transfer model for bond activation. However, it was pointed out that other factors probably also play a major role in determining the size of the activation barriers.

Finally, we would like to point out that the data presented here provide an excellent opportunity for comparison with theoretical calculations. The results are for a simple sp metal, and the dramatic differences observed in the activation barriers for different molecules lead us to believe that the important factors in these reactions could be deduced from quite modest calculations. In contrast, attempts to perform theoretical calculations on, for example, Fe clusters with the precision required to explain why Fe_{18} reacts slower by a factor of 1000 than Fe_{25}[1] are not likely to be very enlightening because the activation barriers only differ by at most 0.2 eV.

Metal Ion Substitution Chemistry in the YBaCuO System as a Probe of the Superexchange Pathway

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Abstract: The effect of substitution for Cu by aluminum, nickel, and zinc in the YBaCuO superconducting system is described in detail. All three metals lower the T_c value and make the superconducting transition less abrupt. However, the strength of the effect varies with the metal, and this is attributed to their different reactivities and site preferences. The most dramatic effect is with zinc, which completely quenches the superconductivity when as few as 10% of the Cu sites are replaced. It is postulated that under these synthetic conditions zinc prefers the five-coordinated "Cu(2)" site, which is presumed to lie on the main superconducting pathway. Nickel has a stronger affinity for the four-coordinated "Cu(1)" sites and is apparently found in both sites at high dopant levels. Magic angle spinning NMR (MAS NMR) and other data indicate that Al prefers the four-coordinate Cu(1) site for initial substitution, although aluminum ions may also aggregate at the twinning boundaries. We suggest the hypothesis that substitution of the Cu(1) sites eliminates their contribution to the superconductivity and thereby makes the system like the related 40 K superconductors, which lack the Cu(1) sites.

Superconductivity was initially discovered in pure metals,[2] but higher transition temperatures, up to $T_c = 23$ K, were observed in alloys, especially with niobium.[3] Searches for new superconductors tended to center on the immediate neighborhood of Nb in the periodic table. The known inorganic superconductors[4] received more limited attention prior to the observation of $T_c =$ 36–50 K in one series of copper oxide perovskites and $T_c > 90$ K in another.[5-8] We report substitution studies in the 90 K system, $YBa_2Cu_3O_{7-\delta}$, with the overall aim of elucidating the nature and mechanism of the superconducting path. This substitution chemistry is also crucially important in understanding and controlling the strong superconductor/substrate interaction during the preparation of thin-films materials. Here, the chemical reaction not only destroys the superconductivity of the deposited film but also dopes it with potentially detrimental impurities, which can degrade the superconducting properties and increase the normal-state resistivity.

Table I. O Content, $7 - \delta$, in $YBa_2Cu_{3-x}M_xO_{7-\delta}$

pure 123 phase	7% Zn	7% Ni	7% Al
6.89 (6.88[a])	6.99	6.92	6.79
6.89 (6.87[a])	6.91	6.89	6.83
	6.88	6.90	6.77

[a] TGA data on same sample.

The $YBa_2Cu_3O_{7-\delta}$ system possesses two crystallographically distinct and chemically dissimilar copper sites[9-11] (Figure 1): the square-planar Cu(1) chains and the square-pyramidal Cu(2) layers, separated by the large Ba^{2+} ions. Local charge neutrality considerations and a greater crystal field stabilization would favor the location of Cu^{3+} in the Cu(1) sites, and this would be balanced by a predominant but not exclusive Cu^{2+} occupancy of the Cu(2) sites. The Cu(2) sites are possessed by both the 40 and 90 K

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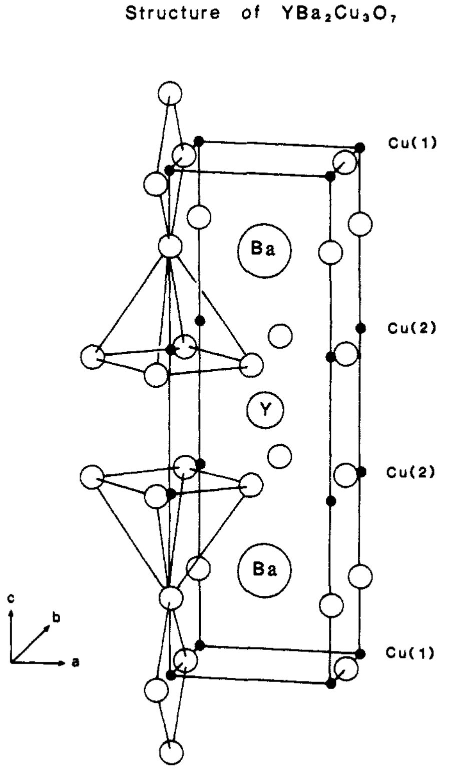

