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# Structure and Superconductivity of Rare Earth Doped $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

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We present results of a detailed investigation of the structural phase transitions and their influence on superconductivity in rare earth doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . The structural transitions are predominantly determined by size differences of the atoms in alternating layers of the structure. In contrast to the findings in Ba-doped  $\text{La}_2\text{CuO}_4$  the influence of the low temperature transition on the electronic properties is not restricted to a narrow hole doping around  $x \simeq 1/8$ . Our data show a strong influence of the buckling of the planar (Cu-O-Cu) bonds on the electronic properties. In particular, superconductivity disappears in the low temperature tetragonal phase if the buckling exceeds a critical strength.

Two well characterized structural phase transitions are observed in doped  $\text{La}_2\text{CuO}_4$  superconductors, both involving collective tilting of the  $\text{CuO}_6$  octahedra [1-5]. These transitions and especially the low temperature (LT) transition between a LT orthorhombic (LTO) and a LT tetragonal (LTT) phase occurring in Ba as well as in rare earth (RE) doped compounds have attracted much attention since the subtle structural changes associated with this transition have a dramatic influence on the superconducting and normal state electronic properties [1-8]. The experimental results obtained on  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$  (LBCO) give strong evidence that the influence of the LT transition on superconductivity (SC) is most pronounced for a particular hole content of  $x \sim 1/8$  [1,4,5]. A much more detailed investigation of both the structure in doped  $\text{La}_2\text{CuO}_4$  and its influence on SC is possible in RE-doped compounds, i.e. in  $\text{La}_{2-x-y}\text{Sr}_x\text{RE}_y\text{CuO}_4$ . In these compounds the LT transition is induced by substitution of the  $\text{La}^{3+}$  ions by smaller but isovalent  $\text{RE}^{3+}$  ions (RE = Nd, Sm, Eu, Gd), i.e. at fixed hole doping of the  $\text{CuO}_2$  planes [2,3,7-10]. Thus the structural properties and the hole doping can be varied rather independently via the RE- and the Sr-doping, respectively.

The structural modifications occurring in doped  $\text{La}_2\text{CuO}_4$  can be characterized by the magnitude and the direction of the tilt of the  $\text{CuO}_6$  octahedra [4]. The octahedra start to tilt at the continuous high temperature (HT) transition between the high temperature tetragonal (HTT) and

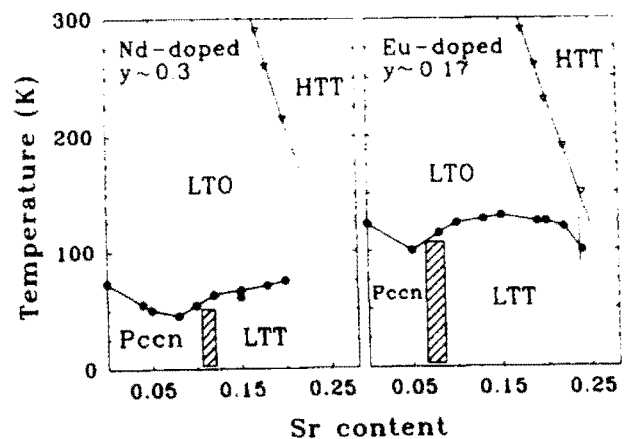


Figure 1. Structural phase diagrams of RE-doped  $\text{La}_{2-x-y}\text{Sr}_x\text{RE}_y\text{CuO}_4$ . Left: RE = Nd ( $y \simeq 0.3$ ). Right: RE = Eu ( $y \simeq 0.17$  [11]). The hatched regions mark the Pccn/LTT phase boundary, which is not well defined due to a broadening of the diffraction peaks measuring the orthorhombic strain [1,2,4,10].

the LTO phase. The tilt axis lies within the  $\text{CuO}_2$  planes and is rotated by  $45^\circ$  with respect to the planar (Cu-O) bonds. At the LT transition temperature  $T_{LT}$  the tilt axis of the octahedra changes without a significant change of the tilt angle  $\Phi$  [10,4]. Two different structural modifications are found below  $T_{LT}$ , a tetragonal phase (LTT), where the tilt axis is parallel to a planar (Cu-O) bond and a further orthorhombic phase with reduced orthorhombic strain (space group Pccn), where the tilt axis is rotated by an angle  $\Theta < 45^\circ$

