Lattice Instabilities in Cuprate Superconductors: A Possible Limiting Mechanism for T_c

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High-resolution thermal-expansion experiments on (i) insulating $La_2CuO_{4+\delta}$, (ii) its Sr- and Ba-doped metallic counterparts with reduced T_c values, and (iii) $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ ($T_c \simeq 24$ K) reveal distinct lattice instabilities at $T_1 = 32 \pm 1$ K and $T_2 = 36 \pm 1$ K. T_2 coincides with T_c^{max} found upon 15 at.% Sr doping. For $YBa_2Cu_3O_{6.5}$ ($T_c = 49$ K), a lattice instability occurs at $T = 90 \pm 1$ K, i.e., again close to $T_c^{max} = 92$ K.

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Among the large variety of theories proposed to explain high-T_c superconductivity (HTS), one line is based on the idea that this phenomenon is triggered by strongly anharmonic electron-lattice coupling. In fact, this was the initial guideline to the discovery of cuprate superconductors by Bednorz and Müller [1]. Whereas the existence of pronounced electronic correlation effects in the normal-state properties of these materials [2] has lead many theoreticians to discard this idea [3], clear indications for strong electron-lattice coupling in the cuprates are provided through measurements of, e.g., phonon renormalization as a function of doping [4] or temperature [5,6], ion channeling [7], and atomic pair distribution functions (APDF) [8,9] at T_c.

Metals with strong electron-lattice coupling tend toward structural instabilities, and already a long time ago it was proposed to search for HTS among systems exhibiting such instabilities [10]. The cuprates belong to this class of systems. A central question is, however, whether these instabilities are caused by the *same* interaction between the free charge carriers and the lattice which possibly mediates superconductivity (as in Re-Mo alloys [10]), or whether they are an intrinsic property of the cuprates, linked to their particular perovskite-derived structure. In the latter case, there would be no direct link between the lattice instability and the occurrence of HTS; the orthorhombic-to-tetragonal (O-T) transition in $(La,Sr)_2CuO_4$ is a prominent example of that [11].

In this Letter, we report the observation of two more lattice instabilities in the "2:1:4" family, occurring in both the undoped (insulating) and the doped (metallic) compounds. In contrast to the O-T transition, the corresponding transition temperatures $T_1 = 31 \pm 1$ K and $T_2 = 36 \pm 1$ K are found to be virtually independent of the degree of doping as well as of the sign of the charge carriers and the actual low-temperature structure. Most surprising, however, is the fact that T_2 coincides with the highest T_c attainable for optimum doping, and that first experiments on $YBa_2Cu_3O_{7-\delta}$ reveal a qualitatively similar behavior.

Our findings are based on high-resolution ($\Delta l \geq 0.01$ Å) measurements of the thermal expansion $\alpha(T)$, using a capacitance dilatometer [12]. Data points were taken in discrete temperature steps, about 10 min after thermalization of the sample. Earlier results [13] already revealed the upper anomaly near T_2 in ceramic $La_2CuO_{4+\delta}$. As shown in Fig. 1(a), this anomaly was found to be of striking similarity (broadened second-order phase transition) to the one occurring in the superconducting $La_{1.85}Sr_{0.15}CuO_4$ sample at $T_c \simeq 36$ K, which is the maximum T_c for any 2:1:4 superconductor when measured via a *bulk* technique, e.g., $\alpha(T)$. Below we present results of a systematic study of single-crystalline and ceramic $La_2CuO_{4+\delta}$ as well as ceramic $La_{2-x}M_xCuO_4$ (M = Sr, $x = 0.1$; M = Ba, $x = 0.115$ and 0.125) and $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$.

For $La_2CuO_{4+\delta}$, two single crystals and three differently prepared ceramic samples have been investigated.

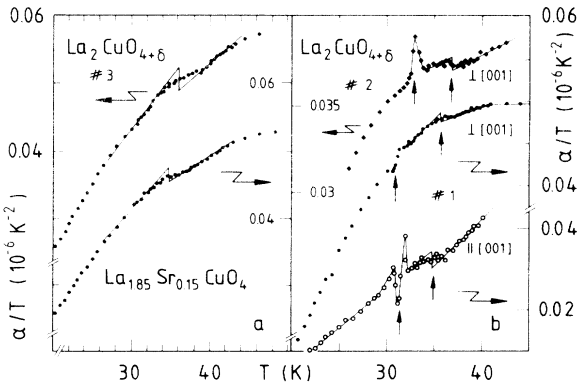

FIG. 1. Coefficient of linear thermal expansion as α/T vs T for (a) polycrystalline $La_2CuO_{4+\delta}$ No. 3 [14] (left scale) and $La_{1.85}Sr_{0.15}CuO_4$ [13] (right scale); and for (b) $La_2CuO_{4+\delta}$ single crystals No. 1 (right scale) and No. 2 (left scale), measured along (○) and perpendicular to (●, ♦) [001].

