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THE EFFECT OF CHEMICAL SUBSTITUTION ON SUPERCONDUCTIVITY IN THE $YBa_2Cu_3O_7$

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ABSTRACT

A systematic survey of published data on the effect of the substitution of more than 50 elements for the four elements of the new high T_c superconductor $YBa_2Cu_3O_{7-\delta}$ ($T_c = 92$ K) is given. Every element in this system may be replaced partially or completely. T_c in all cases either remains unchanged or decreases. The effect of substitution at the Cu sites and, more explicitly, the Cu(2) sites is most effective in reducing T_c. Some substituents do not enter the solid matrix and either strengthen the superconducting properties of the materials or also depress T_c. It is shown that size and/or charge selectivity are at the root of the site selectivity expressed in these chemically complex materials.

INTRODUCTION

Oxide superconductors [1] have provided an unprecedented stimulus for solid state scientists over the past two years. The search for new materials, the efforts to characterize their intrinsic physical properties, and the attempts to explain them theoretically have led to an avalanche of results— a few thousand papers during 1988 alone. The discovery of superconductivity above 90 K in $YBa_2Cu_3O_{7-\delta}$ [2,3] (123) raises many questions about the origin and properties of the superconducting electrons. Among the basic studies characterizing this compound are many involving substitution of all four elements composing the compound. Here I attempt to review results in only one related area-the effect of substitution on the critical transition temperature T_c, which should offer some insight into the contribution of each element to superconductivity. No attempt is made to survey the literature exhaustively. I have simply selected some representative data collected up to January 1989 that are of interest. No attempt is made to describe the effect of substitution on other physically interesting properties, such as critical fields and currents, transport behaviour, specific heat, etc.

So far, it appears that the crystallographic unit cell of $YBa_2Cu_3O_7$ is orthorhombic [4-6], space group *Pmmm*, with $a = 3.827$ Å, $b = 3.893$ Å and $c = 11.679$ Å ($c = 3b$). The structure is conveniently described as "oxygen

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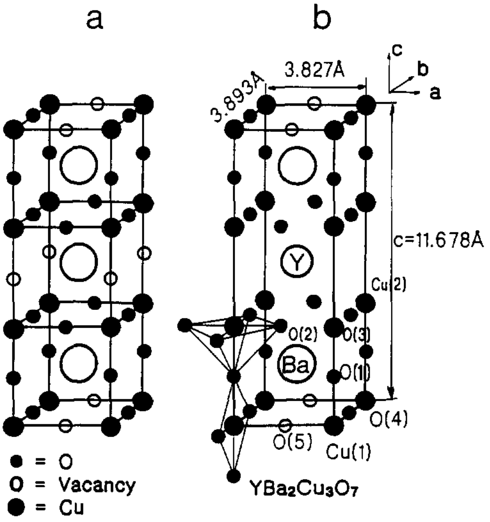

Fig. 1. Crystal structures of (a) a triple perovskite structure and (b) $YBa_2Cu_3O_7$.

deficient pervoskite" (ABO_3) with a tripled unit cell along the c-direction (Fig. 1a). The ordered oxygen vacancies in the structure result in a reduction in the coordination numbers of Cu from the ideal six-fold octahedral site of a stoichiometric perovskite. For $YBa_2Cu_3O_7$ (Fig. 1b) the two oxygen vacancies result in four-fold coordination in the Cu(1) and five-fold coordination in the Cu(2) sites. The Cu(1) atoms form linear chains of corner-shared, almost square planes oriented along the b axis, and the Cu(2) atoms form two-dimensional layers of corner-shared, square-based pyramids as shown in Fig. 1b. The O(1) atom shares both the square plane and the square pyramid. The anisotropy of the oxygen occupation around the Cu(1) sites induces the orthorhombic distortion of the $YBa_2Cu_3O_7$ structure, in order to accommodate one-dimensional Cu(1)–O chains.

It is well established [7,8] that the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ undergoes an orthorhombic-to-tetragonal(I) transition as a result of variation in the oxygen content and oxygen distribution. T_c is dramatically affected by oxygen content and distribution. For $\delta = 0$, $T_c = 92$ K, and when samples are heat-treated at elevated temperatures and/or in a reducing atmosphere, oxygen content and T_c decrease. At $\delta > 0.5$ the samples may be tetragonal and semiconducting. The complete removal of one oxygen ($\delta = 1$) induces a tetragonal unit cell with $a = 3.863$ Å and $c = 11.830$ Å [8] where $c > 3a$. It appears that partial substitution, mainly in the Cu sites, also changes the crystal structure from orthorhombic to tetragonal(II) and it is worth considering the difference between the two tetragonal structures [9]. In the non-superconducting tetragonal(I) phase the oxygen concentration is lower than 6.5 and $c > 3a$. This elongation along the c axis, comparable to $c = 3b$ in the orthorhombic phase, is thought to be the result of oxygen vacancies in the basal plane. On the other hand, the superconducting tetragonal(II) phase is the result of impurities doped into copper or oxygen sites, and oxygen concentration is higher than 7. The c/a ratio remains equal to 3. In other words, the tetragonal(II) has an orthorhombic local symmetry, with accidentally-equal a and b lattice parameters.

As mentioned above, the effort to enhance T_c in the $YBa_2Cu_3O_7$ system, and the attempt to understand the role of each element in superconductivity, led many authors to substitute partially or completely for Y, Ba, Cu or O in the compound. These matters are discussed in detail in the following paragraphs. The T_c values collected from resistivity measurements denote those obtained when zero resistivity is observed.

SUBSTITUTION FOR YTTRIUM

$RBa_2Cu_3O_7$

Following the discovery of superconductivity above 90 K in $YBa_2Cu_3O_7$, it was also found that Y can be replaced by most of the trivalent rare earth elements ($R \equiv$ La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb or Lu) to form superconductors. The same orthorhombic crystal structure is obtained with T_c near 90 K except for $R \equiv$ Ce, Pr or Tb, for which superconductivity has not been observed down to 4 K [3,10–12]. The light rare-earth elements ($R \equiv$ La, Pr or Nd) form compounds that tend to exhibit relatively little orthorhombic distortion in their X-ray patterns. Neutron diffraction studies of orthorhombic $LaBa_2Cu_3O_{7-\delta}$ show that T_c is 93 K only over a very narrow range of oxygen stoichiometry [13–17], and unlike in $YBa_2Cu_3O_7$, T_c varies sharply with δ: it drops dramatically even with a variation of 0.05 in δ. Furthermore, orthorhombicity manifests itself only in the composition range where high T_c is found. This is the reason for some controversial reports of tetragonal structure of $LaBa_2Cu_3O_7$ with $T_c = 76$ K [15], or to a non-superconducting compound above 4 K [11]. $PrBa_2Cu_3O_7$, which is isostructural to $YBa_2Cu_3O_7$, is not superconducting.

The heavy rare-earth elements ($R \equiv$ Nd–Lu except for $R \equiv$ Tb) form compounds which tend to display a rather large orthorhombic splitting in their X-ray diffraction patterns, and all of them have $T_c \approx 92$ K. Moreover, long range magnetic ordering [18–22] has been reported for $R \equiv$ Gd, Dy, Er or Ho.

The Mössbauer measurements on ^{155}Gd provide direct evidence [19] for an absence of conduction electrons at the Gd site in the lattice, and hence no exchange coupling of Gd ion with the conduction electrons. This result explains why the T_c of $YBa_2Cu_3O_7$ is not suppressed by the substitution of Y atoms by magnetic rare-earth atoms, and why superconductivity coexists with long range antiferromagnetic order. Another important feature of these compounds is that at high magnetic fields the magnetic susceptibility data can be fitted to a Curie–Weiss law through the temperature range well below T_c, regardless of whether the sample is in the superconducting or normal state [20]. This means that the magnetic-field-induced paramagnetism in the R sublattice is quite independent of superconductivity in the compound.

The three $RBa_2Cu_3O_7$ compounds with $R \equiv$ Ce, Pr or Tb do not exhibit superconductivity, probably because these ions are not purely trivalent in the $RBa_2Cu_3O_7$ system. While $PrBa_2Cu_3O_7$ is orthorhombic, its Ce and Tb counterparts have quite a different crystal structure. An analysis of the composition of such compounds having the nominal composition $RBa_2Cu_3O_7$ ($R \equiv$ Ce or Tb), prepared with the same solid state reaction method used for the other superconducting $RBa_2Cu_3O_7$ compounds, indicates that these samples are multiphase [23]. On the other hand, the X-ray pattern obtained for $TbBa_2Cu_3O_7$ [9] is reminiscent of the pattern for a perovskite structure with a double unit cell dimension.

