

## Critical Buckling for the Disappearance of Superconductivity in Rare-Earth-Doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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Analysis of the structural, transport, and superconducting properties of Nd-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  reveals a critical tilt angle of the  $\text{CuO}_6$  octahedra for the disappearance of superconductivity in the low temperature tetragonal phase. Our results indicate a strong influence of the tilt of the  $\text{CuO}_6$  octahedra on the electronic properties, suggesting the importance of spin-orbit coupling for the destruction of superconductivity and for the stabilization of a magnetic state.

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The structural phase transition from the low temperature orthorhombic (LTO) to the low temperature tetragonal (LTT) phase, which occurs in  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  (LBCO) at  $x \approx \frac{1}{8}$  as well as in rare-earth-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO), has recently attracted much attention [1–5]. One of the reasons is that in a certain range of compositions this phase transition is accompanied by the destruction of superconductivity. Moreover, it leads to anomalies and drastic changes in the transport properties [1,4,5] as well as to the appearance of local magnetism at finite hole doping [6,7]. It is remarkable that the subtle structural changes at the phase transition, i.e., the rotation of the tilt axis of  $\text{CuO}_6$  octahedra and the related change in the staggered buckling pattern of the  $\text{CuO}_2$  planes, have such pronounced consequences. Hole concentration dependent commensurability effects and charge density wave-like instabilities have been suggested as possible origins [8]; alternatively, a novel transition to a metallic, magnetically ordered ground state has been suggested, when the tilt angle of the  $\text{CuO}_6$  octahedra is increased beyond a critical value [9].

In this Letter we present a detailed analysis of the structural, transport, and superconducting properties of Nd-doped LSCO in order to decide whether the tilt angle is indeed a relevant parameter for the electronic properties of the LTT phase. Such a study is possible in this system, since the structure and in particular the tilt angle can be tuned via the Nd concentration without affecting the charge carrier concentration [10]. Our main result is that the LTT phase is superconducting with no anomalies in the transport properties, if the tilt angle  $\Phi_{\text{LTT}}$  in the LTT phase is smaller than a critical angle  $\Phi_c$ . Vice versa, for  $\Phi_{\text{LTT}} > \Phi_c$  superconductivity is destroyed, and a different electronic ground state, most probably magnetic, is established (Fig. 1). Based on our experiments, we suggest a phase diagram with a crossover from a superconducting to a magnetic and metallic ground state with increasing tilt distortion, i.e., increasing buckling of the  $\text{CuO}_2$  planes.

The preparation and characterization of single phase samples as well as the experimental techniques have been described elsewhere [1,10]. As we have verified with x-ray and neutron diffraction as well as specific heat and thermal expansion measurements, all  $\text{La}_{2-x-y}\text{Sr}_x\text{Nd}_y\text{CuO}_4$  samples with  $y \geq 0.18$  discussed in the present Letter show a low temperature structural transition at a transition temperature  $T_{\text{LT}}$  below 90 K. For low Sr concentrations the transition is to the low temperature orthorhombic  $Pccn$  phase; for all other compositions it is to the low temperature tetragonal LTT phase ( $P4_2/ncm$ ) (Fig. 1). Details of the structure and the structural phase diagram have been reported in Refs. [1,2]. In the following we focus on the electronic properties of the LTT phase.

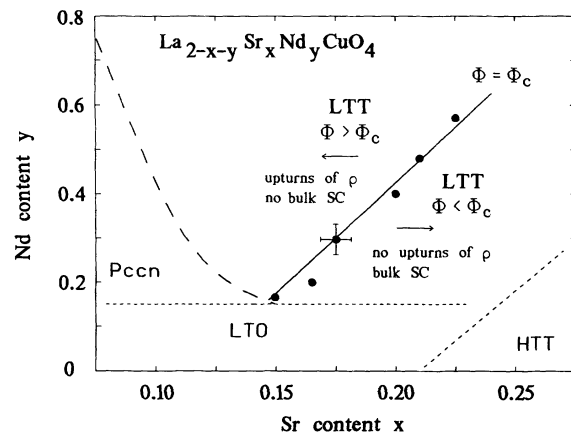


FIG. 1. Schematic low temperature ( $T < 10$  K) structural phase diagram. The phase range of the high temperature tetragonal (HTT) phase was extrapolated from the  $x, y$ -concentration dependence of the  $\text{HTT} \rightarrow \text{LTO}$  transition temperature  $T_{\text{HT}}$ . The solid line  $x_c(y)$  ( $\bullet$ ) is a line of constant tilt angle  $\Phi_{\text{LTT}} = \Phi_c \approx 3.6^\circ$  and separates regions with and without bulk superconductivity (SC) (see text). A typical error bar is also included.

