Superconductor-to-metal transition in overdoped $La_{2-x}Sr_xCuO_4$

J.-S. Zhou, H. Chen, and J. B. Goodenough
Center for Materials Science & Engineering, ETC 9.102, University of Texas at Austin, Austin, Texas 78712-1063
(Received 27 January 1993; revised manuscript received 25 October 1993)

The low-temperature transition from superconductor to metal of overdoped $La_{2-x}Sr_xCuO_4$ has been monitored by measurements of resistivity versus temperature as a function of pressure over the compositional range $0.15 \le x \le 0.30$. Polycrystalline samples were annealed under oxygen for periods up to 1 month to obtain homogeneous, stoichiometric samples. The pressure dependence of the critical temperature is $dT_c/dP > 0$ in the orthorhombic phase found for $x \le 0.22$; it vanishes in the tetragonal phase occurring with $x > 0.22$. Pressure favors the tetragonal phase, lowering the orthorhombic-tetragonal transition temperature T_t and shifting the transitional composition x_t to $x_t < 0.20$ above 10 kbar. This shift is shown to be due to an unusually large compressibility of the Cu-O bonds in the CuO_2 sheets. The persistence of T_c into the tetragonal phase with $x > x_t$ is not due to orthorhombic-phase fluctuations, as has been speculated. Whereas the superconductive transition temperature T_c decreases with increasing x, an elastic transition at $T_d \approx 37$ K persists over the entire compositional range, including the metallic phase at $x = 0.30$. Careful measurements of resistance and Seebeck coefficient across T_d reveal a $T_d \ge T_c$; but superconductive-pair fluctuations may occur below a $T_f > T_d$ where $T_c \approx T_d$, which is consistent with a transition from two- to three-dimensional metallic conduction. The data also suggest that the superconductor-metal transition is not smooth.

INTRODUCTION

The system $La_{2-x}Sr_xCuO_4$ allows an unambiguous study of the evolution of physical properties with oxidation state of the CuO_2 sheets in a copper oxide superconductive system. Problems with maintaining oxygen stoichiometry[1] prevented earlier workers from completing a systematic study over the full range of x from the antiferromagnetic La_2CuO_4 parent through the superconductive phase to the overdoped metallic phase with $x \ge 0.30$. Problems with the segregation of a $La_2SrCu_2O_6$ phase have also been noted for $x \ge 0.20$.[2] These problems can be overcome with proper sample preparation, and single crystals to $x = 0.35$ have been synthesized; single-crystal studies have been limited to rather large increments of x.[3] A recent study[4] of the temperature dependence of the conductivity has used both single-crystal and polycrystalline samples; the polycrystalline data were found to reveal the fundamental features of the evolution with x of the transport properties. Torrance *et al.*[5] used high oxygen pressure to obtain stoichiometric samples to $x \approx 0.35$; they measured the magnetic susceptibility χ and reported the x dependences of T_{max}, the maximum in χ vs T, and of T_c. They reported a smooth decrease of T_c through x_t, where x_t denotes the orthorhombic-tetragonal phase boundary at T_c where it is measurable in this study; both T_c, and T_{max} fall to zero within the tetragonal phase field at $x \approx 0.26$. We[6] have reported Seebeck as well as resistivity data on polycrystalline samples. In the compositional range $x \le 0.10$, we found evidence for large-polaron behavior at higher temperatures and the onset of dynamic charge fluctuations below 150 K. The dynamic phase segregation was between the antiferromagnetic and superconductive phases, which led us to postulate that the superconductive phase is a unique thermodynamic state stabilized by unusual electron-phonon and/or spin-spin interactions. In order to explore similarly the superconductor-metal transition in the overdoped region, we have studied at several pressures the temperature variation of the low-temperature resistance in increments of $\Delta x = 0.01$ over the range $0.15 \le x \le 0.30$.

The transition from the superconductive to the metallic phase with increasing x in the system $La_{2-x}Sr_xCuO_4$ is made complicated by a crossover of T_c and an orthorhombic-tetragonal transition temperature T_t near 30 K at $x = x_t \approx 0.21$. A recent study[7] concluded that superconductivity is associated only with the orthorhombic phase; the persistence of superconductivity to compositions $x > x_t$ was attributed to orthorhombic-phase fluctuations. In this paper, we report high-pressure resistance studies to disprove this postulate; superconductivity extends into the tetragonal phase field. Yamada and Ido[8] have independently come to the same conclusion by measuring the magnetic susceptibility under pressure through the range $0.15 \le x \le 0.22$. The two high-pressure studies show a $dT_c/dP > 0$ for the orthorhombic phase and a $dT_c/dP \approx 0$ for the tetragonal phase, with T_c varying smoothly with x across x_t.

