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Substitution for copper in $YBa_2Cu_3O_y$: The first 3%

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A systematic study of published data on the effects of substitution of transition and nontransition metal ions for copper in $YBa_2Cu_3O_y$ suggests that: (a) limiting behavior can be deduced for its effect on both the critical temperature T_c and the spontaneous strain (SS) from studies on closed-shell dopants (Ga/Al,Zn); (b) the cross correlation between initial values (0%–3%) for $dT_c/d(\%M)$ and $d(\mathrm{SS})/d(\%M)$ provides the definitive discrimination between preferential occupation of the Cu(1) and Cu(2) sites; and, (c) selective doping applies to open-shell [Fe^{3+}, Co^{3+} in the Cu(1) site and Ni^{2+} in the Cu(2) site] ions as well as closed-shell [Ga^{3+} and Al^{3+} in the Cu(1) site and Zn^{2+} in the Cu(2) site] ions. It can be further suggested that charge selectivity may well be at the root of the site selectivity expressed in these chemically complex materials.

Chemical substitution of transition and nontransition metal ions for the two-site [Cu(1); (0,0,0) and Cu(2); (0,0,z)] copper ions in the high-T_c ceramic $YBa_2Cu_3O_y$ has proven to be a rich and varied endeavor. Initial studies[1,2] focused on the effect of a constant level of substitution [3.3% (Ref. 2) and 10% (Ref. 1)] of a variety of metal dopants. For a series of open-shell ions, Xiao *et al.*[1] found that T_c was maximally affected by dopants (Fe,Co) with large, localized paramagnetic moments. Surely the most surprising result of this study,[1] however, was that substitution of the closed-shell ($3d^{10}$), nonmagnetic Zn^{2+} ion had the most deleterious effect on T_c. The results of Maeno, and co-workers[2] were generally consistent with those of Xiao *et al.*, except that the effect of Zn^{2+} doping was not as dramatic and, in fact, was superseded by that for the closed-shell ($3d^{10}$), nonmagnetic Ga^{3+} ion.

Subsequently, several families of metal-substituted ceramics of the form $YBa_2(Cu_{1-x}M_x)_3O_y$, where M has been predominantly Fe, Zn, Ni, and Al and x has ranged from zero to about 0.18, have been investigated. A range of effects have been observed, particularly for the heavily studied Fe-doped ceramics. For example, Tarascon *et al.*[3] reported a strong dependence for T_c on Fe percent and the realization of an orthorhombic-to-tetragonal (O-T) structural transition at ~3% Fe substitution. In contrast, Kistenmacher *et al.*[4] found a significantly weaker dependence (especially at higher Fe content) for T_c on Fe doping, and the structure remained orthorhombic beyond 12% substitution; by 15% Fe doping, however, the structure was tetragonal.

Herein, the plethora of results for a host of metal doped $YBa_2(Cu_{1-x}M_x)_3O_y$ ceramics are critically examined. The results for the Fe-doped ceramics are found to be bounded by the site-selective effects induced by Ga and Al [preferentially Cu(1)] and Zn [preferentially Cu(2)] substitution. Moreover, less extensive data for Ni- and Al-substituted ceramics would seem to indicate a similar variability and similar bounds to the range of the effect. Some of this variation, but perhaps less so than expected, arises from nonselective site substitution, and some arises, more often, from nonideal oxygen stoichiometry. More particularly, it is demonstrated that (a) pronounced differences in the magnitude of the effect on T_c and the spontaneous strain [(SS) defined as $(b-a)/(b+a)$] arise within the first 3% of metal substitution; (b) these differences follow more from the substitution site selected [(Cu(1) or Cu(2)] than the nature (e.g., electronic configuration, magnetism, size, or valence state) of the metal dopant; and (c) it is the cross-correlation of the initial rate of change of T_c and the spontaneous strain with percent metal doping that allows a cogent and systematic interpretation of the accumulated results.