The magnetic susceptibility for samples with a Nd content  $y \approx 0.3$  [11] and varying Sr concentrations [Fig. 2(a)] indicates that superconductivity is strongly suppressed for  $x = 0.15$ . We have shown previously [1] by a comparison to our structural data that this suppression of the Meissner and shielding fraction indicates *the absence of superconductivity in the LTT phase*. The small remaining Meissner fraction visible in Fig. 2(a) for  $x = 0.15$  is due to structural inhomogeneity of the LTT phase, i.e., to orthorhombic parts of the sample still present below  $T_{LT}$ . On the other hand, the data shown in Fig. 2(a) also give evidence that at other Sr concentrations superconductivity is possible in both, in the *Pccn* phase as well as in the LTT phase. This may suggest that the hole concentration is the only crucial parameter. However, in the LTT phase the occurrence of superconductivity at a fixed Sr concentration can be tuned via the Nd content as shown in Fig. 2(b): For  $x = 0.2$  bulk superconductivity is found for Nd concentrations below  $y \approx 0.4$  from ac and dc susceptibility and from specific heat measurements. Since Nd-doping does not influence the hole concentration in the planes [10], it is natural to conclude that there is an additional parameter which is responsible for the suppression of superconductivity in the LTT phase.

In Fig. 3 we show the electrical resistivity  $R(T)$  of samples with a Nd content of  $y \approx 0.3$  and various Sr concentrations.  $T_{LT}$  as obtained from our structural data is indicated in the figure as well. Apparently the small jumplike anomalies of  $R(T)$  at  $T_{LT}$  followed by a strong upturn at lower temperatures occur only in a limited range of Sr concentrations  $0.11 < x < 0.175$ . Notably just in this concentration range we find from Meissner measurements that bulk superconductivity is suppressed. As discussed above the resistively measured superconducting transitions for these samples do not

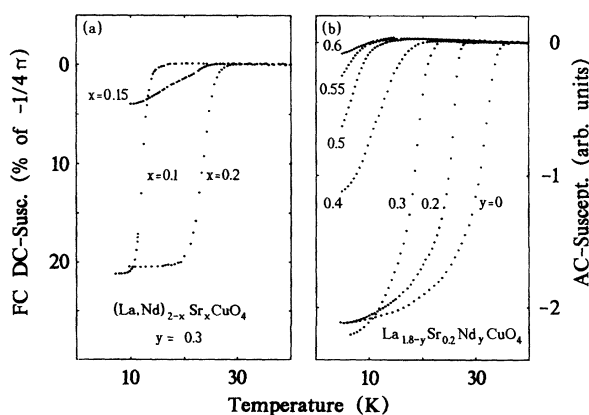


FIG. 2. (a) Field-cooled susceptibility (measured at  $H = 1$  Oe) vs temperature for samples with a Nd content of  $\approx 0.3$  [11] and Sr concentrations of 0.1 (*Pccn*), 0.15, and 0.2 (LTT). (b) ac susceptibility vs temperature of powdered samples with  $x = 0.2$  and various Nd contents. All Nd-doped samples have LTT structure below 40 K.