$Y_{1-x}R_xBa_2Cu_3O_{7-\delta}$ *R ≡ "superconductor" rare-earth element*

Several mixtures of the two superconducting $RBa_2Cu_3O_7$ and $YBa_2Cu_3O_7$ parents demonstrate that $Y_{1-x}R_xBa_2Cu_3O_7$ ($R \equiv$ Sm, Eu, Gd, Dy or Yb) are all superconductors above 90 K [24–25] over the entire range of compositions. In $Y_{1-x}Gd_xBa_2Cu_3O_7$ the Néel temperature of Gd is proportional to the Gd concentration for $x > 0.2$ [25]. A different picture is observed for $R \equiv$ La [26,27]. The characteristic change in T_c with increasing La concentration appears to be a sensitive function of preparation and structural details. For samples prepared at 950 °C, T_c is 90 K up to $x = 0.5$, and decreases sharply to 60 K thereafter [26]. This observation contrasts with a linear decrease of T_c with increasing x reported in ref. 27. The unusual behaviour reported for $Y_{1-x}La_xBa_2Cu_3O_7$ presumably arises from a non-ideal oxygen content and the very narrow range of oxygen stoichiometry needed to achieve the value of $T_c = 93$ K mentioned above [15].

$Y_{1-x}R_xBa_2Cu_3O_7$ *R ≡ Tb, Ce or Sc*

The $RBa_2Cu_3O_7$ compounds where $R \equiv$ Tb, Ce or Sc do not form with the orthorhombic structure, and are not superconductors. However, samples of $Y_{1-x}Tb_xBa_2Cu_3O_7$ for $0 < x \leqslant 0.12$ were prepared having $T_c = 92$ K which does not change with x in this concentration range [27,28]. The small increase in the orthorhombic lattice parameters is attributed to the larger Tb ionic radius, and it is assumed that Tb substitutes for Y as the Tb^{3+} ion. The X-ray diffraction pattern for $x \geqslant 0.12$ samples exhibit weak unidentified lines associated with extra phases [28].

In contrast to the compounds where $R \equiv$ Tb or Ce, $PrBa_2Cu_3O_7$ is orthorhombic yet not superconducting. The crystallographic distortion in

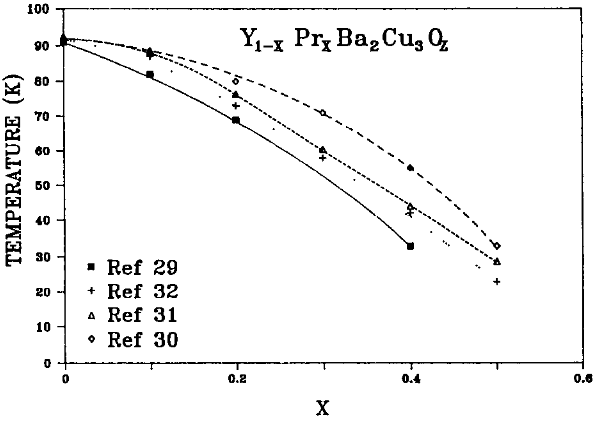

Fig. 2. Variation of T_c in $Y_{1-x}Pr_xBa_2Cu_33O_z$.

the basal plane is very small and the absence of superconductivity will be discussed later. In order to get further insight into the role of the valency of the rare-earth elements in the high T_c compounds, several authors [29–34] prepared the $Y_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ system and measured its electrical and physical properties. The crystal structure is orthorhombic for the entire range of x, and the degree of distortion increases with decreasing x. Figure 2 shows the variations in T_c with increasing x obtained by different groups. Clearly, the trend in T_c is much the same; the variation in data obtained is probably a result of different preparation methods used. There is agreement that for $x > 0.55$ the compounds are not superconductors; resistivity behaviour is typical of a semiconductor material. However, thermopower studies [31] show that the activated regime of resistivity is not intrinsic, and probably arises from interparticle contacts or from a hopping transport mechanism. The valency of Pr in the system is controversial. The depression of T_c as a function of x appears to be associated with nontrivalency of Pr. The magnetic susceptibility measurements reveal that the average valence of Pr is 3.87 in the entire range of x [30]. However, soft X-ray absorption spectroscopy shows [29] that Pr is trivalent, contrary to expectations, thus excluding an obvious mechanism for suppression of superconductivity based on the mixed valency of Pr. The pressure dependence of T_c [34] for the superconducting region $x < 0.5$ measured up to 20 kbar is different for $x < 0.2$ where T_c increases with P, and for $x \geqslant 0.4$, where T_c decreases rapidly with P. These results suggest that the hybridization of Pr 4f electrons and the valence band is expected to be strong for the large Pr ions, and there is a pressure-induced electronic phase transition dependence on Pr concentration. For $x = 0.3$ it occurs at $P = 6$ kbar and for $x \geqslant 0.4$ the transition is shifted to lower pressures [34].

Several mechanisms for the absence of superconductivity in pure $PrBa_2Cu_3O_7$ and for the suppression of T_c in $Y_{1-x}Pr_xBa_2Cu_3O_7$ are available. As mentioned above, the connection of this phenomenon with a Pr valence higher than 3 + cannot be substantiated. It is assumed, rather, that the weakening of superconducting electrons pairs through the strong Coulomb repulsion within the Pr 4f state is responsible for the suppression of T_c. The assumption that the decrease in T_c results from magnetic pair-breaking effect caused by possible partial disorder between Pr and Ba sites is also excluded, since in $Y_{1-x}Gd_xBa_2Cu_3O_7$ no detrimental effect on T_c has been observed [25]. A possible mechanism considers changes in the band structure when a small nonmagnetic Y^{3+} ion (0.93 Å) is replaced by a larger Pr^{3+} ion (1.09 Å), causing hybridization of the Pr 4f electrons and the valence band which is expected to be strong for Pr [34]. In fact Pr is the largest rare-earth ion having 4f electrons which is found as $RBa_2Cu_3O_7$. Although $LaBa_2Cu_3O_7$ is superconducting, La^{3+} has no 4f electrons, and $RBa_2Cu_3O_7$ compound where $R \equiv Ce$ does not form as a single phase.

Powder X-ray diffraction data of $Y_{1-x}Sc_xBa_2Cu_3O_{7-\delta}$ samples show a very good fit to the orthorhombic crystal structure up to $x = 0.25$ [35]. For higher values of x several other phases appear; their relative proportions depend strongly on preparative methods [36]. The effect of Sc substitution on T_c is not clear. It is reported that for $0.1 < x < 0.5$ all the samples are superconductors with T_c within 2 K of that for pure $YBa_2Cu_3O_7$ [36,37]. On the other hand, a progressive decrease in T_c with increasing x is observed by two other laboratories [35,38]. The concentration dependence of T_c for this system is summarized in Fig. 3. Magnetic measurements [35] reveal anomalous magnetic behaviour in this system which is expressed by a large paramagnetic moment. The number of local moments increases proportional to the Sc concentration while the Curie–Weiss temperature, 30 K, is weakly concentration dependent.

It is assumed that the similarity in the ionic radii of Cu^{2+} and Sc^{3+} leads to antisite disorder induced by Sc, namely Sc preferentially occupies Cu(2) sites [35]. Because of the reduced oxygen coordination for Cu occupying an Y site (Fig. 1), it is likely that such a copper ion is in the Cu^{2+} state, which would carry a magnetic moment. That would produce an increased moment with increased Sc concentration and lead to a small decrease in T_c, as in other systems where Cu is replaced by impurities (see discussion below).

