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Superconducting/Non–Superconducting Phase Boundary in the Low Temperature Tetragonal Phase of (La,RE)-Sr-Cu-O

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From measurements of the structural, superconducting and normal state transport properties of rare earth doped $La_{2-x}Sr_xCuO_4$ we find a phase boundary between a superconducting and a non–superconducting state of the low temperature tetragonal phase. This phase boundary is determined by the magnitude of the buckling of the Cu–O–Cu bonds in the CuO_2 layers, suggesting the importance of spin–orbit coupling for the electronic properties of these compounds.

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The structural phase transitions occurring in doped La_2CuO_4 have recently attracted much attention [1-9], since in a certain range of compositions very small structural changes are accompanied by the destruction of superconductivity. As discussed in detail by Axe and Crawford in the previous article,[9] four different phases have been found as function of temperature, pressure, and composition in doped La_2CuO_4. Measurements on Ba doped La_2CuO_4 as well as on rare earth (RE) doped $La_{2-x}Sr_xCuO_4$ clearly show that the change of the buckling pattern of the CuO_2 planes at the low temperature structural (LT) transition between the orthorhombic (LTO) and the low temperature tetragonal (LTT) destroys superconductivity (SC) in some cases. The origin of the very strong sensitivity of the electronic properties on subtle structural changes is the subject of current debate.[9] The LT transition does not always destroy SC and the hole content in particular near $x \sim 1/8$ is often assumed to be the crucial parameter.[9] In the present paper we discuss the properties of the LTT phase of RE doped $La_{2-x}Sr_xCuO_4$ for high Sr concentrations ($0.15 \leq x < 0.25$). For these high Sr contents there is no complication due to the occurrence of the intermediate ("less orthorhombic") Pccn structure which is observed for small hole concentrations in $La_{2-x-y}Sr_x(RE)_yCuO_4$.[5,3]

The preparation and characterization of single phase samples as well as the experimental techniques have been described elsewhere.[10] The determination of the oxygen content and also measurements of the thermopower and the Hall–effect