Figure 1. Idealized structure of $YBa_2Cu_3O_7$ showing Cu(1) and Cu(2) sites.

superconductors, while the Cu(1) chains are unique to the latter. The chemical differences between Cu(1) and Cu(2) suggest the possibility of site-specific substitution for copper, governed by the size, charge, and crystal field requirements of the substituted ions, as well as the chemical reactivities of the precursor compounds.

Experimental Section

Y_2O_3, CuO, $BaCO_3$, NiO, Al_2O_3, and ZnO were used as starting materials, each 99.999% pure (Aldrich). The chemical and phase purity of the starting materials were checked by Cu Kα X-ray powder diffraction (XRD). The powders were thoroughly mixed, ground (agate pestle and mortar), and pressed into pellets, which were fired at 955 °C for 24 h in flowing O_2 in ceramic crucibles and then annealed for a further 6 h at 400 °C in flowing O_2. The propensity for Al substitution militates against the use of alumina crucibles favored by some workers. The samples were characterized by XRD, inductance, and MAS NMR measurements.

The oxygen content of the samples was estimated by thermogravimetric analysis and by iodometric titration, involving thiosulfate titration, followed by titration of the liberated iodine.[12] Typical results are given in Table I. Samples were subjected to thermogravimetric analysis under a flowing H_2/Ar mixture on a Stanton Redcroft TGA/DGA machine. Conversion of the samples to Cu, Y_2O_3, and BaO was confirmed by XRD. Thermogravimetric analysis[13,14] is as accurate as iodometric titration for the pure $YBa_2Cu_3O_{7-\delta}$ ("123") phase. However, for the substituted materials, there were several reaction products, and this yielded TGA curves with rising slopes. Thus, the method was deemed to be less precise for the substituted samples. Iodometric titration is clearly the method of choice for these compounds. The general value of δ was 0.1, except for Al substitution where it was larger, ~0.2; otherwise, there is no sign of variation in oxygen content with metal substitution. ^{27}Al MAS NMR spectra were recorded with a Bruker MSL-400 multinuclear spectrometer operating at 104.26 MHz on samples spun at 4.2 kHz in air. Very short $\pi/50$ pulses were used ($\pi/2$ pulse length was 5.0 μs) and were necessary for quantitative spectral representation of quadrupolar nuclei. Chemical shifts were measured in ppm from $Al(H_2O)_6{}^{3+}$, prepared by acidifying a 1 M $AlCl_3$ with $HClO_4$. Magnetization data were obtained by SQUID magnetometry.[15]

Results and Discussion

Aluminum Doping. The amount of Al that can be substituted is limited by the formation at high doping levels (11%) of $BaAl_2O_4$ as an impurity phase, indicated by the appearance of the characteristic diffraction pattern of $BaAl_2O_4$ in the XRD spectrum. The XRD spectra (Figure 2a) of the Al samples reveal a gradual transition from orthorhombic symmetry, with $a < b$, to tetragonal, with $a = b$, and the unit cell parameter c decreases monotonically with increasing Al concentration Figure 3). The four-coordinated environment is in keeping with Al^{3+} substitution for the nominally Cu^{3+} sites of the Cu(1) planes. The transformation in crystal symmetry is also reasonable since the small Al^{3+} ion (0.39 Å compared to 0.54 Å for Cu^{3+}) will draw the four oxygens closer and mutual repulsion will move these into a somewhat more tetrahedral environment. High-resolution electron microscopic studies are now under way to another parameter, viz. the segregation of some Al ions at the twinning boundaries where a distorted tetrahedral environment is also expected.[16] Some indirect evidence for such segregation is provided by the resistance and inductance measurements (Figures 4 and 5a) for $YBa_2Cu_{3-x}Al_xO_{7-\delta}$. both measurements show a decrease in T_c with increasing Al concentration and hint that the Al is not uniformly dispersed. The inductance data suggest two transitions above 5% nominal dopant concentration. Also at higher concentrations, the normal-state resistivity increases with Al content and a transition from a metallic to a nonmetallic variation of the resistivity with temperature, presumably caused by accumulation of impurity phases such as $BaAl_2O_4$ at the grain boundaries in heavily doped materials. Even in these materials, however, the resistance curves show a drop at ca. 90 K, suggesting that undoped regions of the materials retain superconductivity. The proportion of superconducting material decreases markedly, though not as much as with other substituent ions like zinc, vide infra. This effect on T_c is far smaller than would be expected if Al were situated directly in a principal superconducting path.