EXPERIMENTAL PROCEDURES

Polycrystalline samples were prepared by reacting in air a stoichiometric mixture of the oxides at 1030–1100 °C for 1 week with intermittent grinding. Before the final sintering, the powder samples were ground in a milling machine to obtain a finer powder than is obtainable with regular grinding. Sintering just above the reaction temperature of 1050 °C gave a hard, dense pellet. However, sintering at 1030–1100 °C for times $t < 24$ h is not sufficient to remove $La_2SrCu_2O_6$ as a second phase; single-phase samples were obtained by longer firing times. Annealing at 900 °C for 1 month followed by slow cooling to room temperature gave 3.99±0.01 oxygen atoms per molecule from iodometric titration. After the final sinter, all samples were single phase to x-ray powder diffraction, and slow scans (0.06°/min at steps of 0.005° in 2θ) of several individual peaks—e.g., 004, 110, 200—were made to check the sample homogeneity. A peak-fitting program was used to separate the Cu $K\alpha_1$ and $K\alpha_2$ contributions. Relative to a highly crystalline Si sample giving a full width at half maximum (FWHM) for the (220) peak of 0.05° in 2θ, which was used as an internal standard, the nearby sample peaks showed a FWHM of 0.09° in 2θ with no apparent change over the range $0.15 \le x \le 0.30$. When ground together, the sample powder is always ground to a finer size than the Si-powder standard, which may account for the greater linewidth in the oxide samples. The samples that show a sharp transition at T_c have linewidths similar to those showing a broad transition with more than one shoulder; there is no evidence that the samples with broad transitions are less homogeneous in the La, Sr, and O distribution than the samples like $x = 0.15$ that show sharp transitions at T_c. Moreover, the evolution with x of the lattice parameter a decreases monotonically with increasing x throughout the region $0.15 \le x \le 0.30$. Therefore we conclude that all our samples have a similar and uniform homogeneity at room temperature.

The Meissner-effect measurements were carried out with a superconducting quantum interference device (SQUID) magnetometer. The resistivity of these polycrystalline samples was checked by the van der Pauw method; it is as low as the best values in the literature, for example Ref. 4. Electrical-resistance measurements under nearly hydrostatic pressure were performed with a Be-Cu self-clamping device[9] containing a Teflon cell, a lead manometer, and a 1:1 mixture of n-pentane and isoamyl alcohol as a pressure-transmitting medium. Thin copper wire pressed to the sample's surface made contact via small pieces of indium foil. The sample temperature was measured with a silicon diode attached to a place near the Teflon cell. During a measuring run, the cooling rate was computer-controlled to be less than 0.1 K/min. The Seebeck coefficient was measured with a home-built apparatus that controls the temperature across the sample to within 0.05 K in the temperature range $T < 100$ K.

RESULTS AND DISCUSSION

Although the pressure dependence of T_c, dT_c/dP, has been reported as a function of x,[10,11] it has not been investigated in small increments of x about the orthorhombic-tetragonal phase boundary at x_t. High-resolution synchrotron x-ray diffraction has been used[7] to determine an $x_t = 0.21$ near 30 K. According to neutron elastic scattering,[12] even the short-range orthorhombic fluctuations disappear for $x > 0.22$. Although the inability to observe any orthorhombic fluctuations in samples with $x > 0.22$ cannot rule out their presence, the pressure dependence of T_c would be expected to vary smoothly

