

High-Temperature Superconductivity in Tetragonal Perovskite Structures: Is Oxygen-Vacancy Order Important?

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We used Zn and Ga, two unique dopants having definite valence states and filled $3d$ levels, to substitute preferentially on the Cu(2) and Cu(1) sites in the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor. Small doping of Ga induces an orthorhombic-to-tetragonal structural transition, but the values of T_c are as high as 81 K in the tetragonal phase. Our results indicate that the oxygen-vacancy order, or the linear-chain structure, is not essential. We also find that the Cu(2) sites are much more crucial than the Cu(1) sites in sustaining the high T_c .

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The salient structural features of the new oxide superconductor $\text{YBa}_2\text{Cu}_3\text{O}_7$ are the existence of the Cu-O₂ planes [Cu(2)] and especially the Cu-O chains [Cu(1)], resulting from the oxygen-vacancy order (OVO).¹⁻⁴ The orthorhombic structure is a direct signature of the OVO. As the oxygen stoichiometry is varied from 7 towards 6, the structure gradually undergoes an orthorhombic-to-tetragonal transition¹⁻⁵ as a consequence of the loss of the OVO. Simultaneously, T_c decreases from 92 K to zero,²⁻⁴ with two plateaus around oxygen stoichiometry 6.9 and 6.6.⁵ Because of this feature and other experimental evidence, it has become a prevailing point of view^{1,4,5} that the OVO is essential to high T_c , and any loss or damage of the OVO will affect superconductivity detrimentally.

Another important aspect of the system is the Cu sublattices. There are many theoretical proposals⁶ that rest on the antiferromagnetic correlation between holes in the $3d$ band of the Cu^{2+} ions. The existence of an antiferromagnetic order⁷ and a quantum spin fluid⁸ in La_2CuO_4 gives credence to such models, although the existence of magnetic correlations in the doped La_2CuO_4 and the $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductors has yet to be confirmed. At present, these models are concerned entirely with the quasi two-dimensional motion of the electrons within the Cu-O₂ planes. The contribution of the Cu-O chains is not yet clear. Are the Cu(1) ions antiferromagnetically ordered or correlated? If so, is this correlation important to high T_c ? And moreover, what are the electronic effects of the $3d$ holes of the Cu(1) ions? One effective means of probing the Cu sublattices is to substitute preferentially for the Cu ions on either the planes or chains other ions which have filled $3d$ levels but similar valences. There will be no holes at the impurity sites, and the antiferromagnetic correlation would effectively be turned off.

In this Letter, we present experimental results concerning the effects of both the oxygen-vacancy order and the Cu sublattices on high- T_c superconductivity. The most important result of the present study is that the ex-

istence of OVO in $\text{YBa}_2\text{Cu}_3\text{O}_7$ is *not* a prerequisite in sustaining the high T_c . Conclusive evidence shows that the Cu-O₂ planes are the crucial assemblies, while the Cu(1) site on the Cu-O chains plays a much less important role.

The systems that we have investigated are Zn- and Ga-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$, represented by $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ and $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ ($0 \leq x \leq 0.20$). Among other elements, Zn and Ga are two unique dopants to probe the Cu sublattices. Zn ($3d^{10}4s^2$) and Ga ($3d^{10}4s^24p^1$) have definite valences of 2+ and 3+, respectively, with *completely filled 3d levels*, hence without the complication of a magnetic moment. Their valences are in the vicinity of the average Cu valence in $\text{YBa}_2\text{Cu}_3\text{O}_7$. The replacement of Cu by Zn and Ga, therefore, allows us to study the effects of the $3d$ holes and the valence structure on the oxide superconductors.