Figure 6 shows the ^{27}Al MAS NMR spectrum from samples containing different amounts of aluminum (numbers quoted are nominal weight percentages). Spectra of samples with between 1.67 and 8.33% Al each consist of a single line at 73.70 ± 0.1 ppm, characteristic of the central ($-^1/_2 \rightleftarrows +^1/_2$) transition of four-coordinated aluminum. The MAS NMR spectrum in Figure 6 shows a peak near 80 ppm, which grows with increasing aluminum dopant concentration and is characteristic of a four-coordinated Al site, in contrast with the six-coordination proposed[16] in analogous samples prepared under slightly different conditions. Over the entire composition range, the MAS NMR signal arises from aluminum in 4-fold coordination site. The observed signal could therefore arise from Al substituted at the Cu(1) site (with clear local distortion from square coordination) or from the impurity phase $BaAl_2O_4$. For the lightly doped samples, there is no X-ray evidence for the impurity phase (Figure 2), though very small concentrations of a second phase could escape detection by conventional XRD.

Other workers,[16,17] while agreeing with insertion of dopant ions at the planar Cu(1) sites, have proposed the absorption of additional oxygen in certain doped samples. This has led to proposals that the replacement M^{3+} site is six-coordinated due to filling of the vacant oxygen sites on either side of the planar Cu(1) site. A recent theoretical description of the parent compound suggests Cu^{2+} rather than Cu^{3+} ions in the Cu(1) sites, with holes located on the O sites to balance the charges.[18] Planar geometry com-

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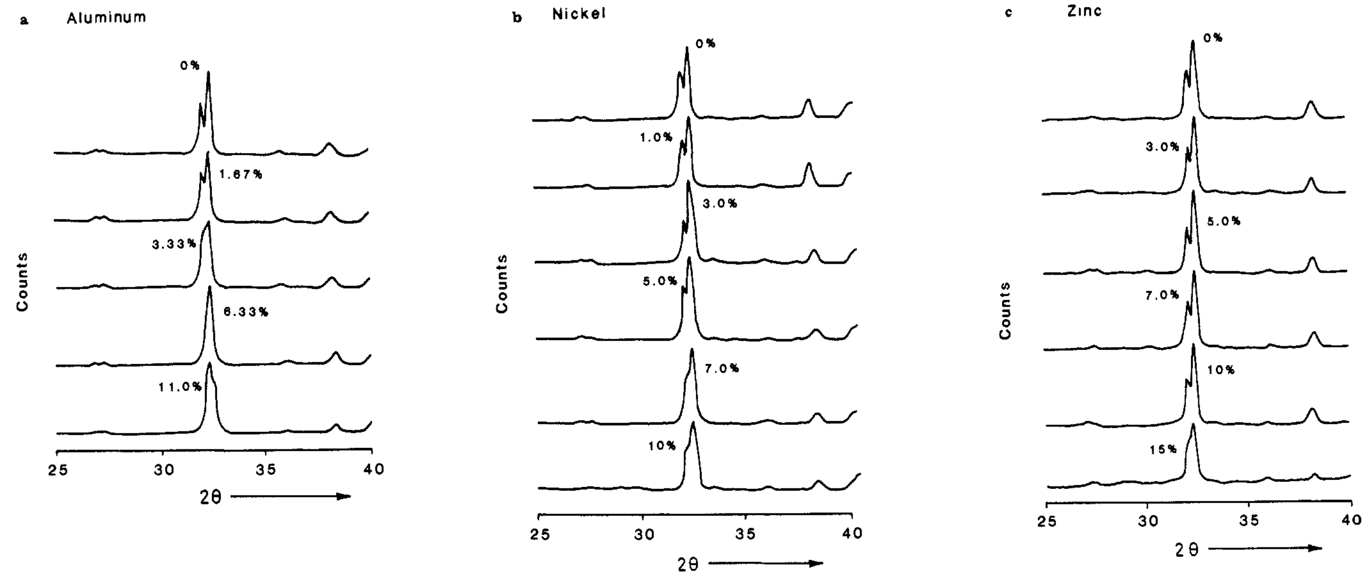

