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Asymmetrical effects of copper-site holes versus oxygen-site holes in La-Sr-Cu-O

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The effects of the copper-site holes and oxygen-site holes on structure, superconductivity, and normal state in $La_{1.85}Sr_{0.15}CuO_4$ have been studied by use of a method in which the hole concentrations at both sites are varied independently. The filling of both the Cu^{2+} holes and the O^- holes induces a tetragonal-to-orthorhombic structural transition. Such a behavior supports strongly the interpretation that the driving force for the bending of Cu—O—Cu bonds is the stabilization of the σ^* antibonding interaction. The two hole-filling processes generate profoundly different effects on T_c, normal-state transport, and magnetic susceptibility. We will discuss the causes of these highly asymmetrical effects.

It is generally accepted that the Cu $3d_{x^2-y^2}$ and O p_σ orbitals, both pointing to each other along the Cu—O bonds in the CuO_2 plane, play a dominant role in the electronic properties of the high-T_c superconducting cuprates. What remains unsettled is whether the CuO_2 plane can be described by an effective Hamiltonian[1] involving a single band with strong on-site Coulomb interaction or multibands involving both the $3d_{x^2-y^2}$ and p bands. The problem is complicated by the fact that the energetics of the orbitals is influenced not only by the hybridization effect but also by the large intrasite and intersite Coulomb repulsion.[2-4] Spectroscopic evidence suggests that the introduced extra holes reside near the O site[5] since these holes have the O p character and the Cu^{3+} state is not found. However, theoretical analysis has indicated that, due to the covalent nature of the Cu—O bonds, a hole on each square of O atoms should be strongly bound to the central localized hole on the Cu^{2+} ion, forming a local singlet whose motion can be modeled by a single-band effective Hamiltonian with a new set of hopping and interaction parameters.[4,6] An important question is how the location (or the character) of the extra holes affects the electronic nature and superconductivity of the cuprates. Of course, the hole location is not a variable which can be readily changed in experiment. Instead, as described in this Rapid Communication, we have used a special method to study the effect of hole location on the structure, superconductivity, and the normal state of (La, Sr)$_2CuO_4$.

Another interesting aspect is the effect of hole doping on structural distortions. It has been established that the CuO_2 planar structure is highly susceptible to symmetry-lowering distortion. For example, the CuO_2 planes are not flat but puckered in both La_2CuO_4 and $YBa_2Cu_3O_{7-\delta}$, resulting from the bending of Cu—O—Cu bonds. In La_2CuO_4, such a distortion causes the structure to be orthorhombic. But hole doping by Sr substitution tends to destroy the distortion.[7] In $La_{1.85}Sr_{0.15}CuO_4$ (with a maximum T_c), the tetragonal-to-orthorhombic (T-O) transition is lowered to $T=190$ K. When Sr content reaches 0.2, the structure becomes tetragonal down to $T=0$ K. It is not clear whether the bending of Cu—O—Cu bonds is important to the superconducting and electronic properties. But the extra holes do affect the T_c and the orthorhombic distortion at the same time. At this stage, it has not been determined what drives such a distortion, and why the extra holes affect the driving mechanism.

It is the intent of this Rapid Communication to address some of the questions raised above. For simplicity, the superconducting CuO_2 plane is considered as one that consists of concentrated localized $3d$ holes (one per Cu^{2+} site) and an appropriate amount of mobile O^- holes. We regard $La_{1.85}Sr_{0.15}CuO_4$ as the *parent* compound with 0.15 O^- holes per square. The effect of the hole location has been studied by doping this parent compound with electrons at the O^- sites and at the Cu^{2+} sites. The former is achieved by reducing the Sr content, the latter by doping the Cu^{2+} $3d^9$ sites with Zn^{2+} $3d^{10}$. For comparison, we also doped the Cu^{2+} sites with Ni^{2+} $3d^8$ ions which is equivalent to doping one more localized hole into $3d^9$. This hole may go to the hybridized $3d_{x^2-y^2}$ orbital, or it may go to the $3d_{z^2}$ orbital should the Coulomb repulsion in $3d_{x^2-y^2}$ be large. As we will demonstrate, dopings at the Cu^{2+} sites and at the O^- sites produce highly asymmetrical effects in $La_{1.85}Sr_{0.15}CuO_4$.