The effects of preferred substitution of Ga^{3+} and Al^{3+} at the Cu(1) site and Zn^{2+} at the Cu(2) site follow most directly from the seminal work of Xiao *et al.*[5] (Ga/Zn) and Tarascon *et al.*[3] (Al/Zn, identified as AT&T). Depicted in Fig. 1(a) are the variations in critical temperature with percent metal substitution for Ga-, Al-, and Zn-substituted ceramics prepared in these laboratories.[3,5] Clearly, the trends in T_c for these Ga- and Al-substituted ceramics are very similar and are employed to deduce what will be called an upper bound limit [upper dashed curve of Fig. 1(a)] characteristic of a weak dependence for T_c on metal doping. Similarly, the Zn-doping results of Xiao *et al.*[5] and Tarascon *et al.*[3] are consistent up to about 4% substitution, after which the results of Tarascon *et al.*[3] show only a weak dependence for T_c on percent Zn substitution. To deduce a lower bound limit [lower dashed curve of Fig. 1(a)] characteristic of a strong dependence for T_c on metal doping, the data of Xiao *et al.*[5] are relied upon. It is emphasized that the discriminating difference between the upper and lower bound limits is the initial (up to ca. 3% substitution) values for $dT_c/d(\%M)$, lying near 0 K/(%M) for the upper bound limit and near -11 K/(%M) for the lower bound limit. In contrast, for metal-doping levels beyond 3%, $dT_c/d(\%M)$ lies close to -4 K/(%M) for both the upper and lower bound limits. It is to be further noted that the Zn-doping results of Takabatake and Ishikawa (T&I)[6] are similar to, but indicate a slightly more deleterious dependence for T_c than the lower bound limit. In addition, the Al-doping results from these same authors[6]

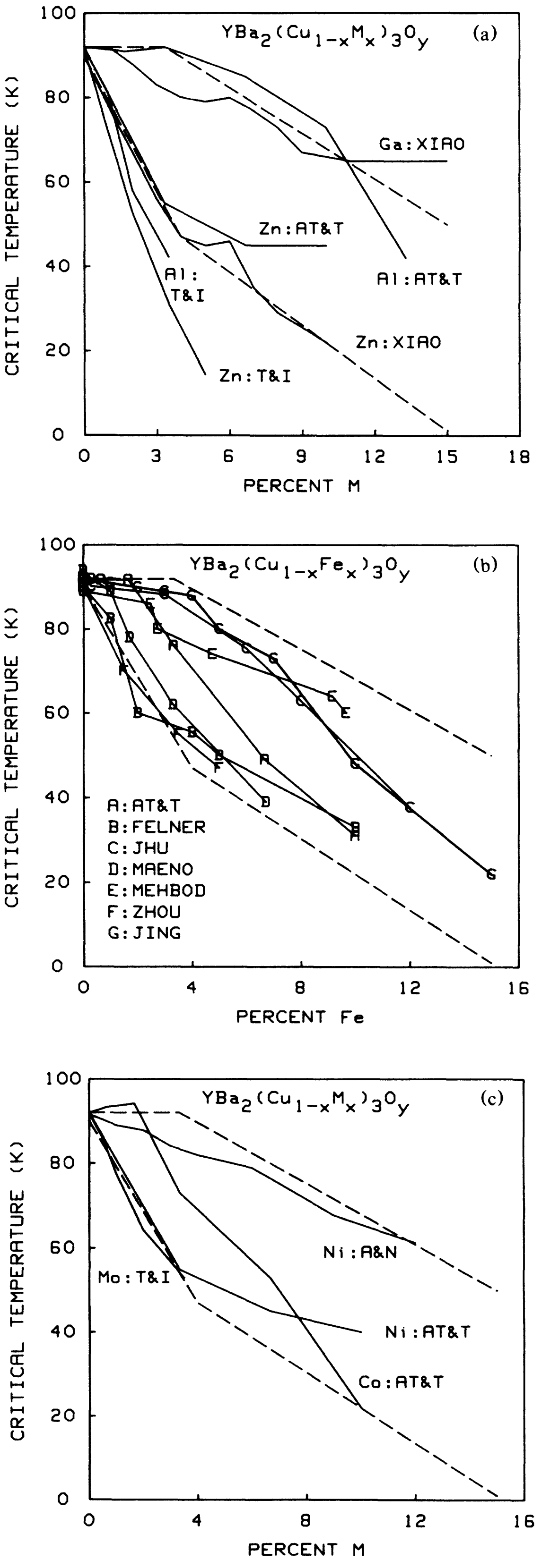

FIG. 1. Effect on the critical temperature of metal substitution for copper in $YBa_2Cu_3O_y$ ceramics for: (a) $M=$Ga, Al, and Zn. Dashed lines represent approximate upper and lower bounds to the effect; (b) $M=$Fe; (c) $M=$Ni, Co, and Mo.

