Dependence of Superconducting Transition Temperature on Doping and Structural Distortion of the CuO_2 Planes in $La_{2-x}M_xCuO_4$ (M = Nd, Ca, Sr)

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By comparing structural and superconducting properties of $La_{2-x-y}Ca_xNd_yCuO_4$ to $La_{2-x}Sr_xCuO_4$ we have separated the effects of structure and doping on the superconducting T_c. At a fixed doping level, the highest T_c is found for flat and square CuO_2 planes in the tetragonal structure. T_c is reduced by the structural distortions of the CuO_2 planes in the orthorhombic structure. The local minimum of T_c vs doping observed around $x \sim 0.12$ indicates the presence of a weakly split singularity of the electronic density of states for the orthorhombic material.

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When substituted with the alkaline earth elements, Ca, Sr, or Ba, the structurally simple La_2CuO_4 material provides a unique opportunity to study the intrinsic properties of the superconducting CuO_2 planes as a function of doping and structural features. For the Sr-substituted compound, the extensively studied dependence of the superconducting transition temperature on doping, which shows underdoped, $0.07 \leq x \leq 0.14$, optimally doped, $x \sim 0.15$ ($T_c \sim 38$ K), and overdoped compositions, $0.16 \leq x \leq 0.27$, is considered typical for all copper oxide superconductors [1]. Considering a larger set of data, which includes T_c vs doping dependence for structurally more complex superconductors, a modified shape of the functional relationship was also proposed and explained using ordered arrangements of holes in the CuO_2 planes [2]. However, the more extensive set of data is subject to considerable uncertainty, since it is difficult to quantitatively measure the competition between charge doping to the CuO_2 planes and to other regions of the complex structures [3].

The dependence of T_c on structural properties is less well understood. For example, a report of a large reduction of the superconducting phase fraction at the orthorhombic-to-tetragonal phase transition boundary, $x \sim 0.21$ at 10 K, proposes that only the orthorhombic phase is superconducting [4]. A similar disappearance of superconductivity in the tetragonal structure was observed for the more complex $YBa_2Cu_3O_{7-\delta}$ system as a function of oxygen content [5]. However, these subtle relationships between the distortion of the tetragonal crystal symmetry and the presence of superconductivity were not supported by subsequent data for the tetragonal and superconducting $La_{2-x}Sr_xCuO_4$ material [6] and by the observation of superconductivity in the tetragonal 123-related and other materials. Recently, we have studied in detail the structural and superconducting properties of the Ca- and Sr-substituted materials using x-ray and neutron powder diffraction, ac susceptibility, and low-field dc magnetization, resistivity, and thermogravimetric measurements [7,8]. Comparison of the Sr- with newly synthesized Ca- and Nd-substituted materials allows, for the first time, a separation of the effects of doping and structural features on T_c. The structural distortions of the CuO_2 planes in the orthorhombic structure, measured most conveniently by the copper-oxygen bond angles, cause suppression of T_c. The local minimum of T_c vs doping observed for orthorhombic $La_{2-x}Sr_xCuO_4$ material around $x \sim 0.12$ is present at $x \sim 0.11$ for the more distorted $La_{2-x}Ca_xCuO_4$. We argue that these features may be related to the variation of the electronic density of states at the Fermi energy.

Polycrystalline samples of $La_{2-x}Ca_xCuO_4$ and $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ were synthesized from nitrates [8]. The calcium solid-solubility limit in $La_{2-x}Ca_xCuO_4$ was extended from $x \sim 0.1$ for material synthesized in air to $x = 0.2$ using synthesis at an oxygen pressure of 600 atm and 1050–1080 °C. The neodymium solid-solubility limit in $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ was found for $y = 1.0$ under high pressure conditions. For strontium, the maximum solubility limit was found to be $x = 0.4$ for synthesis in air at 1170 °C. An oxygen content of 4.00 ± 0.01 was found for all samples considered here from thermogravimetric measurements. Thus, all samples are stoichiometric in metal ions and oxygen content, and the hole doping of the CuO_2 planes is controlled by the amount of the alkaline earths substituted for lanthanum.