$Y_{1-x}A_xBa_2Cu_3O_7$ *(A^{3+} ion ≡ Fe, Bi, Al, Ga, In or Tl)*

Substitution of Y by one of the trivalent rare-earth metal ions does not substantially change the superconducting properties in this class of materials. However, partial substitution by other trivalent ions has been reported. The ionic radius of Fe^{3+} (0.64 Å) is much smaller than that of Y (0.93 Å). The system $Y_{1-x}Fe_xBa_2Cu_3O_7$ was prepared [39]; X-ray diffraction spectra indicate that for $x < 0.3$ the samples are single phases; gradual changes are observed in the spectra with increasing Fe content. A sharp variation in T_c is

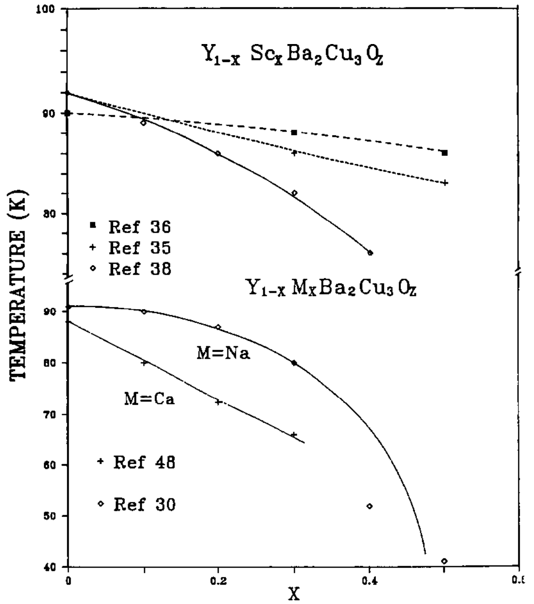

Fig. 3. Variation of T_c in $Y_{1-x}M_xBa_2Cu_3O_z$.

observed with increasing x. It seems that qualitatively similar changes in T_c (and structure) are observed when Fe occupies Cu sites (All these topics will be discussed in depth in the section entitled Substitution for copper). By way of contrast we prepared the same $Y_{1-x}Fe_xBa_2Cu_3O_7$ system in our laboratory using the method reported in ref. 39. We measured the Mössbauer effect for ^{57}Fe on our single phase samples. The spectra obtained were identical to those obtained when Cu is substituted for Fe [40,41] which definitely means that the small Fe ions do not occupy the Y sites. Bi (0.74 Å) substituted for Y does not substantially change the lattice parameters of $YBa_2Cu_3O_7$, suggesting that there is no solubility range of Bi in the Y sites [39].

The systems where $A^{3+} \equiv$ Al, Ga, In or Tl have also been prepared, and it is argued that the trivalent ions substitute for Y^{3+} [39,42–44]. In the case of $A \equiv Al$, for $0 < x < 0.85$, T_c varies between 90 K and 50 K [39]; and for $A \equiv Ga$, T_c decreases gradually with increasing Ga content [42]. For $A \equiv In$, for $x < 0.6$, T_c scarcely changes. Replacement of Y by Tl resulted in improved superconducting transition temperatures [43]. All the X-ray diffraction patterns for $A \equiv Al$, In or Tl reveal the existence of multi-phase materials. The ionic radii of Al^{3+} (0.50 Å) and Ga^{3+} (0.62 Å) are smaller than Y^{3+} (0.93 Å). Significant substitution would entail a decrease in the unit cell parameters, which is in contradiction to the constant lattice parameters and interplanar d values actually found [39,42]. It seems more likely that in all cases A^{3+} occupies the Cu site [45]. It is also possible that

A^{3+} can only partially substitute for Y^{3+}. All substitution at the Cu site is supported by the small observed increase in the cell volume [44].

Partial substitutions of tetravalent ions such as Zr and Hf in the Y site are reported [45–48]. In the system $Y_{1-x}Zr_xBa_2Cu_3O_7$, T_c remains constant at 93 K for $x = 0.15$ [24] and a slight decrease in T_c is observed with increasing x. $T_c = 91$ K for $x = 0.5$ [47]. The X-ray analysis indicates that the materials are multi-phase [47,48], so the amount of Zr occupying Y sites is not clear.

Although X-ray data are not given in ref. 46, the electrical resistivity has been studied in a series of Zr-substituted ($x < 0.4$) and Hf-substituted ($x < 0.5$) systems. With increasing x, T_c decreases: for Zr and Hf, $T_c = 80$ and 78 K for $x = 0.4$, respectively. It is not even clear whether Zr or Hf enters the solid matrix as a genuine substitution, or whether it is segregated in defects. It was observed [46] that after a long period pure $YBa_2Cu_3O_7$ samples had degraded, whereas those doped with even small amounts of Zr or Hf were preserved. Both substitutions improve the sintering of the ceramic and lead to compounds that are much less sensitive to aging and humidity, and are mechanically more resistant.

$Y_{1-x}Ca_xBa_2Cu_3O_{7-\delta}$

Single phase samples containing Ca, $0 \leqslant x \leqslant 0.3$ were prepared and investigated by X-ray diffraction, magnetic susceptibility and conductivity measurements [49,50]. For $x < 0.3$ the crystal structure remains orthorhombic, and the variation with x of the lattice parameters and unit cell volume show an increase in unit-cell volume to be expected for substitution of the larger Ca^{2+} ion (0.99 Å) for Y^{3+}. The calcium solubility in $YBa_2Cu_3O_7$ is limited and samples with $x \geqslant 0.3$ are not single-phase materials. The variation of T_c with x is shown in Fig. 3: an approximately linear decrease with a slope of 0.7 K per 1% of Ca is observed. The oxygen stoichiometry measured by TG shows a tendency to decrease with increasing x; for $x = 0.2$, $\delta = 0.18$. The fact that the unit-cell volume increases with x proves that Ca^{2+} replaces Y^{3+} and not the divalent Ba^{2+}, since Ca^{2+} is smaller than Ba^{2+} and substitution for Ba^{2+} would lead to a decrease in cell volume [51]. The small Y^{3+} ion cannot be replaced by large divalent ions such as Sr^{2+} and Ba^{2+}.

$Y_{1-x}M_xBa_2Cu_3O_7$ ($M^+ \equiv$ Li, Na, K or Rb)

Substitution of trivalent yttrium for mono-valent alkali metal ions depresses T_c below that of pure $YBa_2Cu_3O_7$. The depression of T_c is relatively large for the lighter (Li^+, Na^+) alkali metals but insignificant ($\leqslant 1$ K) for specimens doped with Rb^+ and K^+ [37]. The ionic radii of Na^+ and Y^{3+} are similar (0.95 Å and 0.93 Å respectively), and the X-ray diffraction measurements show that the lattice parameters for $M \equiv Na^+$ are within 0.2%

of those for pure Y. Moreover, the Bragg peaks typical of the orthorhombic structure move closer to one another, overlapping substantially at $x = 0.5$, similar to what has been observed as the oxygen deficiency increases. The similarity between the ionic radii of Na^+ and Y^{3+} permits a higher solubility of Na^+ in the $YBa_2Cu_3O_7$ structure. The variation of T_c for $M \equiv Na$ with x, reported in ref. 30, is shown in Fig. 3. It should be noted that for $x = 0.3$, $T_c = 80$ K and 77 K for $M \equiv K^+$ and Rb^+ respectively, as reported in ref. 52. Since no X-ray data are available, the quality of samples is not known. It is assumed [30] that the presence of monovalent Na^+ ions reduces the oxygen content, to compensate for the trivalent Y^{3+} ions they replace.

From the description above it seems that the high T_c first discovered in $YBa_2Cu_3O_7$ can only be attained in similar systems when Y is partially or completely replaced by a trivalent rare-earth element. Substitution at the Y site by a smaller trivalent ion, such as Sc^{3+}, or by Pr whose valency has not been determined leads to suppression of T_c. The same phenomenon occurs in the case of substitution by divalent Ca^{2+} or monovalent ions (Na^+) whose ionic radii are very similar to Y^{3+}. In all cases, substitution for Y affects T_c much less than substitution for Ba or Cu, and the crystal structure remains orthorhombic. There is no direct evidence that other trivalent ions such as Fe^{3+}, Ga^{3+}, In^{3+} or tetravalent ions such as Hf^{4+} or Zr^{4+}, or large monovalent ions such as K^+ and Rb^+ replace Y^{3+} in this structure. It seems more likely that if substitution really occurs, it is at the Cu sites rather than the Y site.

SUBSTITUTION FOR BARIUM

In the previous section it was shown that the superconductivity of $YBa_2Cu_3O_7$ is not significantly affected by the magnetic character of a rare-earth element substituted at the Y site. T_c did not change significantly when Y was replaced by ions with similar ionic radii but different valencies. Substitution for Ba in $YBa_2Cu_3O_7$ has also attracted considerable attention. Research has concentrated primarily on whether the effect of such substitution is similar to substitution at the Y site, since both Y and Ba represent the same atom in the original perovskite structure (Fig. 1). Partial substitution for Ba ions with different valencies is the focus of the present section.

