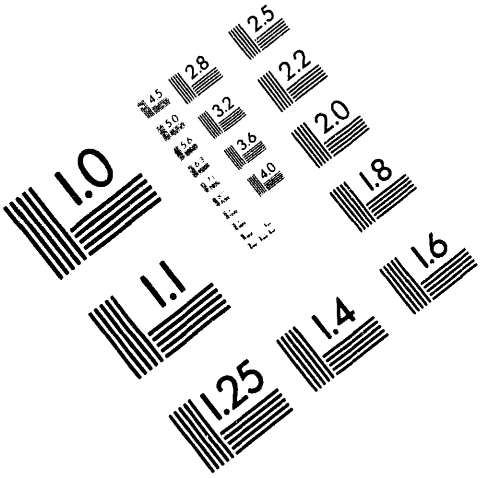

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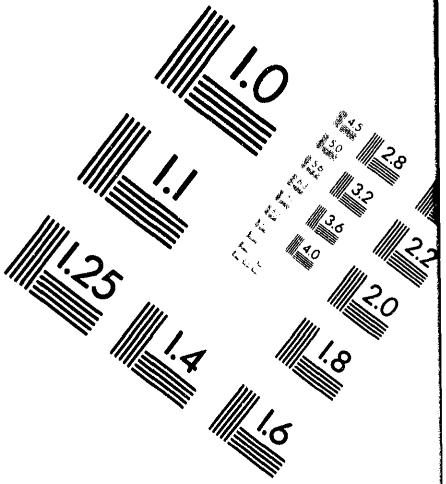

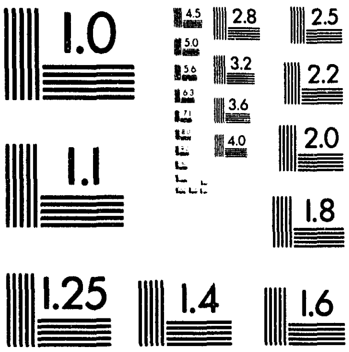

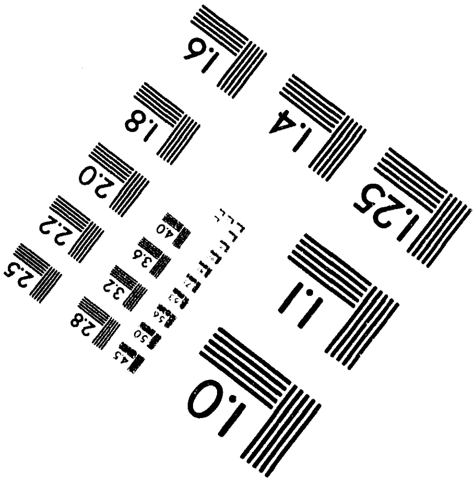

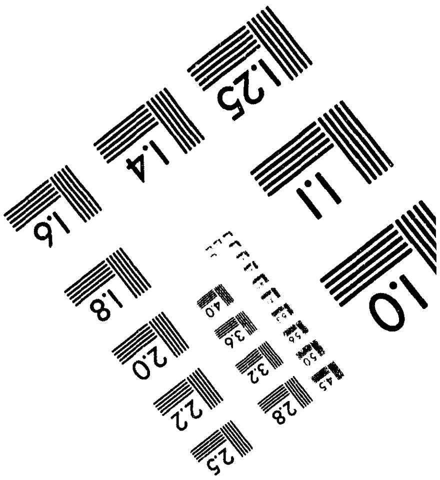

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Suppression of Superconductivity in Orthorhombic $La_{2-x}M_xCuO_4$ (M=Ca,Sr)*

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Suppression of Superconductivty in Orthorhombic $La_{2-x}M_xCuO_4$ (M=Ca,Sr)

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We have extended the calcium solid-solubility limit in $La_{2-x}Ca_xCuO_4$ to x = 0.2 using synthesis at high oxygen pressure. The superconducting transition temperature increases with doping to 34 K at x = 0.15 and is suppressed for x > 0.15, similar to the Sr-substituted material. At a fixed doping level, the optimum superconducting properties (the highest T_c) are found for flat and square CuO_2 planes.

The $La_{2-x}M_xCuO_4$ materials provide 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 T_c on doping, which shows underdoped, $0.07 \leq x \leq 0.14$, optimally doped, $x \sim 0.15$ (T_c~38 K), and overdoped, $0.16 \leq x \leq 0.27$, compositions is considered typical for all copper oxide superconductors.[1] Less understood is the T_c dependence on structural properties. For example, a recent report of a large reduction of the superconducting fraction at the orthorhombic-to-tetragonal phase transition boundary, $x \sim 0.21$, assumes that only the orthorhombic phase is superconducting.[2] We have studied in detail the structural and superconducting properties of the Ca- and Sr-substituted materials using x-ray and neutron powder diffraction, a.c. susceptibility and d.c. magnetization, resistivity and thermogravimetric measurements.[3,4] Comparison of the Ca- and Sr-substituted materials allows a separation of the effects of doping and structure on T_c.

Polycrystalline samples of $La_{2-x}M_xCuO_4$ with M = Ca and Sr were synthesized from nitrates and oxides, respectively. The calcium solid-solubility limit was extended from x = 0.1 for air synthesized material to x = 0.2 using synthesis at an oxygen pressure of 600 atm. and 1110 ^{o}C. For strontium, the maximum solubility limit was found at x = 0.4 for synthesis in air at 1170 ^{o}C. An oxygen content of 4.00 ± 0.01 was found for all calcium and strontium samples up to x = 0.3. Thus, all samples are fully stoichiometric in the superconducting range and the hole doping of the CuO_2 planes is identical for both materials.