Figure 2. XRD patterns as a function of *x*: (a) $YBa_2(Cu_{3-x}Al_x)O_{7-\delta}$; (b) $YBa_2(Cu_{3-x}Ni_x)O_{7-\delta}$; (c) $YBa_2(Cu_{3-x}Zn_x)O_{7-\delta}$. Impurity levels are expressed as a percentage of moles of Cu replaced by dopant metal (33 × %).

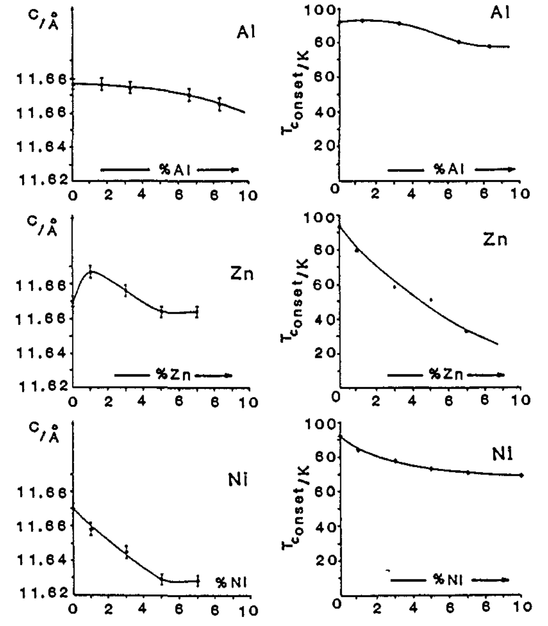

Figure 3. Correlation between *c* parameter and T_c as a function of metal substitution.

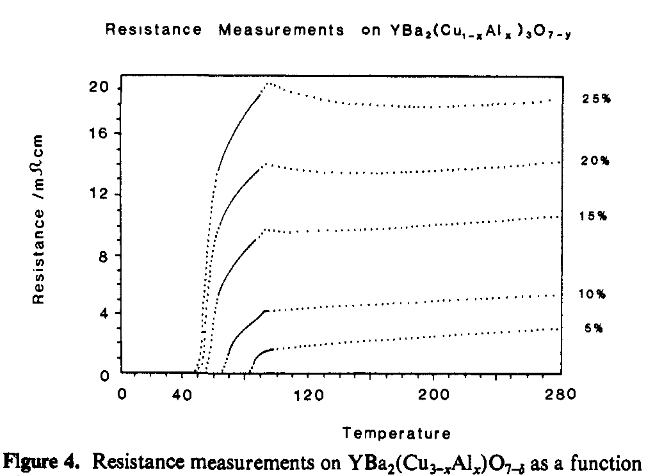

Figure 4. Resistance measurements on $YBa_2(Cu_{3-x}Al_x)O_{7-\delta}$ as a function of *x*.

monly occurs in compounds of both Cu^{2+} and Cu^{3+}, though crystal field stabilization energy produces a stronger preference for this geometry in the trivalent ion. If the Cu(1) site is indeed better described as bivalent, then the increased charge on M^{3+} over Cu^{2+} would be the driving force for attracting the additional oxygen.[19-24] This would raise the coordination number of M^{3+} from 4 to 5 or 6. However, the MAS NMR data do not support this for aluminum: the spectral positions and the integrated intensities indicate a four-coordinated Al^{3+} species whose concentration increases uniformly with the dopant concentration. If additional oxygen ions are present, they must be located outside the first coordination sphere.

