Comment on "Tilting of the CuO_6 octahedra in $La_{1.83-x}Eu_{0.17}Sr_xCuO_4$ as seen by ^{151}Eu Mössbauer spectroscopy"

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We discuss the different characteristic time scales of the X-ray Absorption Fine Structure (XAFS), $\tau_{\rm X}$, and Mössbauer spectroscopy (MS), $\tau_{\rm MS}$, techniques for structural determination at small length scales. We show that XAFS and MS can measure *different* local atomic arrangements in $La_{1.83-x}Eu_{0.17}Sr_xCuO_4$ provided the local structural units are dynamical. Combined knowledge from these complementary techniques is used to determine that the local tilts of the CuO_6 octahedra do not vanish with temperature but are dynamic, with the oxygen atoms at the apex positions (O(2)) hopping among local minima of the energy's surface. Evidence is found for a crossover between different time domains in which the hopping time, τ_0, changes from $\tau_0 < \tau_{\rm MS}$ to $\tau_0 > \tau_{\rm MS}$. We conclude that the Mössbauer results [Phys. Rev. B **54**, R800 (1996)], contrary to the authors' conclusions, do not contradict our XAFS results [Phys. Rev. Lett. **76**, 439 (1996)].

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In a recent report [1], Friedrich *et. al* presented Mössbauer data at the La (Eu) site in the title compound as a function of Sr doping and temperature. The measured reduction in the quadrupole interaction parameter, eQV_{zz}, was attributed to changes in the magnitude of the *local* CuO_6 octahedra tilts consistent with the *average* tilts measured by diffraction techniques [2], i.e., they gradually decrease with increasing Sr doping (at T=300K) and with increasing temperature to vanish at the Low Temperature Orthorhombic (LTO) to High Temperature Tetragonal (HTT) structural phase boundary.

XAFS measurements at the La site have determined [3] that the *local* CuO_6 octahedra tilts in $La_{2-x}Sr_xCuO_4$ persist well into the HTT phase and that the LTO to HTT phase transitions include an order-disorder component, i.e., the CuO_6 octahedra become disorder with one another to result in the *average* zero tilt measured by diffraction techniques. Since both MS and XAFS probe the short range order (SRO) in the atomic arrangement about the probe atoms, it was concluded by Friedrich *et. al* that these findings seem to be contradictory to each other. However, what is relevant to the discussion here is that MS and XAFS probe the SRO with a different *temporal* averaging.

The XAFS "clock" is determined by the lifetime of the core hole, excited after an electron is removed from a deep core atomic state of the probe atoms [4] by the incoming X-ray photon. For the La K-edge ($1s$ state) excitation, this lifetime is $\tau_{\mathrm{X}} \sim 3 \times 10^{-17}$ sec, during which the coherence of the outgoing and backscattered photoelectron waves is preserved. Since this time is much shorter than the time for atoms to move (lattice times $\tau_{\mathrm{Latt}} \sim 10^{-13}$ sec), XAFS measures the instantaneous distribution of atoms around the excited probe atoms, averaged over all such atoms.

The Mössbauer "clock" is determined by the lifetime of the nuclear excited state. For the (7/2) state of ^{151}Eu, $\tau_{\mathrm{MS}} \sim 1.4 \times 10^{-8}$ sec and hence the Mössabuer technique averages over a time much longer than both XAFS and lattice times. If the dominant characteristics of the local structural SRO are static, the local environment measured by both techniques should be equivalent. However, if the local structural units are dynamical, e.g., fluctuating tilts of CuO_6 octahedra over different local minima of the potential energy's surface [7], XAFS and Mössbauer may give different answers that will depend on the characteristic time scale of the dynamical phenomena. In fact, these different time averages can be combined to learn about the time scale of dynamical processes in condensed matter [5].

At low temperature, the system settles in its lowest energy state, i.e., Low Temperature Tetragonal (LTT) for the title compound ($0.09 \lesssim x \lesssim 0.25$), with CuO_6 octahedra tilted about $< 110 >$-type axis (*Bmab* space group notation) and LTO for $La_{2-x}Sr_xCuO_4$, with CuO_6 octahedra tilted about $< 100 >$-type axis. Introduction of Sr ultimately leads to the HTT phase which is stabilized at low temperature for Sr concentrations of $x \gtrsim 0.3, 0.21$ for Eu-doped and undoped $La_{2-x}Sr_xCuO_4$, respectively [2,6]. XAFS revealed that, whereas the Sr induced LTO to HTT phase transition at low temperature is displacive up to $x \sim 0.15$, with the local tilt angle decreasing in agreement with the average structure results [3,6], the tilt angle stops changing and fails to vanish at the phase boundary, with the CuO_6 octahedra remaining tilted in the HTT phase. Hence, for $x \gtrsim 0.15$, the CuO_6 octahedra become disorder relative to each other to result in the zero average tilt of the HTT phase. This disorder at low temperature is most likely quasi-static, as the potential barrier to activate dynamical fluctuations of the CuO_6 octahedra is estimated [7] at about 10 meV$\sim$ 120K. Evidence for static structural disorder introduced with Sr doping was recently found from Sr K-edge XAFS measurements [8].