The samples were made by use of solid-state reaction methods under identical conditions. Fine powders of Y_2O_3 , BaCO_3 , CuO , and ZnO or Ga_2O_3 in appropriate proportions were thoroughly mixed and pressed into pellet forms. The samples were then sintered at 950°C for a total period of about 50 h, with two intermediate grindings and pressings. The final cooling rate was rather slow ($\approx 2^\circ\text{C}/\text{min}$) to prevent the loss of oxygen. Resistivity as a function of temperature was measured on regularly shaped samples by a standard four-probe method. A SQUID magnetometer was used to measure the magnetization of the samples. The structures of the samples were determined with a Phillips model APD3720 automated x-ray powder diffractometer. The diffraction peaks were fitted by modified Gaussian functions, and the lattice parameters were then determined by our fitting the positions of at least 18 diffraction peaks using standard least-squares reduction methods. All of the samples are single phase with an impurity level of less than 1%.

Figures 1(a) and 2(a) show the parameters a , b , and $c/3$ for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ (referred to as Zn123) and $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ (Ga123) systems. The c pa-

parameter for both systems remains essentially unchanged with doping. However, the variation of a and b depends dramatically on the doping element. In the Zn123 system, all of the samples remain orthorhombic, with the distortion $(b-a)/(a+b)$ very close to that of the pure 123 compound. For Ga123, a small amount of Ga rapidly reduces the orthorhombic distortion and induces an orthorhombic-to-tetragonal phase transition at 6 at.% of Ga. This observation indicates that the OVO, or the Cu-O chains, remains intact in the Zn123 system, whereas substitution of Ga quickly destroys the OVO, and above 6 at.% of Ga, the ordered-chain structure no longer exists.

Figures 1(b) and 2(b) display T_c as a function of the Zn and Ga concentrations. The filled squares represent data obtained from magnetization measurement, and the bars are the superconducting transition widths from resistivity measurements (90%-10% resistive drop). The two methods give consistent results. The transition widths gradually broaden with doping, possibly because of the substitutional disorder. The Zn ions suppress the

superconductivity very effectively, with an initial rate of -13 K per at.% of Zn. The superconductivity completely disappears around 12-13 at.% of Zn. This occurs while the Zn123 system retains the same orthorhombic structure as the pure 123 compound. Quite to the contrary, Ga has a very small effect on the superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The initial decreasing rate of T_c is only about 1 K per at.% of Ga. At 6 at.% of Ga, where the structure becomes *tetragonal*, T_c still has a *large* value of 81 K, and in the whole tetragonal region, T_c is in the range of 65-80 K. It should be noted that the Meissner effect of the Ga-doped samples (up to 11 at.% of Ga) remains the same as in $\text{YBa}_2\text{Cu}_3\text{O}_7$ with sharp transitions.

Our results clearly indicate that the existence of the one-dimensional Cu-O chain structure, or OVO, is insignificant to the high- T_c superconductivity. The orthorhombic structure does not assure high T_c , nor is oxygen disorder necessarily detrimental. In the pure 123 compound, T_c is strongly correlated with the oxygen stoichiometry, the change of which also varies the oxy-