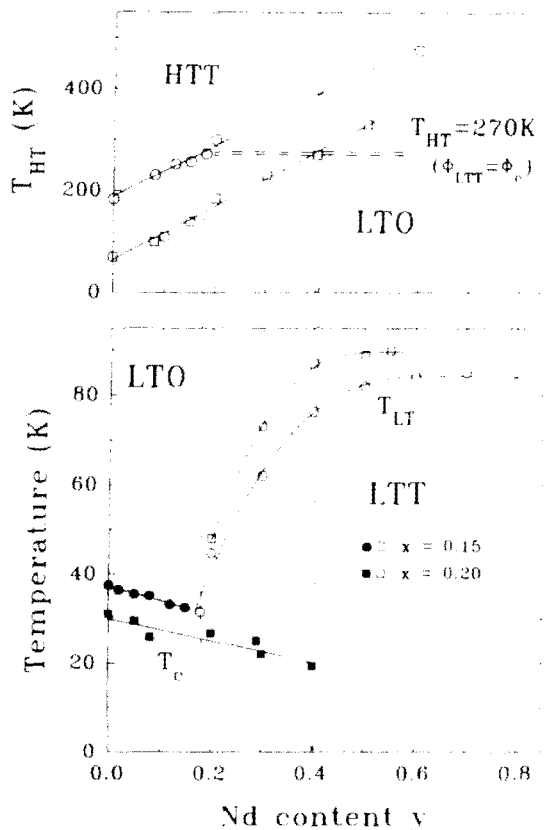


Figure 2. Phase diagram for Nd-doped samples with  $x = 0.15$  (open and filled  $\circ$ ) and  $x = 0.2$  (open and filled  $\square$ ). Upper panel:  $T_{HT}$ . The double dashed line marks  $\Phi_c$  corresponding to  $T_{HT} = 270\text{K}$ . Lower panel:  $T_c$  and  $T_{LT}$ . The dashed vertical lines separate the superconducting from the non-superconducting regions.

with respect to a planar (Cu-O) bond [2-4,10].

Representative structural phase diagrams of RE-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  obtained from x-ray diffraction are shown in Figs. 1,2. The transition temperature  $T_{HT}$  of the HT transition increases with increasing RE-content and strongly decreases with increasing Sr-concentration. At a fixed hole doping  $T_{HT}$  scales linearly with the concentration weighted La,RE ionic radius [2,9], which is very similar for the two series of samples shown in Fig. 1. The concentration dependencies of  $T_{HT}$  are relevant for the discussion of the properties at low temperature, since neutron diffraction data show, that  $\Phi(x, y)$  at a fixed temperature scales

(non linearly) with  $T_{HT}(x, y)$  independent on the tilt axis [10]. This is of course not surprising, since (i)  $\Phi$  can be regarded as the order parameter of the HT transition and (ii)  $\Phi$  does not change at the LT transition.

As shown in Fig. 2 the LT transition does not depend significantly on the hole doping for  $x \geq 0.15$ . It is induced in the Nd-doped compounds for  $y > 0.15$ .  $T_{LT}$  increases strongly with increasing  $y$  for small Nd-contents and saturates for higher doping near  $T_{LT} \simeq 90\text{K}$ . In contrast, for small Sr-concentrations the LT structure changes as function of  $x$  and the intermediate Pccn phase occurs. Nevertheless  $T_{LT}$  is mainly determined by the RE-doping (Fig. 1) and moreover the Pccn/LTT phase boundary (hatched regions in Fig. 1) strongly depends on the RE-doping. Close to this boundary the diffraction patterns yield some evidence for a transition between the Pccn and the LTT phase with decreasing temperature [3,4]. We do, however, not find any evidence for such a "split" LT transition in the specific heat [14].

From the data in Figs. 1,2 it is obvious that there are quite different concentration dependencies of the HT and the LT transition, respectively. The changes of  $T_{HT}$  can be traced back to those of averaged ionic sizes or bond lengths. Its increase with decreasing ionic radius in the  $\text{LaO}$  layers can be attributed to a larger lattice pressure on the (Cu-O) bonds [9]. On the other hand, doping the  $\text{CuO}_2$  planes with holes leads to smaller (Cu-O) bond lengths and thus to a smaller mismatch of the "sizes" of atoms in the different layers. This corresponds to a smaller  $T_{HT}$  [9,12].