$YBa_{2-x}A_xCu_3O_7$ *A = alkaline-earth ion,* Cd^{2+}, Pb^{2+} *or* Sn^{2+}

The chemistry of divalent Ba^{2+}, Sr^{2+}, Ca^{2+} and Mg^{2+} ions, all of which belong to the alkaline-earth group, is very similar. They differ in their ionic radii, which decrease with increasing atomic number. The ionic radii are 1.35 Å, 1.13 Å, 0.99 Å and 0.65 Å respectively. The similarity in the sizes of Ba^{2+} and Sr^{2+} permits a wide solubility range of Sr in the $YBa_{2-x}Sr_xCu_3O_{7-\delta}$

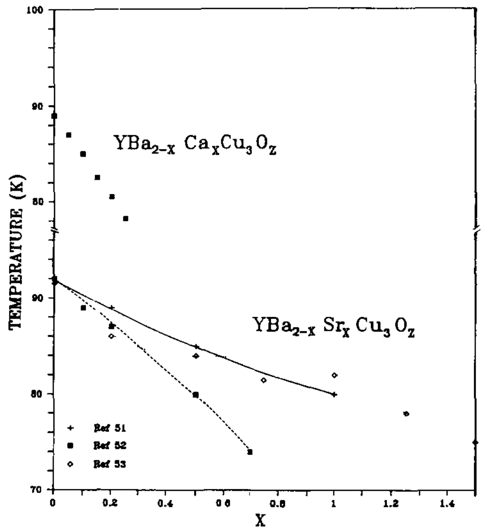

Fig. 4. Variation of T_c in $YBa_{2-x}M_xCu_3O_z$ where M ≡ Ca or Sr.

system, extending to at least $x = 1$. These crystallize in the orthorhombic structure. Samples with $x = 1.25$ and 1.5 showed an additional phase. $YSr_2Cu_3O_7$ was found to be insulating and did not contain any detectable orthorhombic phase characteristic of $YBa_2Cu_3O_7$. The lattice parameters [53,54] and the orthorhombic splitting decrease slightly with increasing Sr, indicating substitution of Sr for Ba [53,54]. This substitution is also indicated by local distortion of the structure, around the Sr atoms, and the four O(1) oxygen atoms are shifted toward the Sr atoms by 0.14 Å. The possibility that an ordered structure is present for $x = 1$, involving an ordering of the Ba and Sr atoms and displacement of the near-neighbour Cu and O atoms, is not ruled out [54].

T_c obtained from resistivity curves for all values of x is depressed monotonically with increasing Sr content. Figure 4 shows the various data obtained. The initial decrease in T_c is larger for low values of x, and is followed by a smaller decrease near $x = 1.0$. T_c continues to decrease even for $x > 1$, where the samples are not single phase. A narrow transition width is observed for $YBaSrCu_3O_7$, which may indicate ordering of Sr ions in the 123 structure [54]. $T_c = 86$ K for $x = 0.5$ was reported in ref. 12, one of the earliest papers published on the 123 phase.

The solubility of Ca^{2+} in the 123 structure is small and limited to $x = 0.25$. As Ca^{2+} is distinctly smaller than Ba^{2+} the orthorhombic unit-cell volume, the orthorhombic distortion and T_c decrease almost linearly with Ca concentration [55] (Fig. 4). The contraction in the unit-cell volume indicates that Ca is indeed substituted for Ba, in striking contrast to the increased unit-cell volume observed when Ca replaces Y [49]. For A ≡ Sr the b lattice parameter decreases while the a parameter remains nearly constant. It is most likely that for both cases, where $A \equiv Ca^{2+}$ and $A \equiv Sr^{2+}$, additional vacancies in the Cu–O chains appear; hence T_c decreases markedly.

In the case of $A \equiv Mg$ [56] the situation is quite different. Single-phase samples of $YBa_{2-x}Mg_xCu_3O_{7-\delta}$ are observed for $x \leqslant 0.4$. However, T_c decreases from 92 K to 82 K with the substitution of even a tiny amount of Mg ($x = 0.04$). All samples up to $x = 1$ have T_c values around 82 K, which means that T_c is not sensitive to Mg concentration. High resolution electron microscopic studies for low Mg concentration show clearly that the small Mg^{2+} ions do not replace Ba^{2+}, but rather occupy oxygen vacancies in the basal plane [56].

Doping of Cd into the 123 structure does not alter the T_c of the system. Moreover, it was found that the presence of Cd in the $YBa_{2-x}Cd_xCu_3O_{7-\delta}$ system leads to a sharp transition above 90 K [57]. Strong hysteretic behaviour is observed in resistivity measurements; it disappears as time goes by. T_c is higher by 21 K when the Cd-doped sample is measured while cooling than when the same sample is measured while heating. Since the lattice parameters for the Cd-doped samples are almost constant up to $x = 1.5$, it is concluded [57] that Cd does not enter the matrix, and the intrinsic properties of the 123 phase are not affected by its presence. Similar behaviour is observed in $YB_{1.7}Pb_{0.3}Cu_3O_7$, $T_c = 90$ K [58]. It is apparent that lead does not substitute for Ba, but rather improves the intergranular contact in sintered ceramic samples. The normal-state resistance of the lead-doped sample is lower than that of the undoped 123 material.

Mössbauer measurements have revealed that Sn in $YBa_{1.8}Sn_{0.2}Cu_3O_7$ resides in two sites, possibly those of Ba and Y [59]. A typical resistivity curve for a single-phase compound indicates zero resistance at 85 K, suggesting that the incorporation of Sn depresses T_c. As the Sn concentration is increased, T_c is further reduced. Marked variations in the intensity of the Mössbauer line corresponding to Sn in the Ba site are observed in the region 82–115 K. This means that there are changes in lattice rigidity at the superconducting transition. This observation indicates the important role of phonons in superconductivity phenomena in high T_c systems.

$YBa_{2-x}R_xCu_3O_{7-\delta}$ $R \equiv Y$ or La

Efforts have been made to raise the oxygen stoichiometry beyond 7 by partial replacement of the divalent barium by trivalent Y or La ions. Since Y and Ba sites in the 123 structure are interchangeable, it is thought that La^{3+} is a better choice as a substituent that Y because the ionic radii of La^{3+} and Ba^{2+} are very close, 1.33 Å and 1.35 Å respectively. The $Y_{1+x}Ba_{2-x}Cu_3O_7$ system [60] was prepared at relatively low temperatures. Although Y^{3+}, by virtue of its small size, cannot occupy the Ba site, low temperature preparation yields metastable phases. For $x > 0$ up to $x = 0.5$ a tetragonal structure

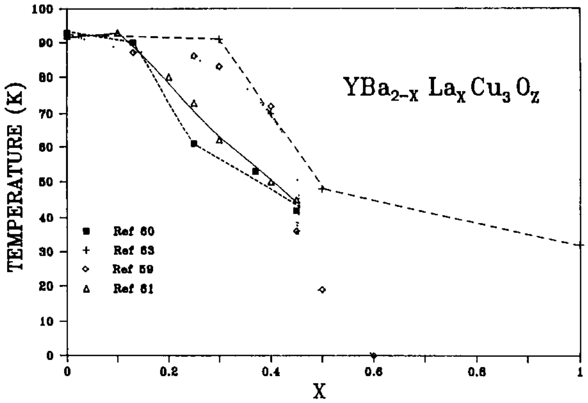

Fig. 5. Variation of T_c in $YBa_{2-x}La_xCu_3O_z$.

was observed, although some evidence of a slight orthorhombic distortion is suggested in some of the samples [60]. On the other hand, substitution of Ba^{2+} by La^{3+} in $YBa_{2-x}La_xCu_3O_{7-\delta}$ leads to a structural transition from orthohombic to tetragonal at $x = 0.4$ [61–64]. In both cases the oxygen content is increased with increasing x, and the extra oxygen atoms occupy the O(5) vacancies in the basal plane (see below).

The onset of superconductivity for R ≡ Y is in the region of 75 K, and zero resistance is observed around 50 K regardless of x, up to $x = 0.5$ [60]. It is noted that the La content dependency of T_c [61–65], shown in Fig. 5, differs from the other doped systems described above. The general feature of the curves in Fig. 5 is a constant value of T_c for low $x < x_c$ (x_c is different in the various papers) followed by a sharper decrease for $x > x_c$. These two regions are not connected to the crystallographic transition that occurs. It was also observed [64] that for $x < x_c$ the normal resistivity exhibits metallic behaviour, which changes to semiconducting behaviour for $x > x_c$. Because La^{3+} cannot replace Cu, and also because of the weak interaction between Ba and Cu sites, the effect of La doping on T_c can only be interpreted either (a) by a change of hole concentration or (b) by a change in oxygen concentration and coordination number of the Cu(1) atoms. Hall effect measurements do not show a change of carrier concentration at $x = x_c$ [61]. It seems therefore that the excess oxygen atoms in the O(5) sites form a second pyramid in the 123 structure with the Cu(1) atoms, where the O(1) oxygen is common to the first pyramid with Cu(2) already existing in the structure [61]. The increase in the coordination number of Cu(1) from 4 to 5 (or 6) leads to an increase in the Cu(1)–O(1) distance, so that O(1) is shifted relatively toward Cu(2). Above a critical composition x_c, these Cu(2) atoms connected with Cu(1) pyramid have a different electronic state; they behave like impurities doped into the Cu site and depress T_c.