strongly emulate the lower bound limit—in stark contrast to the very definition, in large measure, of the upper bound limit in terms of the Al-doping results of Tarascon *et al.*[3]

In Fig. 1(b), the results of seven systematic studies on the effect of Fe substitution on T_c are depicted. Evidently, all results lie within the upper and lower bound limits deduced from the Ga/Al and Zn studies (see above). It could be implied from Fig. 1(b) that Fe substitution, in the absence of other effects, is nonselective, with the results of Kistenmacher *et al.* (for Johns Hopkins University)[4] and Jing *et al.*[7] most closely approximating the upper bound limit [preferential Cu(1) substitution] and those of Felner, Nowik, and Yeshurun,[8] Maeno *et al.*,[2] and Zhou *et al.*[9] most closely approximating the lower bound limit [preferential Cu(2) substitution]. The intermediate results of Tarascon *et al.*[3] and Mehbod *et al.*[10] would then be understood in terms of significant substitution at both the Cu(1) and Cu(2) sites.

As implied by the dichotomy for the Al-doping results[3,6] of Fig. 1(a), the variability of the situation for Fe doping is not unique. This point is reinforced by data from two different laboratories on the effect of Ni doping. In Fig. 1(c), it is seen that the results of Adrian and Nielsen (A&N)[11] can be strongly identified with the upper bound limit, while those of Tarascon *et al.*[3] are reminiscent of the lower bound limit and the Zn-doping results from this same laboratory. Also shown in Fig. 1(c) are the results of Takabatake and Ishikawa[6] for Mo doping, which are readily associated with the lower bound limit, and the Co substitution results of Tarascon *et al.*,[3] which (as for their Fe-doping data) are intermediate between the upper and lower bound limits.

In a first attempt to penetrate the origins of the variability in results for different metal-doped ceramics and, more importantly, the variability in results from different laboratories for the same metal dopants, initial (0%–3%) and intermediate (ca. 3%–10%) values for $dT_c/d(\%M)$ are plotted versus *d*-electron count in Figs. 2(a) and 2(b), respectively. One motivation for examining such a correspondence extends from the speculation[1,5] that band filling might possibly play an important role in differentiating the effects of various metal dopants, especially those with closed-shell electron configurations. As can be readily seen, no such correspondence can be implied from the results displayed in Fig. 2. The mode of presentation in Fig. 2 does serve, however, to emphasize the rather strong differentiation among the results through their initial values of $dT_c/d(\%M)$ and their less dramatic differentiation via their intermediate values of $dT_c/d(\%M)$. Focusing on Fig. 2(a), it is recognized that (a) there is a clear grouping of results for which $dT_c/d(\%M)$ is very small and includes the essentially equivalent results for four[3,4,7,10] of the seven studies on Fe doping; (b) there is a much wider diversity for the other three[8–10] Fe-doping experiments that exhibit large magnitudes for their initial values of $dT_c/d(\%M)$. In fact, the initial slope $[-15\ \mathrm{K}/(\%M)]$ for the results of Felner *et al.*[8] lies near to that $[-18\ \mathrm{K}/(\%M)]$ exhibited for Fe doping of the 40-K superconducting ceramic $La_{1.85}Sr_{0.15}CuO_4$.[12] In that system, there is only one copper site