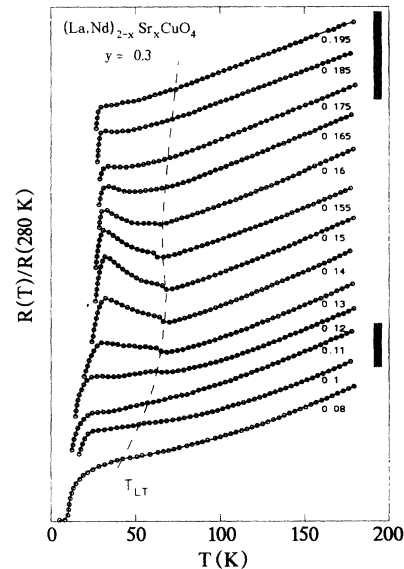


FIG. 3. Normalized electrical resistivity  $R(T)/R(280\text{ K})$  for Nd-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  with  $y \approx 0.3$  [11] and various Sr concentrations. The curves are shifted along the y axis. The vertical bars mark the Sr concentrations for which bulk superconductivity is found.  $T_{LT}$  as measured by x-ray diffraction is indicated by the dashed line.

signal bulk superconductivity but are due to the structural inhomogeneity below  $T_{LT}$  [1].

Data similar to those presented in Figs. 2 and 3 have also been obtained for other series of samples with fixed Nd contents of  $y = 0.2, 0.4, 0.5,$  and  $0.6$ . From all data we find that the occurrence of the resistivity anomalies and the suppression of superconductivity depend on both, the Sr *and* the Nd concentration. We therefore define a critical Sr concentration  $x_c(y)$ , below which the LTT phase is nonsuperconducting. In the Nd/Sr phase diagram (Fig. 1) the line  $x_c(y)$  as extracted from our resistivity and Meissner measurements separates a region in the LTT phase with bulk superconductivity from a region without bulk superconductivity and with transport anomalies. Obviously, the crossover between these regions is not determined by the hole concentration alone.

The physical meaning of the separation line in Fig. 1 emerges from a comparison with structural data [1,10]: The separation line is a line of constant tilt angle  $\Phi_c \approx 3.6^\circ$  of the  $\text{CuO}_6$  octahedra in the LTT phase. This is inferred directly from neutron diffraction measurements of the concentration dependence of the tilt angle, and it can also be extracted from x-ray diffraction results.

The determination of the tilt angle with x-ray diffraction, which has been used for the majority of our samples, relies on the correlation between the magnitude of  $\Phi$  with the orthorhombic strain  $[a - b]$  in the LTO phase and with the transition temperature  $T_{HT}$  of the  $\text{HTT} \rightarrow \text{LTO}$  transition. These correlations are well known for the LTO phase:  $\Phi$  can be regarded as the order parameter

of the continuous HTT  $\rightarrow$  LTO transition, and therefore  $\Phi(x, y, T)$  scales (nonlinearly) with  $T_{\text{HT}}(x, y) - T$  in the LTO phase [12]. In addition,  $\Phi^2$  scales linearly with  $[a - b]$ . This has been demonstrated for pure LSCO [12], and we have verified by neutron diffraction that it holds also in Nd-doped compounds (up to  $y = 0.6$ ). We find that  $\Phi^2(x, y, T) = \alpha[a - b](x, y, T)$  where  $\alpha$  is a constant [13].

In the LTT-phase the tilt angle  $\Phi_{\text{LTT}}$  can similarly be extracted from the x-ray diffraction results, since neutron diffraction shows that (i) there is no significant change of  $\Phi$  at  $T_{\text{LT}}$ , and (ii) the temperature dependence of  $\Phi$  below  $T_{\text{LT}}$  is very weak in the Nd-doped compounds [13–15]. Given that there are no significant changes of  $\Phi$  at and below  $T_{\text{LT}}$ ,  $\Phi_{\text{LTT}}$  is of course related to the orthorhombic strain  $[a - b](T_{\text{LT}})$  just above the LTO  $\rightarrow$  LTT transition, as well as to  $T_{\text{HT}}$ . A critical tilt angle  $\Phi_{\text{LTT}} = \Phi_c \approx 3.6^\circ$  corresponds to  $[a - b](T_{\text{LT}}) \approx 0.035 \text{ \AA}$  and to  $T_{\text{HT}} \approx 270 \text{ K}$ ;  $\Phi_{\text{LTT}} > (<) \Phi_c$  corresponds to larger (smaller) values of  $[a - b](T_{\text{LT}})$  and  $T_{\text{HT}}$ .