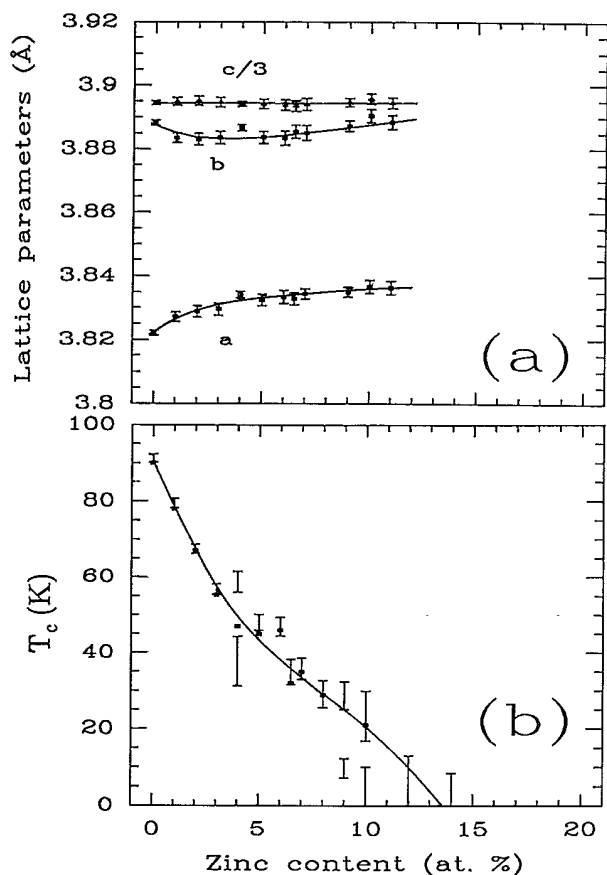


FIG. 1. (a) Lattice parameters of $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ as functions of Zn content. (b) Variation of T_c with Zn content. The filled dots are T_c 's obtained from magnetization measurements under a field of 30 Oe, and the bars represent the resistive transition (90%-10%).

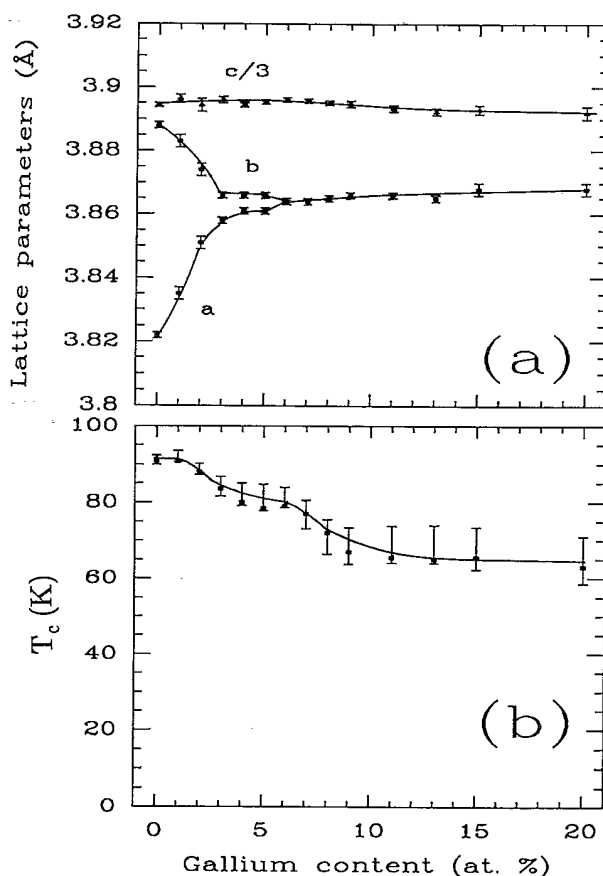


FIG. 2. (a) Lattice parameters of $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ as functions of Ga content. (b) Variation of T_c with Ga content. The filled dots are T_c 's obtained from magnetization measurements under a field of 30 Oe, and the bars represent the resistive transition (90%-10%).

gen configuration.^{1,5} We believe that the behavior of T_c in the pure 123 compound is determined by the actual oxygen content, rather than its configuration.

Our analysis suggests that the oxygen content in the Zn123 and Ga123 systems remains unchanged from that of the parent 123 compound. Cava *et al.*⁵ have determined the lattice parameters of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with various oxygen content ($0 < \delta < 0.7$). The lattice parameter c , most sensitive to δ , is linearly dependent on δ having a slope of $c^{-1}\Delta c/\Delta\delta = -1.37\%/(\text{O atom})$. The c parameters in the Zn123 and Ga123 systems are essentially constant. We estimated the variation of oxygen content from the largest error bar of c , and δ came out to be ± 0.03 , which should have a negligible effect on T_c . The different superconducting behaviors of Zn123 and Ga123 are, therefore, due to the intrinsic electronic structures of Zn and Ga.