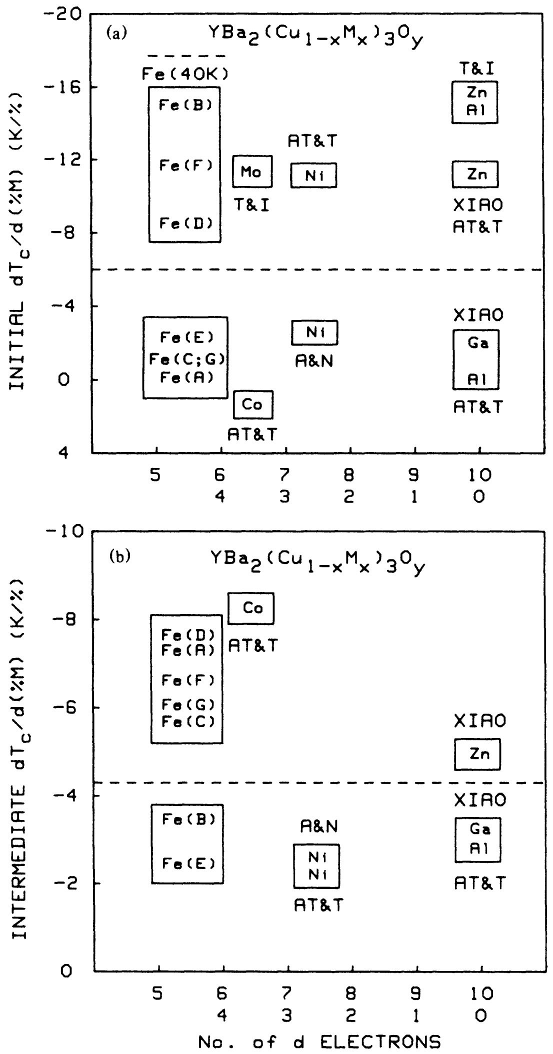

FIG. 2. (a) Initial (0%–3%) $dT_c/d(\%M)$ vs d electron count for Ga-, Al-, Zn-, Fe-, Ni-, Co-, and Mo-substituted ceramics. Also shown (short-dashed line) is the result of iron substitution for copper in $La_{1.85}Sr_{0.15}CuO_4$ ($T_c = 40$ K); (b) Intermediate (3%–10%) $dT_c/d(\%M)$ vs d electron count. For each case, the long-dashed line separates the results into two classes.

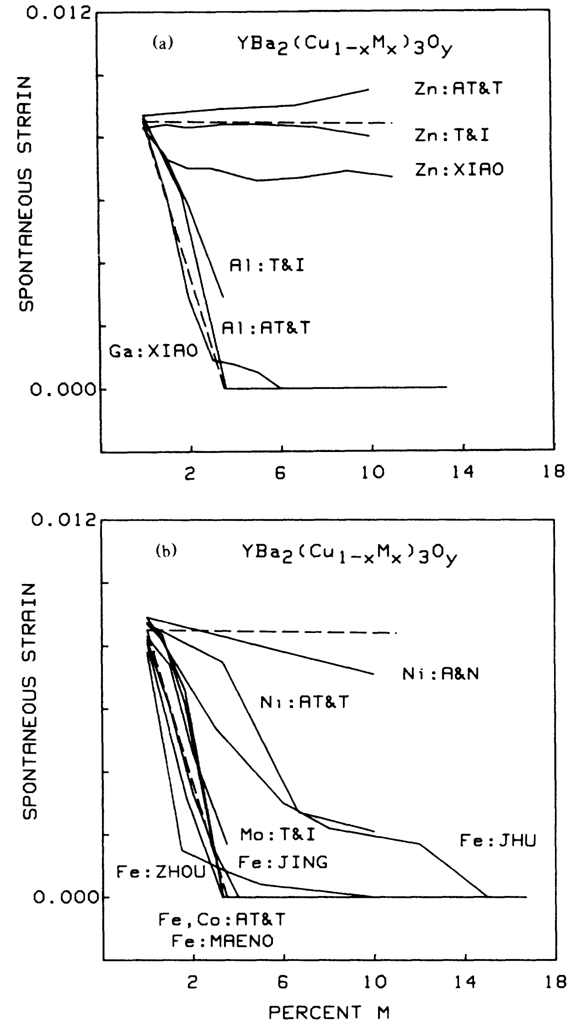

FIG. 3. Spontaneous strain $[(b-a)/(b+a)]$ vs percent metal substitution for (a) $M=$Ga, Al, and Zn; (b) $M=$Fe, Co, Ni, and Mo.

whose geometric surroundings (sheets of Cu-O polyhedra) are closely approximated by the Cu(2) site in the $YBa_2Cu_3O_y$ ceramics. Lastly, it is recognized that the initial values of $dT_c/d(\%M)$ for the two Ni studies differ by a factor of four, while their intermediate values of $dT_c/d(\%M)$ are nearly identical.