A similar clear-cut correlation with averaged structural parameters is impossible for the LT transition. There are several contradictory experimental findings. Even for rather small  $y$  the  $T_{LT}$  of Eu-doped samples is higher than in all Nd-doped compounds and there is no LT transition in Pr-doped compounds up to  $y = 0.85$  [13]. Thus the occurrence of the LT transition, its transition temperature as well as the relative stability of the LTT phase compared to the Pccn phase are not determined by averaged bond lengths, tilt angles, etc.. The LT transition depends strongly on the ionic radius of the doped RE and the stabi-

lity of the LTT phase as extracted from the phase diagrams increases with the difference of the ionic radii of the La and the RE suggesting the importance of local deviations from the averaged structure. On the other hand measurements of the specific heat clearly show that the enthalpy jump  $\Delta H$  at  $T_{LT}$ , i.e. the energy scale of the LT transition, systematically increases with increasing tilt angle [2,14].  $\Delta H$  shows the same concentration dependence as  $T_{HT}$  [2,14]. Moreover, Sr-doping is obviously no precondition for the LT transition and influences  $T_{LT}$  only weakly. However, the stability of the LTT phase compared to that of the Pccn structure depends sensitively on small changes of  $x$ .

The structural phase diagrams (Figs. 1,2) give little evidence that specific electronic properties of the  $\text{CuO}_2$  layers are important to provide a driving force for the LT transition. Still, the LT transition leads to pronounced changes of the electronic properties indicating a significant coupling between structural and electronic degrees of freedom [2,4–8]. Fig. 3 shows the AC-susceptibility of Eu-doped samples with  $y \simeq 0.17$  [11]. The  $T_c(x)$ -curve in these compounds strongly differs from that in pure  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ . There is no SC for  $x < 0.14$  and the small diamagnetic signals up to  $x = 0.17$  indicate “minority phase” SC due to compositional and structural inhomogeneity of the samples [9,2]. On the other hand large diamagnetic signals and sharp phase transitions are present for  $x \geq 0.18$ . In this concentration range  $T_c$  decreases with increasing  $x$  and SC disappears for  $x \simeq 0.25$  (not shown in the figure) as in overdoped RE-free compounds [13].

It is apparent from the data in Fig. 3 that the influence of the LT transition on SC is not restricted to a narrow hole concentration range of  $x \simeq 1/8$ . Moreover, SC reappears as function of  $x$  without any qualitative change of the structure. The LT transition destroys SC only in some regions of the phase diagram. The parameter, which controls the appearance of SC in the LTT phase has been determined by a thorough study of Nd-doped compounds [8,7,2]. The corresponding data are summarized in a low temperature phase diagram (Fig. 4), which shows the structural pha-

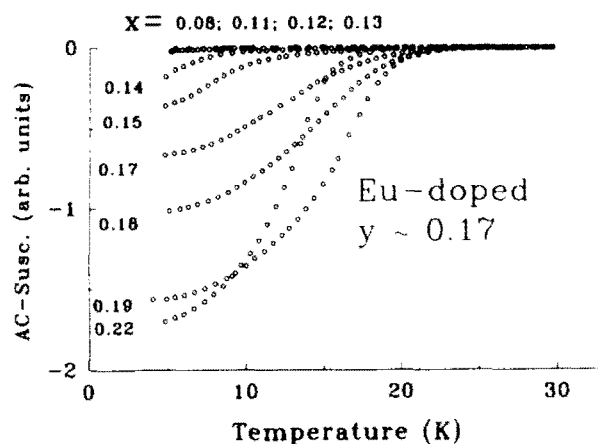


Figure 3. AC-susceptibility of powdered Eu-doped samples with fixed  $y \simeq 0.17$  [11] and various hole concentrations.

se boundaries as determined from x-ray diffraction as well as an additional separation line within the LTT phase. This line separates a superconducting region from a non-superconducting one, where in addition pronounced changes of the transport properties are present at and below  $T_{LT}$ . It corresponds to a line of constant  $T_{HT} \simeq 270\text{K}$ . This criterion also holds in the Eu-doped samples discussed above: SC reappears in the LTT phase at  $x \simeq 0.18 \pm 0.01$  (Fig. 3), where  $T_{HT} = 270\text{K}$  (see Fig. 1).