$YBa_{2-x}A_xCu_3O_7$ $A \equiv$ *mono-valent alkali metal cation*

The similarity in the ionic radii of Ba^+ and K^+ 1.35 Å and 1.33 Å respectively, caused several laboratories to substitute potassium for barium in the 123 compound [59,66–70]. From the chemical point of view, the synthesis temperature is reduced because the reaction rate of the mixture containing alkali ions is expected to increase [70]. From the physical point of view, any reduction in the cationic charge will change the carrier concentration and affect the electronic structure of the Cu–O network, or decrease the oxygen concentration, which will produce a vacancy in the Cu–O chains, provided the orthorhombic structure of the 123 host is not altered. It appears that in $YBa_{2-x}K_xCu_3O_7$ a single orthorhombic phase persists up to $x = 1$ [68,69]. Since the ionic radii of Ba^{2+} and K^+ are similar, differences in lattice parameters are small, and only a small change in lattice constant was observed with increasing x [68,70]. T_c remains unchanged regardless of K concentration. At low K concentration the superconducting transition appeared to be sharper than in the undoped samples [67].

In the case of $A \equiv Cs$ there are several indications [70] that this large ion (1.69 Å) does not substitute for Ba. For $A \equiv Li$ a marked change in T_c is observed, suggesting that, owing to its smaller ionic radius (0.60 Å), Li^+ replaces Cu^{2+} and not Ba^{2+}. For $A \equiv Na$, T_c remains constant up to $x = 0.25$ [69], and then drops to lower temperatures for higher concentrations. It is not clear whether the Na^+ substitutes for Ba^{2+} or Y^{3+}, which have similar ionic radii [30]. Several values of T_c for different alkali-cation-doped samples are given in ref. 53, but the quality of samples is not reported.

SUBSTITUTION FOR COPPER

Chemical substitution of transition and nontransition metal ions for the two-site Cu(1) and Cu(2) copper ions in 123 compound has proven to be a rich and varied endeavour. The effect of impurities in the Cu sites on the electrical, mechanical and thermal properties of the high T_c materials is of great importance for understanding the superconducting state. Even though there are many theoretical proposals to explain high T_c superconductivity, there is wide agreement that the Cu–O layers and/or chains play the dominant role in the mechanism of this phenomenon. In ordinary superconductors magnetic impurities such as Fe and Co significantly depress T_c owing to their pair-breaking action. It was shown in the previous sections that replacement of Y by magnetic rare-earth ions (Gd, Dy, etc.) has no influence on T_c. On the other hand, it will be shown here that atoms which are able to substitute preferentially for the Cu ions in either planes or chains, or to replace Cu randomly on both crystallographic sites, clearly influence T_c. In most cases partial substitution for Cu (3–5%) induces a structural change from orthorhombic to tetragonal symmetry. The most striking fact is that Zn impurities, which are not magnetic, unexpectedly alter the superconducting properties more drastically than magnetic impurities, without changing the orthorhombic symmetry of the crystal structure.

Some contradictory results are observed in the literature concerning the behaviour of the 123 phase doped with impurities. Superconducting properties appear to be inconsistent from investigation to investigation. Some of this variation, but perhaps less than expected, arises from non-selective site substitution; and some arises, more often, from non-ideal preparative methods, which lead to extra phases or to a varied oxygen stoichiometry. Disagreement on the definition of T_c also produces ostensibly different results. A plethora of results of substitution effects for Cu by different metal ions on T_c is summarized here. For the sake of convenience the dopants are divided into two categories: magnetic and non-magnetic ions. The survey is based mostly on recently published papers.

Substitution for copper by non-magnetic ions

Zn

Zn and Cu are next-door neighbours in the Periodic Table and have similar ionic radii (Zn^{2+}, 0.74 Å; and Cu^{2+}, 0.69 Å). The pioneering research of Maenu et al. [71] and Xiao et al. [72] showed that despite the fact that Zn is not magnetic, the rate of T_c depression with Zn substitution is the largest known to date. This fact induced several authors to perform a more systematic investigation of the replacement of Cu by Zn. In $YBa_2(Cu_{1-x}Zn_x)_3O_7$ up to $x = 0.1$ the crystal structure remains orthorhombic [73] with the distortion very close to that of the pure 123 compound. A slight increase in the a lattice parameter is observed, but the b and c lattice parameters do not change with x. This means that oxygen stoichiometry, the linear Cu–O chains, and oxygen vacancy order are hardly disturbed by Zn substitution, and Zn ions preferentially substitute for Cu in the Cu(2) sites [73]. Neutron diffraction data confirm this observation [74]. Quantitative analysis carried out on different compositions and components made with an electron probe microanalyser clearly shows that Zn atoms replace Cu, and that the final Zn content in the 123 phase is always lower than the initial nominal concentration. The upper limit for Zn solubility in the matrix is 8% [74].

The variations in T_c with percent Zn substitution reported in several recent papers [73–79] are presented in Fig. 6. Clearly the trends in T_c obtained for low Zn concentration up to 3% are very similar, and a sharp drop in T_c is observed, with $dT_c/d(\%Zn)$ lying between 11–16 K $\%Zn^{-1}$. For higher x values, a plateau at about 50–60 K is observed in most investigations. The Zn doping results obtained in refs. 75 and 78 show a

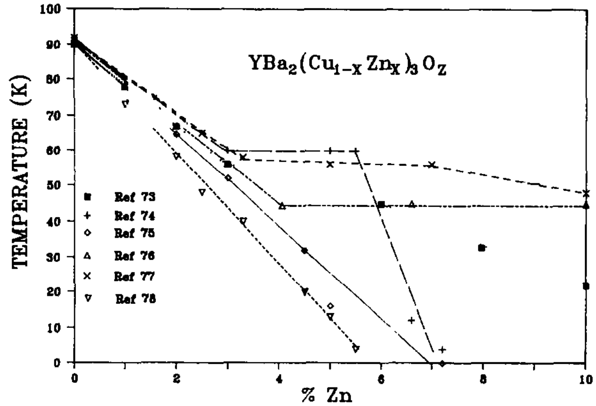

Fig. 6. Variation of T_c in $YBa_2(Cu_{1-x}Zn_x)_3O_z$.

continuous decrease of T_c down to zero and for $x > 5$–7%, T_c drops to zero. The different results exhibited in Fig. 6 probably arise from the limited solubility range of Zn and to the inability to prepare single-phase materials for $x > 5\%$. A similar plateau of $T_c(x)$ is observed in Ga-doped samples [73], but this was never found in 123 compounds doped with magnetic 3d ions.

The sharp decrease in T_c for $0 < x < 3\%$ suggests that it is the Cu–O planes which are the crucial structures in high T_c superconductors, whereas the Cu(1)–O chains play a much less important role than was formerly believed. The Cu–O chains act as an electron reservoir which serves to minimize T_c when oxygen is removed. This assessment is by no means in conflict with the observations [8] that T_c correlates with the number of oxygen ions along the Cu–O chains. It is commonly agreed that the electron hole in the 3d level of Cu^{2+} is crucial to high T_c superconductivity [80,81]. The holes either provide an antiferromagnetic background, coupled to the superconducting carriers, or become the itinerant charge carriers themselves, forming superconducting pairs. The 3d level of Zn is completely full, and Zn substitution for Cu eliminates 3d holes. The Fermi level shifts quickly into a local minimum of the density of states. This might explain the rapidly decreasing T_c caused by Zn substitution.