Continuing the pursuit of the antecedents of the variations in materials response, trends in structural parameters with percent metal substitution were examined. In Fig. 3(a), the variation in spontaneous strain with percent metal substitution for the Ga-, Al-, and Zn-doped ceramics of Fig. 1(a) are presented. Here, as for the variation in T_c, all of the Zn-doped materials[3,5,6] show a consistent behavior: The spontaneous strain is essentially independent of the Zn concentration. The variation in a and b themselves for the Zn-doped ceramics of Xiao *et al.*[5] is shown in Fig. 4(a). Similarly, as for the variation in T_c of Fig. 1(a), the Ga-doped ceramics of Xiao *et al.*[5] and the Al-doped ceramics of Tarascon *et al.*[3] show [Fig. 3(a)] analogous behavior; a strong decrease in spontaneous strain, leading to or implicating an O-T structural transition near 3%. An example of the variation in a and b for this type of behavior is depicted in Fig. 4(b) for the Fe-doped results of Tarascon *et al.*[3] Surprisingly, the Al-doped ceramics of Takabatake and Ishikawa[6] follow this same pattern, even though their T_c dependence [Fig. 1(a)] is nearly analogous to the Zn-doped ceramics. As for the breadth of T_c dependencies, limiting behavior [indicated by the dashed lines in Fig. 3(a)] for the variation in spontaneous strain with percent metal substitution were ascertained.

In Fig. 3(b), the variation in spontaneous strain with percent metal substitution for a variety of metal-doped ceramics is presented. Most of these substituted ceramics show a dependence for the spontaneous strain on dopant level that is typified by the Ga and Al results of Fig. 3(a); a strong decrease, leading to or implicating an O-T structural transition near 3% metal substitution. The con-

