

**SUPERCONDUCTIVITY IN ORTHORHOMBIC AND TETRAGONAL  
YBa<sub>2</sub>(Cu<sub>1-x</sub>A<sub>x</sub>)<sub>2</sub>O<sub>7</sub> SYSTEMS (A = Zn, Ga, Al and Co)**

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**Abstract**

Preferential substitution of the Cu sites by other elements have been studied to elucidate the importance of structure (orthorhombic vs. tetragonal) and sites (plane vs. chain) in superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> oxide. X-ray and neutron diffraction measurements show that Ga<sup>3+</sup>, Co<sup>3+</sup> and Al<sup>3+</sup> exclusively substitute the Cu(1) sites and Zn<sup>2+</sup> substitutes only the Cu(2) sites. The resulting superconducting properties show that the integrity of the Cu-O<sub>2</sub> planes is far more important than that of the Cu-O chains in sustaining high T<sub>c</sub> superconductivity, and oxygen vacancy order is not essential to high T<sub>c</sub> superconductivity.

**I. Introduction**

Shortly after the discovery of high T<sub>c</sub> superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, it was found that the Y-site can be replaced by most rare earth elements which have large localized magnetic moments.<sup>1-3</sup> The superconducting transition temperature remains close to 90 K, while the rare earth moments order antiferromagnetically at low temperatures (< 2 K). The Ba-site also plays a relatively unimportant role and can be substituted by Sr to a large extent<sup>4</sup>, and the resulting compounds suffer only modest decreases in T<sub>c</sub>. The Cu-site however is crucial.<sup>5-8</sup> Xiao et al.<sup>5</sup> showed that by substituting only 10% of Cu by a number of 3d transition metals (Fe, Co, Zn, ...), the value of T<sub>c</sub> decreases greatly. It was further observed that the reduction of T<sub>c</sub> anti-correlates with the magnetic susceptibility or moment of a dopant, suggesting the existence of a magnetic pair-breaking mechanism. Zn was found, however, to be exceptional; it depresses T<sub>c</sub> far more than any other 3d elements, yet it does not carry a magnetic moment. As shall be described below, this is due to the unique role of Zn in Cu oxide superconductors.

The YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> oxide has an orthorhombic structure (b>a) with two Cu-sites as shown in Fig. 1. It contains the warped Cu-O<sub>2</sub> planes on which the Cu(2) (plane site) is located. In addition, there are the Cu-O chains along the b-axis upon which the Cu(1) (chain site) is situated. There are twice as many Cu(2) as Cu(1) sites. There are five oxygen sites as shown in Fig. 1. The O(2) and O(3) sites are located on the Cu-O<sub>2</sub> planes, and O(1) is the bridging oxygen along the c-axis, giving rise to the five-fold coordination of Cu(2). The O(5) sites in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> along the a-axis are vacant, giving rise to an orthorhombic distortion. With this oxygen vacancy order, a chain structure of Cu(1)-O(4)-Cu(1) is formed along the b-axis. It should be noted that in some published structure the oxygen site designations of O(1) and O(4) are reversed. The oxygen content (y), which can be varied between 6 and 7 in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>, plays a crucial role.<sup>9,10</sup> Below y = 6.3, the sample is insulating and antiferromagnetic. The value of T<sub>c</sub> increases with y and reaches 92 K when y is close to 7. When oxygen stoichiometry is reduced from 7 towards 6, the O(1), O(2) and O(3) sites remain filled but oxygens are removed from the O(4) sites. This results in a reduction of the orthorhombic distortion and a partial filling of the O(5) sites. Near

$y=6.3$ , the O(4) and O(5) populations are sufficiently disordered and become equal, the structure transforms from orthorhombic to tetragonal and  $T_c$  approaches 0 K. The lattice parameters of  $YBa_2Cu_3O_y$  with various oxygen content ( $0 < \delta < 0.7$ ) have been determined. The lattice parameter  $c$ , most sensitive to  $\delta$ , is linearly dependent on  $\delta$  having a slope of  $\frac{1}{c} \left( \frac{\Delta c}{\Delta \delta} \right) \approx 1.4\%/O \text{ atom}$ .<sup>10</sup> The oxygen depletion studies have also been made by quenching the samples from high temperatures.<sup>9</sup> The orthorhombic samples are found to be superconducting whereas the tetragonal samples are not. Because of these results, a great deal of emphasis has been placed on the integrity of the chains, and the orthorhombic structure for high  $T_c$  superconductivity. There are also theoretical models<sup>11</sup> for high  $T_c$  superconductivity which are based on the Cu-O chains.

