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STRUCTURAL ANALYSES ON La$_{2-x}$Sr$_x$CuO$_{4-\delta}$ CRYSTALS

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We present results of single crystal neutron diffraction experiments on La$_{2-x}$Sr$_x$CuO$_{4-\delta}$. The analysis of the temperature dependence of the La-O bond lengths shows that almost the entire thermal contraction of La$_2$CuO$_4$ between 540 K an 50 K is due to the decrease of the LaO$_9$ polyhedron, the Cu-O bond distances remain almost constant. Doping of La$_2$CuO$_4$ with Sr (or additional O) decreases both Cu-O bond lengths.The large thermal parameters especially of the apical O indicate the instability of all examined crystals against a second phase transition.

1. INTRODUCTION

(La/RE)$_{2-x}$M$_x$CuO$_{4-\delta}$ with M=Sr,Ba shows a variety of different structural modifications depending on RE metal concentration, doping, temperature and pressure[1]. Most of the stability boundaries between these phases can be discussed in the frame of the tolerance factor based on the RE/La-O and the Cu-O bond distances[2]. At very high temperatures these bonds agree with each other, but due to the different thermal expansion for La-O and Cu-O they mismatch at low temperatures. One possibility of the system to reduce this mismatch is the structural transition from the high temperature tetragonal (HTT, I4/mmm) into the low temperature orthorhombic (LTO, Abma) phase. It is now evident that the previous explanations of this transition based on a Peierls instability[3] are incorrect. However the relation between the structural transition and the electronic system (and hence superconductivity) is still unclear. In this paper we present structural results of neutron diffraction experiments emphasizing the aspects of the structural phase transition.

2. EXPERIMENTAL

Large ($\sim$10-20mm^3) single crystals of La$_{2-x}$Sr$_x$CuO$_{4+\delta}$ with $\delta\sim$0.0; x=0.0,0.08 and $\delta\sim$0.005; x=0.0 were prepared by the standard flux growth technique[4]. Our stochiometric La$_2$CuO$_{\sim4.00}$ crystal shows antiferromagnetic ordering at T$_N$=296 K and La$_2$CuO$_{\sim4.005}$ at T$_N$=250 K. In the oxygenated crystal some traces of superconductivity were observed (dc suscpetibility) with an onset at 35 K. A La$_{1.85}$Sr$_{.15}$CuO$_4$ crystal was prepared using a zone melting method[5], its excellent superconducting properties are described in ref. 5. Neutron diffraction experiments were performed at the ORPHEE reactor, CEN Saclay. For complete structure analyses the intensities of Bragg reflections were measured up to $sin(\theta)/\lambda < 0.92$Å^{-1} on the P110 four-circle diffractometer (λ=0.831Å). The model refinements were performed in the spacegroups F4/mmm (HTT) and Abma (LTO) taking into account the twinning in the orthorhombic case. The lattice parameters were obtained with the triple axis spectrometer VALSE at λ=2.47Å. Details of the different measurements and refinements will be described elsewhere[6].

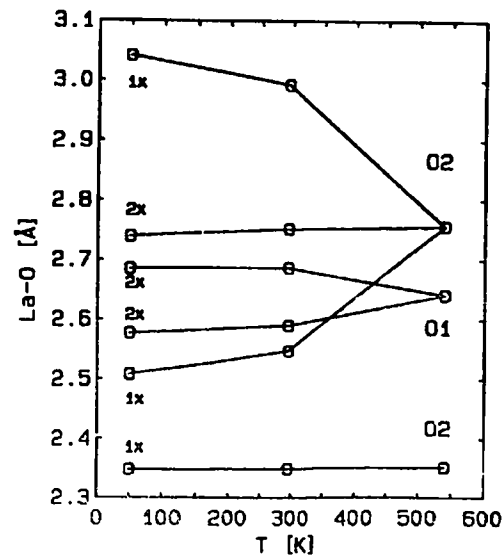FIGURE 1
Temperature dependence of the La-O bond lengths for La$_2$CuO$_{\sim4.00}$, the multiplicity of the bonds is indicated

3. RESULTS AND DISCUSSION

Fig. 1 shows the different La-O bond distances for the La$_2$CuO$_{\sim4.00}$ crystal at three temperatures (540 K, 295 K and 50 K). The HTT-LTO phase transition for this crystal occurs at about T$_{t-o}\sim$530 K. There are three different La-O distances in the HTT phase, which split into six La-O bonds in the LTO phase. The variation of the averaged La-O bond can be seen from the strong volume decrease of the LaO$_9$ coordination polyhedron: from 42.00(4)Å^3 at 540 K to 41.75(4)Å^3 at 295 K and 41.54(4)Å^3 at 50 K. The CuO$_6$ octahedron remains almost constant over this temperature range (11.71$_5$(2)Å^3 at 540 K and 11.70(2)Å^3 at 50 K). It is evident that the thermal contraction of the La$_2$CuO$_4$ lattice in the LTO phase is almost completely due to the variation of the LaO$_9$ polyhedron. This supports the formalism of the tolerance factor and the bond length mismatch between
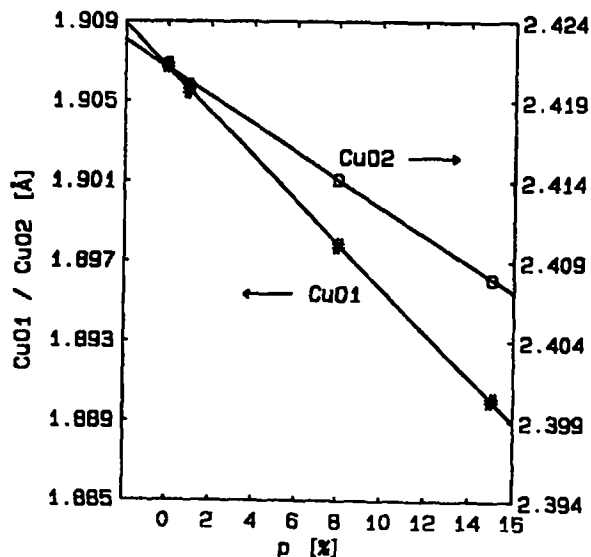
FIGURE 2