Energy-dispersive fluorescence analysis, performed in a transmission electron microscope, on over 100 spots of the samples revealed that the substitutions are uniform down to at least 300 Å (electron-beam size). The fact that all of the samples in our substitution ranges are single phase also supports the Ga and Zn replacement of the Cu sublattices. Otherwise, if Y or Ba are replaced, the extra Y or Ba and deficient Cu atoms (compared with the formula $\text{YBa}_2\text{Cu}_3\text{O}_7$) inevitably lead to off stoichiometry, resulting in multiphase samples with a non-123 phase level of 10%–30%. This would be clearly visible in the x-ray spectra. Furthermore, the small ionic sizes of Ga and Zn make them very unlikely substitutes for Y or Ba ($r_{\text{Zn}^{2+}} = 0.75$ Å, $r_{\text{Ga}^{3+}} = 0.62$ Å, $r_{\text{Cu}^{2+}} = 0.73$ Å, $r_{\text{Y}^{3+}} = 0.89$ Å, and $r_{\text{Ba}^{2+}} = 1.36$ Å).⁹

The most interesting question is why the behaviors of T_c for the two systems are so dramatically different. As mentioned earlier, the $3d$ levels of both the Zn and Ga ions are completely full; the difference lies in their valence states (2+ and 3+). It is commonly agreed upon that the electron hole in the $3d$ level of Cu^{2+} is crucial to the high- T_c superconductivity⁶; the holes either provide the antiferromagnetic background (in the ordered or quantum-spin-fluid state) coupled to the superconducting carriers, or become the itinerant charge carriers themselves forming the superconducting pairs. This explains the rapidly decreasing T_c caused by the Zn substitution which eliminates the $3d$ holes. However, the ineffectiveness of Ga substitution on T_c remains anomalous, where the d levels at the impurity sites are also filled.

After examining the structural data shown in Figs. 1(a) and 2(a) and their correlation with the superconducting behaviors, we believe that the Ga and Zn are substituting *preferentially* on the Cu(1) and Cu(2) sites, respectively. In the case of the Ga123 system, the Cu-O chain structure is quickly destroyed by doping. Such an effect can be achieved much more easily by the Ga replacement of the Cu(1) ions on the chains than of the

Cu(2) ions on the planes. On the other hand, the fact that the orthorhombic structure of the Zn123 system remains unchanged indicates that the Cu(1) site in the lattice is hardly disturbed. Therefore, Zn would most likely be doped into the Cu-O₂ planes. Such preferential doping is accommodated by the different valence states of Zn and Ga. The Cu(2) site has a valence of 2+, well suited for the Zn^{2+} ions. The Cu(1) site, although uncertain at this moment, may be in the 3+ state or in the mixed-valence state of 3+ and 2+, making it more favorable for the Ga^{3+} ions. It is difficult to observe the preferential substitution with x-ray diffraction, since the scattering powers of Zn and Ga are very similar to that of Cu. But neutron-diffraction measurement, which is planned, is capable of making the distinction.

The results of the Zn123 and Ga123 systems suggest that the Cu-O₂ planes are the crucial assemblies in the high- T_c superconductors, whereas the Cu(1) site on the Cu-O chains plays a much less important role. It should be pointed out that our assessment is by no means in conflict with the observation^{2,5} that T_c correlates with the number of oxygen ions along the Cu-O chains.