However, Hall effect measurements<sup>12</sup> show that when the oxygen stoichiometry is changed from 7 towards 6, the carrier density also decreases in a manner similar to that of  $T_c$ . At about 6.3, the carrier density reduces precipitously and the sample becomes insulating. Thus the oxygen content is clearly of crucial importance for superconductivity in  $YBa_2Cu_3O_y$ . When the oxygen stoichiometry is reduced from 7 to 6, not only the Cu-O chains are destroyed, but the carrier concentration is also reduced. Understanding whether the Cu-O chains or the carrier concentration plays a more fundamental role in high  $T_c$  superconductivity is extremely important. Preferential substitution of the Cu sites by other elements while maintaining the oxygen content close to 7 is an attractive means to investigate this question.

It is now generally agreed that the  $Cu^{2+}$  ions, with a  $3d^9$  configuration having one hole in the d-band, is crucial for high  $T_c$  superconductivity. In the non-superconducting state the  $Cu^{2+}$  moments are ordered antiferromagnetically.<sup>13</sup> In the superconducting state, the antiferromagnetic correlation associated with the 3d holes is featured prominently in many proposed superconductivity mechanisms.<sup>14,15</sup> In this respect  $Zn(3d^{10}4s^2)$  and  $Ga(3d^{10}4s^24p^1)$  are two unique dopant elements for the Cu sites. They have definite charge states of  $Zn^{2+}$  and  $Ga^{3+}$ , therefore having a full d-shell configurations of  $3d^{10}$ . Upon substituting the Cu-sites, the local d-hole will be eliminated. Furthermore, the  $3d^{10}$  configuration is non-magnetic and there is no magnetic pair-breaking complications. For these reasons the samples doped with Zn and Ga are particularly useful in understanding the role of the Cu sites.

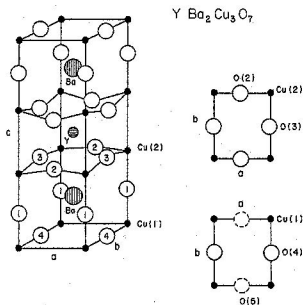


Fig.1: Crystal structure and site identifications of  $YBa_2Cu_3O_7$ . The O(5) sites are vacant in the orthorhombic cell.

When an element A is intended to substitute Cu as in  $YBa_2(Cu_{1-x}A_x)_2O_7$ , where x is the atomic percent of Cu substituted by A, a number of questions are of importance. First of all, it must be ascertained that the element A is substituting the Cu sites. Secondly, it is desirable to have A preferentially substituting either the Cu(1) or the Cu(2) site. Indiscriminately substitution of both Cu sites would not be of particular interest in elucidating the relative importance of the two sites. Thirdly, the charge state of A, its electronic structure, and its magnetic moment if any, are also of crucial importance. Finally, to eliminate effects associated with oxygen deficiency, the oxygen content of the sample should be maintained close to  $y=7$ .

If only the Cu(1) sites, the chain sites, are substituted, the actual substitution level of the chain sites is 3 times the value of x. Due to the presence of a foreign atom (A), the oxygen vacancy order is expected to be disrupted. The structure may transform from orthorhombic ( $b > a$ ) to tetragonal ( $b = a$ ) when the dopant level is increased. On the other hand, if only the Cu(2) sites, the plane sites, are substituted, the actual substitution level of the plane sites is 1.5 times the value of x. One anticipates that the structure remains orthorhombic and the oxygen vacancy order in the plane containing the chains to be intact. These expectations are indeed born out by experiments. In this work, we discuss only those cases where the substituting ions occupy either the Cu(1) sites or the Cu(2) sites. The resulting properties, both structural and superconducting, have been studied.