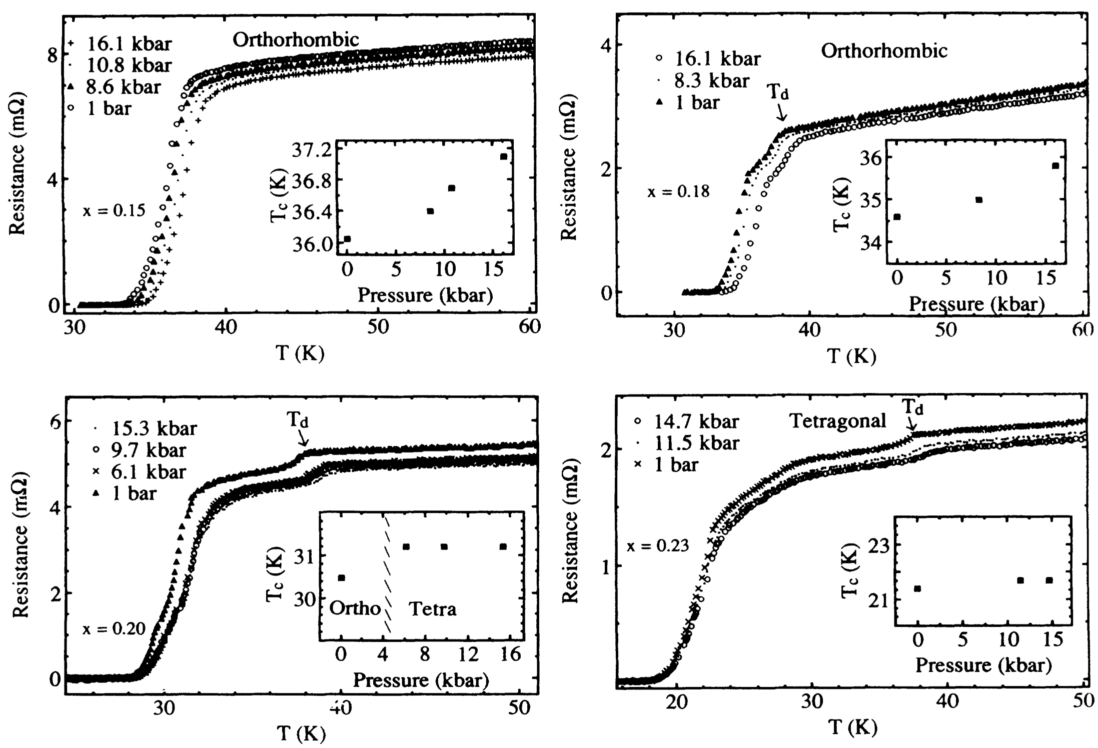

FIG. 1. Temperature dependence of the resistance of $La_{2-x}Sr_xCuO_4$ pellets under different hydrostatic pressures. Insets: Pressure dependence of T_c.

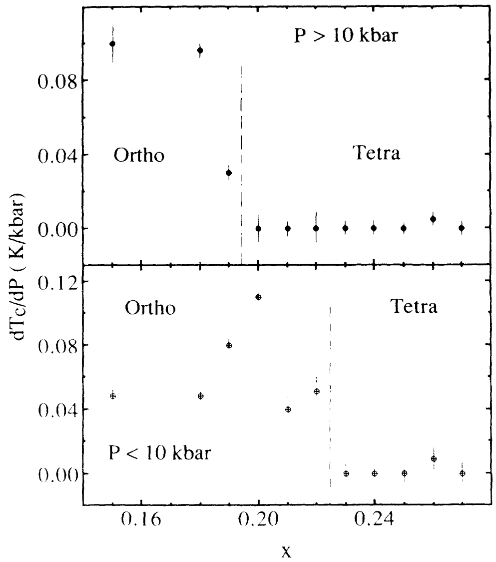

FIG. 2. Variation with x of the pressure dependence of T_c for $P > 10$ kbar and $P < 10$ kbar in the system $La_{2-x}Sr_xCuO_4$.

with x if any T_c for $x > x_t$ is associated with orthorhombic fluctuations.

Typical curves of resistance versus temperature as a function of pressure are shown in Fig. 1 for four compositions spanning the orthorhombic-tetragonal transition at x_t. In this figure, T_c is defined as the midpoint of the resistance drop due to the superconductive transition. This transition is to be distinguished from the resistance drop occurring at the temperature marked T_d in the figure. The resistance drop at $T_d \approx 37$ K is well resolved from the superconductive onset temperature in all samples $x \geq 0.18$; it is obscured by a $T_c \approx T_d$ in the $x = 0.15$ sample.

Figure 2 summarizes the measured dT_c/dP versus x over the compositional range $0.15 \leq x \leq 0.27$. Since the slope of T_c versus pressure P changes in the vicinity of 10 kbar, we show dT_c/dP for the ranges $P < 10$ kbar and $P > 10$ kbar. Where there is an orthorhombic-tetragonal phase change below 10 kbar, the slope dT_c/dP is taken for the orthorhombic phase. For $P < 10$ kbar, the $x = 0.19$ and $x = 0.20$ samples show an anomalously high value of dT_c/dP in Fig. 2. In these two samples, the R-versus-T curves in Fig. 1 and Fig. 3 indicate the presence of two superconductive phases having nearly the same T_c, which results in a step in the resistive drop at T_c. Pressure changes the ratio of the resistive drops for the two steps, which gives too high a value of dT_c/dP for a T_c defined as the midpoint of the resistivity drop, since the midpoint includes in this case both steps. For $x \geq 0.23$, where the samples remain tetragonal to lowest temperatures,[7] a $dT_c/dP \approx 0$ is found whereas in the $x = 0.15$ sample, which retains the orthorhombic structure to the highest pressures used in this study (22 kbar), T_c increases with pressure with a maximum $dT_c/dP = 0.11$ K/kbar above $P = 10$ kbar; this value for dT_c/dP is consistent with literature data.[13] The samples with $0.2 \leq x \leq 0.22$ showed an increase in T_c with pressure only in the range $P < P_c$, where P_c decreases with increasing x. We therefore interpret the sharp drop in dT_c/dP versus x at a critical composition to signal the composition x_t for which $T_c = T_t$, where T_t is the orthorhombic-tetragonal transition temperature. Room-temperature x-ray diffraction under high pressure[14] has established that pressure favors the tetragonal phase, i.e., $dT_t/dP < 0$. Where T_t approaches T_c, a $dT_c/dP > 0$ in the orthorhombic phase and a $dT_t/dP < 0$ give rise to a pressure-dependent $x_t = x_t(P)$ with $dx_t/dP < 0$, since x_t is defined as the orthorhombic-tetragonal transitional composition at T_c. This experiment gives two important deductions. First, the sharp drop from $dT_c/dP > 0$ to $dT_c/dP = 0$ at x_t demonstrates that the superconductive compositional range extends from the orthorhombic phase into the tetragonal phase. Second, although pressure suppresses any orthorhombic fluctuations in the tetragonal phase, both T_c and the superconductive shielding fraction (as measured by ac susceptibility under pressure)[8] increase on going from the orthorhombic to the tetragonal phase for a given composition $x \leq x_t$. These two deductions provide unambiguous evidence that the superconductivity observed for $x > x_t$ is to be associated with the tetragonal phase and not with orthorhombic-phase fluctuations. At lower pressure ($P < 10$ kbar), we find an abrupt drop in dT_c/dP at $0.22 < x_t < 0.23$ in our samples, which is to be compared with an $x_t \approx 0.21$ obtained by Takagi *et al.*[7] At higher pressure ($P > 10$ kbar), dT_c/dP decreases linearly with increasing x, dropping abruptly to zero at $0.19 < x_t < 0.20$.

