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Effects of Th doping on structural and superconductive properties of $La_{2-x}Ba_xCuO_4$

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The striking suppression of superconductivity of $La_{2-x}Ba_xCuO_4$ in a narrow range of x around 0.125 is known to be a consequence of a structural transition to a low-temperature tetragonal phase below about 60 K. Study of low-temperature lattice instabilities by x-ray diffraction revealed that in $La_{2-y-x}Th_yBa_xCuO_4$ the development of the low-temperature tetragonal phase, as well as the sharp suppression of superconductivity, is centered at $x-y \cong 0.125$, instead of $x \cong 0.125$. Therefore, the anomalous low-temperature behavior is essentially characterized by the density of carriers rather than local ionic forces, which couples with the lattice instabilities.

Recently high-temperature superconductor[1] $La_{2-x}Ba_xCuO_4$ has drawn renewed intensive interest because it became evident that the disappearance of bulk superconductivity[2] in a narrow range of x around 0.12 is related to the structural transition from a midtemperature orthorhombic (OMT) phase to a low-temperature tetragonal (TLT) phase at temperature $T_{d2} \approx 60$ K.[3,4] A striking change in various normal-state properties occurs below about 60 K: the electrical conduction becomes nonmetallic and modification of the density of states $N(E)$ near the Fermi energy E_F is suggested from Seebeck and Hall coefficients.[5] The anomalous suppression and subsequent recovery of high-T_c superconductivity with varying carrier concentration has so far been found only in $La_{2-x}Ba_xCuO_4$ and $La_{2-x}Sr_xCuO_4$, and for the latter the magnitude of the anomaly is much reduced.[6,7] Nevertheless, it is envisaged that the clarification of this anomaly holds a clue to the mechanism of superconductivity in *all* high-T_c Cu oxides, because the phenomenon is intimately related with a delicate configurational change within CuO_2 planes.

In this paper, we present the low-temperature structural and superconductive properties of $La_{2-y-x}Th_yBa_xCuO_4$ and demonstrate that the condition for the lattice instabilities, which is responsible for the strong suppression of high-T_c superconductivity, is essentially specified by the amount of hole concentration $p \approx x-y$.

Various attempts have been made to control the carrier density in $La_{2-x}Ba_xCuO_4$ by a method other than the amount of divalent ions in La site.[8-10] Empirically, substitution for ions having smaller valency is best accomplished if the substitute has a somewhat smaller ionic radius, and vice versa. Examples are smaller Y^{3+} in the 8 coordination of oxygen with ionic radius[11] of 1.02 Å substituting for Ca^{2+} (1.12 Å) in $Bi_2Sr_2CaCu_2O_{8+\delta}$, and 9-coordinated Sr^{2+} (~1.29 Å), rather than Ca^{2+} (1.18 Å), substituting better for La^{3+} (1.20 Å) in La_2CuO_4. On the basis of these considerations, we devised Th doping in $La_{2-x}Ba_xCuO_4$ because Th is known to be stable in a +4 ion state in the 9 coordination (1.09 Å) and seems an ideal dopant for the La site in La_2CuO_4. In contrast, Ce^{4+} would be stable in the 8 coordination (0.97 Å) as in $Nd_{2-x}Ce_xCuO_4$.

Samples used in this study are polycrystals prepared by solid-state reaction. To enhance the homogeneity of Th, we adopted slightly higher final-reaction temperature, 1130 °C, compared to 1100 °C used for $La_{2-x}Ba_xCuO_4$.[12] The total reaction time was 120 h and sintered samples were annealed in oxygen flow at 400 °C for 24 h.

Powder x-ray analysis at room temperature indicates that with $y=0.020$, a trace of ThO_2 is detected only for $x \leq 0.11$. The solubility of Th apparently enhances for greater x, and for $x \geq 0.12$, a very systematic change in the lattice parameters is observed by Th doping. With $y=0.020$ the lattice parameter a increases by about 0.06% and c decreases by about 0.07% for given x, resulting in the increase of the unit-cell volume by about 0.05%. For this reason, we will present here the physical properties of $La_{2-y-x}Th_yBa_xCuO_4$ only for $x \geq 0.12$.

The oxygen content of these samples was determined by iodine titration to be 3.988 ± 0.011 per formula unit for $y=0.020$ and $0.12 \leq x \leq 0.17$. This indicates that the change in oxygen content is insignificant by Th doping, and a Th^{4+} ion acts to compensate the hole carrier introduced by Ba^{2+}.