## II. Experimental

The samples have been fabricated using the standard solid-state reaction methods. Appropriate amounts of  $Y_2O_3$ ,  $BaCO_3$ ,  $CuO$  and various metal oxides ( $ZnO$ ,  $Ga_2O_3$ ,  $Al_2O_3$ ,  $Co_2O_3$  etc.) are mixed, ground, pressed into a pellet and annealed in flowing  $O_2$  at  $950^\circ C$ . The process was repeated and slowly cooled ( $2^\circ C/min$ ) in  $O_2$ . The resulting samples in disk form were cut into appropriate shapes using a diamond saw.

Structural information has been obtained from powder x-ray diffraction and neutron diffraction. X-ray diffraction has been performed by a Philips 3720 automatic ( $\theta$ - $2\theta$ ) powder diffractometer using  $CuK_\alpha$  radiation, with an internal  $Al_2O_3$  standard. The lattice parameters (a,b,c) have been determined by fitting at least 18 peak positions of the diffraction pattern. It is sometimes useful to inspect portions of the diffraction pattern to obtain qualitative information of the structure. The diffraction pattern between  $46^\circ \leq 2\theta \leq 48^\circ$  is one such example. In the orthorhombic structure, three peaks (006), (020), and (200) are resolved. It is immediately obvious that the lattice parameters  $c/3 > b > a$ . However, when the value of c/3, b and a are not sufficiently distinct, e.g. near O-T transition when the value of b and a are approaching each other, an extended diffraction pattern is essential for a reliable determination of the lattice parameters.

For polycrystalline specimens, powder x-ray diffraction provides mainly the information of the lattice parameters a, b and c. Neutron diffraction, on the other hand, provides detailed information within the unit cell. It gives valuable information of the site occupancy of the metal ions, the various oxygen sites, and the total oxygen content. Neutron diffraction measurements of the samples were carried out at the National Bureau of Standards reactor. The scattering intensities were refined using a modified Rietveld analysis procedure. Only the essential neutron diffraction results will be mentioned here, the details will be published elsewhere.

The superconducting properties were measured by both resistivity and SQUID magnetometry on precision-cut samples. The resistivity measurements were performed on bar-shape samples using a four-probe technique with forward and reversed current. In the following section, the value of  $T_c$  from resistivity measurements is illustrated by a vertical bar denoting the 10%-90% resistive transition. A commercial

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SQUID magnetometer was used to measure the samples in both field-cooled (Meissner effect) and zero-field-cooled (superconducting shielding) modes. The value of  $T_c$  determined from the magnetometry measurement is denoted by a filled dot in the figure. Good agreement between the two measurements have been obtained in all samples studied.

### III. Results

#### 1. Zn-substituted samples

The lattice parameters of Zn-substituted samples  $YBa_2(Cu_{1-x}Zn_x)_2O_7$  are shown in Fig. 2(a). All the samples are orthorhombic with similar distortions  $(b-a)/(b+a)$  as in the pure 1-2-3 compound. This is consistent with the expectation if Zn substitutes the Cu(2) sites. As mentioned earlier, the lattice parameter  $c$  of  $YBa_2Cu_3O_{7-\delta}$  depends sensitively on the oxygen content. The  $c$ -axis of the Zn samples is unchanged throughout the doping range, suggesting that the oxygen content is close to 7.

These expectations are indeed confirmed by the neutron diffraction measurements at 295 K on  $YBa_2(Cu_{0.99}Zn_{0.01})_2O_7$ . The essential results are the following. It has a space group of Pmmm same as that of  $YBa_2Cu_3O_7$ . Zn is found to occupy only the Cu(2) sites, with occupancies Zn(2)=0.20(8) and Cu(2)=1.80(8). These values are in good agreement with the theoretical occupancies of Zn(2)=0.18 and Cu(2)=1.82. There are no measurable Zn(1) on the chain sites. The structure is orthorhombic with a large value of  $(b-a)/(b+a)=7.55 \times 10^{-3}$ . The populations of O(4) = 0.84(2) and O(5) = 0.06(1) indicate that the oxygen vacancy order is intact. The total oxygen content ( $y$ ) is 6.80(6), a value commonly observed in pure superconducting  $YBa_2Cu_3O_7$ . The structure data thus conclusively show that Zn occupies only the Cu(2) plane sites, leaving the oxygen vacancy order intact. Neutron diffraction measurements were also made at 10 K with essentially the same results.