Samples of $La_{1.85}Sr_{0.15}(Cu_{1-x}A_x)O_4$ (A=Zn,Ni) were made by using the standard solid-state reaction method.[8] Every sample was carefully characterized by x-ray diffraction and confirmed to be single phase. The oxygen content was not determined, but it should remain unchanged, since both Zn and Ni ions are divalent as Cu^{2+}. A structural study[9] by Hilscher *et al.* has shown that as much as 45 at.% of Zn can replace the Cu site in La-Sr-Cu-O without affecting the oxygen content. The com-

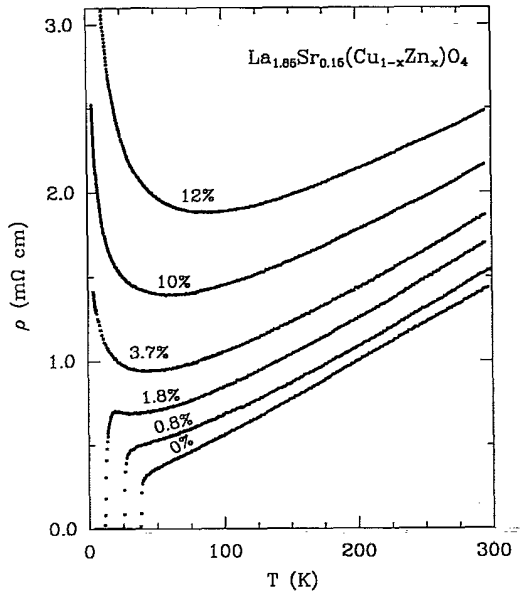

FIG. 1. The temperature dependence of resistivity of $La_{1.85}Sr_{0.15}(Cu_{1-x}Zn_x)O_4$.

pound La_2NiO_4 with the same oxygen content also exists. Zn and Ni dopants definitely substitute for the Cu site as demonstrated by the fact that the samples with Zn or Ni content as high as 30 at.% remain single phase. The localization nature of the $3d$ states of the Zn and Ni dopants ensures that the extra $3d$ charges go to the substituted Cu sites.

Figures 1 and 2 show the temperature dependence of the resistivity for the Zn- and Ni-doped $La_{1.85}Sr_{0.15}CuO_4$ systems. Overall, both systems exhibit similar transport behavior. At high temperatures resistivity is linear in T with a positive temperature coefficient, typical of high-T_c samples. The slope of the resistivity remains approximately constant. The residue resistivity, $\rho(0\ \mathrm{K})$, obtained by extrapolating $\rho(T)$ in the linear region to $T=0$ K, increases linearly with doping, consistent with an impurity-scattering mechanism. At low temperatures, doping of Zn or Ni induces a resistivity upturn and suppresses T_c.

In Fig. 3, the data of lattice parameters (a,b,c), T_c, normal-state conductivity $\sigma(300\ \mathrm{K})$, and magnetic susceptibility $\chi(50\ \mathrm{K})$ are presented for the $La_{2-x}Sr_xCuO_4$, $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$, and $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_4$ systems. The data are plotted in a special way, in which the middle line represents the parent material $La_{1.85}Sr_{0.15}CuO_4$. To the left-hand side of the line, electrons are doped into the O^- sites (by reducing the Sr content), whereas to the right-hand side of the line, electrons (or holes) are doped into the Cu^{2+} $3d^9$ sites by Zn (or Ni) doping. The data for the $La_{2-x}Sr_xCuO_4$ system and some data (denoted by crosses in Fig. 3) for the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_4$ system at high doping levels were tak-