Diamagnetic susceptibility was measured by a superconducting-quantum-interference-device magnetometer after cooling in a field of 2.5 Oe. As shown in Fig. 1 for the Th-doped samples, a strong Meissner signal is recovered for $x=0.125$. Sharp depression of T_c occurs at $x=0.145$, but in comparison with $La_{2-x}Ba_xCuO_4$ with $x=0.125$, the onset of diamagnetism with $T_c \cong 12$ K is much sharper and the Meissner volume fraction is substantial.

Figure 2 compares the x dependence of T_c as determined at 1% of the perfect-diamagnetic volume fraction for $La_{2-x}Ba_xCuO_4$ and $La_{2-y-x}Th_yBa_xCuO_4$ ($y=0.020$). It is clear that the center of sharp depression of T_c shifts from $x \cong 0.125$ for $La_{2-x}Ba_xCuO_4$ to $x \cong 0.145$ for $La_{2-y-x}Th_yBa_xCuO_4$ with $y=0.020$. Persistence of 30 K superconductivity at $x=0.170$ is also consistent if the transition temperature is approximately described as $T_c = T_c(x-y)$. Correspondingly, the distinctive minimum in resistivity ρ at about 60 K, reproducibly present in $La_{2-x}Ba_xCuO_4$ with $x=0.125$, no longer exists for a Th-doped sample with $x=0.125$. Instead, the resistivity minimum appears at 50–60 K for $x=0.145$. For greater x the resistivity minimum disappears again and the metallic behavior persists down to T_c.

Figure 3 shows a portion of the powder x-ray spectra of

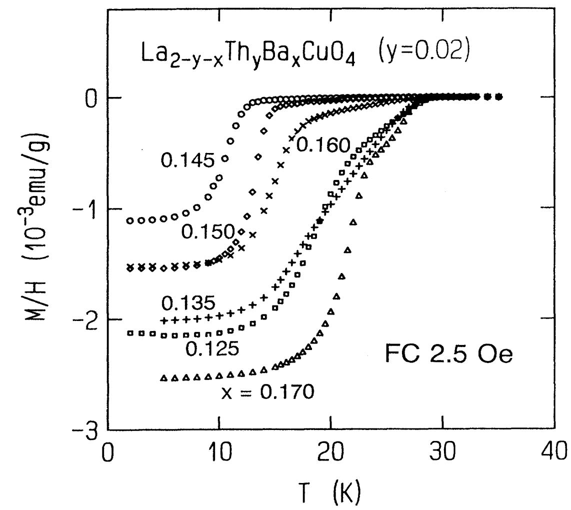

FIG. 1. Magnetization of $La_{2-y-x}Th_yBa_xCuO_4$ with $y=0.020$. For $x=0.145$ a strong suppression of T_c is evident, but the onset of superconductivity remains sharp and a substantial Meissner volume fraction is retained.

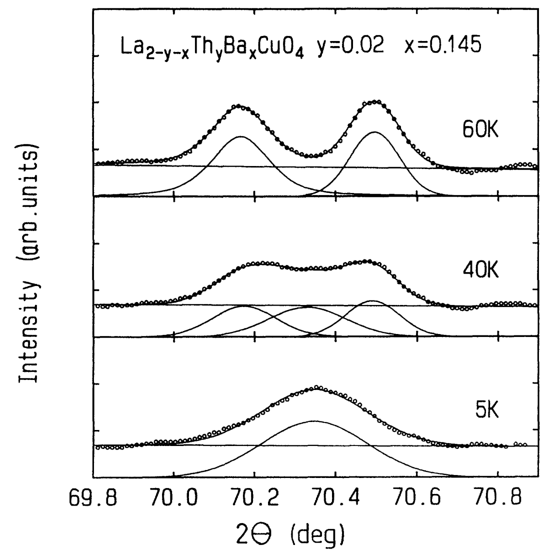

FIG. 3. Powder x-ray-diffraction patterns of $La_{1.980-x}Th_{0.020}Ba_xCuO_4$ with $x=0.145$ at selected temperatures. The split (400) and (040) reflections of the OMT phase are overtaken by a single peak of the TLT phase at lower temperatures. The circles represent the data points and solid curves indicate the results of multiple-peak fitting.