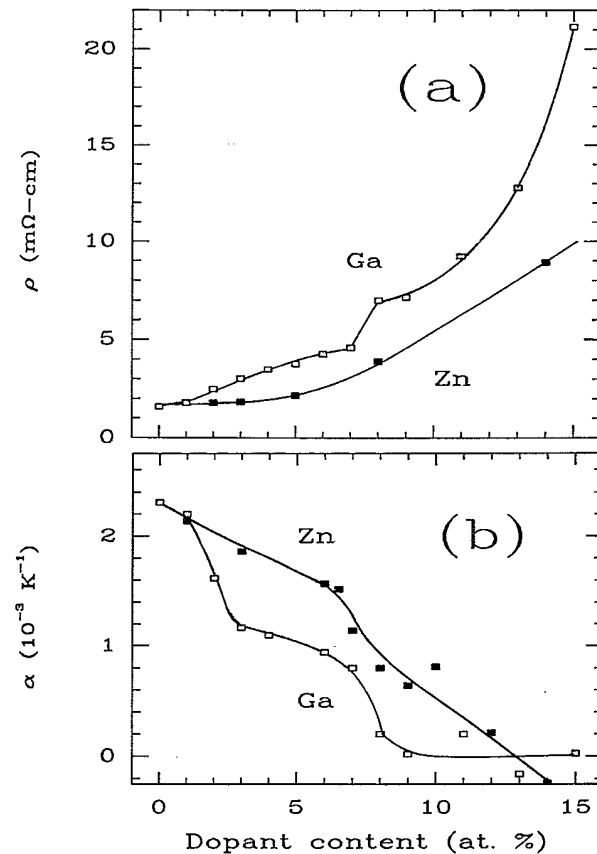


FIG. 3. (a) Resistivity (ρ) and (b) temperature coefficient of resistivity (α) at $T=296$ K of $\text{YBa}_2(\text{Cu}_{1-x}\text{Zn}_x)_3\text{O}_7$ and $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_3\text{O}_7$ as functions of dopant content.

There the oxygen deficiency effectively reduces the carrier densities and the possible coupling inside the (Cu-O₂)-(Cu-O)-(Cu-O₂) assembly.

The Zn and Ga concentration dependence of the resistivity ρ and the temperature coefficient of resistivity (TCR, $\alpha = \rho^{-1} d\rho/dT$) at $T = 296$ K are shown in Figs. 3(a) and 3(b). Clearly, these normal-state properties are quite different in the two systems. The values of ρ of the Ga123 system are much higher than that of the Zn123, despite the fact that the Ga123 samples are much better superconductors. The correlation of T_c with ρ , hence, is not obvious. In contrast to the relatively smooth change in ρ with the Zn content, the Ga concentration dependence of ρ has an abrupt jump at 7 at. % of Ga. This feature is not an experimental artifact, but rather is closely related to the orthorhombic-to-tetragonal structural transition, which correspondingly induces a change in the electronic structure. Remarkably, the values of ρ of the Ga123 system increase over 1 order of magnitude, while T_c maintains at relatively high values (> 65 K).

All of the samples are metallic in the doping range $0 \leq x \leq 0.12$ as indicated by the positive TCR. The Ga123 system always has a smaller TCR than the Zn123 system, implying that the high- T_c Ga123 system is, in fact, somewhat less metallic than the T_c -depressed Zn123 system, consistent with the ρ data. A special point of interest is that the variation of TCR with Ga content follows closely with that of T_c ; both parameters have three plateaus at approximately the same locations. It should be noted that the structure at these plateaus undergoes delicate changes. The orthorhombic distortion rapidly decreases at the first plateau, followed by a small but relatively constant orthorhombic distortion region. Finally, the structure becomes tetragonal at the last plateau. Oxygen disordering apparently has a small effect on T_c , but it induces considerable changes of the normal-state behaviors, especially the TCR.

In summary, we have observed sharply different and contrasting structural, superconducting, and electronic properties between the Zn- and Ga-doped Y-Ba-Cu-O oxides. Superconductors with T_c as high as 81 K were obtained in tetragonal perovskite structures. Contrary to the common belief, oxygen-vacancy order was found to be insignificant to the high- T_c superconductivity. Preferential replacement on the Cu sites by Zn and Ga ions leads to the conclusion that the most important feature in the superconductor is the Cu-O₂ planes, while the role of the Cu(1) site on the chains is rather minor.

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Note added.—After submission of this paper, we have completed neutron-diffraction measurement on the Zn- and Ga-doped samples at both 4.2 and 300 K. The data fully support the results presented in this paper. Specifically, in the Ga-doped sample, the oxygen-vacancy order is lost.

Second note added.—We have also substituted Zn and Ga on the Cu site in the La_{1.85}Sr_{0.15}CuO₄ system, where there is no Cu-O chain and only Cu-O₂ planes. The value of T_c is found to be severely affected by both Zn and Ga doping. Specifically, La_{1.85}Sr_{0.15}CuO₄ ceases to be superconducting with only 2.5% Zn and Ga doping. Therefore, Ga is equally detrimental to superconductivity if it is substituted into the Cu-O₂ planes. These results support our conclusions that Cu-O₂ planes are the most important assemblies in high- T_c superconductor, and the oxygen-vacancy order is not essential.

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