According to x-ray-diffraction measurements, the single crystals are microtwinned with nearly equally distributed twin orientations within the basal plane. Therefore, we expect the corresponding in-plane expansion coefficient to be in good agreement with α_{110}, which would be measured on an untwinned crystal along [110]. The dimensions of the crystals were $9\times1\times1$ mm^3 (No. 1) and $4\times1\times1$ mm^3 (No. 2), respectively. For measurements along the [001] axis, a stack of four pieces of crystal No. 1 was used in order to increase the signal-to-noise ratio. Ceramic samples were rods of $10\times1\times1$ mm^3. Details concerning the sample preparation and the determination of the oxygen content are given in [14]. The samples were characterized by means of high-resolution dc magnetization measurements using a SQUID magnetometer.

Figure 1(b) shows $\alpha(T)/T$ for $La_2CuO_{4+\delta}$ single crystals No. 1 and No. 2 measured perpendicular to (α_{110}) and, for No. 1, along (α_{001}) the [001] axis. For both orientations, a plateau in $\alpha(T)/T$ is found at $T_2=36\pm1$ K. Using the standard equal-area construction, we replace these broadened transitions by idealized jumps $\Delta\alpha_{110}$ and $\Delta\alpha_{001}$. The size of the anomalies at T_2 is similar for different samples and orientations. Estimating for crystal No. 1 the change of the volume-expansion coefficient as $\Delta\beta=2\Delta\alpha_{110}+\Delta\alpha_{001}$, we find $\frac{1}{3}\Delta\beta=(0.67\pm0.2)\times10^{-7}$ K^{-1}, in close agreement with the results for the ceramic samples [ranging between $\frac{1}{3}\Delta\beta=(1.3\pm0.2)\times10^{-7}$ K^{-1} and $(0.8\pm0.2)\times10^{-7}$ K^{-1}] for different oxygen-excess concentrations, $\delta=(3\pm0.5)\times10^{-4}$ to $(4\pm0.5)\times10^{-4}$. On going from No. 1 to No. 2, a 25% decrease in $\alpha_{110}(T)$ values is found, pointing to a moderate change in the distribution of a-b microtwins. In summary, strain fields due to either twins or grain boundaries appear to have *no* significant effect on T_2 and $\Delta\alpha_{110}$.

Slightly below the anomaly at T_2, a second anomaly can be resolved around $T_1=31$ K, in all samples and independent of the orientation. This anomaly manifests itself only in time-dependent phenomena: Within a small temperature interval (T_1-1 K, T_1+1 K), drift effects in the sample length occur, which are absent outside. We note that, in contrast to the anomaly at T_2, the T_1 anomaly is not accompanied by a change of the overall T dependence of α.

The same drift effects as in the single crystals are observed in the ceramic $La_2CuO_{4+\delta}$ samples, in addition to the broad second-order transition found already in [13]. The size of $\Delta\alpha_2$, the idealized jump at T_2, is larger for smaller O-excess concentration. This indicates that the upper phase transition is a true property of the insulating, near-stoichiometric compound, a conclusion which is strongly supported by results of elastic-constant and specific-heat $C(T)$ measurements on $La_2CuO_{4+\delta}$ ($\delta\approx0$) single crystals, recently reported by Migliori *et al.* [15]. These authors observed in both quantities features near 30 and 37 K which most likely correspond to the lattice anomalies in $\alpha(T)$ at T_1 and T_2. In addition, they found the $C(T)$ peaks to be strongly suppressed upon increasing the oxygen excess δ [16]. In fact, specific-heat measurements on our $La_2CuO_{4+\delta}$ samples which all contain a small amount of excess oxygen, $\delta>0$, did not resolve any anomaly within a resolution of $\Delta C\geq80$ mJ/K mole.

Next we discuss the $\alpha(T)$ results on the ceramic samples of doped $La_{2-x}M_xCuO_4$ in which either the low-temperature tetragonal (LTT) structure (M=Ba) or a nonoptimum hole concentration (M=Sr) fixes T_c well below $T_c^{max}=36$ K. Figure 2(a) displays $\alpha(T)/T$ of $La_{2-x}Ba_xCuO_4$ for $x=0.115$ and 0.125. At $T^*=58$ K ($x=0.115$) and 59 K (0.125), $\alpha(T)$ shows a distinct minimum which is most likely due to the structural phase transition from the low-temperature orthorhombic (LTO) structure into the LTT phase [17]. For the sample with $x=0.115$ the superconducting transition is reflected by a small positive $\alpha(T)$ jump at $T_c=6$ K, whereas $T_c=4$ K is found for $x=0.125$. The magnetization results, shown in the upper part of Fig. 2(a), indicate the presence of a minority phase with $T_c\simeq32$ K, most likely the LTO phase, as commonly observed in the x-ray pattern of samples in this concentration range [17]. The results for three different measurements on $La_{1.885}Ba_{0.115}CuO_4$, shown in the lower part of Fig. 2(a), highlight a very similar behavior as in the undoped compound, i.e., irreproducible data points caused by strong drifts near $T_1=32\pm1$ K and a distinct change of slope in $\alpha(T)/T$ at $T_2=36\pm1$ K. The fact that a discontinuity $\Delta\alpha_2$ cannot be resolved appears to be a peculiarity of the LTT phase,