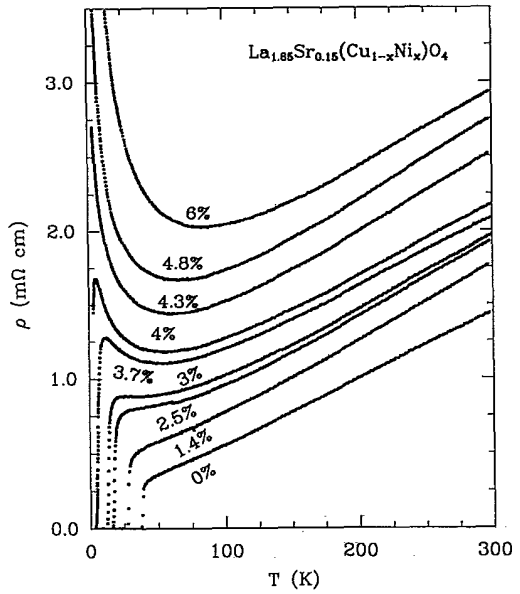

FIG. 2. The temperature dependence of resistivity of $La_{1.85}Sr_{0.85}(Cu_{1-x}Ni_x)O_4$.

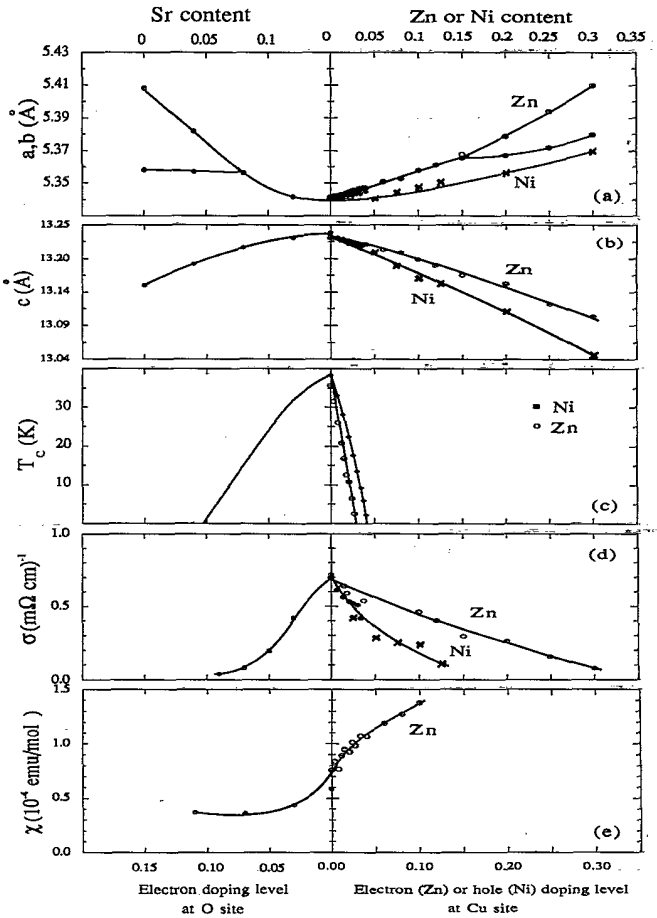

FIG. 3. Lattice parameters $(a,b,$ and $c)$, T_c, conductivity σ, magnetic susceptibility χ as functions of Sr content in $La_{2-x}Sr_xCuO_4$, Zn content in $La_{1.85}Sr_{0.15}Cu_{1-x}Zn_xO_4$, and Ni content in $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_4$. The central line represents the parent compound $La_{1.85}Sr_{0.15}CuO_4$. The data for the $La_{2-x}Sr_xCuO_4$ system and some data (denoted by crosses) for the $La_{1.85}Sr_{0.15}Cu_{1-x}Ni_xO_4$ system are taken from Refs. 10 and 11, respectively. All the remaining data are obtained from this study.