Nickel Doping. Unlike what is observed with Al, insertion of Ni can be continued to quite high levels. XRD and inductance data for Ni-substituted samples (Figures 2b and 5b) are similar to those for Al in comparable concentrations. T_c decreases with Ni concentration but only down to about 74 K for nominal 10% Ni doping. The Ni appears to have an initial preference for the same site, Cu(1), as does Al, and it therefore has no dramatic effect on T_c. The planar geometry in this site is one for which nickel(II), d^8, is ligand field stabilized. In its diamagnetic planar form, d^8 nickel substitution is analogous to doping with diamagnetic metals or metalloids like Zn, Al, B, and Si. Each has the effect of increasing the overall magnetic susceptibility in the normal region above T_c, by disrupting the antiferromagnetic exchange, as will be described in detail elsewhere. Thus, low-level nickel doping raises the magnetism in any case, but a further rise in magnetism is important at high dopant levels, indicating a rising level of paramagnetic ion doping, viz. five- or six-coordinated nickel. Paramagnetic dopants, like Ni, Fe, or Cr,[24] have their higher electron spins coupled less completely with neighbors than are the copper spins they replace. The increased level of paramagnetic ions at high Ni dopant levels indicates high-spin nickel in the five-coordinated Cu(2) sheet sites. Nickel could not be paramagnetic in the planar Cu(1) chain sites unless additional oxygen were absorbed to form octahedral sites. However, unlike the observation with iron doping,[19-24] there is no appreciable rise in oxygen concentration with dopant level (Table I). Thus, at

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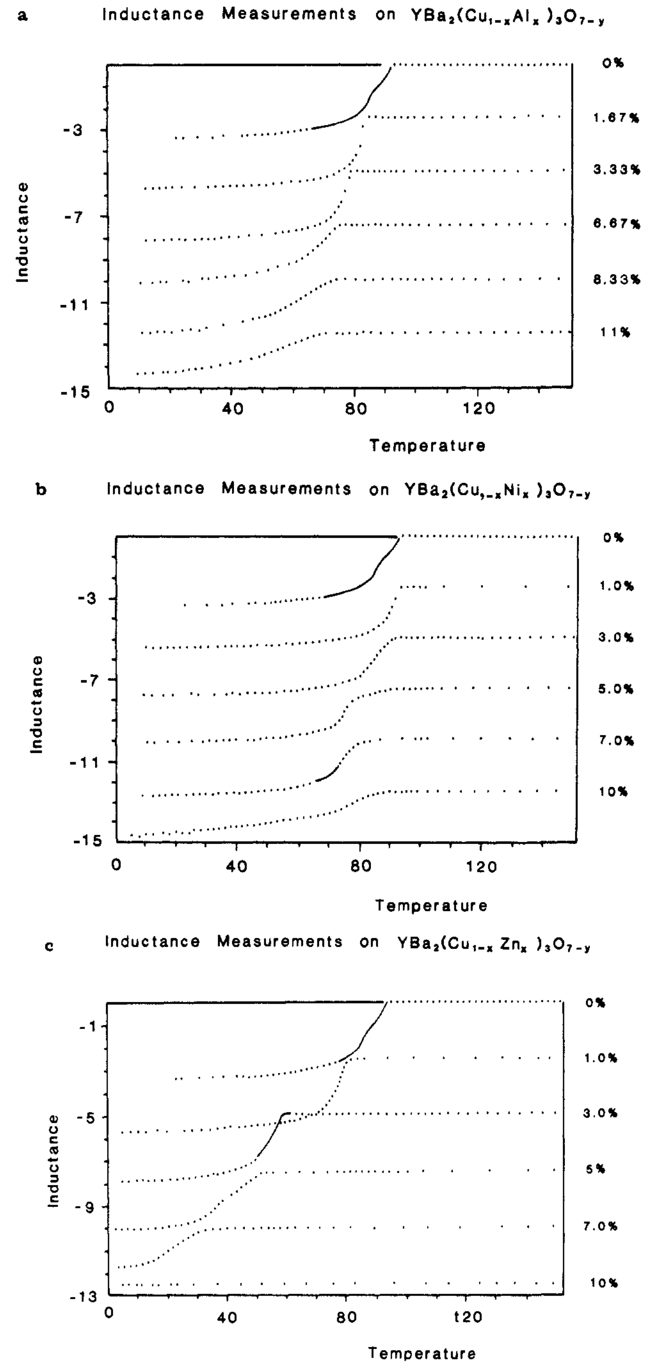

Figure 5. Inductance measurements as a function of x for: (a) $YBa_2(Cu_{3-x}Al_x)O_{7-\delta}$; (b) $YBa_2(Cu_{3-x}Ni_x)O_{7-\delta}$; (c) $YBa_2(Cu_{3-x}Zn_x)O_{7-\delta}$. The curves are displaced 2.5 units.

high concentrations there is heavy occupation at both sites, though the depression of T_c is small compared to that of other substituents.