As mentioned above  $T_{HT}(x, y)$  scales with  $\Phi(x, y)$  at low temperature and from neutron diffraction [10] a critical tilt angle  $\Phi_c \simeq 3.6^\circ$  is inferred along the separation line in Fig. 4. Only if  $\Phi(x, y)$  exceeds  $\Phi_c$  in the LTT phase is SC destroyed in RE-doped  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ .

The interplay between structure and SC is also demonstrated in the phase diagram in Fig. 2, showing the structural phase boundaries and  $T_c$  as function of the Nd-content for  $x = 0.15$  and  $x = 0.2$ . The Sr-concentration  $x = 0.15$  turns out to represent a special situation, since  $\Phi(T_{HT})$  reaches the critical value of  $\simeq 3.6^\circ$  (270K) just at the LTO/LTT phase boundary and thus SC and LT transition mutually exclude each other [2]. In the more general case represented by the series with  $x = 0.2$  SC is observed in the LTO as well as in the LTT phase. It disappears within the LTT phase at a critical Nd-content ( $y \simeq 0.4$ ) [7,8], at

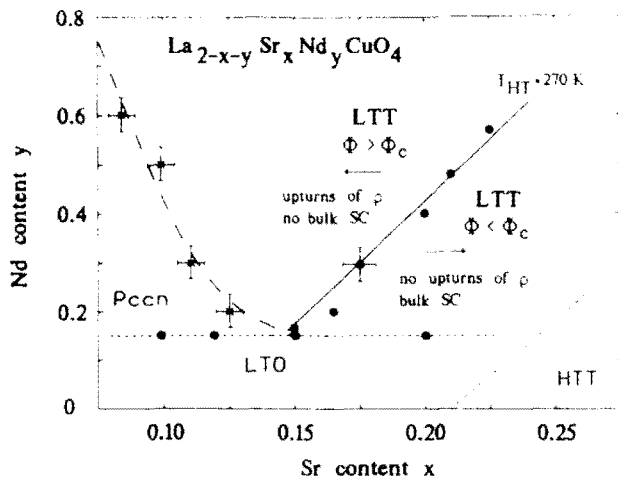


Figure 4. Low temperature ( $T < 10\text{K}$ ) structural phase diagram of  $\text{La}_{2-x-y}\text{Sr}_x\text{Nd}_y\text{CuO}_4$ . The phase range of the HTT phase was extrapolated from  $T_{HT}(x, y)$ . The solid line ( $\bullet$ ) separates regions with and without bulk SC (see text).

which  $\Phi(T_{HT})$  amounts to  $\simeq 3.6^\circ$  (270K). The phase diagrams at fixed Nd-content as function of  $x$  are more complicated, since the LTT phase occurs only in a restricted range of Sr-contents (Fig. 4). In these series of samples SC is present at small  $x$  in the Pccn phase as well as at large  $x$ , when  $\Phi$  in the LTT phase is smaller than the critical value [8,7]. Note that the data on the Eu-doped samples (Figs. 1,3) clearly show that the SC for small  $x$  in Nd-doped compounds correlates with the presence of the Pccn structure.

It is very appealing to relate the experimental evidence for a critical tilt and the observation of (local) antiferromagnetic (AF) order in the non-superconducting LTT phase [15] to recent model calculations of Bonesteel et al. [16] for a spin-orbit coupling  $t-J$  model. They found a crossover from a spiral magnetic pattern to a commensurate AF state at a critical tilt angle. However, these model calculations can not account for differences between LTO and LTT tilt distortions. The model is therefore not sufficient to explain our experimental findings, since the influence of the tilt distortion is different in the LTO (Pccn) and LTT phases. For example SC occurs in the Pccn phase as well as in the LTO phase for  $\Phi > \Phi_c$  [13,7,2].

Nevertheless, the model of Bonesteel et al. may provide a good starting point to study the close relationship between structural and electronic properties of doped  $\text{La}_2\text{CuO}_4$ .

In conclusion we have shown that RE-doping of  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  allows for a systematic study of the interplay between structural distortions of the  $\text{CuO}_2$  planes and their electronic properties. Subtle structural changes are found to destroy superconductivity. In particular in the LTT phase superconductivity disappears at a critical buckling of the  $\text{CuO}_2$  planes.

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