Most strikingly, as shown in Fig. 2(b), the superconducting transition temperature ( $T_c$ ) decreases sharply with Zn doping, with an initial rate of -13 K per at. % of Zn. This is the sharpest decrease of any metal dopant that we are aware of. Superconductivity completely disappears near 13% at.% of Zn while the orthorhombic structure and the linear chains are maintained.

Jee et al.<sup>16</sup> have recently reported the results of the Zn-doped samples which are in excellent agreement with ours. In addition to resistivity, they have also measured the specific heat. The specific heat peak at  $T_c$  shifts progressively to lower temperatures with increasing Zn dopant level.

#### 2. Ga-substituted samples

The characteristics of the  $YBa_2(Cu_{1-x}Ga_x)_2O_7$  samples are completely different from that of the Zn-doped samples. Drastic changes of the lattice parameters occur at even 1% dopant level as shown in Fig. 3 for the diffraction pattern within  $46^\circ \leq 2\theta \leq 48^\circ$ . At 3% the structure is already nearly indistinguishable from tetragonal. Fitting the full diffraction pattern shows that the O-T transition occurs at 6-7% Ga as shown in Fig. 4(a). One observes that the  $c$ -axis is essentially unchanged, while the  $a$  and  $b$  axes converge rapidly.

A sample of  $YBa_2(Cu_{0.92}Ga_{0.08})_2O_7$  was investigated by neutron diffraction. The data was refined by both orthorhombic and tetragonal structures. In the orthorhombic (Pmmm) refinement, we obtained a very small value of  $(b-a)/(b+a) < 1 \times 10^{-3}$  which is near the instrumental resolution. The populations of O(4) = 0.66(5) and O(5) = 0.35(4) show that the oxygen vacancy order is mostly destroyed. In a tetragonal refinement, one of course finds O(4) = O(5). The total oxygen content is  $y=7.01$ . Unfortunately the neutron scattering amplitudes of Cu and Ga are 0.772

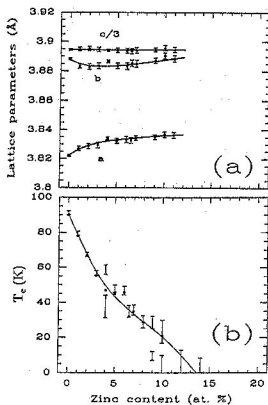


Fig.2: Lattice parameters and  $T_c$  as a function of dopant content for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ .

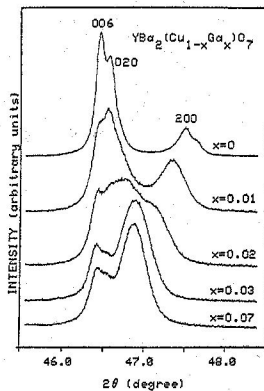


Fig.3: X-ray diffraction patterns of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$  within the range of  $46^\circ \leq 2\theta \leq 48^\circ$ .

and 0.729 respectively, differing by only a few percent. Consequently, we are not able to conclusively assign the site location of Ga. However, from the drastic structure changes observed, it is virtually certain that Ga occupies only the Cu(1) site.

The value of  $T_c$  for the Ga-doped samples changes very little as shown in Fig. 4(b). Most interestingly, across the O-T transition,  $T_c$  remains very high ( $\sim 80$  K). Even in the tetragonal region  $T_c$  is in the range of 65-80 K. This indicates that the oxygen vacancy order is insignificant to high  $T_c$  superconductivity. The Meissner effect in all of the Ga-doped samples remains large as in  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

### 3. Al-substituted samples

The lattice parameters of the  $\text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_7$  samples are shown in Fig. 5(a), similar to those of the Ga-doped samples. The  $c$ -axis remains unchanged, while the  $a$  and  $b$  axes converge rapidly upon doping with Al. At  $x = 0.05$ , the sample is already essentially tetragonal, above  $x = 0.07$ , the structure becomes fully tetragonal. The values of  $T_c$  are insensitive to Al doping as shown in Fig. 5(b). Al does not have a  $d$ -band.  $T_c$  is about 90 K in the orthorhombic phase, and is only weakly dependent on the Al content in the tetragonal phase. Across the O-T transition,  $T_c$  suffers no discernible degradation. Al and Ga are similar in many respects, they are located in the same column of the periodic table, and having identical valence state ( $3+$ ).