The correlation of the suppression of superconductivity with  $[a - b](T_{\text{LT}})$  is demonstrated in Fig. 4. The upper panel of this figure shows the change of the orthorhombic splitting  $\Delta[a - b] \equiv [a - b](T_{\text{LT}}) - [a - b](T \rightarrow 0)$  as a function of the Sr concentration for samples with different Nd content. Note that we plot  $\Delta[a - b]$  rather than  $[a - b]$  since at low Sr doping the *Pccn* phase occurs with a reduced, but finite  $[a - b](T \rightarrow 0)$ .

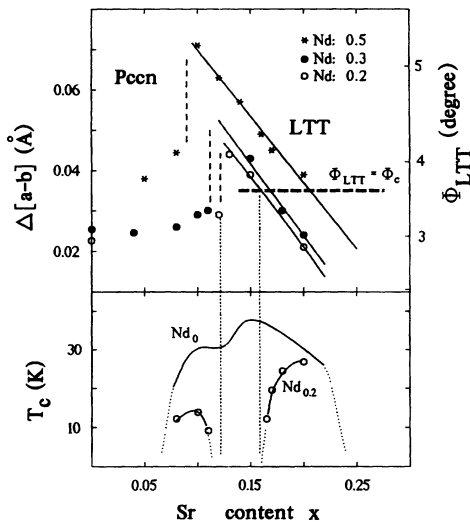


FIG. 4. Upper panel:  $\Delta[a - b]$  (left scale) and  $\Phi_{\text{LTT}}$  (right scale) vs  $x$  for samples with various Nd content. The *Pccn*/*LTT* phase boundary is indicated by the vertical dashed lines for each Nd concentration.  $\Phi_c \approx 3.6^\circ$  corresponding to  $\Delta[a - b] \approx 0.035 \text{ \AA}$  is indicated by the double dashed line. Lower panel:  $T_c$  as a function of  $x$  for  $y = 0$  and  $y = 0.2$  (○) as extracted from magnetic susceptibility data. The Sr range where superconductivity is suppressed coincides with  $\Delta[a - b] > 0.035 \text{ \AA}$  or, equivalently, with  $\Phi_{\text{LTT}} > \Phi_c$  as indicated by the vertical dashed lines for samples with  $y = 0.2$ .

For the LTT structure, on the other hand,  $\Delta[a - b] = [a - b](T_{\text{LT}}) \propto \Phi_{\text{LTT}}^2$ . The corresponding values of the tilt angles are given in the right scale of the figure. The lower panel of the figure shows  $T_c$  as a function of Sr concentration for pure LSCO and for samples with  $y = 0.2$ . For  $y = 0.2$  and  $y = 0.3$  superconductivity is suppressed in a narrow Sr concentration range in the LTT phase where  $\Phi_{\text{LTT}} > \Phi_c$ , whereas for a higher Nd concentration of  $y = 0.5$   $\Phi_{\text{LTT}} > \Phi_c$  even for  $x = 0.2$ .

The magnitude of the tilt of the  $\text{CuO}_6$  octahedra is therefore found to be a crucial parameter for the transport and superconducting properties of the LTT phase. In particular, if  $\Phi_{\text{LTT}}$  exceeds the critical angle  $\Phi_c \approx 3.6^\circ$  there is no superconductivity in the LTT phase.

For the discussion of this result we recall that the tilt distortion in LSCO and LBCO also affects the magnetic properties: In the undoped, antiferromagnetic (AF) insulator  $\text{La}_2\text{CuO}_4$  the tilt leads to a canting of the Cu spins out of the  $\text{CuO}_2$  planes and results in weak ferromagnetism [16]. This can be attributed to the spin-orbit coupling induced antisymmetric Dzyaloshinskii-Moriya (DM) interaction [17] between the Cu spins. It has been suggested by Bonesteel, Rice, and Zhang that in the doped metallic compounds the motion of the charge carriers is coupled to the tilt displacements via spin-orbit scattering [9,18]. In this model large tilt angles stabilize a two sublattice AF metallic ground state against a nonmagnetic ground state with spiral spin correlations [9]. It is very appealing to relate this transition predicted in the *t*-*J* spin orbit coupling model of Bonesteel *et al.* to the disappearance of superconductivity at the critical buckling found in our experiments. This is further supported by the observed (local) AF order in  $\mu\text{SR}$  [6] and Mößbauer measurements [7] in the nonsuperconducting LTT phase.