Neutron powder diffraction data were collected for single-phase samples at the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source, and the structures were refined by the Rietveld technique. Data were obtained at several temperatures from 10 to 300 K for ~6 g samples placed in sealed vanadium cans filled with helium exchange gas. For all compositions studied, the structural phase diagram contains only two crystallographic phases, the low-temperature orthorhombic (LTO), *Cmca*, and high-temperature tetragonal, *I*4/*mmm* phases [7,8]. The O-T transition develops

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due to the mismatch of the La-O and Cu-O(1) bond lengths in the *a*-*b* plane and occurs at 550 K for pure La_2CuO_4 [9]. At low temperatures, the La-O and Cu-O(1) bonds are under tension and compression, respectively [10]. With increasing amounts of Ca^{+2} or Sr^{+2} substitution for La^{+3}, the O-T transition temperature decreases due to the improved match of the La-O and Cu-O(1) bond lengths. The substitution leads to the shrinkage of the Cu-O(1) bond length due to the hole doping into the antibonding copper-oxygen orbitals. In fact, the decrease of the Cu-O(1) bond length is a measure of the hole doping to the CuO_2 planes because the Cu-O(1) bond length is only weakly constrained by the lattice parameters in the LTO structure and can relax to a preferred value [7]. The observed Cu-O(1) bond contractions are almost identical, 0.103 and 0.105 Å/mol, for Sr and Ca substitution, respectively [see Fig. 1(a)]. However, for the same amount of substitution, the O-T transition occurs at higher temperatures for the Ca- than for the Sr-substituted material [8]. The temperature difference is an effect of the larger ionic size of the Sr ion, i.e., the larger average length of the La(Sr)-O bonds compared to the La(Ca)-O bonds, which relieves part of the tension for the Sr-substituted material and increases it for the Ca-substituted material. Figure 1(b) shows the normalized orthorhombic strain, $(a - b)/(a + b)$, at 10 K for both materials. The larger orthorhombic distortion observed for the Ca-substituted material is a consequence of the higher temperature of the O-T transition, i.e., the larger mismatch of the La(Ca)-O and Cu-O bond lengths. All Ca-substituted samples are orthorhombic at 10 K.

The CuO_2 planes are flat and the copper and oxygen atoms are distributed on a square lattice for the tetragonal phase. For the LTO phase, two distortions of the CuO_2 planes are present: the almost rigid rotation of the Cu-O octahedron around the $\langle 110 \rangle$ axes of the tetragonal phase and the scissors-mode distortion within the CuO_2 planes. The rotation of the Cu-O octahedron causes the O(1) ions to shift out of the planes defined by the positions of the copper ions, distorting the Cu-O(1)-Cu bond angle from 180°. The scissors mode, which is present within the CuO_2 planes, distorts the O(1)-Cu-O(1) bond angle from 90°. The Cu-O(1)-Cu bond angle defines the flatness of the CuO_2 planes and the O(1)-Cu-O(1) bond angle, the distortion from the square network. Figure 1(c) shows that the Cu-O(1)-Cu bond angles at 10 K are more distorted for the Ca-substituted material consistent with this material being "more orthorhombic" than the Sr-substituted material for the same substitution level x. Figures 2(b) and 2(c) show that at 10 K, the isoelectronic substitution of the smaller Nd cations for La increases both the orthorhombic distortion and the bending of the Cu-O(1)-Cu bond angles at a fixed charge doping level for the $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ samples. The increase of the distortion is caused by the decrease of the average La(Nd)-O bond lengths, while the Cu-O(1) bond undergoes only minor contraction, 0.006 Å/mol(Nd) which is about 20 times smaller than the change due to the charge doping by Ca or Sr substitution [see Fig. 2(a)]. No transition to the low temperature tetragonal (LTT) phase, observed for barium- $(x \geq 0.125)$ [11] and strontium with neodymium- $(x = 0.15$ and $y \geq 0.18)$ [12] substituted systems, is present for the $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ samples to $y = 1$.