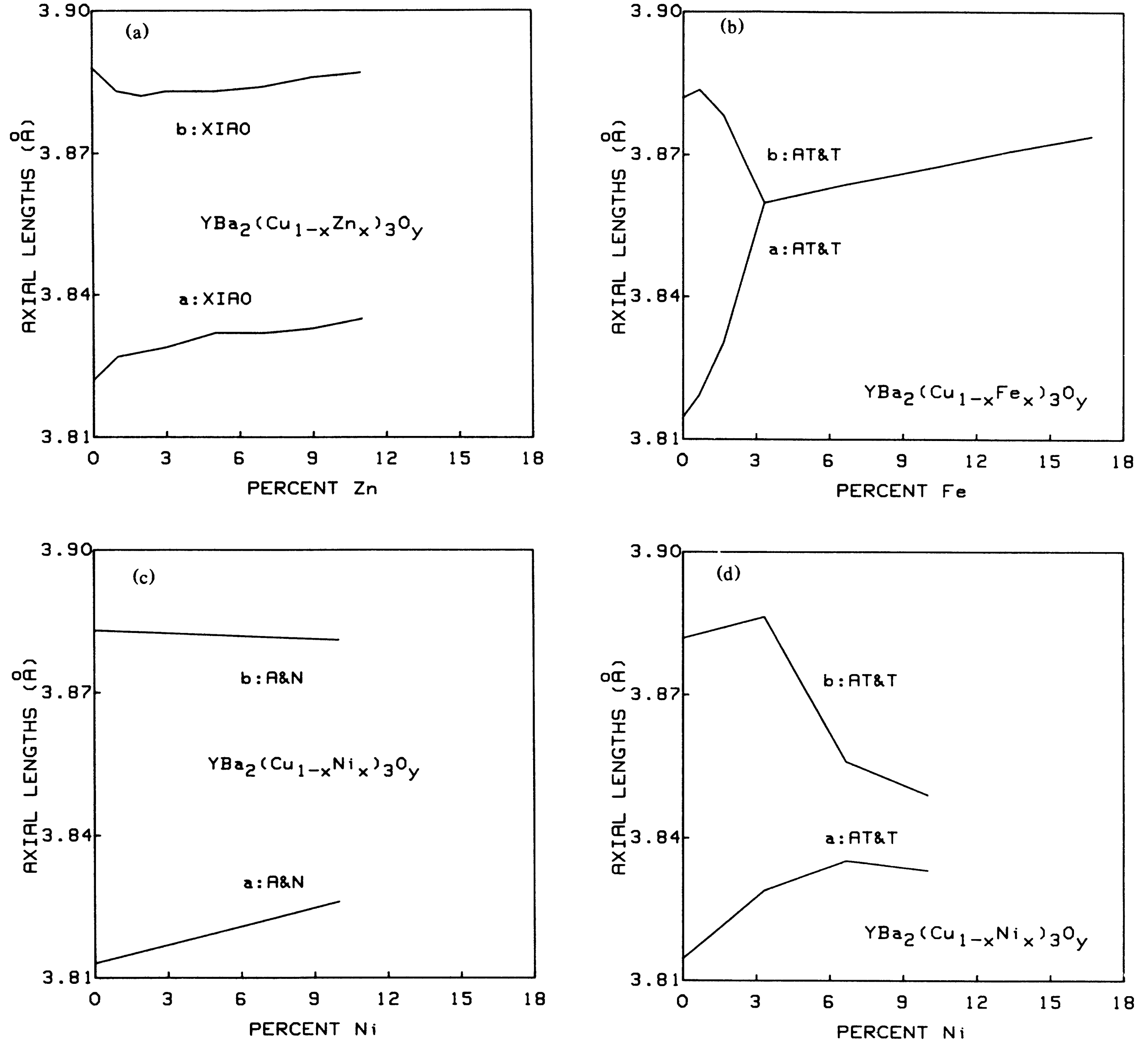

FIG. 4. Examples of the variation in the cell axes a and b with metal substitution for (a) the $YBa_2(Cu_{1-x}Zn_x)_3O_y$ ceramics of Xiao *et al.* (Ref. 5); (b) the $YBa_2(Cu_{1-x}Fe_x)_3O_y$ ceramics of Tarascon *et al.* (Ref. 3); (c) the $YBa_2(Cu_{1-x}Ni_x)_3O_y$ ceramics of Adrian and Nielsen (Ref. 11); and (d) the $YBa_2(Cu_{1-x}Ni_x)_3O_y$ ceramics of Tarascon *et al.* (Ref. 3).

trasting aspects of the two studies on Ni doping[3,11] [viz. Fig. 1(c)] are highlighted by their rather striking difference in the dependence of the spontaneous strain on percent Ni dopant [Fig. 3(b)] and the contrasting variation in the a and b axis lengths on Ni doping shown in Figs. 4(c) and 4(d).

Combining the deductions represented in Figs. 2 and 3, it becomes obvious that the cross correlation between the initial values of $dT_c/d(\%M)$ and $d(\mathrm{SS})/d(\%M)$ should provide a cogent basis for the interpretation of the diversity of results and such a cross correlation is presented in Fig. 5. It is readily ascertained that two regions of this diagram are heavily populated. (1) The region where the initial value of $dT_c/d(\%M)$ is large [on the average -13 K/(%M)] and, in contrast, the initial value of $d(\mathrm{SS})/d(\%M)$ is small [near 0.5/(%M)], and is populated by all the Zn-doped ceramics[3,5,6] and the Ni-doped ceramics of Tarascon *et al.*;[3] and, (2) the region where the initial value of $dT_c/d(\%M)$ is small [ca. 0 K/(%M)] and the initial value of $d(\mathrm{SS})/d(\%M)$ is large [on the average 2.5/(%M)], is populated by the Ga-doped ceramics of Xiao *et al.*,[5] the Al-, Fe-, and Co-doped ceramics of Tarascon *et al.*,[3] and the Fe-doped ceramic of Jing *et al.*[7] If these limiting regions are taken as indicative of strongly preferred site substitution at the Cu(1) and Cu(2) sites, as indicated in Fig. 5, then at first blush, metal-doped ceramics lying outside these regions could be implied to have mixed-site substitution. However, such a notion may still be only partially correct. In Fig. 6(a), the variation in the c-axis length with percent metal substitution is displayed for a variety of doped ceramics. It has been argued in numerous places[3,13-15] that the magnitude of the c