Nickel is not as effective as other dopants, like Zn, in blocking the superconductivity. Even at 33% Ni, or $YBa_2Cu_2NiO_{7-\delta}$, a relatively high T_c, 57 K, is observed, and a weak superconductivity level of about 1% continues to be allowed (Table II). It is interesting to consider a mechanism to allow this, which does not apply to the diamagnetic dopants. Paramagnetic nickel in the sheets may transmit electron pairs less well than does copper but better than do diamagnetic dopants like Si. An antiferromagnetic mechanism for superconductivity would account for this for a metallike nickel, which takes part in the magnetic coupling. Of the various transition-metal ions with multiple unpaired electrons, nickel(II) exhibits the strongest magnetic coupling.[25,26]

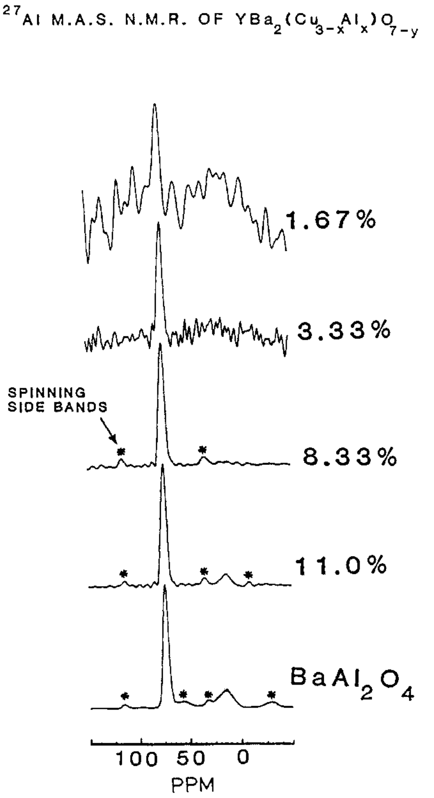

Figure 6. ^{27}Al MAS NMR of $YBa_2(Cu_{3-x}Al_x)O_{7-\delta}$ as a function of dopant concentration x, expressed as a percentage of moles of Cu replaced by Al.

Table II. T_c and Percent Superconductor for Doped Samples

% M	T_c(onset)[a]	% superconductor
15% Ni	71	3.5
20% Ni	63	2.3
33% Ni	57	0.8
1% Zn	78	23.5
5% Zn	53	4.7
7% Zn	34	1.6
3% Al	90	23.1
8% Al	90	21.1
11% Al	90	15.2

[a] Field = 100 G. [b] Maximum values per unit volume in a 0.16-cm³ container filled with sample.

Zinc Doping. Inductive measurements for $YBa_2Cu_{3-x}Zn_xO_{7-\delta}$ show a dramatic effect on T_c for small Zn doping levels (Figure 5c). At a Zn concentration of 15%, no transition can be detected down to 4 K. In contrast to the behavior of nickel and aluminum, there is no orthorhombic to tetragonal transition at Zn replacement levels of up to 15% (Figure 2c) despite the large drop in T_c. These results suggest that Zn is substituting in the five-coordinated Cu(2) plane, and, indeed, there is precedent for this type of substitution in the related Y_2BaCuO_5 compound. It is generally observed that, in five-coordinated sites, Cu^{2+} prefers four short bonds and one long bond, while, with identical ligands, the five bonds to Zn^{2+} are more equal to each other, though the larger ion size (0.68 Å compared with 0.65 Å for Cu^{2+}) makes them slightly longer.[27] When ion size permits, zinc shows a slightly stronger preference for five-coordination. Zn^{2+} should tend to pull in the apical oxygen ion and push out those in the *ab* plane (Figure 3). This would tend to alter *a* and *b* by similar amounts, hence not changing the crystal symmetry. Above 10% Zn concentration, the structure

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converges to tegragonal. Whether this is an indication of the onset of zinc substitution into the planar Cu(1) sites is not defined by the present data and is under investigation. Thus, the possibility arises that site-specific substitution may be a feature of the detailed firing conditions, whereby sustitution at Cu(1) and Cu(2) sites is dictated by kinetic factors. Such a possibility may be the source of conflicting reports on the location of impurity ions.