Ga, Al, In and Mo

The superconducting properties of $YBa_2(Cu_{1-x}Ga_x)_3O_{7-\delta}$ appear to be inconsistent from investigation to investigation. A crystallographic transition to tetragonal is obtained for $x > 0.03$–0.04; and Ga substitutes preferentially for Cu in the Cu(1) sites [73]. The observed systematic variation of lattice parameters suggest that Ga (0.62 Å) is incorporated into the 123 compound at least below $x = 0.05$. Extra phases are revealed above this concentration by X-ray measurements. Electron microprobe studies of several samples show that the 123 phase in all cases contains significantly less Ga than the

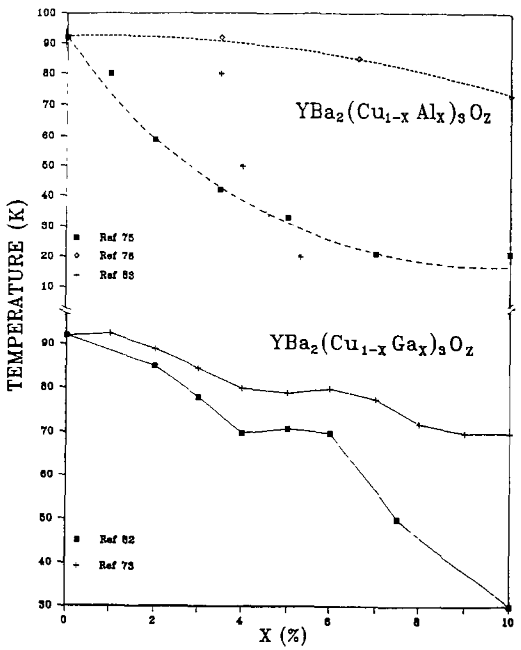

Fig. 7. Variation of T_c in $YBa_2(Cu_{1-x}A^{3+}_x)_3O_z$ where A ≡ Ga or Al.

nominal composition. It is concluded that no more than about 1% of Ga is incorporated into the 123 structure, and that the X-ray diffraction data may be misleading [82]. The variation of T_c with Ga content is shown in Fig. 7; the discrepancies among the data are obvious, and are not explained. It should be added that $T_c = 53$ K for $x = 0.1$ is reported in ref. 71.

Surprisingly, although the ionic radius of Al^{3+} is much smaller than that of Cu^{2+} (0.50 Å and 0.69 Å, respectively), X-ray diffraction measurements carried out on single crystals [45] indicate that aluminium substitutes for copper, and that the solid solubility limit of Al is above 4% [75]. Samples containing higher concentrations of Al ions contained other phases. The orthorhombic structure changes to tetragonal at around 4% Al. Refinement of the structure made on single crystals indicates that Al (like Ga) replaces copper preferentially at only one site, viz., Cu(1) in the Cu–O chains. The presence of Al^{3+} in the lattice produces local octahedral sites around the Al^{3+} ions, disordering the regular O(4) chains and leading to an orthorhombic tetragonal transition.

The variations of T_c with Al content are shown in Fig. 7. T_c drops gradually to 80 K for 3.3% Al, then decreases sharply [45]. The transition width is increased with Al content, which may reflect microscopic inhomogeneity. T_c suppression is seen only after a threshold Al concentration is reached, which is approximately the same composition where the crystallographic transition occurs. The data cited from refs. 44, 75 and 76 are quite different; the discrepancies among the conflicting data are not explained. It is worth mentioning that Al substitution reduces the in-plane resistivity and upper critical fields compared to the pure parent compound [83].

The solubility of Mo in the 123 phase is limited to 5%, and at the same concentration a structural phase transition to the tetragonal structure is observed [75,84]. T_c is 72, 60 and 50 K for 1, 2 and 5%, respectively, and above this concentration a multi-phase material is obtained.

For In substitution for copper, no X-ray data or other measurements which define the structure are available [44]. As usual T_c is reported to decrease with increasing In content.

Ag, Au, Pd, Nb and Pb

Ag substitution for Cu occurs rarely in oxide materials, as can be seen from examination of naturally occurring minerals. Contrary to Cu^{2+} only mono- and trivalent Ag exists in oxides. The larger size of Ag^+ (1.26 Å) compared with Cu^{2+} (0.69 Å) can be expected to limit substitution to very low levels. The size factor makes it very unlikely that Ag will substitute for Y. It has been reported that substitution of Cu by Ag rapidly destroys superconductivity, but also that up to 5% copper can be replaced by silver without any change in T_c [85,86]. A systematic study of Ag substitutions has shown that for $x = 0.1$, 0.15 and 0.2, T_c is 63, 55 and 48 K, respectively [87], but the samples seem to be multi-phase, and there is no clear evidence for substitution. Suprisingly, superconductivity with the onset at 50 K has been observed in a multi-phase mixture with the composition $YBa_2Ag_3O_x$ [88]. At room temperature the sample showed a weight gain, and after several days, superconductivity disappeared. Properties such as machineability, malleability, and soldering may improve considerably by preparing a composite material of 123 and Ag. The effect of Ag on the surface barrier for depletion of oxygen from the 123 phase was also reported recently [89,90].

In the $YBa_2(Cu_{1-x}Au_x)_3O_7$, Au^{3+} is introduced into the 123 structure and the orthorhombic structure exists up to $x = 0.1$. The a and b parameters of the unit cell remain unchanged, but the expansion of the c lattice parameter which correlates well with Au doping level is observed [91]. It is assumed that the substitution occurs at the Cu(1) sites. No significant effect on T_c has been observed ($T_c = 89$ K for $x = 0.1$) to date. Au is evidently an exceptional substituent, since it is argued that it occupies the Cu(1) site, but neither T_c nor crystal structures are changed. It is shown too that T_c is unaffected by the presence of Au as a composite [92]. The composites with gold exhibit low normal state resistivity and much improved ductility.

It is also reported that for $YBa_2Cu_{2.5}Pd_{0.5}O_{6.8}$ as a major phase $T_c = 49$ K, which shows that Pd destroys superconductivity. The sample is metastable: a month after sample preparation no superconducting transition was observed down to 4 K [93].

Two main phases were observed in the Nb^{5+} (0.70 Å) doped into the 123 system. It was found that in $YBa_2Cu_{2.5}Nb_{0.5}O_z$ the 123 structure exists together with a f.c.c. structure with $a = 8.4153$ Å and $T_c = 90$ K, and it is not clear whether Nb^{5+} ions enter into the structure [94].

Multi-phase materials are obtained in $YBa_2Cu_{3-x}Pb_xO_z$. Although T_c does not change, the normal state resistivity and the critical current densities J_c are sensitive to the amount of lead. For $x = 0.1$, J_c is more than twice as high as that of the sample with $x = 0$ at 77 K [95]. Intergranular contact is improved and the behaviour of this system is similar to the system in which Pb was substituted for Ba [58].

Sn, V, Ti, Cr, Cd and Hg

An attempt to prepare $YBa_2Cu_{3-x}Sn_xO_{7-\delta}$ reveals that the critical dopant concentration x_c for Sn, at which superconductivity disappears, is approximately 1. T_c is almost independent of x for $x < 1$ and decreases only 5 K as x varies from 0 to 0.9. For all samples with $x > 1$ superconductivity is not found down to 4 K and the samples exhibit semiconductive properties [94]. The specimens were found to be single phases, but neither crystallographic data nor the valence or occupation sites of Sn were reported. In a recent research, single phases and a positive Hall coefficient in the normal state were observed for $x \leqslant 0.3$. For $x = 0.05$, 0.1, 0.2 and 0.3, $T_c = 90$, 88, 85, and 81 K, respectively. For $x = 0.4$, $T_c = 77$ K but the sample contained impurity phases [96].

Vanadium was introduced into the 123 phase additionally and then substitutionally for Cu. In both cases the orthorhombic structure was the main phase up to $x = 0.2$, and a scanning electron microscopic analysis revealed that V was introduced into the lattice substitutionally for Cu. It is assumed to be tetravalent [97]. T_c practically remains unchanged at 91.8, 87.4 and 85 K for $x = 0.02$, 0.06 and 0.1, respectively; and the fact that the critical current density J_c with $x = 0.033$ is similar to J_c for pure 123 casts doubt on the substitution of V for Cu. The same $T_c = 83$ K for $x = 0.1$ is given in ref. 72 together with $T_c = 74$ K for $YBa_2(Cu_{0.9}Ti_{0.1})_3O_{7-\delta}$.

Cr substitution leads to homogeneous materials over the range of $x < 0.1$. Materials with $x \geqslant 1$ form with a different structure [98]. The decrease in T_c is only about 3 K for $x = 0.05$ [99] and for $x = 0.1$, $T_c = 85$ K [72]. The reason for the relatively mild decrease of T_c with increasing Cr content is explained by the conventional spin exchange mechanism [91].