In the case of quasi-static disorder, XAFS and MS should measure equivalent local environments for the probe atoms. As can be seen in Fig. 3 of Ref. [1] for the ($T = 4.2$K, x) curve, the reduction in eQV_{zz} with Sr is not nearly as fast as expected from the average structure results [2]. If the *local* tilt were the same as the *average* one, the $x = 0.26$ sample would have shown a much larger reduction in eQV_{zz} as this sample is very close to the HTT boundary ($x \sim 0.3$). Any reasonable extrapolation of the ($T = 4.2$K, x) curve to eQV_{zz}=-4 mm/sec (the lowest value measured and hence assumed to be the closest to zero tilt angle) will give $x \gg 0.3$. This behavior implies that the local tilts fail to vanish at the phase boundary, consistent with the XAFS results at low temperature.

Now we direct our attention to the temperature dependence of eQV_{zz}. Again it is argued in Ref. [1] that the measured T-dependence is consistent with the *local* tilts following the *average* tilts measured by diffraction. However, Figs. 3 and 4 of Ref. [1] show, e.g., for $x = 0.26$, that eQV_{zz} changes by $\sim$ 40% in going from 150K to 300K. The phase diagram shows [2], however, that this sample is already in the HTT phase at about T=100K so eQV_{zz} should have remained constant above this temperature if the *local* tilts were the same as the *average* tilts, i.e., zero. The big changes observed, however, indicate that the picture presented in Ref. [1] is inadequate.

XAFS showed no change in *local* tilt angle as the temperature is raised in $La_{1.85}Sr_{0.15}CuO_4$ across the LTO to HTT phase transition [3]. The decreasing and ultimately vanishing *average* tilt angle measured by diffraction was attributed to increasing disorder of the CuO_6 with temperature. XAFS can directly measure and quantify disorder in the arrangement of the CuO_6 octahedra *only* if the correlation length of octahedra tilts, ζ, is smaller than the photoelectron mean free path, λ, at photoelectron energies corresponding to the XAFS regime, i.e., 20-1000 eV ($\lambda \approx 5 - 10\,\text{Å}$). However, even if not "visible" for XAFS, disorder in the atomic arrangement must be present if the local structure differs from the average structure. It is important to notice that since XAFS is so fast ($\tau_{\rm X} \gg \tau_{\rm Latt}$), it can not distinguish between static and dynamic disorder. In the case of Ref. [3], no change in *local* tilts was observed in the whole temperature range 10-300 K (LTO$\rightarrow$ HTT boundary $\sim$ 200K) implying $\zeta > 5-10$ Å. If the temperature induced disorder was static, MS and XAFS should have given equivalent answers since they probe similar length scales. That is certainly not the case as the temperature dependence of eQV_{zz} in Ref. [1] is quite large. This implies that the disorder is dynamic.

The following picture arises: at low temperature the *local* tilts are frozen in the LTT configuration. As the temperature is increased thermally activated hopping of the O(2) apical oxygens among neighboring local minima of the energy surface [7] is allowed. Preferential occupation of two of the four equivalent LTT-like minima leads to the LTO average structure while equal occupation leads to the HTT structure with zero tilt average angle [9]. At each temperature, MS will measure an effective eQV_{zz} which will depend on how the temperature-dependent hopping time, $\tau_0(T)$, compares with τ_{MS}. As mentioned before, Fig. 3 of Ref. [1] shows for $x = 0.26$ a significant change in eQV_{zz} from 150K to 300K, even though diffraction shows the HTT phase is present above 100K. Based on the diffraction results, the four LTT sites are equally populated above 100K. The hopping time, however, must be changing from $\tau_0 < \tau_{MS}$ to $\tau_0 > \tau_{MS}$ when going from 150 to 300K, since the measured effective eQV_{zz} decreases in the HTT phase to saturate at about 240K. A low value of eQV_{zz} together with saturation of the $(x = 0.26, T)$ curve in Fig. 3 of Ref. [1] is indicative of MS averaging over the four equally populated sites. The crossover between these two time domains is expected to occur at a lower temperature for higher Sr concentrations as introduction of Sr stabilizes the HTT phase. This is indeed observed in Fig. 3 of Ref. [1] where the $(x = 0.17, 0.22; T)$ curves didn't saturate up to T=300K, even though diffraction shows the HTT phase above 300K and 180K, for $x = 0.17$ and $x = 0.22$, respectively.

To conclude, we showed that the pure displacive model used to interpret the MS results fails to explain several features of the MS data. The MS and XAFS results are not contradictory to each other, but complementary. When the different time scales of both techniques are considered, a dynamical picture for the CuO_6 octahedra tilts is mandatory to reconcile the XAFS and MS results. The hopping time of the CuO_6 apical oxygens between equivalent local minima shows a crossover from $\tau_0 < \tau_{MS}$ to $\tau_0 > \tau_{MS}$ at T$\approx$ 240K for $x = 0.26$ and at $x \approx 0.21$ for T=300K.

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