The observation that $dT_c/dP > 0$ is only associated with the orthorhombic phase indicates that T_c is sensitive to the Cu-O-Cu bond angle. In the orthorhombic phase, this angle is bent from 180°; the angle increases with pressure, becoming 180° in the tetragonal phase where T_c reaches its maximum value for a given composition x. Thus T_c increases with decreasing distortion of the CuO_2 plane in this system, where there is no charge transfer from a nonsuperconductive reservoir layer. This conclusion is consistent with the situation found for the n-type systems. In the infinite-layer $Sr_{1-x}Nd_xCuO_2$ system,[15] for example, a $dT_c/dP > 0$ could be attributed to an oxygen-atom displacement from the CuO_2 planes.[16] Where the Cu-O-Cu bonds are straight, as in the n-type $L_{2-x}Ce_xCuO_4$ T' tetragonal phase, a $dT_c/dP = 0$ is found.[17] This correlation of T_c with structure, and specifically with the Cu-O-Cu bond angle, is also a clear indication that strong electron-phonon interactions are implicated in superconductive-pair formation. Models of the pairing mechanism that are based on electron-electron interactions alone do not provide this correlation.

As argued elsewhere,[18] the origin of the orthorhombic-tetragonal transition in the $La_{2-x}Sr_xCuO_4$ system is a temperature-dependent mismatch between the La-O and Cu-O bond lengths. The tolerance factor $t = (\text{La-O})/[\sqrt{2}(\text{Cu-O})]$ is a good measure of this mismatch, and the La-O bond has the larger thermal expansion. In most ABO_3 perovskites, the A-O bond is also the more compressible; the result is a predictable pressure dependence of the transitions from one perovskite polytype to another where there is a $t > 1$.[19] However, a more compressible La-O bond would call for a $dT_t/dP > 0$ in the $La_{2-x}Sr_xCuO_4$ system. Observation of a $dT_t/dP < 0$ signals that the Cu-O bond is more compressible in this case. We believe this nonintuitive deduction follows from the fact that the superconductive phase falls in a compositional range where the Cu-O bond length has a double-well potential, one Cu-O bond length occurring in the regions of antiferromagnetic spin fluctuations where the charge carriers occupy crystal-field orbitals and a smaller Cu-O bond length being stabilized by stronger covalence where the charge carriers are distributed more equally between cation and anion in a molecular orbital.[6] A first-order phase change with a straightening and shortening of the Ni-O-Ni bond has been observed at an antiferromagnetic-metallic phase change in $NdNiO_3$.[20] This compound also exhibits a pressure dependence of T_t that requires a more compressible Ni-O bond in the ionic phase.[21,22] An unusually large compressibility of the Cu-O bond would support the idea that ionic and covalent Cu-O bonds coexist; a double-well potential makes each potential anharmonic and gives a high compressibility where there is a large fraction of ionic bonding. It would be useful to have a measurement of the relative compressibility of the La-O and Cu-O bonds in this system. The best available data are from Gupta and Gupta[23] for $La_{1.85}Sr_{0.15}CuO_4$. They calculate from the data of Nelmes *et al.*[24] a slight increase (+0.08%) in the La-O(1) bond length, but a strong decrease (−0.16%) in the Cu-O(1) bond length at 1.0 GPa, which appears to confirm our analysis.

The transition from the superconductor to the metallic phase in the overdoped region is generally believed to be smooth.[5,25] Even in the recent work of Takagi *et al.*,[7] a discontinuity in Meissner fraction at x_t was attributed to the orthorhombic-tetragonal phase change; the superconductivity found for $x > x_t$ was assumed to be associated with orthorhombic-phase fluctuations that decrease smoothly to zero with increasing $(x - x_t)$ in the range $0.22 \le x \le 0.3$. A dynamic phase segregation between superconductive and metallic phases would be smooth if only the mean size of the superconductive domains were changing. In order to check whether the transition from the superconductive to metallic compositions in the tetragonal phase is smooth or shows evidence of a series of superconductive phases, we have taken measurements of low-temperature resistance versus temperature at steps of $\Delta x = 0.01$ over the narrow compositional range $0.15 \le x \le 0.3$. In Figs. 1,3 we present typical data. Before discussing the details, we call attention to two principal features: (i) a small, but marked resistance change at the transition to $T_c \approx 37$ K marks a transition that is distinguishable from the superconductive phase below T_c, and (ii) several samples exhibit two superconductive onset temperatures. From our x-ray data, we cannot attribute this feature to sample inhomogeneity at room temperature. Therefore we interpret the data to mean that the superconductor-metal transition is not smooth, but occurs through a two-phase region containing not only superconductor and metallic domains, but also a stepwise series of superconductive phases with increasing x.