Antiferromagnetism and Superconductivity. There is growing sentiment in favor of an antiferromagnetic mechanism for the superconductivity in the high-T_c perovskites,[18,28,29] thereby reviving interest in their magnetic properties. Samples of $YBa_2Cu_3O_{7-\delta}$ are generally incompletely (<80%) transformed into superconductors even when they show sharp magnetic transitions and reproducible T_c values, 90 K.[7,8] This incomplete transformation could be attributed to flux trapping within the material or to the presence of impurity phases, and the magnetic data indicate that the latter phenomenon is at least partly responsible. Impurity phases could consist of $YBa_2Cu_3O_{7-\delta}$ regions with higher than average δ values or of the phases Y_2BaCuO_5, $BaCuO_2$, and CuO. However, the amount of the latter detected by XRD tends to be small or zero compared to the incomplete Meissner effect, indicating the importance of flux trapping the superconductor.

Measurements over a range of temperatures, magnetic field strengths, and superconducting fractions allow approximate separation of the magnetic contributions from the superconducting and nonsuperconducting phases. Above T_c, non-Curie magnetic behavior is observed. The samples become more magnetic with decreasing concentration of the superconducting material, indicating that the impurity phase is the more strongly magnetic. On the basis of the limited data, the superconducting phase has a shallow Neel point near 200 K and a low μ_{eff} (<0.3 μ_B), i.e. a high degree of magnetic ordering, near T_c. Detailed examination of these properties is continuing, but it is important to note that quite large amounts of the impurity phases may be present with no significant effect on T_c,[7,8] presumably due to separate existence of the phases in separate domains. By contrast, we have shown that very small amounts of metallic impurities substituting for copper in the structure have a major effect on the superconducting properties. These substitution effects are more dramatic than those of rare earths, even when metals like Pr, with a stable tetravalent state, are used.[30]

The observation that T_c is readily quenched by doping in the Cu(2) layers, common to both the 40 and 90 K systems, indicates that these layers are essential to the superconductivity. The Cu(1) chains are a distinguishing feature of the 90 K systems, and the expected limiting effect of Cu(1) doping is to reduce T_c to the 50 K range without quenching T_c, provided not too many dopant ions stray into the Cu(2) layers.

In an antiferromagnetic mechanism, a formally $Cu^{III}O_4$ site is viewed as a $Cu^{II}O_4$ center, spin coupled with a labile positive hole located near the site. Normally, the $Cu^{II}O_4$ has its spin locked in place by the opposing spins of the adjacant Cu sites. But when coupled with the hole spin, it is nonmagnetic and can invert, taking the hole spin with it. Now the hole spin couples equally well with any of the neighbors and can move to one of them without energy loss or activation. Pairs of magnetically linked positive holes moving thus could constitute superconductivity. The base-linked square-pyramidal structure is expected to provide the strong coupling required for this process. The spin information is carried by the $d_{x^2-y^2}$ orbitals, which reside predominantly in the basal planes of the Cu(2) pyramids. Disruption of the coupled sheets could be accomplished either by thermal randomization of spins or by substitution of the copper with a metal that takes no part in the magnetic coupling. Doped sites or thermally randomized spins constitute lattice end points for magnetic coupling. These would then disrupt hole-pair propagation, consistent with experiment. Like other models,[31] this model and ultrahigh T_c are mutually exclusive. Confirmation of persistent rumors of T_c values of 220–260 K, high compared to the Neel temperature, in this system would invalidate it.

The enhancing effect of the Cu(1) chains is more mysterious. The Cu(1) planes are optimally oriented for magnetic coupling, but the Cu(2) pyramids orient relatively little spin information in that direction.

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