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Understanding the Role of the Local Structure in the Second Order Structural Phase Transition of $\text{La}_{2-x}\text{A}_x\text{CuO}_4$ ($\text{A}=\text{Ba}, \text{Sr}$)

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ABSTRACT

We have studied the *local* atomic structure of $\text{La}_{2-x}\text{A}_x\text{CuO}_4$ ($\text{A}=\text{Ba}, \text{Sr}$) through the high-temperature tetragonal (HTT) to low temperature orthorhombic (LTO) structural phase transition using the atomic pair distribution function technique. Although long-range ordered tilts disappear in the average structure, we show that significant local tilts persist. We propose an order-disorder model which reconciles both the local and long-range structural observations.

INTRODUCTION

The atomic structure of high-temperature superconductors (HTS) plays an important, and as yet poorly understood, role in their interesting properties [1]. For example, the different structural phases of the first discovered [2] "214" superconductors, $\text{La}_{2-x}(\text{Sr}, \text{Ba})_x\text{CuO}_4$, seem to have a direct affect on their superconductivity [1]. The barium doped compound loses its superconducting properties over a narrow range of doping around $x = 1/8$ [3]. This may be related to the fact that in this material the direction of the collective octahedral tilts which exist is [110] (the so-called LTT-phase) rather than [100] (the LTO phase) as in all the well superconducting variants [1,3]. It has been suggested that in the LTT phase, a critical buckling angle for the tilts destroys superconductivity [4], possibly due to spin-lattice coupling [5]. There may also be a relationship of the tilt direction to the mobility of charge stripes which have been seen in related 214 materials [6].

Most of the structural analyses have been carried out to study the average long-range order of the tilts using conventional crystallographic methods. This gives the average, long-range ordered tilt magnitude, $\langle\theta\rangle$. If there is disorder in the tilts, then $\langle\theta\rangle$ will not be the same as the real, local tilt magnitude, $|\theta|$. However, it is the *local* tilt amplitude and direction which have the largest effect on the properties, for example, through spin-lattice coupling.

To study the *local* tilts directly it is necessary to use a local probe such as the pair distribution function analysis (PDF) of powder diffraction [7,8] data or XAFS [9]. Such studies indicate that significant disorder exists in the tilts [10,11,12,13] and that locally the tilts may even be in a different direction than the average tilts [11]. It is clearly important to fully characterize the nature of the local tilts.

Figure 1: Schematic view of the tilt distortions. Top part of the scheme gives side view of the CuO_6 octahedra in the HTT and LTO phases, showing the local tilt angle. Shaded circles are in-plane oxygen ions (O1) and the black circles are the apical oxygens (O2). The top-view of the same tilts is shown schematically below. Note that the structure in the top view is 45° rotated with respect to the side view.

Figure 2: Schematic view of the different tilt models: (a) HTT, (b) HTTLS, (c) LTO, and (d) LTOLS, which are described in the text. (a) and (c) are the conventional displacive models. (b) and (d) are the order/disorder tilt models, where (d) is actually identical to (c). Figures give the top view of a few neighboring CuO_6 octahedra indicated by the dashed lines. Crosses indicate the average positions of the apical oxygen atoms (O2) obtained crystallographically. Squares indicate the positions of atoms in the local structural models. These displaced sites have partial occupancies ranging from zero to 1 (see text). The size of the O2 displacements are greatly exaggerated.

In this paper, we study the behavior of the *local* tilts as the sample goes through the transition from the high-temperature tetragonal (HTT) phase to the low-temperature orthorhombic (LTO) phase using the PDF method. We find that, despite the fact that the average tilts disappear at this phase transition, the local tilts remain with essentially their full amplitude. This agrees with earlier qualitative observations from the PDF [10,12] and recent XAFS data [13]. This suggests that the LTO-HTT phase transition is order-disorder in nature rather than displacive. Furthermore, we find that there is significant lateral tilt disorder in directions perpendicular to the average tilts suggesting large amplitude static or dynamic disordered displacements perpendicular to the tilts.