Dependence of the two Cu-O bond lengths on the charge carrier concentration p per Cu atom introduced by Sr (p=8% and 15%) and additional O (p=0 and 1%)

FIGURE 3

Dependence of the thermal parameters U11 and U22 of O2 on p introduced by Sr (p=8% and 15%) and additional O (p=0 and 1%)

La-O and Cu-O bonds[2]. In the tetragonal structure the possibilties to reduce the volume of the LaO_9 polyhedron without decreasing the CuO bonds are limited. The resulting strain, which cause the transition into the LTO phase, can be seen in a bond-strength/bond-length analysis. Our structure parameters at 295 K and the empirical coefficients of Brown et al.[7] yield a bond-valence sum of +2.66 for La and +2.43 for Cu.

The position of the O2 site between Cu and La seems to have an essential influence in this context. Already in the HTT structure there is a large Jahn-Teller effect which deplaces O2 from the Cu site towards La. The corresponding La-O2 bond of 2.3484(11)Å at 295 K is significantly shorter than all the other La-O bonds and even smaller than the sum of the ionic radii[8]. Due to the Jahn-Teller effect the bond mismatch in the tetragonal structure can be reduced up to a certain limit, where the crystal transforms into the LTO phase without further change of the La-O2 distance, which has a very small thermal expansion of $\Delta La O2/La O2$=.0017(7) between 50 K and 540 K.

The temperature dependency of La_2CuO_4 can be compared to the influence of the hole doping. In Fig. 2 we show the bond distances from Cu to O1 and O2 as a function of the charge carrier concentration p per Cu atom, p=x+2δ. Due to the uncertainties of all occupation factors, the absolute error in p may amount to 1% (but the difference between the two $La_2CuO_{4+\delta}$ crystals is supported by the variation in T_N^9). As shown in Fig. 2 both Cu-O bond lengths are strongly reduced by the doping. This indicates a charge transfer into the CuO planes for $La_{2-x}Sr_xCuO_{4-\delta}$, similar to findings in $YBa_2Cu_3O_{7-\delta}$[10].

Both, Sr/Ba and excess oxygen doping, reduce T_{t-o} strongly[1]. One reason is the difference in the ionic radii in the case of Sr (and Ba) and the additional atom in the case of O. However there must be further mechanisms,
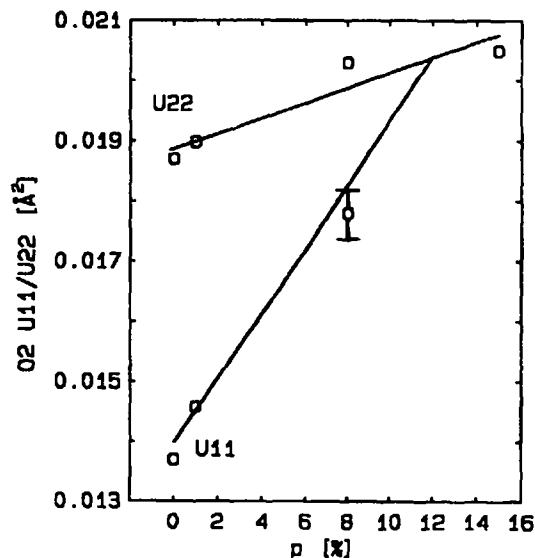
as Sr and Ba behave almost similar in spite of quite different ionic radii. The observed contraction of the CuO_6 octahedron due to the doping offers another explanation for the stabilization of the HTT phase, as it reduces the bond length mismatch. Therefore, the HTT-LTO transition is also connected to the electronic structure in these compounds and not only to structural properties.

In Fig. 3 we show the room temperature mean square displacements of O2 parallel to the a and b-axis as a function of p. For p=0.15 the crystal is tetragonal and therefore U11=U22. The value is quite large due to the low lying optical phonon which becomes soft at T_{t-o}. For the other crystals in the LTO phase U11≠U22. The mean square displacement U11(parallel a) decreases rapidly with decreasing p (and increasing T_{t-o}) as the soft mode hardens in the LTO phase[11]. U22(parallel b) decreases only slightly, it remains large even in the La_2CuO_4 crystal, where the phase transition occurs at 530 K. This indicates that all crystals are instable against a second phase transition into P4₂/ncm (or Pccn), which is observed in $La_{2-x}Ba_xCuO_4$ and isostructural compounds[12].

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