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The lattice parameters (a,b,c) are shown in Figs. 3(a) and 3(b). There is a striking resemblance in the evolution of the structural distortion between electron doping at the O^- site and at the Cu^{2+} site. A tetragonal-to-orthorhombic transition at the left-hand side (Sr doping) of the parent compound is well known. Most interestingly, we have also uncovered such a transition upon Zn doping, on the right-hand side. In general, disorder induced by dopants tends to suppress a phase transition. But here the disorder inherent to Zn doping does not prevent the phase transition from appearing. Contrary to Zn doping, the structure of the Ni-doped samples remains tetragonal up to at least 30 at.% of Ni. Thus, there is a distinct difference between electron doping and hole doping at the Cu^{2+} sites as far as the structural distortion is concerned. Figures 3(a) and 3(b) also show that the lattice constants a,b always increase and c decreases as the system is moved away at both sides from $La_{1.85}Sr_{0.15}CuO_4$. In other words, the lattice parameters of $La_{1.85}Sr_{0.15}CuO_4$, which exhibits the highest T_c, also attain extreme values.

As mentioned earlier, the orthorhombic distortion is due to the puckering of the plane. There are a few proposed mechanisms for the distortion. One argument[13] is that the bending of Cu—O—Cu bonds is due to the stabilization of the π^* antibonding interaction which is the admixture of Cu $3d\,t_{2g}$ orbitals and O p_π orbitals. The bending of Cu—O—Cu bonds reduces the overlap integral between the $3d$ and $2p$ orbitals; consequently there is a drop in the energy of the π^* interaction. Since the π^* band is far below the Fermi level, the T-O transition in La_2CuO_4 should have practically no effect on the electrical properties according to this model. The bond-bending mechanism due to the π^* interaction is also found in ether, where the π^* interaction between the p orbitals on carbon and oxygen forces the C—O—C bonds to bend.[12] Another argument[13] for the bending is that it can also be due to the σ^* antibonding interaction, i.e., admixture of Cu $3d_{x^2-y^2}$ and O p_σ, whose energy can also be lowered by reducing the overlap of the Cu and O orbitals. To find out the actual mechanism responsible for the distortion is of importance not only for the structural aspect, but also for the possible interplay between the structural distortion and other properties, such as superconductivity, normal state, and energetics of various bands.

Obviously, the model of distortion should not only explain the distortion itself, but also account for the T-O transition shown in Fig. 1(a) as electrons are doped into the O^- sites or Cu^{2+} sites. Since the π^* states are below the Fermi level, the doping process should have a negligible effect on π^*. Thus, it is implausible to invoke the role of π^* interaction in the bending of Cu—O—Cu bonds. On the other hand, the Fermi level lies in the σ^* band. Doping electrons either at the O^- or the Cu^{2+} sites have the same effect of filling up the σ^* band. Therefore, it is more likely that the distortion mechanism is related to the σ^* band. This is strongly supported by the data in Fig. 1(a). The stabilization energy due to bond bending is strongest when both the Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals are filled. In $La_{1.85}Sr_{0.15}CuO_4$, where the $3d_{x^2-y^2}$ band is half-filled and the O $2p_\sigma$ band is not full, the stabilization energy in this case is not large enough to sustain the orthorhombic distortion (at 300 K). However, as electrons are doped into the O^- sites or into the Cu^{2+} sites to fill the σ^* band, stabilization energy increases, and eventually, a T-O transition occurs. Based on this mechanism, Burdett and Kulkarni[13] have recently calculated the energy difference between the tetragonal and orthorhombic structures of $La_{1.85}Sr_{0.15}CuO_4$ as a function of $3d$ electron count. Indeed, they found that the orthorhombic form is most stable for $3d^{10}$ (i.e., Zn^{2+}). In the case of Ni doping, substitution does not cause any structural transition up to at least 30 at.% Ni [see Fig. 3(a)]. This is again consistent with the σ^* interaction mechanism. Hole doping at Cu^{2+} sites actually reduces further the stabilization energy of the σ^* interaction which makes the tetragonal structure more favorable.