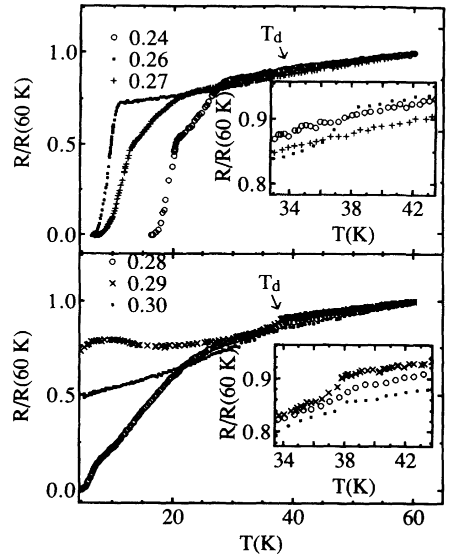

FIG. 3. Resistance versus temperature for six different values of x in the system $La_{2-x}Sr_xCuO_4$.

The feature at $T_d \approx 37$ K is independent of composition x; however, its presence is not so obvious in the tetragonal-phase samples $x = 0.24$ and 0.27, each of which exhibit multiple superconductive-onset temperatures. A T_d is also not resolved in the $x = 0.15$ sample where $T_c \approx T_d = 37$ K. A larger separation between T_d and T_c was found in samples with $x > 0.15$; a linear R-versus-T dependence was also observed below T_d, but with a different slope compared with that above T_d, which would seem to indicate that the anomaly at T_d is not due to a superconductive transition caused by an impurity phase. Although a decrease in the dc susceptibility under high magnetic field appears below T_d, it is extremely weak, and any difference between the field-cooled and zero-field-cooled susceptibility fell within the experimental error of our measurements. The ac susceptibility showed no change at T_d.

In order to gain insight into the character of the transition at T_d, we made careful measurements of the Seebeck coefficient as a function of temperature across T_d. For these measurements, the temperature on one side of the sample was held at 43 K while the temperature on the other side was controlled to vary over 25–43 K in steps of 0.5–1.0 K. The Seebeck coefficient α was obtained from the slope of the curve of thermopower voltage V versus $\Delta T = (43 - T)$ K across the sample. The data are presented in Fig. 4.

In the $x = 0.15$ sample, α shows an abrupt drop at about 40 K; we designate as T_f the initiation temperature for this drop and as T_0 the temperature at which both α and the resistance R go to zero. For $x = 0.15$, $R(T)$ shows a deviation from linear behavior at a $T_f > T_c$; this variation is gradual, producing a rounded shoulder, in accordance with theory for the onset of superconductive-

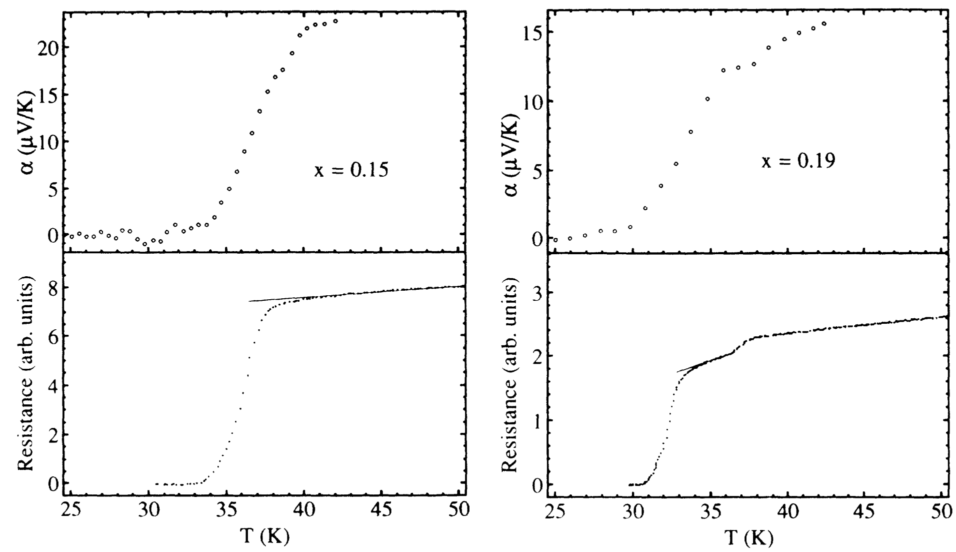

FIG. 4. Temperature variation of Seebeck coefficient α and resistance R for samples $x=0.15$ and $x=0.19$ of $La_{2-x}Sr_xCuO_4$.