X-ray phase and lattice constant analysis of Cd- and Hg-containing compounds of the 123 system indicated a restricted solid solution for much larger Cd^{2+} (0.97 Å) and Hg^{2+} (1.10 Å) ions when substituted for Cu, and there are homogeneous solutions for $x \leqslant 0.02$ [100]. The deterioration of superconductivity as a result of Cd and Hg substitution appears to be fairly small.

There is no direct proof that the ions mentioned in this section really replace copper and form solid solutions with the 123 phase.

Substitution for copper by magnetic ions

Since the discovery of high T_c superconductivity a large variety of possible explanations concerning the basic interactions and the nature of the superconducting state have been published. So far no generally accepted concept has emerged. A promising way to probe the superconducting state is to study samples with compositional variations. It is commonly accepted that superconductivity results mainly from the hybridization of Cu d-states and O p-states in a Cu(2)–O layer. Of special importance in this respect is the substitution for Cu by an element that has a magnetic moment or different number of valence electrons. Magnetic ion substitution has been of particular interest, since it may provide a test of the importance of magnetic pair-breaking or magnetic pairing, and hence to shed some light on the superconducting mechanism.

Subsequently, several families of metal substitutions of the form $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$, where M is a magnetic 3d ion such as Mn, Fe, Co and Ni, and x has ranged from 0 to about 0.2, have been investigated. A wide range of effects have been observed in the heavily studied Fe-doped system, mainly because ^{57}Fe is a suitable nucleus for Mössbauer measurements. A systematic survey of substitution for copper up to 3% has been published already [101]. In the following an extension is made to higher x values, and the dopants will be described in the same order they appear in the Periodic Table.

Mn

Manganese is an antiferromagnetic element and a systematic study of $YBa_2(Cu_{1-x}Mn_x)_3O_{7-\delta}$ indicates [100] that up to $x = 0.2$ the 123 orthorhombic structure is preserved. An accurate analysis of X-ray data shows the amount of additional intergranular phases increases proportionally to the Mn content, but shows modifications indicative of Mn substitution for Cu.

The onset of the resistive transition is almost invariant with the Mn concentration. T_c (defined as the temperature at which the resistivity is zero) decreases non-linearly with the Mn content. T_c remains constant 91 K up to $x = 0.075$ and then decreases to 89, 77 and 73 K for $x = 0.1$, 0.15 and 0.2 respectively [102]. $T_c = 79$ K is given in ref. 72. The T_c suppression resulting from Mn substitution is explained by the classical spin exchange between the local magnetic moment and the Cooper-pair electrons.

Fe

A large number of investigations [101,103–113] of the general composition $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ have been undertaken primarily because Mössbauer measurements on ^{57}Fe provide direct, useful information on the local environment of Fe. The crystal structure of this system has been investigated using a variety of techniques. Commonly samples with $x \leqslant 0.03$

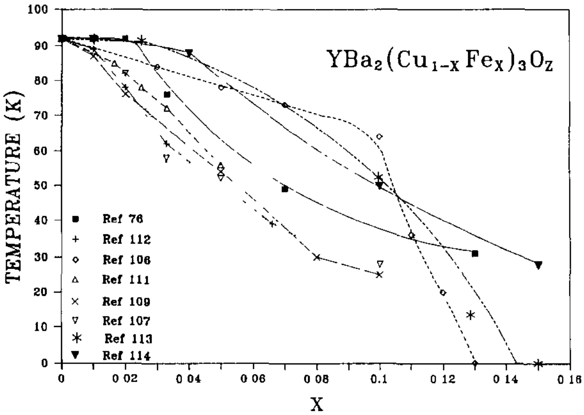

Fig. 8. Variation of T_c in $YBa_2(Cu_{1-x}Fe_x)_3O_z$.

are found to have an orthorhombic structure similar to undoped materials, while samples having $x \geqslant 0.05$ are found to be tetragonal. The formal valence of Fe in this system is three [40]. Although Fe^{3+} (0.64 Å) is smaller than Cu^{2+} (0.69 Å) the volume of the unit cell surprisingly increases [76] with increasing dopant concentration.

Mössbauer measurements prove definitely [40,41] that for low values of x, Fe replace Cu preferentially in the Cu(1) sites whereas for higher concentrations, $x > 0.05$, 10–20% of Fe ions also occupy Cu(2) sites. The chemical composition has been determined using scanning electron microscopy [103], and it was found that the concentration of Fe in the 123 phase is in accord with the nominal composition. Since Fe^{3+} substitutes for Cu^{2+} in the Cu(1) sites, the oxygen concentration is increased with Fe content. For $x = 0.1$ the oxygen concentration [111] is 7.13. The Cu(2) atoms retain a formal valence of +2. Fe ions in the Cu(1) site show a preference for higher coordination than four, and induce disorder in the intercalated oxygen on the *a* and *b* axis. The resultant expansion of the unit cell volume and tetragonal structure are presumably connected directly with the extra oxygen content.

In Fig. 8 the results of eight systematic studies on the effect of Fe substitution on T_c are depicted. It was shown [101] that the weak dependence of T_c on dopant concentration in the Ga substituted samples may be taken as an upper bound, and the strong dependence of T_c in the Zn-doped samples (only for low concentration) may be taken as a lower bound. Evidently all the results of Fig. 8 lie within these upper and low bound limits. Focussing on Fig. 8, one can see a clear grouping of results where a decrease in T_c is associated with an increase in Fe content. The data from ref. 103 show a linear reduction in T_c with x up to 0.1, with a constant slope of 2.8 K $\%Fe^{-1}$. Above a certain concentration T_c drops rapidly to zero. Three different areas are distinguished in ref. 109: Up to $x \leqslant 0.023$, T_c

remains constant: a moderate linear decrease of 5.4 K $\%\mathrm{Fe}^{-1}$ for $0.023 < x < 0.1$ is followed by a sharp decrease to zero of 9 K $\%\mathrm{Fe}^{-1}$ for $0.1 < x < 0.16$. It was shown that substitution for Cu in the Cu(2) sites (Zn) affects T_c much more strongly than substitution for Cu in the Cu(1) sites (Ga), see Fig. 7. Since Mössbauer measurements show that for high Fe concentrations a multiple-site substitution may be inferred, the wide diversity of the results of Fig. 8 would then be understood in terms of significantly different distributions of Fe between Cu(1) and Cu(2) sites, caused by different preparative methods. Beyond the range of variation of T_c found among the several investigators, my own experience indicates that even for the same composition prepared in the same way, different results are obtained: e.g., for $x = 0.1$, $T_c = 38$ K [104] and 69 K [105]. The plateau observed in refs. 76 and 109 for low Fe concentration is presumably a result of an absence of Fe in the Cu(2) sites.

Co–Ni

The solubility limit of dopants in $\mathrm{YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}}$ was found to be $x = 0.2$ and $x = 0.15$ for $\mathrm{M} \equiv \mathrm{Ni}$ and Co respectively [114]. Above these concentrations different materials begin to precipitate. A striking difference is that the Ni (like Zn) samples remain orthorhombic throughout the range of possible compositions, whereas the Co samples (like Fe and Ga) undergo an orthorhomic–tetragonal transition over a narrow range of composition, at about $x = 0.03$. At $x = 0.025$, the product is a two-phase mixture of tetragonal and orthorhombic phases [115]. A continuous lengthening of the a-axis is observed with increasing cobalt concentration, although its trivalent ionic radius is smaller than that of Cu (0.63 Å and 0.69 Å respectively). The oxygen content of the Co-substituted materials remains constant for low values of x but increases to a value of 7.19 to 7.25 for $x = 0.30$ [111]. This fact has become important for understanding the nature of the structural transition. It is well established that Co substitutes for Cu preferentially on the Cu(1) sites [76]. On the other hand, for $\mathrm{M} \equiv \mathrm{Ni}$ the orthorhombic structure persists; Ni only reduces the distortion. The unit cell volume is reduced with increasing Ni content [76] as expected from its small ionic radius (0.62 Å). The oxygen content of Ni-substituted materials remains constant throughout the range of solid solution [114]. The preferred site for Ni in the 123 compound is the Cu(2) site [98].