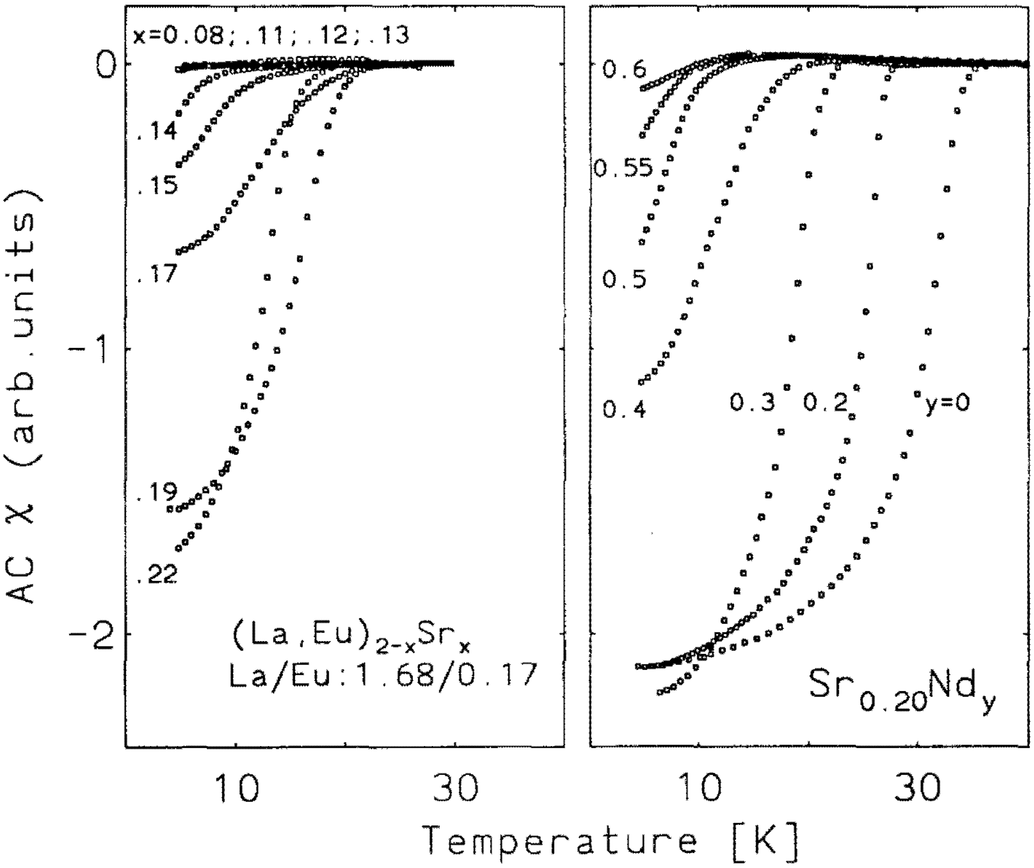

Fig. 1. AC susceptibility vs. temperature of powdered samples with a fixed *La*/*Eu* ratio[11] of 1.68/0.17 and various *Sr* concentrations x (left part) and samples with a fixed *Sr* concentration of 0.2 and various *Nd* contents y (right part). All *RE* doped samples are in the LTT phase.

prove that the hole content of the CuO_2 planes does not change by doping with the trivalent rare earths.[10] We mention that in all *RE* doped samples discussed in the present paper a low temperature structural transition towards a LTT structure has been found from x-ray diffraction. In the following we will discuss the influence of this structural transition on SC and normal state transport properties.

In Figure 1 we plot the AC susceptibility, measured on fine powders of two series of samples. In the left part of the figure data obtained for *Eu* doped compounds with a fixed *La*/*Eu*-ratio of 1.68/0.17[11] and various *Sr* concentrations are shown. It is obvious that the hole concentration dependence of T_c in this series of samples differs drastically from that in pure $La_{2-x}Sr_xCuO_4$ (LTO phase). Note that these data yield no evidence that SC is suppressed for a particular hole content only. Instead, the data indicate a strong suppression of SC below a "critical" *Sr* concentration $x_c \sim 0.18$. There is no bulk SC for $x < x_c$, whereas rather sharp diamagnetic transitions with a x dependence of T_c similar to pure $La_{2-x}Sr_xCuO_4$[6] are present for higher hole doping.

The right part of Figure 1 shows data obtained on *Nd* doped samples with a fixed *Sr* concentration of $x = 0.2$. The LTO/LTT phase boundary is found at $y \sim 0.15$ similar as for $x = 0.15$[2,4] (see Figure 3 below). There is no measurable influence