A sample of  $\text{YBa}_2(\text{Cu}_{0.99}\text{Al}_{0.07})_3\text{O}_7$  has been measured by neutron diffraction. The space group is tetragonal  $P4/mmm$ , with the population  $O(4) = 1.03(1)$ . All Al are found to occupy the chain sites with occupancies  $\text{Cu}(1) = 0.82(1)$  and  $\text{Al}(1) = 0.18(1)$ . The total oxygen content is  $\gamma = 7.03$ .

#### 4. Co-substituted samples

A sample of  $\text{YBa}_2(\text{Cu}_{0.9}\text{Co}_{0.1})_3\text{O}_7$  was studied by x-ray and neutron diffraction. In both cases, the structure was found to be tetragonal. The space group is tetragonal  $\text{P4/mmm}$ . All of the Co ions are found to occupy the Cu(1) sites. The measured populations of  $\text{Cu}(1) = 0.72(5)$  and  $\text{Co}(1) = 0.28(2)$  are in excellent agreement with the theoretical occupancies of  $\text{Cu}(1) = 0.70$  and  $\text{Co}(1) = 0.30$ . The O(4) population is 1.06(3), resulting a total oxygen content of  $y = 7.06(8)$ . Susceptibility measurements in the normal state show that  $\text{Co}^{2+}$  carries a sizable magnetic moment of about  $3\mu_B$ .<sup>5</sup>

The O-T transition of  $\text{YBa}_2(\text{Cu}_{1-x}\text{Co}_x)_3\text{O}_7$  occurs at  $x \approx 0.03$  as reported by Miceli et al.<sup>17</sup> In the orthorhombic phase,  $T_c$  is essentially unchanged ( $\approx 90$  K). Above the O-T transition,  $T_c$  decreases rapidly and linearly with Co content. At about  $x = 0.14$ , the sample is no longer superconducting. The value of  $T_c = 21$  K of the  $x = 0.10$  sample is in excellent agreement with an earlier result reported by Xiao et al.<sup>5</sup>

#### IV. Discussion

From Figs. 2, 4, 5, it is clear that the superconducting behaviors are entirely different when Cu(1) sites or Cu(2) sites are preferentially occupied. When the Cu(1) sites are substituted, there is little change in  $T_c$ . In fact, at low dopant level, there is virtually no change of  $T_c$  while the oxygen vacancy order and the Cu-O chains are progressively being disrupted.  $T_c$  remains high ( $\approx 80$  K) even when the O-T transition has been induced. Quite the contrary, when the Cu(2) sites are substituted,  $T_c$

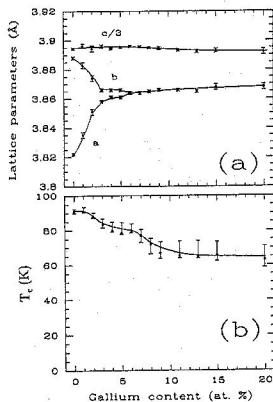


Fig.4: Lattice parameters and  $T_c$  as a function of dopant content for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ .

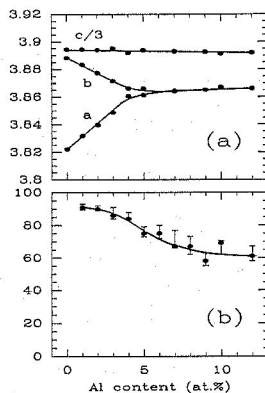


Fig.5: Lattice parameters and  $T_c$  as a function of dopant content for  $\text{YBa}_2(\text{Cu}_{1-x}\text{Al}_x)_3\text{O}_7$ .

decreases sharply. The reduction of  $T_c$  is approximately proportional to the dopant concentration. Thus the tetragonal structure without well-defined Cu-O chains is not detrimental to high  $T_c$ . The orthorhombic structure, where well-defined oxygen vacancy order and Cu-O chains are preserved, does not assure high  $T_c$  superconductivity either. The most important result is that the integrity of the Cu-O<sub>2</sub> planes is far more important than that of the Cu-O chains in sustaining high  $T_c$  superconductivity.