Figure 9 shows superconducting transition temperatures as a function of Co and Ni concentrations. For both systems essentially equivalent results are obtained. T_c for the Co-doped materials remains fairly constant for $x < 0.03$ and then drops off rapidly with variously reported constant slopes: from 7K $\%\mathrm{Co}^{-1}$ in ref. 115 to about 13.7 $\%\mathrm{Co}^{-1}$ in ref. 116. Note that $x = 0.03$ coincides with the observed structural transition from orthorhombic to tetragonal symmetry. A similar trend can be seen in the data shown in Fig. 8 (refs. 76 and 109). The similarity in the data reported in Fig.

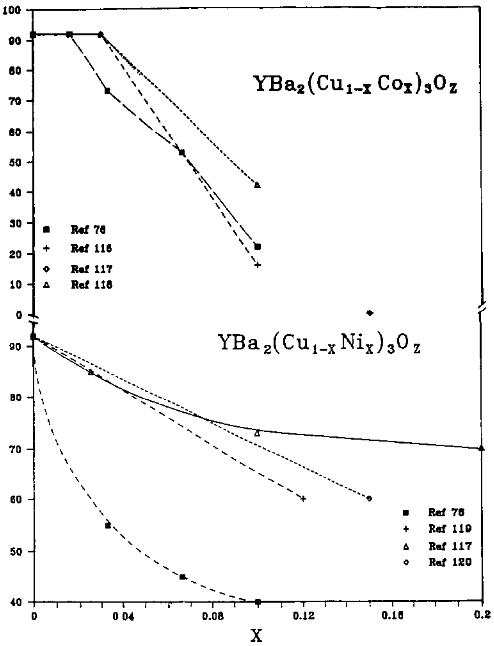

Fig. 9. Variation of T_c in $YBa_2(Cu_{1-x}M_x)_3O_z$ where M ≡ Co or Ni.

9 is assumed to be result of a complete absence of Co ions from the Cu(2) sites. For the Ni-doped samples, T_c decreases fairly smoothly (except for data in ref. 76) with an average slope of 3.5 K $\%Ni^{-1}$. The depression of T_c by Ni is explained by two different mechanisms: variation in the density of states near the Fermi level, since Ni^{2+} has one 3d electron less than Cu^{2+}, or to a pair-breaking effect, as in the conventional BCS theory, owing to the localized magnetic moment of Ni [117].

Summary

In the current view of these materials the structural features which appear vital to superconductivity are (i) the existence of two crystallographically independent Cu sites, namely Cu(2) and Cu(1); (ii) the ability of oxygen atoms O(5) to diffuse in and out of the structure and thus govern the coordination number and oxidation state of the Cu(1) site. While the role of oxygen in determining structural symmetry and its correlation with T_c has been established, the specific roles and relative importance of the CuO_2 planes and Cu–O chains are more controversial. It may be argued that charge selectivity is the direct antecedent of site selectivity in these chemically complex materials. It is apparent that Al, Fe, Co and Ga ions differ in their oxidation number from Ni and Zn ions. The former are formally trivalent and the latter are divalent. An ion in a higher oxidation state is usually expected to be found in a site with high oxygen coordination (ochahedral). Since the coordination number of the Cu(2) sites is limited to 5, one would expect trivalent ions will prefer the Cu(1) sites, to attract oxygen in order to compensate for the increased ionic charge. Since a non-magnetic ion such as Ga affects T_c in the same way as a magnetic ion (Fe, Co, etc.), it is likely that neither the observed behaviour of T_c nor the crystallographic transition is a result of magnetic effects, but rather results from a convolution of oxygen-dependent and dopant-dependent effects. More explicitly, the breakdown of T_c is related to disorder of the chain oxygens O(4) among the previously unoccupied O(5) and the O(4) sites. On the other hand, for divalent dopants Zn and Ni, the substitution for Cu occurs in the Cu(2) sites, both orthorhombicity and oxygen content are maintained. Doping at the Cu(2) site is most effective in reducing T_c, regardless of whether the dopant is a magnetic ion or not, which emphasizes the important role of the Cu–O planes in the mechanism of superconductivity.

SUBSTITUTION FOR OXYGEN

Normal-state conductivity as well as superconductivity in $YBa_2Cu_3O_{7-\delta}$ depends strongly on oxygen concentration. For $\delta = 0$ the crystal symmetry is orthorhombic and $T_c = 92$ K. When samples are heat-treated at elevated temperatures and/or in reducing atmospheres, oxygen is depleted and T_c decreases. For $\delta > 0.5$ the samples may be tetragonal and semiconducting. Depletion of the oxygen also leads to reduction of the formal oxidation state of Cu(1). In tetragonal $YBa_2Cu_3O_6$, Cu(1) appears to have a formal charge of +1 and two-fold coordination with oxygen along the *c* axis of the unit cell [7,8]. The main topic of this section is substitution for oxygen by other anions such as fluorine or sulphur.

F^-

The first report of enhanced superconductivity in fluorine-doped 123 material $YBa_2Cu_3O_8F_2$ with zero resistance near 155 K [118] motivated a prediction [119] that the average Cu oxidation state in this compound is the same as in the undoped 123 compound. It has been proposed, based on simple chemical and charge considerations (similar ionic radii: 1.29 Å for F^- and 1.35 Å for O^{2-}) that two F^- anions could substitute for one oxide ion (O^{2-}) in the basal planes. This would destroy the one-dimensional ordering of the Cu–O chains, and replace them with two-dimensionally ordered CuF_2 planes, which would decrease the orthorhombic distortion.

Since this first report of enhanced superconductivity many groups have attempted to synthesize these materials, with mixed results [120–122]. A small systematic increase in T_c from 90.8–92.5 K with increasing fluorine content was observed [121]. On the other hand no enhancement of superconducting properties was observed in fluorine-doped materials prepared by solid state synthesis methods at high temperatures [122]. The conflicting data are probably the result of difficulties inherent in the methods employed. The solid fluorine starting materials, whether BaF_2, CuF_2 or YF_3, are generally difficult to decompose and to incorporate into the 123 structure. Fluorine-doped materials $YBa_2Cu_3O_7F_y$, where $y = 0.08–1.1$, have been prepared recently by annealing the 123 phase in NF_3 gas at 300 °C [123]. These materials exhibit a significant increase in the diamagnetic Meissner effect as a function of F^- content, but no enhancement of T_c. At sufficiently long annealling times y exceeds 1.2 and the material undergoes an orthorhomic-to-tetragonal phase transition and is no longer superconducting. Neutron-diffraction studies show that the fluorine is structurally incorporated into the vacant O(5) sites along the a-axis [122].

S^{2-}

Single phase $YBa_2Cu_3O_6S$ has been prepared and investigated [104,124]. An expansion of the lattice parameters for the orthorhombic structure relative to the undoped material was observed [104], indicating that the bigger sulphur atoms substitute for oxygen. T_c is not changed; in fact, the transition is sharper and displays the full Meissner effect. Electron microscopic studies [125] indicate that samples measured within one day of preparation probably have the composition of $YBa_2Cu_3O_6S$. This phase does not contain twins. On the other hand, in "old" samples several phases can be seen indicating that samples with sulphur are unstable.

Cl^-

$T_c = 90$ K was reported for $YBa_2Cu_3O_{6.5}Cl_{0.5}$, but the quality of the sample is not given [126].

CONCLUSIONS

Every element in the $YBa_2Cu_3O_{7-\delta}$ system has been replaced by chemical substitution. T_c in all cases reported so far either remains unchanged or is reduced and the transition broadened. The effect of substitution at the Cu sites is more conspicuous that at the Y or Ba sites: i.e., the same amount of dopant will reduce T_c much more drastically when it is substituted for Cu. An impurity ion at the Cu(2) site is most effective in reducing T_c. The oxygen content increases and exceeds 7 when trivalent ions such as Al, Co, or Fe substitute for Cu(1), or when La^{3+} substitutes for Ba^{2+}. In the former case, the additional oxygen satisfies the increased demand for octahedral coordination at the Cu(1) site. The reduction of T_c is related to a disordering redistribution of oxygen among the O(4) and O(5) sites. With this type of substitution the compound evolves from an orthorhombic to tetragonal structure. Several dopants do not enter the solid matrix as substitutions at all, but are segregated in defects, acting as an agent which strengthens the mechanical properties of the sample as well as the intergranular superconducting coupling. On the other hand, some other dopants appear as impurities. In that case the stoichiometry of the compound is changed and T_c is reduced.

It was shown that there is a depression of T_c with increased dopant concentration, whether the dopant ion that replaces the Cu is magnetic (Fe, Co or Ni) or diamagnetic (Zn or Al). This suggests that the behaviour of the new high T_c materials with respect to magnetic impurities is different from that of conventional BCS-type superconductors.

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