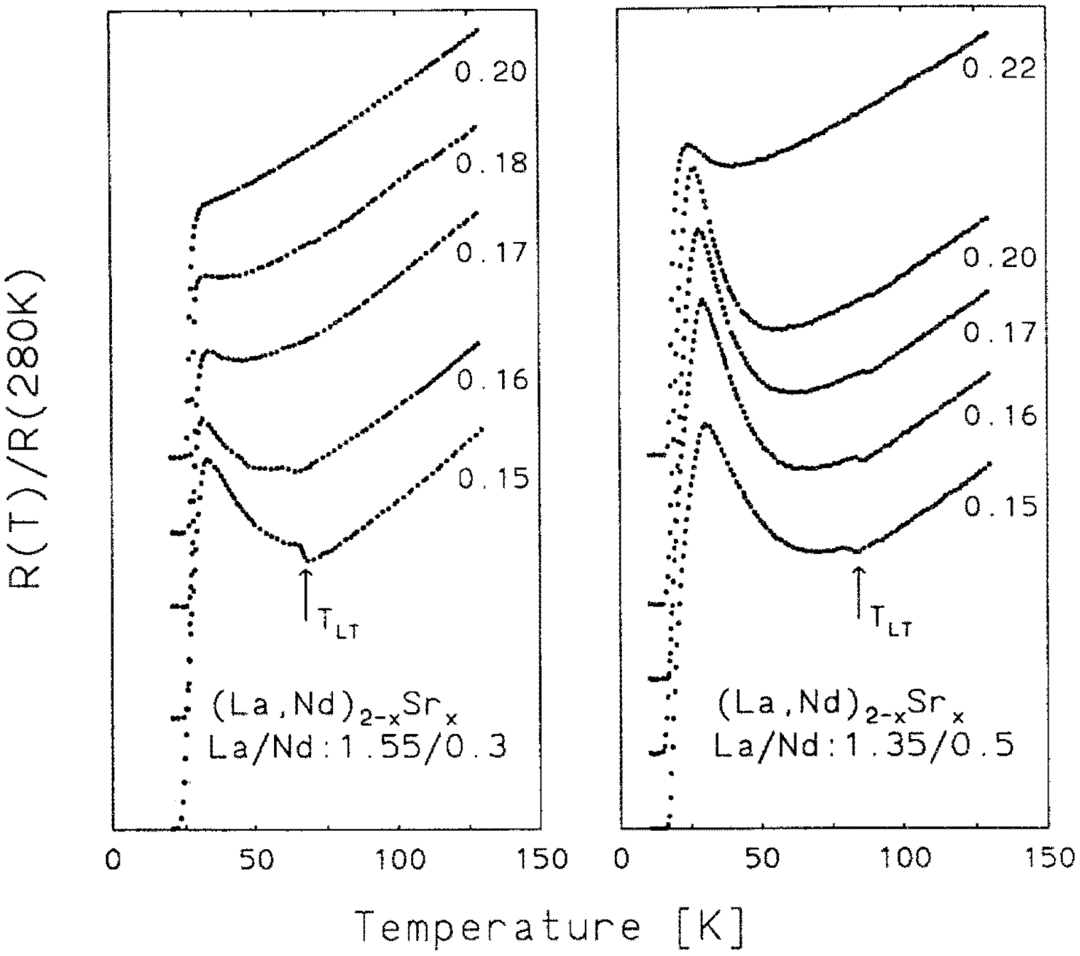

Fig. 2. Normalized electrical resistivity as a function of temperature for Nd doped $La_{2-x}Sr_xCuO_4$ with a La/Nd ratio of 1.55/0.3 ($y \sim 0.3$)[11] (left part) and a La/Nd ratio of 1.35/0.5 ($y \sim 0.5$)[11] (right part) for various Sr concentrations. The curves are shifted along the y–axis for clarity.

of this structural phase boundary on the SC. The AC susceptibility data shown in Figure 1 as well as DC susceptibility[2,4] and specific heat measurements[13] clearly show bulk SC with $T_c > 20K$ for all samples with Nd concentrations $y < y_c \sim 0.4$. On the other hand, for higher Nd concentrations the transitions broaden and the diamagnetic signal strongly decreases with increasing y. There is only minority phase SC[14] for high Nd contents $y > y_c$. This means, that in the LTT phase at a fixed hole doping a superconducting state changes into a non–superconducting one with increasing y. Similar results are obtained for other Sr concentrations $0.15 < x < 0.2$ in Nd as well as in Sm and Eu doped compounds.

Not only SC but also the normal state transport properties of doped La_2CuO_4 strongly change below T_{LT} in certain ranges of concentrations.[7,3] We emphasize that the occurrence of anomalies in the transport properties below T_{LT} and the suppression of SC have a very similar concentration dependence. In Figure 2 we plot the electrical resistivity $R(T)$ of samples with various Sr concentrations and fixed La/Nd ratios[11] of 1.55/0.3 and 1.35/0.5, respectively. At the Sr content $x \sim 0.15$, where SC is suppressed in the LTT phase,[2,4] we find small jumplike anomalies at

T_{LT} followed by a strong upturn towards lower temperatures in both series of samples shown in Figure 2. In contrast, at a Sr doping of $x \sim 0.2$ pronounced anomalies of $R(T)$ are present only for the high Nd content $y \sim 0.5$, whereas in the superconducting compound ($y \sim 0.3$) the structural transition has no measurable influence on $R(T)$. Also we find that in the series of samples with $y \sim 0.5$ the anomaly of the resistivity in the LTT phase is dramatically smaller at a Sr concentration of $x = 0.22$.

Thus, from our measurements we conclude that it is not the structural transition alone that destroys SC and leads to anomalies in the normal state transport properties of doped La_2CuO_4. Separately, the electronic properties of the LTT phase are obviously not determined merely by the hole content or the RE concentration. Instead the data are suggestive of an additional parameter which controls the suppression of SC in the LTT phase.

To determine this parameter we have extracted pairs of critical concentrations from various series of samples, i.e. the concentrations, where the electronic properties strongly change as function of the hole doping and the RE content. In Figure 3 these pairs of critical concentrations for Nd doped samples are plotted in a (Sr, Nd) phase diagram together with the structural phase boundaries at T < 10K obtained from x–ray diffraction. Within the LTT phase we find a line which separates a region with bulk SC from a region without bulk SC plus additional transport anomalies (see also Ref.[8]).