Neutron powder diffraction data were collected at several temperatures from 10 to 300 K and the structure was refined by the Rietveld technique. The structural phase diagram contains only two crystallographic phases, the low-temperature orthorhombic, Cmca, and high-temperature tetragonal, I4/mmm. The O-T transition for the Ca-substituted material occurs at higher temperatures, or larger doping levels, than for the Sr-substituted material. The CuO_2 plane is flat and the copper and oxygen atoms are distributed on a perfect square lattice for tetragonal phase. For the orthorhombic phase two distortions of the CuO_2 plane are present: the rigid rotation of the Cu-O octahedron around the 100-axis and the scissors-mode distortion within the CuO_2 plane. The rotation of the Cu-O octahedron causes the oxygen ions O(1) to move out of the CuO_2 plane, distorting the Cu-O(1)-Cu bond angle from 180 deg. The scissors mode, that is present within the CuO_2 plane, distorts the O(1)-Cu-O(1) bond angle from 90 deg. The Cu-O(1)-Cu bond angle defines the flatness of the CuO_2 plane and the O(1)-Cu-O(1) bond angle, the perfection of the square network. Figure 1 shows that the Cu-O(1)-Cu bond angle is more distorted for the Ca-substituted material consistent with the Ca-substituted material being "more orthorhombic" than the Sr-substituted material for the same substitution level, x.

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. No discontinuity in the superconducting volume fraction and T_c versus x curve were observed at the O-T phase boundary. Figure 2 shows T_c's (determined from the half point of the resistive transition) and the O-T phase boundary for both materials. Both systems show a maximum T_c for compositions close to $x = 0.15$. For the Ca-substituted material, the O-T structural transition is shifted far away from $x = 0.15$ and thus, the tetragonal phase can not be responsible for the suppression of superconductivity. The suppression of Tc for $x \geq 0.15$ is not related to the structural transition to the tetragonal phase but instead is caused by some intrinsic behavior common to both compounds. The observed lower T_c for the Ca system is a structural effect, resulting from the larger distortion of the Cu-O(1)-Cu and O(1)-Cu-O(1) bond angles which determine the electronic hybridization between the copper $d_{x^2-y^2}$ and oxygen $p_{x,y}$ orbitals. Since the band structure near the Fermi energy is entirely due to the 2D band composed of these orbitals, it seems appropriate to relate all relevant electronic properties of the $La_{2-x}M_xCuO_4$ materials (and other 2D copper oxides) to the structural properties of the CuO_2 plane rather then to the global crystal symmetry.

A conclusion that an increase of the orthorhombic distortion (an increase of the distortions of the copper-oxygen bond angles) at a fixed doping level decreases T_c is supported by measurements on $La_{2-x}Sr_xCuO_4$ samples under pressure.[5] Hydrostatic pressure reduces the orthorhombic distortion and eventually results in a transition to the tetragonal structure (with the flat and square CuO_2 plane). With increasing pressure, T_c increases as the orthorhombic distortion is reduced and then remains constant in tetragonal phase. The increased T_c's observed under pressure for the tetragonal phase are shown on Fig. 2. Pressures of 20 kbar were necessary to transform the orthorhombic $x = 0.15 - 0.21$ samples to the tetragonal structure at low temperatures. Present data for the superconducting $La_{2-x}Sr_xCuO_4$ system with the tetragonal structure, $0.15 \leq x \leq 0.27$, shows that there is a continuous decrease of T_c with doping over the whole range. By extrapolation 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 for the optimum composition for superconductivity at $x = 0.15$ for the tetragonal material. The commonly observed maximum of T_c for $x = 0.15$ under ambient conditions might be caused by the overall suppression of T_c with increased doping and by suppression of T_c by structural and electronic distortion of the flat and square CuO_2 plane at lower doping levels in the orthorhombic structure.

This work was supported by the NSF Science and Technology Center for Superconductivity under grant #DMR 91-20000 (BD, ZW, JLW, BAH, PGR) and the U.S. Department of Energy, BES - Materials Sciences under contract No. W-31-109-ENG-38 (JDJ, RLH, DGH)

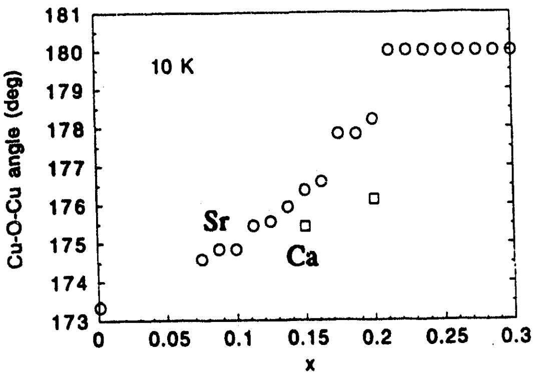

Fig. 1. Composition dependence of the Cu-O(1)-Cu bond angle for $La_{2-x}M_xCuO_4$ at 10 K.

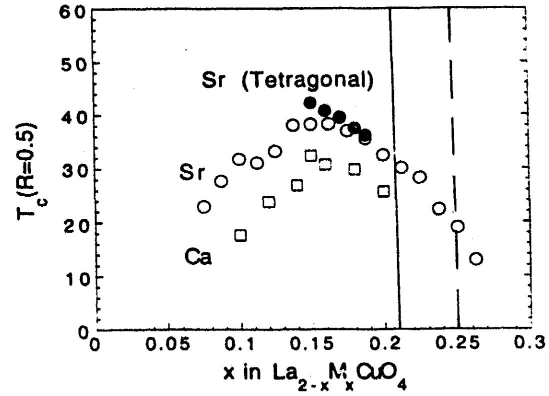

Fig. 2. Superconducting T_c's and the T-O phase boundary for $La_{2-x}M_xCuO_4$ materials.

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