The values of T_c are plotted in Fig. 3(c). The effect of doping at different sites is markedly asymmetrical. To suppress T_c, the critical electron content is $x_c = 0.1$ (measured from $La_{1.85}Sr_{0.15}CuO_4$) at the O^- sites, and only $x_c = 0.028$ at the Cu^{2+} sites as in the Zn doping. Extra holes at the Cu^{2+} sites also lower T_c rapidly ($x_c = 0.04$) as in the Ni doping. This is a very strong indication that the localized holes on the Cu^{2+} sites play a significantly different role than those on the O^- sites in superconductivity.

The asymmetrical effect is further evident in normal-state conductivity σ. Figure 3(d) shows the room-temperature conductivity σ versus Sr, Zn, and Ni doping. On the left-hand side, σ decreases with increasing electron doping at the O^- sites. Near an electron content of 0.1, the Fermi level is pushed up to the mobility edge, causing a metal-insulator transition and the disappearance of superconductivity. Therefore the O^- holes are more directly associated with the carrier transport and affect T_c in a gradual fashion. On the right-hand side of Fig. 3(d), electron doping by Zn^{2+} at the Cu^{2+} sites reduces σ much more slowly. In particular, when T_c is suppressed to zero, σ is reduced by only 15% for Zn doping (35% for Ni doping). As seen in Figs. 1 and 2, when Zn- or Ni-doped samples become nonsuperconducting, they are still metallic in nature at high temperatures as indicated by the almost constant positive slopes of resistivity. At any rate, the localized Cu^{2+} holes are intimately related to the superconductivity mechanism, but affect the conductivity in a much lesser degree.

While the electron doping at different sites have similar, although asymmetrical, effects on the properties mentioned above, it affects the susceptibility of the doped system in a completely different fashion. Figure 3(c) shows the susceptibility (χ) at $T = 50$ K (above T_c) as functions of electron doping at O^- and Cu^{2+} sites. Since the diamagnetic contribution ($\sim -1\times10^{-4}$ emu/mol) of the ionic cores is approximately constant for different samples, the variation in χ in Fig. 3(c) is a consequence of the magnetic spin susceptibility. As electrons are doped into the O^- sites, χ is reduced. But electron-doping at the Cu^{2+} sites has the opposite effect of increasing χ, even though a filled $3d$ band is not supposed to carry a magnetic moment. This can be explained as follows. In the re-

gion where the Sr content is between 0.02 and 0.15, there is no long-range magnetic order. $\chi(T)$ can be well-described by the short-range two-dimensional (2D) antiferromagnetic (AF) fluctuation[14] which is enhanced with increasing Sr content. In the AF-fluctuating state, the Cu^{2+} magnetic moments are compensated (net spin=0). However, electron doping at the Cu^{2+} sites destroys the moment compensation, hence, inducing a localized Cu^{2+} moment which enhances $\chi(T)$. A detailed analysis of $\chi(T)$ is presented elsewhere.[15]

The strong and deleterious effect on T_c due to Cu-site doping serves as a good probe for the superconductivity mechanism. This effect which underscores the significance of the CuO_2 plane[16] has not been understood. The short coherence length does not lead to an extreme sensitivity of T_c to impurity. In fact, the strong magnetic-pairing effect in conventional superconductors is in part related to the large coherence length. An important characteristic of the oxide superconductor is its poor electron screening, which may enhance the impurity effect. Both the nonmagnetic Zn^{2+} and magnetic Ni^{2+} induce or carry a local moment in the CuO_2 planes, and it is expected that the dynamics of the magnetic background in CuO_2 be affected by such local moments.[15] Together with the poor local screening, the disorder in the exotic magnetic state may effectively suppress T_c. The extreme sensitivity of T_c to the filling of the d holes clearly indicates the strong interaction between the localized d holes and the carriers. Cu-site doping also affects severely the virtual processes such as $p^5d^9p^6 \rightarrow p^5d^{10}p^5 \rightarrow p^6d^9p^5$ and $p^5d^9p^6 \rightarrow p^6d^8p^6 \rightarrow p^6d^9p^5$, whose importance has been emphasized in some models.[3] In addition, we suggest another scenario which may be detrimental to superconductivity. In the case of Zn, for example, in the CuO_2 plane the $d_{x^2-y^2}$ level of the local Zn site should be lower than that of Cu, otherwise the extra electron would not go to the Zn site to fill the $3d$. Due to hybridization, the lowered $d_{x^2-y^2}$ level may also drag down the neighboring p_σ level, creating a barrier for the conducting holes. Consequently, carriers tend to stay away from the Zn sites, generating a much larger effective interaction between the carriers and the dopants.