Although there is no qualitative difference in the structure found of the compounds in these two regions of the phase diagram, the separation line correlates with structural properties. The separation line is identified as a line of constant transition temperature T_{HT} of the high temperature structural (HT) transition, whose concentration dependence we have discussed previously in Ref.[10,3,12]. From our x–ray diffraction data we find $T_{HT} = 270K \pm 20K$ for all samples with compositions which correspond the separation line shown in Figure 3.

This correlation between T_{HT} and the change of the electronic properties also holds for compounds doped with other REs. For example, in the series of Eu doped samples with $y \sim 0.17$ (Figure 1) our diffraction measurements yield $T_{HT} >$ 270K for $x < 0.18$ and $T_{HT} <$ 270K for $x \geq 0.18$, respectively. The pronounced change of SC as function of the hole content again occurs at the concentration where $T_{HT} \sim 270K$.

Before we discuss the meaning of the correlation between T_{HT} and the electronic properties we mention two special cases. The line defined by $T_{HT} =$ 270K and the LTO/LTT structural phase boundary cross each other in the Nd doped compounds at $x \sim 0.15$. This leads to a special phase diagram as a function of y for this Sr concentration: the LT structural transition and bulk SC mutually exclude each other.[4,2] However, this is only a special case of the more general phase diagram at higher Sr doping, where bulk SC is observed not only in the LTO phase but also in the LTT phase up to a critical Nd concentration defined by $T_{HT}(x, y) \sim 270K$. In compounds doped with smaller RE ions this more general phase diagram is also found for $x = 0.15$, since the LTT/LTO phase boundary is observed for compositions, where T_{HT} is smaller than 270K.[12]

A second "special" hole concentration is extracted from Figure 3 by the extrapolation of the separation line to $y = 0$. The criterion $T_{HT} \sim 270K$ is found

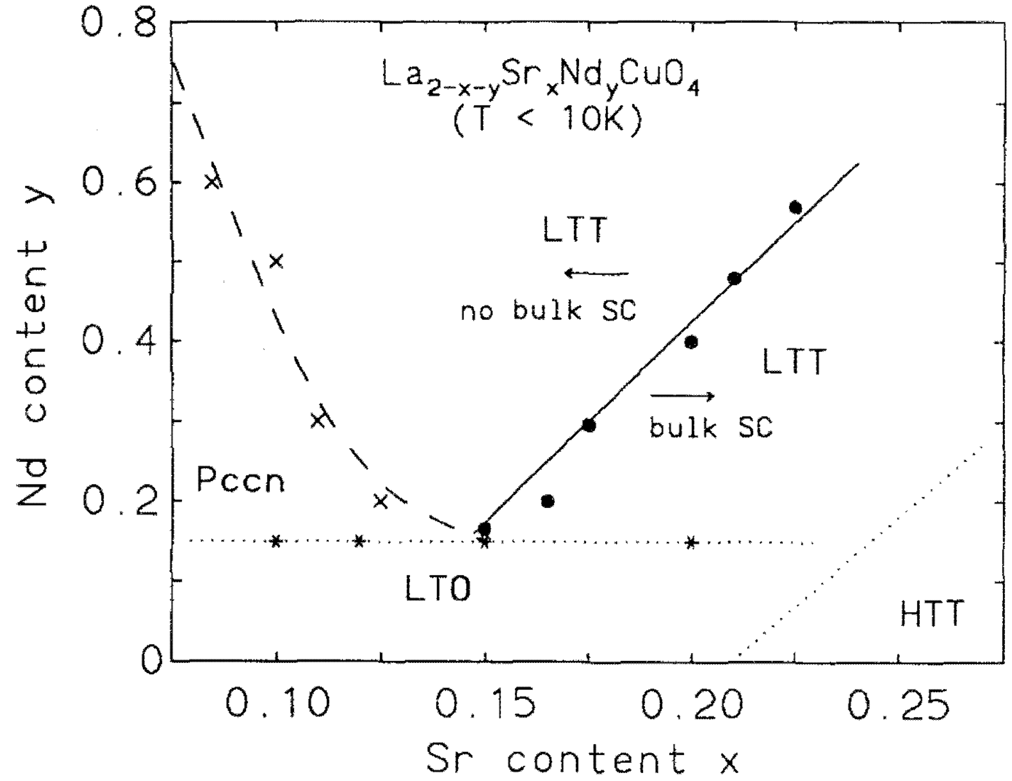

Fig. 3. Low temperature structural phase diagram extracted from our structural investigations. The phase range of the high temperature tetragonal (HTT) phase has been extrapolated from the x, y concentration dependence of T_{HT} at higher temperatures. The experimentally observed boundaries between the different structural phases are marked by × (Pccn/LTT) and ⋆ (LTO/Pccn and LTO/LTT). At the phase boundaries a mixture of different structural phases is present.[2] The dashed and the dotted lines are guides to the eye. •: Critical Nd and Sr concentrations in the LTT phase as extracted from Fig. 1 and Fig. 2 and similar data (see text). The separation line in the LTT phase is a line of constant $T_{HT} = 270K$.