pair fluctuations.[26] We emphasize two points: first, α versus T provides a sensitive test of the onset of superconductive-pair fluctuations; second, a small step in the α-versus-T curve can be seen at about 37 K, which corresponds to the temperature T_d found in all samples $x \geq 0.18$. The $x=0.15$ sample apparently has a $T_c \approx T_d < T_f$. In the $x=0.19$ sample, on the other hand, the anomaly at $T_d \approx 37$ K is well separated from the onset temperature for superconductivity. For $x>0.15$, a small drop in α and a change in slope of $R \sim T$ occurs on lowering T through T_d. In these samples, a $T_f < T_d$ is signaled where there is a deviation from a linear $R \sim T$ behavior below T_d, and there is no small step in α in the range $T_0 < T < T_f$, as occurs in the $x=0.15$ sample; for $x \geq 0.18$ a $T_d > T_f > T_c$ is found.

The fact that $T_f \approx 40$ K $> T_d$ in the $x=0.15$ sample has decreased to $T_f = 35$ K $< T_d$ at $x=0.19$ shows that T_f tracks the bulk T_c. A $T_d > T_f$ reveals an $R \sim T$ in the domain $T_f < T < T_d$ as well as in the domain $T > T_d$ (see, for example, the curve for $x=0.26$ in Fig. 3), but there is a discontinuity in dR/dT on crossing T_d; therefore T_d is to be associated with a bulk transition and not with a superconductive impurity phase. In the case of $T_d > T_f$, no pair fluctuations are present in the temperature domain $T_f < T < T_d$; therefore a linear R-vs-T curve should be expected, as is observed. We conclude that T_d marks an intrinsic transition that is not associated with the onset of superconductive-pair fluctuations. Moreover, the data indicate that superconductivity is restricted to the temperature range $T_c \leq T_d$ whereas superconductive-pair fluctuations are found below a $T_f > T_d$ in the optimally doped samples where $T_c = T_d$. Such a situation would be expected should T_d mark a transition from two-dimensional to three-dimensional polaron coupling.

The fact that T_d is independent of x shows that the transition at T_d is not controlled by electronic factors, but by an elastic coupling, so we can anticipate the presence of an elastic anomaly at T_d. Support for this deduction is found in the thermal-expansion data,[27,28] which show an anomaly at 37 K that, like T_d, is independent of x. Anderson[29] has emphasized the importance of c-axis coupling to stabilize superconductivity; however, pair fluctuations can be stabilized in two dimensions. We note that the temperature range $\Delta T = T_f - T_c$ of pair fluctuations increases from $\Delta T < 3$ K for $T_f < T_d$ in the $x=0.19$ sample to a $\Delta T = 4.2$ K in the $x=0.15$ sample where a $T_f > T_d = T_c$ is found.

From Fig. 1, a $dT_d/dP \approx 0.1$ K/kbar can be obtained for all values of x independent of whether the structure is orthorhombic or tetragonal. In the $x=0.15$ sample, where $T_c = T_d$, both T_c and T_d have the same pressure dependence; for $x>0.15$, a $dT_c/dP < dT_d/dP \approx 0.1$ K/kbar is found. This observation shows that T_d indeed represents an upper limit for T_c.

Evidence for a weakly first-order transition at a $T_d > T_c$ has been reported by Butera[30] and by Inderhees *et al.*[31] on the basis of specific-heat data for $YBa_2Cu_3O_{6.9}$. The fact that two peaks have not been generally observed could well be due to a lack of resolution in the samples with an optimum T_c. In addition, a recent report by Early *et al.*[32] of a double resistive transition in n-type $Sm_{2-x}Ce_xCuO_{4-y}$, which was interpreted to represent the onset of pair fluctuations below the upper critical temperature, could represent a T_d. We believe a $T_d \geq T_c$ will prove to be a universal feature of the high-T_c copper oxide superconductors and that it signals a change in the lattice vibrational spectrum.

CONCLUSIONS

In conclusion, we have established a $dT_c/dP > 0$ for the orthorhombic phase and $dT_c/dP = 0$ for the tetragonal phase. The superconductivity observed in the tetragonal phase field is therefore not to be associated with orthorhombic-phase fluctuations, which would exhibit a $dT_c/dP > 0$. The association of a $dT_c/dP > 0$ only with a bent Cu-O-Cu bond angle indicates that T_c decreases sensitively with any distortion of the CuO_2 planes. For a given composition x, T_c is higher in the tetragonal phase than in the orthorhombic phase.

