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LETTER TO THE EDITOR

Observation of Superconductivity in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6$

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Substitution of Ca^{2+} for Y^{3+} in $YBa_2Cu_3O_6$ converts this tetragonal semiconductor into a tetragonal superconductor with a T_c of 50 K. Furthermore, the structure of $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$, determined by neutron powder diffraction, is fully consistent with partial oxidation of the Cu(2)–O sheets, whereas the linear O–Cu(1)–O units do not undergo oxidation. Observation of a limited solid solubility for Ca^{2+} in this structure is attributed to a maximum allowed oxidation state for Cu(2). This implies that in the superconductor $YBa_2Cu_3O_7$ the Cu–O chains are responsible for the T_c of 90 K, whereas the Cu–O sheets alone produce superconductivity at 50 K in $YBa_2Cu_3O_{6.5}$.

The role of the Cu–O chains in $YBa_2Cu_3O_7$ has been debated continuously since the discovery of this material (*1*). The fact that $YBa_2Cu_3O_6$ is a semiconductor whereas $YBa_2Cu_3O_7$ is a superconductor with a critical temperature T_c above 90 K, has led many to speculate that the Cu–O chains present in the oxidized structure are necessary for high temperature superconductivity. Furthermore, the variation of T_c with oxygen content is quite complex, and the formation of a 60 K superconducting phase near an oxygen stoichiometry of $O_{6.5}$ has been interpreted as evidence for superconductivity solely in the Cu–O sheets (*2*). In this scenario, the oxygens in the chains would serve only to dope holes into the sheets, increasing the average oxidation state of the Cu^{2+} ions[1], yielding a 60 K metallic superconductor rather than a semiconductor. If this is correct, it should be possible to produce the same effect by chemical doping in either the Y^{3+} or the Ba^{2+} site. Here we report the superconducting properties and structure of $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$, demonstrating the effectiveness of doping the Y^{3+} site.

Samples of $(Y_{1-x}Ca_x)Ba_2Cu_3O_6$ and $(Y_{2-x}Ca_x)BaSrCu_3O_6$ were prepared from the binary oxides by first forming the fully oxidized materials in air at 950°C and subsequently reducing them in flowing Ar at 725°C. Manthiram *et al.* (*3*) first studied the substitution of Ca^{2+} for Y^{3+} in $YBa_2Cu_3O_7$ and found that a solid solution existed for $0 \leq x \leq 0.3$, and that the T_c decreased as x increased. We obtained comparable results for the fully oxidized materials. Upon reduction of the oxidized materials to $Y_{1-x}Ca_xBa_2Cu_3O_6$, however, we observed that the Ca-substituted materials continue to superconduct at temperatures as high as 50 K (for $x = 0.2$).

In Fig. 1 we compare the powder pat-

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[1] There is still considerable controversy concerning the location of the holes in the Cu–O framework; i.e., does one produce Cu^{3+} or O^- by doping the High T_c superconductors? Here we will assume that Cu^{3+} is present, although the exact percentage of Cu^{3+} character for the hole states is not known.

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terns of $YBa_2Cu_3O_7$ and $YBa_2Cu_3O_6$ with that of $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$. This figure emphasizes the structural similarity of the reduced materials. In Fig. 2 we show flux exclusion and resistance measurements for $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_6$. The reduced material clearly exhibits bulk superconductivity with a T_c of ~50 K.