a Th-doped sample with $x=0.145$ at selected temperatures. Contribution from Cu $K\alpha_2$ radiation has been analytically subtracted. At 60 K, split (040) and (400) peaks of the OMT phase are evident. Below 50 K, a third peak becomes visible between the two peaks. We assign this to (400) peak of the TLT phase. As the temperature decreases it grows with the expense of the intensities of the OMT peaks. To estimate the volume fraction of each phase, we have fitted the spectra by multiple Gaussian peaks with a linear background, as shown by solid curves in Fig. 3. The integrated intensity ratios for both phases are plotted as functions of temperature in Fig. 4. The transition width is about 20 K and only a very small hysteresis is observed between cooling and heating measurements. The transition temperature for $La_{2-y-x}Th_yBa_xCuO_4$ with $x=0.145$ and $y=0.020$ is $T_{d2}=38$ K if defined at the volume fraction of 50%, and the volume fraction of the OMT phase is negligible below 30 K. For $La_{2-y-x}Th_yBa_xCuO_4$ with $x=0.125$ and $y=0.020$,

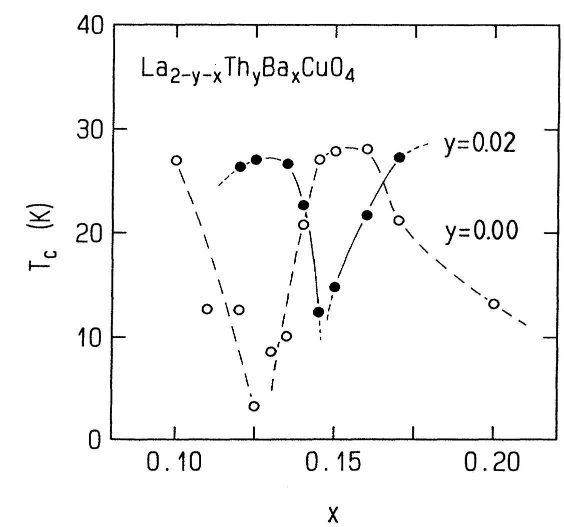

FIG. 2. The x dependence of T_c for $La_{2-x}Ba_xCuO_4$ (○) and $La_{2-y-x}Th_yBa_xCuO_4$ with $y=0.020$ (●). T_c is defined at the temperature of 1% volume fraction of perfect diamagnetism. In both systems, the anomalous suppression of T_c is centered at $p \approx x-y \cong 0.125$.

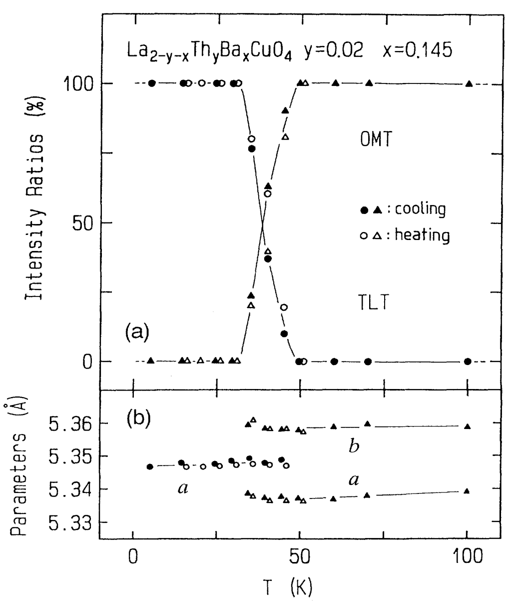

FIG. 4. Temperature dependence of (a) the integrated intensity ratios, $I(\mathrm{TLT})/[I(\mathrm{TLT})+I(\mathrm{OMT})]$ and $I(\mathrm{OMT})/[I(\mathrm{TLT})+I(\mathrm{OMT})]$, and (b) the lattice parameters for $La_{1.980-x}Th_{0.020}Ba_xCuO_4$ with $x=0.145$.

T_{d2}=30 K is lower than that for x=0.145. Moreover, the TLT volume fraction never reaches 80% even at 5 K for that sample. For x=0.170, $T_{d2} \approx 20$ K and a substantial OMT fraction persists down to 5 K. This is direct evidence that the structural anomaly at low temperatures is controlled by the condition $x-y \approx 0.125$, rather than by the amount of divalent ions x or of nontrivalent ions in the La site $x+y$. The results also imply that the TLT phase is thermodynamically stable only in a very narrow range of $x-y$. Judging from the volume fractions of the Meissner signal and of the TLT phase, we infer that the bulk superconductivity with reduced T_c is sustained even in the TLT phase in Th-doped $La_{2-x}Ba_xCuO_4$.