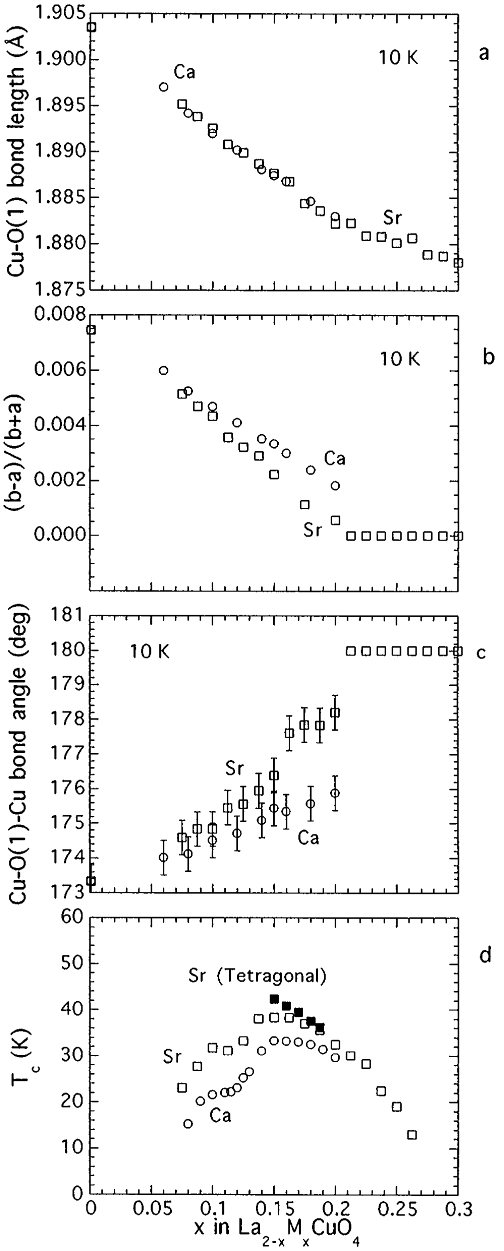

FIG. 1. Composition dependence at 10 K of (a) the in-plane copper-oxygen, Cu-O(1), bond lengths; (b) the orthorhombic strain; (c) the Cu-O(1)-Cu bond angles; (d) the superconducting T_c's for $La_{2-x}Sr_xCuO_4$ and $La_{2-x}Ca_xCuO_4$ systems. The increased T_c's (Ref. [13], Fig. 4) for tetragonal $La_{2-x}Sr_xCuO_4$ system under applied pressure are marked by solid squares.

From the magnetic measurements, the single-phase samples are bulk superconductors for $0.08 \leq x \leq 0.20$ and $0.08 \leq x \leq 0.27$ for Ca-and Sr-substituted materials, respectively [7,8]. Figure 1(d) shows T_c's determined from

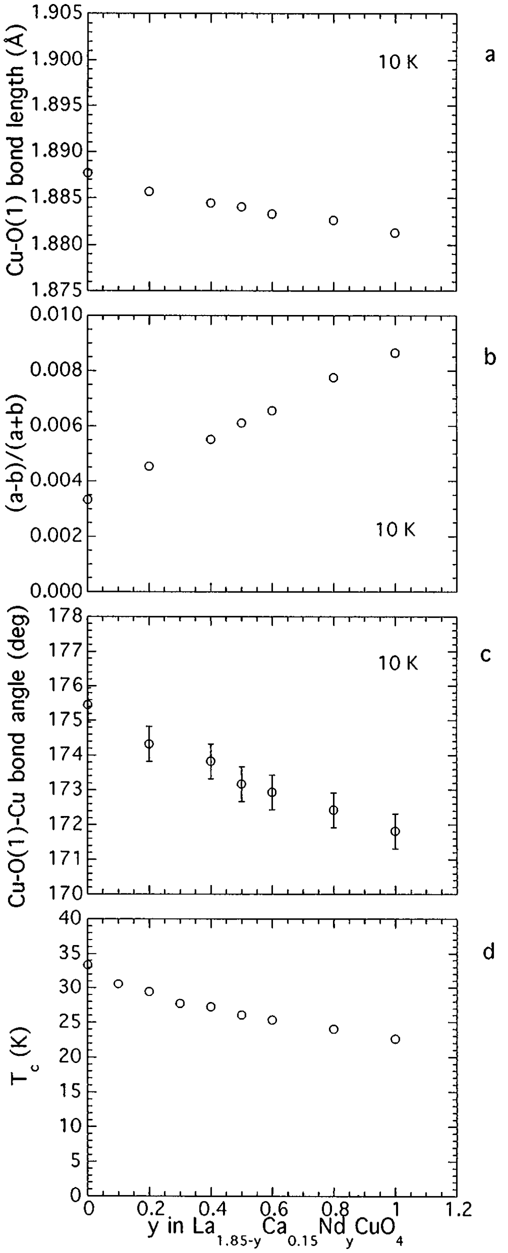

FIG. 2. Same as Fig. 1 for the $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ system.