While the mere existence of  $\Phi_c$  agrees with the results obtained from this model, we know, however, that the *magnitude* of the tilt angle does not change at the LTO  $\rightarrow$  LTT transition (see the discussion above). It is only the tilt *axis* that changes. Thus, the influence of the tilt angle on the electronic properties is obviously more pronounced in the LTT phase than in the LTO phase, i.e., it must depend on the *direction* of the tilt axis. This cannot be explained by the one band model of Bonesteel *et al.* [9], in which the *magnitude* of  $\Phi$  is the only parameter that characterizes the tilt distortion. On the other hand, the change in the tilt axis alone has been shown to markedly increase the strength of the exchange anisotropies, inducing an increased in-plane spin wave gap almost twice as large below the structural transition in  $\text{La}_{1.65}\text{Nd}_{0.35}\text{CuO}_4$  [14]. To account for this effect it may be necessary to include the symmetric exchange anisotropies in the theoretical models in addition to the antisymmetric DM interaction between the Cu moments [19].

We mention that the destruction of superconductivity above a critical buckling strength may be interpreted as a pair-breaking effect of the tilt of the  $\text{CuO}_6$  octahedra [20].

Spin-orbit coupling preserves time reversal symmetry. Therefore, according to Anderson's theorem [21], spin-orbit coupling cannot suppress superconductivity in an orbital  $s$ -wave pairing state. On the other hand, as has been worked out recently by Bonesteel [20], the octahedral tilt will act as an effective pair-breaking mechanism if the pairing state has  $d_{x^2-y^2}$  symmetry.

We summarize our results in the phase diagram shown in Fig. 5, which shows  $T_c$ ,  $T_{LT}$ , and  $T_{HT}$  versus the Nd content for  $x = 0.15$  and  $x = 0.2$ . The data suggest a crossover with increasing Nd content from a superconducting ground state towards a metallic, nonsuperconducting ground state with probably (local) AF order. The magnetic state is stabilized, if the tilt angle, and equivalently  $\Delta(a - b)$  and  $T_{HT}$ , exceed a critical value. According to this phase diagram the Sr concentration of 0.15 represents a special situation, in which the appearance of a magnetic ground state as a function of the Nd concentration coincides with that of the LTO  $\rightarrow$  LTT transition.

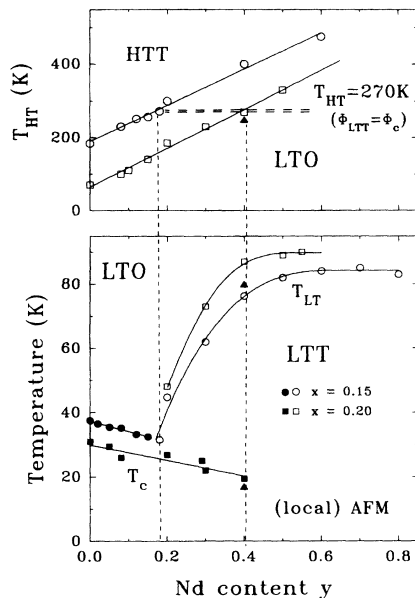


FIG. 5. Phase diagram for samples with  $x = 0.15$  ( $\circ, \bullet$ ) and  $x = 0.2$  ( $\square, \blacksquare$ ). Data points from Nakamura and Uchida [5] (single crystal) for  $x = 0.2$ ,  $y = 0.4$  are indicated in the figure as well ( $\blacktriangle$ ) [5]. Upper panel:  $T_{HT}$ . The double dashed line marks  $\Phi_c$  corresponding to  $T_{HT} = 270$  K. Lower panel:  $T_c$  ( $\bullet, \blacksquare$ ) and  $T_{LT}$  ( $\circ, \square$ ). The dashed vertical lines separate the superconducting from the nonsuperconducting regions of the phase diagram for each Sr concentration.

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