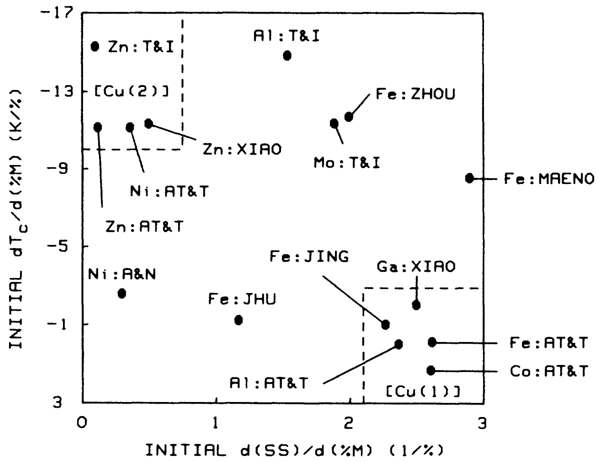

FIG. 5. Initial (0%–3%) $dT_c/d(\%M)$ vs initial $d(\mathrm{SS})/d(\%M)$ for $\mathrm{YBa_2(Cu_{1-x}M_x)_3O_y}$ ceramics. The dashed boxes represent two limiting cases: (a) large initial $dT_c/d(\%M)$, small initial $d(\mathrm{SS})/d(\%M)$—characteristic of Cu(2) substitution; and (b) small initial $dT_c/d(\%M)$, large $d(\mathrm{SS})/d(\%M)$—typical of Cu(1) substitution.

axis tracks (inversely) with the total oxygen content y for the ceramic preparation. Within this interpretation, only nominal variations in oxygen content with percent metal dopant are indicated for several families of doped ceramics in Fig. 6(a) and amplified upon in Fig. 6(b). There are, however, notable cases [the Mo- and Al-doped ceramics of Takabatake and Ishikawa,[6] and the Fe-doped ceramics of Jing *et al.*[7] and Zhou *et al.*,[9] and, the Ni-doped ceramics of Adrian and Nielsen[11] whose trend in c with percent Ni is too large to be shown within the borders of Fig. 6(a)] for which the c axis (and, by implication, the oxygen content) show anomalous trends. All of these ceramics (except for the Fe-doped ceramics of Jing *et al.*[7]) fall outside the limiting regions outlined in Fig. 5, and it is likely that both their observed trends in T_c and spontaneous strain result from a convolution of oxygen-dependent and dopant-dependent effects. If these metal-doped ceramics are dropped from consideration in Fig. 5, then only the Fe-doped ceramics of Kistenmacher *et al.*[4] and Maeno *et al.*[2] remain outside the regions of limiting behavior. For both of these results, it is possible that multiple site substitution may be implicated. Such a conjecture is reasonable for the Fe-doped ceramics of Kistenmacher *et al.*,[4] as only the weak variation in the b-axis length [typical of Cu(2) substitution] prevents the initial value for $d(\mathrm{SS})/d(\%M)$ from being more characteristic of preferred Cu(1) site selection. In contrast, it is more likely that the sharp upturn in c (implying a sharp downturn in oxygen content) at very low Fe percent may lead to the somewhat too large a value for $dT_c/d(\%M)$ for the Fe-doped ceramics of Maeno *et al.*[2]