To confirm the structure and oxygen content of the reduced material we collected neutron diffraction data[2] on a sample of nominal composition $Y_{0.5}Ca_{0.5}Ba_2Cu_3O_x$. The diffraction pattern exhibited tetragonal symmetry and was refined in the space group *P4/mmm*. The starting atomic positions for the refinement were taken from the $YBa_2Cu_3O_6$ structure described in Ref. (*4*). The Cu, O(1), and O(2) sites were assumed to be fully occupied. The remaining metal atom and the O(3) site occupanices were refined. While the Ba site refined to full occupancy (within one standard deviation), refinement of the Y site suggested partial occupancy by Ca (~20(5)%). The O(3) atom at 0, ½, 0 refined to a partial occupancy of 0.11(4). The formula derived from the neutron data is thus $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.1}$. Atomic positional and thermal pa-

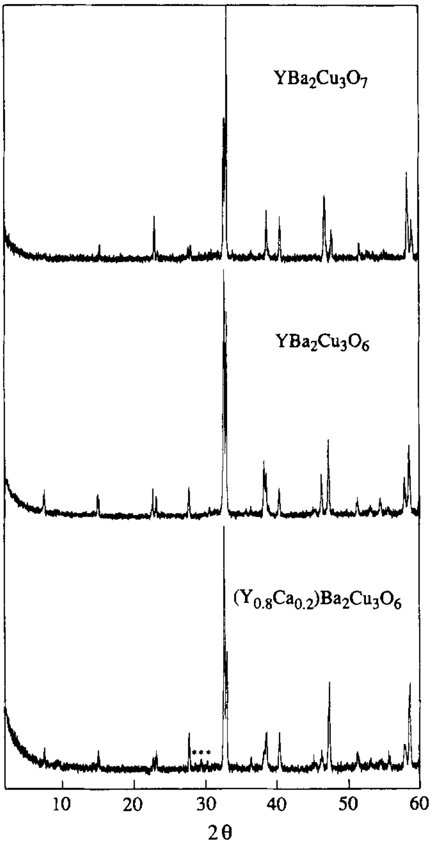

FIG. 1. X-ray diffraction powder patterns for $YBa_2Cu_3O_7$, $YBa_2Cu_3O_6$, and $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$. Asterisks denote $BaCuO_2$ impurity.

TABLE I

ATOMIC POSITIONAL AND THERMAL PARAMETERS FOR $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.1}$

Atom	*x*	*y*	*z*	*b* (Å²)
Y/Ca[a]	½	½	½	0.8(2)
Ba	½	½	0.1911(5)	0.2(1)
Cu(1)	0	0	0	2.0(2)
Cu(2)	0	0	0.3626(4)	0.4(1)
O(1)	0	0	0.1527(8)	2.2(2)
O(2)	0	½	0.3744(4)	0.8(1)
O(3)[b]	0	½	0	0.5

$a = 3.8611(3)$; $c = 11.826(1)$; Space group *P4/mmm* (123)
$R_I = 0.062$; $R_{WP} = 0.105$; $R_e = 0.048$; $S_p^2 = 4.8$; $S_I^2 = 6.2$

[a] Site occupancy refinement is consistent with the formulation $(Y_{0.8}Ca_{0.2})$ assuming a fully occupied site.

[b] Site occupancy refined to 0.11(4).

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[2] The data was collected at room temperature at the Brookhaven National Laboratory High-Flux Beam Reactor. The beam conditions were as follows: Si monochromator; graphite (004) analyzer; collimation, 40 feet in pile; 20 feet, monochromator–sample; 20 feet, sample–analyzer; 40 feet, analyzer–detector; & = 1.3596 Å (calibrated using CeO_2); 5° $< 2\theta <$ 113°, 0.1° step size. Several regions containing impurity peaks were identified and excluded from the refinement, as was the region below $2\theta = 20°$ where peaks deviated from Gaussian shape due to asymmetry. The remaining peaks were treated as Gaussian. Neutron scattering factors were taken from L. Koester and H. Rauch, Int. Atomic Energy Agency Report 2517/RB (1981). Background values were obtained by linear interpolation of average values between peaks. In all, the refinement included 2θ variable parameters (a scale factor, 12 structural parameters, three half-width parameters, two unit cell parameters, a zero-point correction, and a preferred orientation correction) and 107 reflections.