We note that the (400) diffraction peak of the TLT phase of $La_{2-y-x}Th_yBa_xCuO_4$ is broader than the corresponding peaks of the OMT and high-temperature tetragonal (THT) peaks, although it is somewhat narrower than the TLT peaks of the $La_{2-x}Ba_xCuO_4$ samples. An electron-diffraction study of our $La_{2-x}Ba_xCuO_4$ samples[13] shows that for x=0.125 the TLT sample is composed almost entirely of tetragonal domains. Without such characterization, however, it is not possible to clarify the precise symmetry and microstructure of the TLT phase of $La_{2-y-x}Th_yBa_xCuO_4$.

Even if each Th^{4+} ion were paired with a Ba^{2+} ion at an adjacent site, such a pair would not compensate for the local ionic distortion because Ba^{2+} has a commandingly greater ionic radius (1.47 Å) in comparison with matching La^{3+} and Th^{4+}. The present results demonstrate that the structural and superconductive anomaly is centered at $x-y \cong 0.125$ despite the fact that the system contains a greater amount of large Ba^{2+} ions. Therefore we conclude that the hole concentration $p \approx x-y$ is the essential parameter which governs the lattice instabilities at low temperatures.

Theories of the electronic mechanism of the low-temperature lattice instability consider the importance of the Van Hove singularity,[14,15] as well as the in-plane oxygen-oxygen charge transfer.[16] So far, there has been no decisive experimental evidence for the presence of a Van Hove-like singularity in $N(E)$ either in the THT or the OMT phase. The magnetic susceptibility M/H near room temperature increases with x as a consequence of decrease in the effective exchange energy J between Cu spins by the increase in hole concentration. M/H would also reflect the x dependence of $N(E_F)$. A close examination of M/H of $La_{2-x}Ba_xCuO_4$, $La_{2-y-x}Th_yBa_xCuO_4$, and $La_{2-x}Sr_xCuO_4$ at 300 K as a function of x (present study and Refs. 6–8) indicates that the variation of M/H with x is smooth and within experimental resolution there is no evidence for the anomalous enhancement. The same is true for the OMT samples at 100 K. Although this behavior of static, uniform susceptibility does not immediately negate the presence of the proposed singularity in $N(E)$, it is unlikely that $N(E_F)$ sharply peaks at $x \approx 0.12$.

Condensation of the X-point phonon in the TLT phase, which has survived in the OMT phase, is an attractive explanation for the suppression of superconductivity based on electron-phonon coupling mechanism. It would, however, be difficult to account for the observed change in the normal-state properties by this condensation alone.

In the THT and OMT phases all the in-plane oxygen sites are equivalent; so are the corresponding Cu—O bond lengths. In contrast, there are two distinctive sites in the TLT phase: Half of the oxygen ions reside precisely in the plane, while the other half slightly above or below the plane. Since the critical value of the carrier concentration per Cu for the instability is very close to 1/8, it is plausible that a band instability commensurate with the lattice triggers the lattice deformation to lift this degeneracy. We speculate that the states in the charge-transfer gap ("midgap states," or more recently called "in-gap states") around E_F, generated by hybridization of O $2p$ and Cu $3d$ orbits, develop an additional gap structure with reduced $N(E_F)$ in the TLT phase by this deformation and lower the energy of the system. We believe that this reduction in $N(E_F)$ is the main reason for the strong suppression of T_c, as well as for the change in the normal-state properties. As we argued in our previous paper[12] on $La_{2-x}(Ba,Sr)_xCuO_4$, however, such electronic instability does not always result in static and long-range lattice distortion at the same temperature. This scheme is quite different from the band filling with a Van Hove singularity by varying p.

In summary, we have demonstrated that by partially substituting Th for La in $La_{2-x}Ba_xCuO_4$ the low-temperature lattice instability, together with the change in the normal state and the sharp suppression of T_c, is centered at $x-y \cong 0.125$, instead of $x \cong 0.125$. Therefore, it is experimentally established here that the lattice deformation is triggered through coupling to carriers if $p \approx 1/8$ for the carrier concentration per Cu is satisfied.

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