STRUCTURAL MODELS

The Cu atoms reside at the centers of oxygen octahedra that form a 2-D plane by corner sharing oxygen atoms which lie on the equatorial planes of the octahedra (O1). The apical oxygen atoms (O2) are at the top and the bottom position of each octahedron (Fig. 1).

Figure 3: The [023] superlattice peak for $\text{La}_{1.85}\text{Ba}_{0.15}\text{CuO}_4$ sample, compared for 10 K (solid line) and 325 K (dashed line) data. Peak clearly disappears in the high temperature phase of the material. Lines are guides to the eye. The background slopes as a result of the incident spectrum. Neutron data collected at Manuel Lujan Jr. Neutron Scattering Center (MLNSC), Los Alamos National Laboratory.

Figure 4: Temperature dependence of the square of the octahedral tilt-angle amplitude, determined independently from both O1 (triangles) and O2 (squares). This represents the *local* behavior of the octahedra. Temperature dependence of the superlattice peak intensity (open circles) is shown to compare the local with the long-range behavior of the octahedral tilts.

For the case of the LTO model, octahedra rotate by 3.5° - 4° about the [100] axis, causing displacements of the apical oxygens in [010] directions. In the HTT model the octahedral rotations disappear. In this average crystallographic picture the HTT-LTO transition can be thought of as being a "displacive" transition. This is shown schematically in Figs. 2(a) and (c).

While, in the "displacive" representation certain single fully occupied atomic positions are displaced, in the "order-disorder" representation these atomic positions are replaced with two (or more) atomic positions that are partially occupied, and whose occupancies add up to one. The occupancies of the new atomic positions, as well as their spatial coordinates can be varied, and their linear superposition should be considered in order to obtain the average atomic position. This is shown schematically in Figs. 2(b), and (d) as the HTTLS, and LTOLS models, where the LS stands for "linear superposition". Two atomic positions, situated apart from each other along the [010] direction, replace each apical oxygen site. The HTTLS model assumes equal occupancies of 0.5 for each displaced site. In the LTOLS model, at the lowest temperature, the occupancies are set to zero and 1, recovering the LTO model.

RESULTS

The HTT-LTO structural phase transition in the average structure is clearly evident in our data from the disappearance of the [023] superlattice peak shown in Fig. 3. The intensity of

the peak is proportional to $\langle \theta \rangle^2$, and is an order parameter for the HTT-LTO phase transition. However, we would like to stress that it gives the *long-range average* octahedral tilt, $\langle \theta \rangle$, and does not necessarily reflect the actual local tilt angle, $|\theta|$.

We have obtained the local octahedral tilt amplitude from full profile refinements of the PDF. This approach is described elsewhere [8,14]. An independent measure of the tilts can be obtained from measured displacements of either O1 or O2. If the octahedra are tilting rigidly these values will be the same. The temperature dependence of the tilts is shown in Fig. 4 as obtained from the barium doped sample. It is clear that the local tilt amplitude, $|\theta|$, is temperature independent and significant local tilts persist well into the high-temperature phase.

The "order-disorder" LS-models reconcile both the local and long-range results. However, at all temperatures large displacement (thermal) factors are observed in directions perpendicular to the [010] tilts which suggests that there is significant tilt amplitude perpendicular to the LTO tilt directions. We find that models which allow for displacements along both [100] and [010] directions give better agreement than the displacive or LS models described above for the same number of fitting parameters.

CONCLUSION

The PDF results suggest that the HTT phase in $\text{La}_{2-x}(\text{Sr,Ba})_x\text{CuO}_4$ consists of disordered, and possibly dynamically fluctuating, finite octahedral tilts. On the basis of the observations we therefore suggest that in the HTT phase, finite tilts persist but the axes of the CuO_6 octahedra precess about the *c*-axis of the crystal. Because the octahedra share corners, this must be a collective precessional mode of low energy.

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