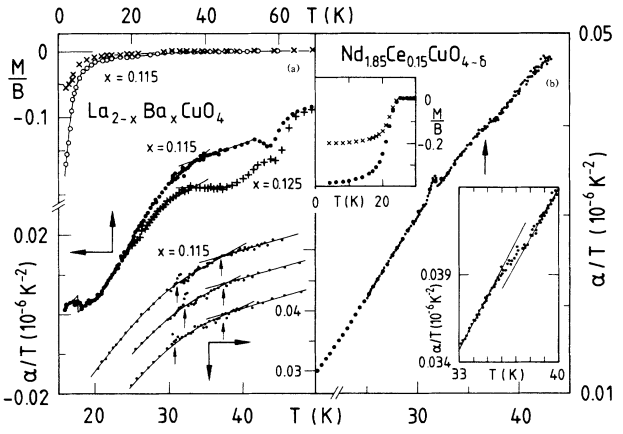

FIG. 2. (a) Coefficient of thermal expansion for $La_{2-x}Ba_xCuO_4$, $x=0.115$ (●) and $x=0.125$ (+), as α/T vs T. Upper part: dc magnetization for $x=0.115$ as M/B vs T after zero-field cooling [shielding signal (○)] and field cooling [Meissner signal (×)], measured in a field $B=10$ G. Lower part: α/T vs T for three consecutive runs on $x=0.115$. (b) α/T vs T for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. Lower inset: Blowup of $\alpha(T)/T$ between 33 and 40 K. Solid lines are extrapolations from high- and low-T data. Upper inset: Shielding (●) and Meissner (×) signals taken at $B=10$ G on the same sample.

another one being a very strong dopant dependence of $\alpha(T)$ in the temperature range 25 K $\leq T \leq$ 60 K [Fig. 2(a)]. For $La_{1.9}Sr_{0.1}CuO_4$ (not shown), an S-shaped anomaly implying a substantially reduced $\Delta\alpha_2$, i.e., $(0.4 \pm 0.1) \times 10^{-7}$ K^{-1}, near $T_2 = 37 \pm 1$ K and a "time-dependent" sample length in the vicinity of $T_1 = 31$ K are observed.

Figure 2(b) shows α/T vs T for $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$. Results of the dc magnetization, indicating a superconducting transition with $T_c^{\text{onset}} = 24$ K, are plotted in the upper inset. No corresponding discontinuity can be resolved in $\alpha(T)$ within our resolution of $\Delta\alpha \geq 10^{-8}$ K^{-1}. This is in accordance with the Ehrenfest relation, $\Delta\alpha \sim (\partial T_c/\partial p)_{p \to 0}$, since T_c of $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ has been shown to be pressure independent [18]. At $T_1 = 31 \pm 1$ K and $T_2 = 36 \pm 1$ K the same anomalies as in $La_2CuO_{4+\delta}$ show up in this electron-doped superconductor. Additional evidence for local structural changes between 30 and 40 K in this system was recently provided through APDF measurements [9].

Our thermal-expansion results on $YBa_2Cu_3O_{6.5}$ are shown in Fig. 3. Both $\alpha(T)/T$ and the magnetization, plotted at the top of Fig. 3(a), demonstrate a bulk superconducting transition at $T_c = 49$ K and the absence of any minority phase with higher T_c. Figure 3(b) displays the $\alpha(T)/T$ results between 75 and 100 K for four consecutive runs. Clear indications of a lattice anomaly can be resolved around 90 K, i.e., a break in the slope with a reduced $\alpha(T)$ below 90 K and distinct time dependences in the sample length within $\Delta T = \pm 1$ K around 90 K. Both characteristics clearly distinguish this anomaly from the superconducting transition observed in oxygen-rich ceramic samples [19] where $\alpha(T)$ increases upon cooling through T_c without any measurable time dependence [20,21].