in pure $La_{2-x}Sr_xCuO_4$ at $x \sim 1/8$, i.e. for this Sr concentration T_{HT} is larger than 270K in all RE doped compounds. Thus, from our findings at higher hole doping we conclude that there is no SC in the LTT phase for $x = 1/8$ in RE doped $La_{2-x}Sr_xCuO_4$. This is in agreement with a particularly strong suppression of SC at this hole content.[9] In addition we find some evidence for a special role of the hole content $x \sim 0.12$. As we will show elsewhere,[15] there is a large negative thermopower of $S \sim -10\mu V/K$ in the LTT phase at $x = 0.12$ independent of the RE concentration (see also Ref.[7]). A similar but less pronounced behaviour of the thermopower is also present for larger Sr concentrations.[3] However, a sign change does not occur for lower hole contents $x \leq 0.1$; in this case S remains positive even at very high Nd concentrations.[15]

Regarding the correlation between T_{HT} and the electronic properties, a line of constant T_{HT} in the (x, y) phase diagram obviously corresponds to a line of a similar magnitude of the order parameter of the continuous HT transition at a fixed temperature in the LTO phase.[8] As discussed by Axe and Crawford in the previous article,[9] the tilt angle Φ of the CuO_6 octahedra serves as an order parameter of the HT transition. From neutron diffraction data it is found that Φ does not change significantly at the LT transition, where the tilt direction changes.[9,16] This means, that the line of constant T_{HT} in Figure 3 is a line of constant Φ in the LTT phase. In other words, *all critical hole or RE concentrations* found in the various series of samples correspond to a *single critical magnitude* Φ_c of the octahedral tilt.[8]

Interestingly, the existence of a critical tilt angle for the electronic properties of the doped CuO_2 planes has been predicted by Bonesteel, Rice and Zhang.[17] In their spin–orbit coupling t–J model they find a stabilization of an antiferromagnetic ground state for large tilt angles. Indeed, μSR[18] and Mößbauer measurements[19] yield evidence for (local) antiferromagnetic order in the non–superconducting LTT phase below $T_N \sim 32K$. Thus, it is very appealing to relate the evidence for a critical tilt angle found in our experiments to the transition predicted in the calculations. However, in the single band model of Bonesteel et al. Φ is the only parameter, which determines the influence of the buckling of the CuO_2 layers on the electronic properties: there is no difference between the LTO and the LTT phase in this respect.

This is obviously in disagreement with the experimental findings, since pronounced changes of the transport properties occur at T_{LT}. However, we note that a similar disagreement between theory and experiment is present already in the description of the magnetic properties of the undoped antiferromagnetic compounds. Whereas the calculations predict no influence of the tilt direction on the strength of the exchange anisotropies,[20] inelastic neutron scattering yields a dramatic increase of the in–plane spin wave gap by almost a factor of two at the LTO to Pccn transition in Nd doped La_2CuO_4.[21] Nevertheless, the evidence for a critical tilt angle described by Bonesteel et al.[17] and the observation of local antiferromagnetic order in the non–superconducting LTT phase[18,19] indicate that the spin orbit t–J model is a good starting point to explain the close relationship between subtle structural changes and SC in doped La_2CuO_4.

In conclusion, we have shown that there is a phase boundary between a superconducting and a non–superconducting groundstate in the LTT phase of RE doped $La_{2-x}Sr_xCuO_4$. The boundary is determined by the *magnitude of the buckling* of the CuO_2 planes. Bulk SC occurs if the tilt angle of the CuO_6 octahedra is smaller than a critical value regardless whether the structure is LTO or LTT and SC is destroyed in the LTT phase for larger tilt angles. It is both, the occurrence of the LT transition and the tilt angle, which controls superconductivity in RE doped $La_{2-x}Sr_xCuO_4$.

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