The culmination of these correlations for metal doping of the copper sites in $\mathrm{YBa_2Cu_3O_y}$ ceramics may be succinctly stated: If one allows for oxygen stoichiometry (common) or site (less common) dependent effects, then a rather strong case can be made for general site, and possibly charge, selectivity, a rendition of which is expressed in Table I. It is noted that the charge preference suggested is identical to that espoused by Tarascon *et al.*[5] and directly akin to a commonly advocated formal charge distribution in the parent all-copper ceramic—$\mathrm{Cu^{3+}}$ in the Cu(1) site and $\mathrm{Cu^{2+}}$ in the Cu(2) site. In fact, it might be argued that charge selectivity is the direct antecedent of site selectivity in these chemically complex materials. The presence of both open-shell, magnetic [Fe and Co in the Cu(1) site; Ni in the Cu(2) site] and closed-shell, nonmagnetic [Ga and Al in the Cu(1) site; Zn in the Cu(2) site] ions in both limiting regimes suggests that neither exchange nor band filling is the predominant pair-breaking

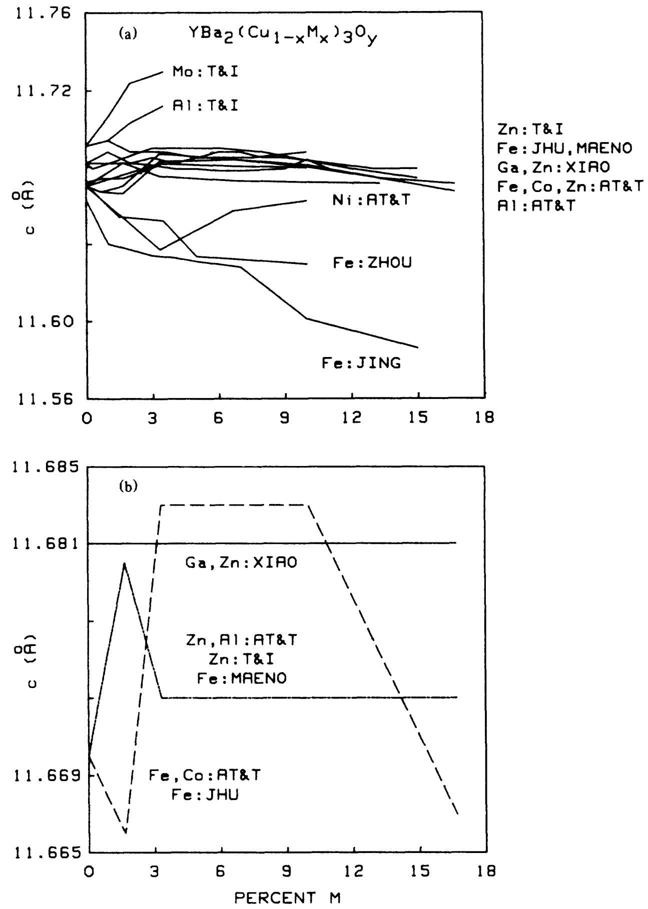

FIG. 6. (a) Variation in the c-axis length with metal substitution for M = Al, Ga, Zn, Fe, Co, Ni, and Mo; (b) schematic expansion for the ceramics with small changes in c on metal substitution.

TABLE I. Preferential site and charge substitution for copper in $\mathrm{YBa_2(Cu_{1-x}M_x)_3O_y}$ ceramics.

Cu(1) site	Cu(2) site
$\mathrm{Ga^{3+}}$	$\mathrm{Zn^{2+}}$
$\mathrm{Al^{3+}}$	$\mathrm{Ni^{2+}}$
$\mathrm{Fe^{3+}}$	
$\mathrm{Co^{3+}}$	

mechanism leading to the loss of superconductivity in these high-T_c ceramics. Rather, it appears to be the sensitivity of these structurally low-dimensional materials[16] to the random potential induced by the locally disordered (at least at low metal-doping levels) metal substitution that diminishes their superconducting properties, as similarly suggested by Tarascon *et al.*[5] Doping at the Cu(2) site (Zn^{2+}, Ni^{2+}) is most effective in reducing T_c, while doping at the Cu(1) (Ga^{3+}, Al^{3+}, Fe^{3+}, and Co^{3+}) site is most effective in promoting the O-T structure transition.[3,5,17] Finally, the differentiation in the magnitude of these effects appears early in the substitution process, ideally within the first 3%.

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