the half point of the resistive transition, which corresponds to an onset of the diamagnetic transition for the ac susceptibility. Both systems show a maximum T_c for compositions close to $x = 0.15$. For the Ca-substituted material, the extrapolated O-T structural transition is shifted far away from $x = 0.15$ and thus, in agreement with our data for the $La_{2-x}Sr_xCuO_4$ system [7], the tetragonal phase cannot be responsible for the suppression of superconductivity. The decrease of T_c for $x > 0.15$ is not related to the structural transition to the tetragonal phase but instead is caused by some intrinsic electronic behavior common to both compounds. Superconducting transition temperatures are lower for the Ca system than for the Sr system. All $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ samples are bulk superconductors with T_c gradually decreasing with an increasing amount of Nd [see Fig. 2(d)].

The lower T_c's observed for the more distorted Ca system and the suppression of T_c at a fixed doping level with increasing orthorhombic distortion for $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ indicates that these effects are related to the distortions of the CuO_2 planes. The conclusion that an increase of the distortion at a fixed doping level decreases T_c is supported by measurements on $La_{2-x}Sr_xCuO_4$ samples under pressure [13]. With increasing pressure, T_c increases as the orthorhombic distortion is reduced and then remains approximately constant in the tetragonal phase. The increased T_c's observed under pressure for the tetragonal phase are shown on Fig. 1(d). For a fixed charge doping, the maximum T_c's are found for the tetragonal structure with the flat and square CuO_2 planes [8].

It is now possible to quantitatively describe the intrinsic T_c dependence on the charge doping or structural distortion by separating these effects. The data marked by solid squares on Fig. 1(d) for the superconducting $La_{2-x}Sr_xCuO_4$ system with the tetragonal structure, $0.15 \leq x \leq 0.27$, show a continuous decrease of T_c with doping over the whole range. Higher T_c's might be expected at lower doping levels ($x < 0.15$), since there is no apparent saturation of T_c at $x = 0.15$; i.e., there is no indication that the optimum composition for superconductivity occurs at $x = 0.15$ for the tetragonal material. The suppression of the superconducting transition temperature, ΔT_c, by structural distortion measured at 10 K (distortions at 10 K and at T_c are almost identical, since they change very weakly with temperature below 50 K) is shown in Fig. 3 for samples with fixed charge doping, $x = 0.15$. Data for tetragonal (20 kbar, $T_{c\,\max} = 42$ K) and LTO (ambient conditions) $La_{1.85}Sr_{0.15}CuO_4$ and for LTO $La_{1.85-y}Ca_{0.15}Nd_yCuO_4$ samples were used to define the $\Delta T_c = T_{c\,\max} - T_c(y)$. T_c is suppressed by 20 K with the distortion of the Cu-O(1)-Cu bond angles from 180° to 172°.

An observation that both tetragonal and LTO $La_{2-x}M_xCuO_4$ structures can be superconducting shows

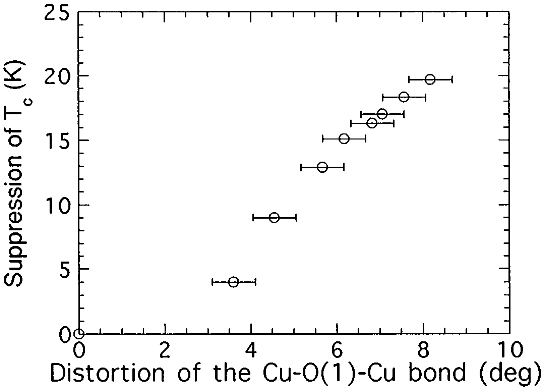

FIG. 3. Suppression of the superconducting transition temperature by structural distortion of the Cu-O(1)-Cu bond angle.