The cases of Zn and Ga-doped samples are particularly illuminating because both have a full  $3d^{10}$  configuration and without the complications of a magnetic moment. Upon substituting a Cu<sup>2+</sup> site, the d-hole will be eliminated, a feat that can be accomplished by both Zn and Ga. Because the correlation among holes of Cu<sup>2+</sup> ions in the Cu-O<sub>2</sub> plane is crucial for high  $T_c$  superconductivity, the substitution of the Cu(2) sites by Zn with filled d-band sharply reduces  $T_c$ . The Ga ions, substituting only the less important Cu(1), have a minor effect on  $T_c$ . In the 2-1-4 compound of (La<sub>1.85</sub>Sr<sub>0.15</sub>)CuO<sub>4</sub>, there is only one Cu site located on the Cu-O<sub>2</sub> plane. Recently we have also substituted Cu by Zn<sup>18</sup> and Ga<sup>19</sup>. The values of  $T_c$  have been found to be severely depressed by both Zn and Ga substitutions. Quantitatively,  $T_c$  reduces to zero as 2.5% of Zn or Ga is doped into the Cu-O<sub>2</sub> planes.

The Al-doped samples show results similar to those of the Ga-doped samples. Like Ga<sup>3+</sup>, the Al<sup>3+</sup> ions do not carry a magnetic moment either, and it has no d band. The Co-doped samples, however, are different in that Co<sup>2+</sup> carries a sizable magnetic moment in excess of  $3\mu_B$ . Indeed, the depression of  $T_c$  of the Co-doped samples is considerably greater, particularly beyond the O-T transition, than those of the Ga and Al samples. This result clearly indicates that the magnetic pair breaking mechanism exists in high  $T_c$  superconductors, and the charge carriers in the plane and chains are not decoupled.

A few words should be mentioned about the tetragonal structure as determined from x-ray and neutron diffraction measurements. Both diffraction methods are insensitive to local orthorhombic distortion, if existing, in the tetragonal samples containing Ga, Co or Al. Therefore, there exists a possibility that the Cu-O chains may persist locally, even though the global structure appears tetragonal. However, at  $x=0.07$  and beyond, all samples doped with Ga, Co, or Al have become tetragonal from diffraction measurements. Because of preferential substitution, more than 20% of the Cu(1) sites have been occupied by foreign ions. The Cu-O chains structure, if persists at all, cannot be extended by more than a few unit cells. Since superconductivity originates from the planes, it is hard to imagine that local order can have any significant effect.

Another important observation that can be made from this study is the association of the charge states of the substituting ions and the Cu sites they preferentially occupy. Al, Co and Ga all have 3+ states and they substitute only the Cu(1) sites. Zn has a 2+ state and substitutes only the Cu(2) sites. Recalling the formal charge states arguments that have been made earlier about Cu(1) and Cu(2) in YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>, this is perhaps not surprising. However, because the actual formal charge state of Cu(1) in pure YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> is less than 3+, in the Co, Al, and Ga-doped samples where the substituting ions all have a 3+ states, additional oxygen have been drawn into the unit cell, and the total oxygen content is found to be in excess of  $y = 7$ .

A major conclusion in this work is that the integrity of the Cu-O<sub>2</sub> plane is essential for high  $T_c$  superconductivity. Recently two new superconductors Bi-Sr-Ca-Cu-O<sup>20,21</sup> and Tl-Ba-Ca-Cu-O<sup>22</sup> with  $T_c$  in excess of 100 K have been discovered. Structural determinations indicated that both structures contain the crucial two dimensional Cu-O<sub>2</sub> planes but not the Cu-O chains.<sup>23,24</sup> Thus Cu-O<sub>2</sub> planes are a common feature of all four high  $T_c$  oxide superconductors. Only YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> contains the intriguing Cu-O chains which we conclude are not an essential feature for high  $T_c$  superconductivity.



### Acknowledgements

This work has been supported by NSF Grant Nos. DMR86-07150 and MEM87-18496. We thank F.H. Streitz, A. Gavrin and A. Bakhshai for their assistance.

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