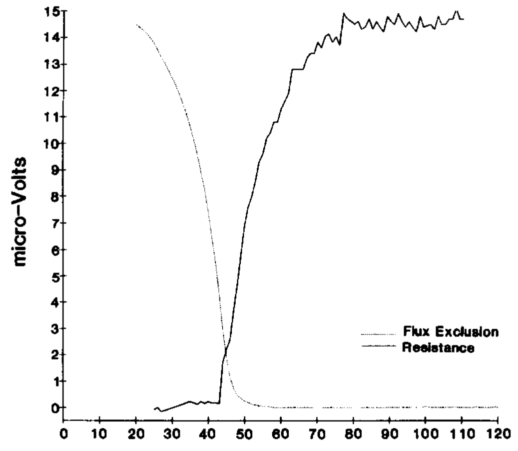

FIG. 2. Flux exclusion and resistance measurements of T_c for $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$.

TABLE II

SELECTED INTERATOMIC DISTANCES[a] (Å) FOR $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.1}$

Y/Ca–O(2)	2.436(3)	[2.403]	Cu(1)–O(1)	1.806(9)	[1.803]
Ba–O(1)	2.768(2)	[2.774]	Cu(2)–O(1)	2.483(5)	[2.450]
–O(2)	2.903(6)	[2.920]	–O(2)	1.936(1)	[1.946]
Average	2.836	[2.847]			

[a] Numbers in brackets are the average values for $YBa_2Cu_3O_6$ taken from Refs. (*11–13*).

rameters are given in Table I and selected interatomic distances appear in Table II. Calculated and observed diffraction patterns appear in Fig. 3.

The neutron structure may also be used to infer the oxidation states of the Cu(1) and Cu(2) ions when Ca is incorporated into $YBa_2Cu_3O_6$. The replacement of ~20% of Y^{3+} by Ca^{2+} decreases the Cu(2)–O(2) distance from 1.946[3] to 1.936(1) Å (see Table II), whereas the Cu(2)–O(1) distance increases from 2.450[3] to 2.483(5) Å. These changes are consistent with the production of Cu^{3+} in the planes due to Ca^{2+} substitution.[4] The Cu(1)–O(1) bond distances, however, remain relatively constant (1.806(9) Å[3] vs 1.803 Å), which indicates a nearly constant oxidation state for Cu(1). Thus Ca^{2+} doping of $YBa_2Cu_3O_6$ is analogous to Sr^{2+} doping of La_2CuO_4 in that holes are stoichiometrically doped into the Cu–O sheets. It is interesting that the T_c of $YBa_2Cu_3O_{6.4-6.6}$, which is near 60 K (*5*), is not much higher than the T_c we observe in $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$, and this is probably due to superconductivity which is primarily localized in the Cu–O planes for both materials. In $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$, for a Cu(2) oxidation state of ± 2.1, we observe a $T_c \approx 50$ K, somewhat higher than in $La_{2-x}Sr_xCuO_4$ for an equivalent doping level. This may reflect an interaction between the adjacent Cu–O planes in $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_6$.

The fact that the solid solubility of Ca in $(Y_{1-x}Ca_x)Ba_2Cu_3O_6$ is limited to about $x = 0.3$ is somewhat surprising since in the Bi and Tl based superconductors, which contain multiple Cu–O sheets, there are pure Ca layers separating these sheets. Further-

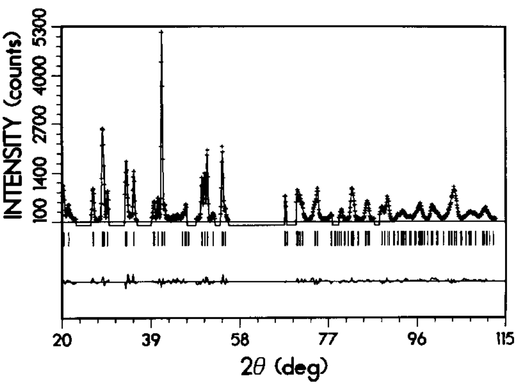

FIG. 3. Calculated and observed powder neutron diffraction patterns for $(Y_{0.8}Ca_{0.2})Ba_2Cu_3O_{6.1}$. Short vertical markers below the pattern represent allowed reflections. Peaks from impurity phases have been excluded.