that the structural properties of the CuO_2 planes rather than the crystal symmetry is important in controlling the electronic properties of these and other 2D copper oxides. This observation is further supported by the superconducting properties of the tetragonal $La_{2-x}M_xCuO_4$ materials for which the CuO_2 planes are not flat, for example, the LTT phase of the barium-substituted ($x = 0.125$, nonsuperconducting and $x = 0.15$, superconducting) system [14]. The only distortion of the CuO_2 planes for the LTT phase is the rigid rotation of the Cu-O octahedron around the $\langle 100 \rangle$ axes of the high temperature tetragonal phase. This rotation causes half of the oxygen ions O(1) to shift out of the CuO_2 planes, distorting half of the Cu-O(1)-Cu bond angles from 180° by an amount which is larger than the distortion for the corresponding LTO structure. The increased distortion may in part be responsible for the suppression of T_c to $\sim$27 K for $La_{1.85}Ba_{0.15}CuO_4$. However, the complete suppression of superconductivity for $La_{1.875}Ba_{0.125}CuO_4$ cannot be explained by bond angle distortion alone. For these lower doping levels, $x \sim 0.12$, other electronic effects must also play a role as can be observed by a similar but weaker anomaly in T_c vs x curves for the Sr- and Ca-substituted materials, which do not show the LTT phase or any other structural anomaly at these compositions.

Irrespective of the coupling mechanism responsible for high temperature superconductivity, the T_c is usually related to the electronic density of states at the Fermi energy. Band structure calculations as well as angle-resolved photoemission data show "extended" saddle point singularities yielding high density of states (DOS) near the Fermi energy [15,16]. Calculations showed that octahedral tilts in the LTO structure cause little change in the DOS singularity around E_F, whereas tilts in the LTT structure open a large notch in the DOS whose depth and width are quadratic in tilt magnitude [17]. The difference between LTT and LTO tilts arises from the asymmetry of the LTT distortion which produces two different Cu-O(1) bond lengths, while there is only one bond for the LTO structure. The split singularity of the DOS in the LTT structure may be responsible for the complete suppression of T_c observed for barium- [14] and also for the more distorted strontium with neodymium- substituted [12,18] systems when the Fermi energy passes through the DOS singularities as a function of doping. The weaker anomaly of T_c vs x curves for the Sr- and Ca-substituted materials indicates a smaller but not negligible splitting of the singularity in the DOS for the LTO structure. Improved band structure calculations which will include both the $\langle 110 \rangle$ tilts and scissors-mode distortions and the nonlinear tilt-DOS coupling are required for comparison.

The model presented here for the dependence of T_c on the DOS at E_F, which is controlled by the hole doping (the relative position of the E_F with respect to the maximum of the DOS) and bucking of the CuO_2 planes (splitting of the maximum of the DOS), indicates that for fixed doping level the highest DOS and T_c should be found for flat and square CuO_2 planes in the tetragonal structure, which is consistent with experimental data. The decrease of T_c in the tetragonal $La_{2-x}Sr_xCuO_4$ system as a function of doping for $x > 0.15$ may be due to the lowering of the density of states at E_F as the Fermi energy moves below the maximum of the DOS. The observed anomaly in T_c vs x for $x \sim 0.12$ can be interpreted as the crossing of the Fermi energy through the weakly split peak in the DOS at this composition for the LTO structure and more strongly split peak for the LTT structure. Within this scenario, the application of pressures in excess of 20 kbar should bring $x \sim 0.12$ compositions to the tetragonal structure with a single maximum of $T_c \sim 45$ K appearing in place of the anomalously low T_c.

By comparing structural and superconducting properties of the alkaline earth-substituted $La_{2-x}M_xCuO_4$ materials we conclude that at a fixed doping level, the highest T_c is found for flat and square CuO_2 planes, and T_c is suppressed by the structural distortions of the CuO_2 planes. The local minimum of T_c vs doping observed for LTO and LTT materials around $x \sim 0.12$ may be related to the split singularity of electronic density of states.

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