygen could share one electron from each of the Co neighbors. This pairing would not imply conventional short-range ordering with the tendency to form clusters (ultimately leading to the insolubility of Co), because once a pair is formed, there will be no further attraction among the Co. The axial nature of these pairs, however, might be expected to cause short-range orientational ordering of pairs. Because powder diffraction measures only long-range order, we cannot directly infer such pairing from these experiments.

It is tempting to argue that the additional oxygen brought in by Co drives the orthorhombic-tetragonal transition by filling vacancies adjacent to the "chains." However, the vacuum-annealed sample, $YBa_2Cu_{2.2}Co_{0.8}O_{6.9}$, is tetragonal while the oxygen stoichiometry has a value expected for an orthorhombic structure. These facts might be explained if Co insists on having an oxygen coordination higher than fourfold, although, this would not necessarily explain why the transition occurs for very low Co concentration, corresponding to low additional oxygen $(\leq 0.05)$. It is clear that the orthorhombic-tetragonal transition for the Co substitutions is qualitatively different than for the oxygen-deficient undoped material—the latter being entropic in origin while in the former, the

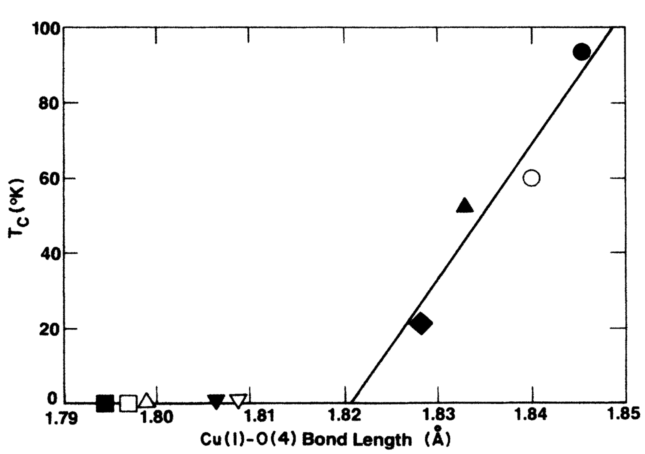

FIG. 3. The continuous decrease of $T_c$ with Cu(1)–O(4) bond length suggests that the superconducting properties are correlated to the local electronic environment.

transition is evidently driven by an effective "applied field." Such a field could arise from Co—O bonds forming elastic dipoles which would have, on average, tetragonal symmetry. Further experiments are required to clarify these points.

While the electronic properties may depend in a complicated manner on many effects, the Cu(1)—O(4) bond length, which is also the shortest bond length in the structure, may be an important parameter reflecting the local electronic properties. Figure 3 shows a plot of $T_c$ versus Cu(1)—O(4) bond length for both the oxygen-deficient and the Co-doped materials. It is clear that $T_c$ decreases systematically with decreasing Cu(1)—O(4) bond length for both. Although these data appear to be consistent with a single line, the variation of $T_c$ with bond length could be quantitatively different for each defect system. The essential point is that the change in $T_c$ is correlated to the local electronic properties, as reflected by the Cu(1)—O(4) bond length. In particular, the change in $T_c$ is more likely to be related to the hybridization of the orbitals rather than to valence changes, since the region of decreasing $T_c$ is coincident with the region of constant Cu(1)—O octahedral volume. We conclude that the suppression of superconductivity in this compound may be more strongly coupled to the details of the chemical bonds among the ions, and less affected by the presence of paramagnetic substitutional ions.

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