An abrupt change in dT_c/dP at the orthorhombic-tetragonal phase transition allows us to obtain at atmospheric pressure an $x_t \approx 0.22$, where $T_t = T_c$ at x_t, in our samples, as compared to an $x_t \approx 0.21$ reported by Takagi *et al.*[7] It also allows us to define a critical pressure for P_c for given x and hence $x_t(P)$ and a $dx_t/dP < 0$, corresponding to a $dT_t/dP < 0$. A $dT_t/dP < 0$ would seem to require that the Cu-O bond be more compressible than the La-O bond, and available data support this conclusion. In fact, they indicate an unusually high compressibility for the Cu-O bond, which supports our postulate of a first-order transition from "ionic" to covalent Cu-O bonding.[6]

The peculiar transition at T_d deserves further attention. The data presented here and for the n-type system $Sm_{2-x}Ce_xCuO_{4-y}$ indicate a $T_c \leq T_d$; and specific-heat data from $YBa_2Cu_3O_{6.9}$ suggest that the phase transition at T_d is a universal phenomenon in the high-T_c copper oxide superconductors. Although no symmetry change has been observed in the crystal structure below T_d, a remarkable change in the thermal expansion at 37 K (Refs. 27,28) indicates the presence of an important change in elastic properties. Measurement of the resistance R and Seebeck coefficient α as a function of temperature through T_d and T_c reveal that pair fluctuations exist above T_d where $T_c \approx T_d$. These data are consistent with a transition at T_d from two-dimensional to three-dimensional polaron coupling. Moreover, the anomaly at T_d appears to be a general phenomenon that occurs in other high-T_c copper oxides. For example, thermal-expansion anomalies have been reported near T_c in orthorhombic $YBa_2Cu_3O_{6.9}$.[33]

We believe it is also significant that sharply defined superconductive transition temperatures T_c in samples $0.15 \leq x \leq 0.19$, $x \approx 0.22$, and $0.25 \leq x \leq 0.26$ alternate with broad transitions exhibiting more than one shoulder in samples $0.20 \leq x \leq 0.21$, $0.23 \leq x \leq 0.24$, and $0.27 \leq x \leq 0.29$ since we were unable to detect any room-temperature variation of inhomogeneity in our samples. Moreover, increasing the current only decreased T_0 without changing T_c or the general features of the curves, which would seem to rule out grain-boundary effects. In view of the evidence that below 300 K the optimally doped superconductive compositions appear to represent a thermodynamically distinguishable phase,[6] we interpret our data to signal a low-temperature segregation via cooperative atomic displacements of metallic and superconductive phases in the overdoped region, consistent with the sharp drop-off of Meissner fraction with x that is observed in this region. Niedermayer *et al.*[34] have used muon spin rotation to monitor a decrease in the superconductive condensate density n_s/m^* with increasing hole density in overdoped $Tl_2Ba_2CuO_{6+\delta}$, which is quite consistent with a two-phase model. However, a gradual decrease in the mean size of the superconductive domains should simply result in a broadening and lowering of the superconductive transition as was found for $x = 0.28$ in Fig. 3. The appearance of successive shoulders in the transition for alternate compositions would seem to require either a greater stability for superconductive domains with specific sizes or a superconductivity that changes in steps with charge-carrier concentration, which is quite different from BCS superconductivity in conventional metals.

Note added in proof. The observation by Dabrowski *et al.*, Physica C **217**, 455 (1993), of a $T_c(\max) \approx 34$ K for $x = 0.15$ in the $La_{2-x}Ca_xCuO_4$ system is consistent with this deduction since the Cu-O-Cu bond angle was shown to be about 2° smaller at $x = 0.15$ than in the $La_{2-x}Sr_xCuO_4$ system.

ACKNOWLEDGMENTS

We gratefully acknowledge the support of the Robert A. Welch Foundation, Houston, Texas, the Texas Advanced Research Program, and the National Science Foundation.

[1] M. W. Shafer, T. Penney, and B. L. Olson, Phys. Rev. B **36**, 4047 (1987); N. Nguyen, J. Choiset, M. Herviell, and B. Raveau, J. Solid State Chem. **39**, 120 (1981).

[2] J. D. Jorgensen, P. Lightfoot, Shiyou Pei, B. Dabrowski, D. R. Richards, and D. G. Hinks, in *Advances in Superconductivity III,* Proceedings of the Third International Symposium on Superconductivity, Sendai, Japan, 1990, edited by K. Kajimura and H. Hajakawa (Springer-Verlag, Berlin, 1991), p. 337.

[3] S. Uchida, T. Ido, H. Takagi, T. Arima, Y. Tokura, and S. Tajima, Phys. Rev. B **43**, 7942 (1991).

[4] H. Takagi, B. Batlogg, H. L. Kao, J. Kwo, R. J. Cava, J. T. Krajewski, and W. F. Peck, Jr., Phys. Rev. Lett. **69**, 2975 (1992).

[5] J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. Parkin, Phys. Rev. Lett. **61**, 1127 (1988); J. B. Torrance, A. Bezinge, A. I. Nazzal, T. C. Huang, S. S. Parkin, D. T. Keane, S. J. LaPlaca, P. M. Horn, and G. A. Held, Phys. Rev. B **40**, 8872 (1989).