Our central result is the finding that the structural instabilities detected in the various 2:1:4 cuprates always occur at $T_1 = 31 \pm 1$ K and $T_2 = 36 \pm 1$ K, irrespective of the degree of doping, i.e., of the density of free charge carriers. For common metals or alloys, this would be highly surprising: There, lattice structures as well as structural instabilities are governed by the density of the conduction electrons and the shape of their Fermi surface, the martensitic phase transitions observed in $A15$ compounds or Chevrel phases being good examples. In the doped cuprates, however, a straightforward explanation is at hand: Even at doping levels of $x \sim 0.1$, the density of free charge carriers is 1–2 orders of magnitude below that of common metals, resulting in a relatively large screening length. If the observed instabilities are triggered by local or short-range distortions restricted to one unit cell, the charge carriers are unable to screen out these distortions. This point of view is strongly corroborated by recent investigations of the lattice dynamics in $La_{2-x}Sr_xCuO_4$ ($x = 0$ and 0.1) [4] which clearly demonstrate the absence of screening for large wave numbers,

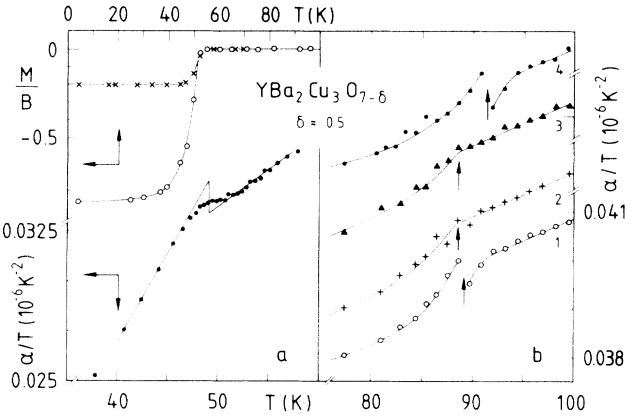

FIG. 3. (a) Upper part: Shielding (○) and Meissner (×) signal for $YBa_2Cu_3O_{6.5}$, taken at $B = 0.2$ and 0.1 G, respectively. Lower part: α/T vs T for the same sample near the superconducting transition at $T_c = 49$ K. (b) α/T vs T for four consecutive runs on the same sample between 75 and 100 K.

i.e., for short-range displacements, in $La_{1.9}Sr_{0.1}CuO_4$. It is no surprise that a similar insensitivity to doping has also been observed for structural instabilities in $SrTiO_3$ [22]. We, thus, infer from our results that the two instabilities detected in our experiments are linked to local distortions, e.g., of CuO_6 octahedra or CuO_4 squares. This is consistent with the fact that these instabilities are also independent of the actual structure of the cuprates (LTO or LTT). Furthermore, the observation of the lattice instabilities in the T' structure of $Nd_{1.85}Ce_{0.15}CuO_4$, i.e., in the absence of apical oxygen atoms, suggests structural changes *within* the CuO_2 planes.

The question of to what extent lattice instabilities are contributing to Cooper pairing can only be answered by a detailed analysis of the phonon modes and their coupling to the free charge carriers. It often turns out that only one phonon branch in some restricted part of the Brillouin zone (e.g., near to the Γ point or to the zone boundary) is affected by the instability, and in that case its contribution to T_c is negligibly small. As discussed in detail in [11], this is actually the case for the O-T phase transition in $La_{2-x}Sr_xCuO_4$. (This very important phase-space argument has been ignored by various authors when suggesting double-well potentials as a possible source for high-T_c superconductivity.) Regarding our observed instabilities, no such conclusions can be drawn so far: Dilation measurements probe only lateral dimensions of the unit cell but cannot provide information on atomic displacements within, the latter being a necessary ingredient for any lattice-dynamics analysis. Such information could be gained by inelastic-neutron-scattering experiments.

However, irrespective of the special nature of pairing, our data suggest a particular mechanism manifested by these lattice instabilities and limiting T_c: For the 2:1:4

system this mechanism, being an intrinsic property of the undoped parent compound La_2CuO_4, arrests the increase of T_c on doping at $T_c^{max} < T_2$. Our additional observation of a structural instability in ceramic $YBa_2Cu_3O_{6.5}$ ($T_c = 49$ K) around $T = 90$ K as well as the disappearance of the Cu^{2+} ESR signal below $T = 90$ K in an oxygen-reduced single crystal of $YBa_2Cu_3O_{7-\delta}$ ($T_c^{onset} \simeq 30$ K) observed by Shaltiel *et al.* [23] lend further support to this speculation.

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[20] If the drop in $\alpha(T)/T$ seen near $T_1 = 90$ K [Fig. 3(b)] were due to the superconducting transition of some minority phase (with $T_c = 90$ K), the most conservative estimate would require a mono-domain (aligned along the a axis) contributing $\simeq 5\%$ to the sample volume [21]. However, the upper bound for such a minority phase set by our SQUID measurement is 1 vol.%. Also, *no* time dependences in $\alpha(T)$, which are very pronounced at $T_1 \simeq 90$ K, were resolved near $T_c = 90$ K in single crystalline O-rich samples [21].

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