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[3] Distances averaged from values given in Refs. (*11–13*).

[4] The argument is based upon the ionic radii of eight coordinate Y (1.019 Å) and Ca (1.12 Å) taken from (*14*). Although no value is listed for square planar Cu(III) it is assumed to be less than that of Cu(II) (0.57 Å). The value for linearly coordinated Cu(I) is 0.46 Å.

more, it is possible to substitute Y^{3+} for Ca^{2+} in these systems, although one then induces semiconducting rather than superconducting behavior (*6*). Based upon these structural observations it would appear to be possible to fully substitute Ca^{2+} for Y^{3+} in $YBa_2Cu_3O_6$. We surmise, however, that there is a maximum oxidation state for the Cu(2) site which can be accommodated in this structure due to the Cu–O bonding and this limits the Ca solubility.[5] In the Bi and Tl systems the Cu–O sheets are nearly (or completely) planar (*7*) and may therefore accept higher doping levels (more Cu^{3+}), yielding higher T_c's.

In a recent study (*8*) of the systems $Y_{1-x}Ca_xBa_2Cu_3O_y$ and $Y(Ba_{2-x}La_x)Cu_3O_y$, results similar to ours were obtained for the Ca-doped samples having low oxygen content. Evidence was presented that in $YBa_2Cu_3O_7$, the Cu(1) site cannot be oxidized beyond +2.5 (i.e., alternating Cu^{2+} and Cu^{3+}). Above this oxidation threshold it is energetically more favorable to dope the Cu(2) site, which seems to be a reasonable assumption. If we then assume, based upon our results, that the Cu(2) site cannot be oxidized (doped) above an average charge of $\sim+2.15$ (as determined from the Ca^{2+} solubility limit), then a second threshold exists beyond which charge will again be injected into the Cu(1) chains, the chains become superconducting and the T_c rises to 90 K. It is this second threshold which appears as the ~60 K plateau region in the plot of T_c vs x in $Y(Ba_{2-x}La_x)Cu_3O_7$ in Ref. (*8*). The fact that the Cu–O chains do participate in the metallic conductivity of $YBa_2Cu_3O_7$ is demonstrated both by magnetic resonance studies, which observe Korringa-type Cu(1) relaxation for oxygen stoichiometries above about $O_{6.5}$ (*9*), and by band structure calculations (*10*). It seems reasonable that to obtain high Cu oxidation states (i.e., Cu^{3+}) it is favorable to have square *planar* coordination, as found in the Cu(1) site in $YBa_2Cu_3O_7$. In the Bi and Tl systems the Cu–O sheets are nearly planar (*7*) and may therefore accept a higher Cu charge state. The high T_c's observed in these systems may then reflect the high Cu oxidation state allowed by the planar structure.

In summary, superconductivity in the absence of Cu–O chains has been demonstrated in $YBa_2Cu_3O_6$. This has been achieved by partial oxidation of Cu^{2+} to Cu^{3+} specifically within the copper oxygen sheets via substitution of Ca^{2+} for Y^{3+}. Since the Cu(1) ions are electronically decoupled from the Cu(2) ions when the chains are not present, this result implies that there is a superconducting pairing mechanism operating in the Cu–O sheets. The Cu–O chains are, however, apparently necessary to achieve 90 K superconductivity in this structure. We are currently attempting to extend this work to the presumably analogous substitution (doping) in the Ba site.

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[5] The Cu(2)–O(1) distance increases with Ca doping and this increase is associated with flattening of the Cu–O sheets with increasing hole concentration. As the sheets flatten the difference between the z axial parameters for Cu(2) and O(2) decreases. This difference in 0.22 Å for undoped $YBa_2Cu_3O_6$ (*11–13*) and 0.14 Å for $(Y_{0.8}, Ca_{0.2})Ba_2Cu_3O_6$.

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