The data presented in Fig. 3 provide support for the multiband description[17] of the CuO_2 plane. In this model, there is one half-filled localized band (holes predominantly on the Cu site) and other partially filled bands with carriers (holes on the O^- site). The strong interaction between these bands may give rise to superconductivity. Whether this multiband model could be reduced to a single-band effective Hamiltonian cannot be resolved here, because the holes in the single-band picture are mixtures of Cu^{2+} and O^- holes. The filling of either the Cu^{2+} or O^- holes generates different sets of energy parameters in the Hamiltonian,[6] which could result in the asymmetrical properties seen above. However, regardless of whether or not the two approaches are equivalent, the large asymmetrical effects of Cu^{2+} and O^- holes have to be accounted for by any viable theory. In this sense, the data presented in Fig. 3 serve as strong constraints to the theoretical models.

Note Added. We have recently carried out Hall-effect measurements of a few Zn-doped samples (up to 4 at.%). The carrier concentration near room temperature remains basically unchanged. Therefore, the strong suppression of T_c due to Zn cannot be caused by any change in the carrier concentration, and the oxygen content should not be affected by Zn doping.

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[1]P. W. Anderson and Y. Ren, in *High Temperature Superconductivity,* edited by K. S. Bedell *et al.* (Anderson-Wesley, Redwood City, 1990), p. 3.

[2]Mark S. Hybertsen, Michael Schlüter, and Niels E. Christensen, Phys. Rev. B **39**, 9028 (1989).

[3]E. B. Stechel and D. R. Jennison, Phys. Rev. B **40**, 6919 (1989).

[4]T. M. Rice, Phys. Scr. **T29**, 72 (1989).

[5]J. M. Tranquada *et al.*, Phys. Rev. B **36**, 5263 (1987); Z. X. Shen *et al.*, Phys. Rev. B **36**, 8414 (1987).

[6]F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988).

[7]K. C. Hass, in *Solid State Physics,* edited by H. Ehrenreich and D. Turnbull (Academic, Boston, 1989), p. 213.

[8]M. Z. Cieplak, Gang Xiao, A. Bakhshai, and C. L. Chien, Phys. Rev. B **39**, 4222 (1989).

[9]G. Hilscher *et al.*, Z. Phys. B **72**, 461 (1988).

[10]J. B. Torrance *et al.*, Phys. Rev. B **40**, 8872 (1989); Phys. Rev. Lett. **61**, 1127 (1989).

[11]J. M. Tarascon *et al.*, Phys. Rev. B **36**, 8393 (1987).

[12]A. W. Sleight, Science **242**, 1519 (1988).

[13]J. K. Burdett and G. V. Kulkarni, Phys. Rev. B **40**, 8908 (1989).

[14]David C. Johnston *et al.*, Phys. Rev. Lett. **62**, 957 (1989).

[15]Gang Xiao, M. Z. Cieplak, J. Q. Xiao, and C. L. Chien, Phys. Rev. B. **42**, 8752 (1990).

[16]Gang Xiao *et al.*, Nature (London) **332**, 238 (1988).

[17]V. J. Emery, Phys. Rev. Lett. **58**, 2794 (1987).