[6] J. B. Goodenough, J.-S. Zhou, and J. Chan, Phys. Rev. B **47**, 5275 (1993).

[7] H. Takagi, R. J. Cava, M. Marezio, B. Batlogg, J. T. Krajewski, W. F. Peck, Jr., P. Bordet, and D. E. Cox, Phys. Rev. Lett. **68**, 3777 (1992).

[8] N. Yamada and M. Ido, Physica C **203**, 240 (1992).

[9] J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1984).

[10] J. E. Schirber, E. L. Venturini, J. F. Kwak, D. S. Ginley, and B. Morosin, J. Mater. Res. **2**, 421 (1987).

[11] N. Tanahoshi, Y. Iye, T. Tamegai, C. Murayama, N. Mori, S. Yomo, N. Okazaki, and K. Kitazawa, Jpn. J. Appl. Phys. **28**, L762 (1989).

[12] T. R. Sendyka, T. Egami, B. A. Hunter, J. D. Jorgensen, D. G. Hinks, A. W. Mitchell, B. Dabrowski, R. L. Hitterman, P. G. Radaelli, and J. L. Wagner, in *Lattice Effects in High-T_c Superconductors,* edited by Y. Bar-Yam, T. Egami, J. Mustre de Leon, and A. R. Bishop (World Scientific, Singapore, 1993), p. 111.

[13] C. W. Chu, P. H. Hor, J. G. Lin, Q. Xiong, Z. J. Huang R. L. Meng, Y. Y. Xue, and Y. C. Jean, in *Frontiers of High-Pressure Research,* Vol. 286 of *NATO Advanced Study Institute, Series B: Physics,* edited by H. D. Hochheimer and R.

D. Etters (Plenum, New York, 1991), p. 383.

[14]H. J. Kim and R. Moret, Physica C **156**, 363 (1988).

[15]C. L. Wooten, Beom-hoen O, J. T. Markert, M. G. Smith, A. Manthiram, J.-S. Zhou, and J. B. Goodenough, Physica C **192**, 13 (1992).

[16]S. J. L. Billinge, P. K. Davies, T. Egami, and C. R. A. Catlow, Phys. Rev. B **43**, 10 340 (1991).

[17]M. A. Crusellas, J. Fontcuberta, S. Piñol, J. Beille, and T. Grenet, Physica C **209**, 537 (1993).

[18]J. B. Goodenough, Supercond. Sci. Technol. **3**, 26 (1990).

[19]J. B. Goodenough, J. A. Kafalas, and J. M. Longo, in *Preparative Methods in Solid State Chemistry,* edited by P. Hagenmuller (Academic, New York, 1972), p. 1.

[20]J. L. Garcia-Munoz, J. Rodriguez-Carvajal, P. Lacorre, and J. B. Torrance, Phys. Rev. B **46**, 4414 (1992).

[21]X. Obradors, L. M. Paulius, M. B. Maple, J. B. Torrance, A. I. Nazzal, J. Fontcuberta, and X. Granedos, Phys. Rev. B **47**, 12 353 (1993).

[22]P. C. Canfield, J. D. Thompson, S.-W. Cheong, and L. W. Rupp, Phys. Rev. B **47**, 12 357 (1993).

[23]M. Gupta and R. P. Gupta, Physica C **173**, 381 (1991).

[24]R. J. Nelmes, N. B. Wilding, P. D. Hatton, V. Caignaert, B. Raveau, M. I. McMahon, and R. O. Piltz, Physica C **166**, 329 (1990).

[25]H. Takagi, T. Ido, S. Ishibashi, M. Uota, S. Uchida, and Y. Tokura, Phys. Rev. B **40**, 2254 (1989).

[26]W. J. Skocpol and M. Tinkham, Rep. Prog. Phys. **38**, 1049 (1975).

[27]M. Lang *et al.*, Phys. Rev. Lett. **69**, 482 (1992).

[28]M. Lang *et al.*, Z. Phys. B **74**, 3 (1989).

[29]For example, P. W. Anderson and J. R. Schreiffer, Phys. Today, June 1991, p. 55.

[30]R. A. Butera, Phys. Rev. B **37**, 5909 (1989).

[31]S. E. Inderhees, M. B. Salamon, N. Goldenfeld, J. P. Rice, B. G. Pazol, D. M. Ginsberg, J. Z. Liu, and G. W. Crabtree, Phys. Rev. Lett. **60**, 1178 (1988).

[32]E. A. Early, C. C. Almasan, R. F. Jardin, and M. B. Maple, Phys. Rev. B **47**, 433 (1993).

[33]C. Meingast, O. Kraut, T. Wolf, H. Wuhl, A. Erb, and G. Muller-Vogt, Phys. Rev. Lett. **67**, 1634 (1991).

[34]Ch. Niedermayer, C. Bernhard, U. Binninger, H. Glückler, J. L. Tallon, E. J. Ansaldo, and J. I. Budnick, Phys. Rev. Lett. **71**, 1764 (1993).