Structural Ground-State of La$_2$CuO$_4$ in the LTO Phase: Evidence of Local Disorder

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We present neutron scattering data which indicate that the local structure of La$_2$CuO$_4$ in the LTO phase is disordered. Data from two different diffractometers are compared and systematic differences between the pair distribution functions (PDF) of the LTO model and the data are reproduced in both cases.

1. INTRODUCTION

At high temperature and/or high doping La$_2$-xA$_x$CuO$_4$ (A=Ca, Sr, Ba), has a tetragonal structure (HFT phase) [1] and the CuO$_2$ planes are flat. On cooling the planes distort (LTO phase): they strain orthorhombically and they buckle due to a collective tilting of CuO$_6$ octahedra [1]. However, recent studies of the local structure reveal that this behavior represents an average and that, locally, the tilt persists into the tetragonal phase [2,3]. Furthermore, in the Ba doped material we showed that in the LTO phase at low temperature the local tilts are homogeneous and that the crystal structure of the LTO phase is, itself, an average of locally disordered tilts [3]. In this model the ground-state structure of the LTO phase is a disordered "tilt phase". Clearly it is important to establish the validity of this observation. Here we report measurements of the local structure of undoped La$_2$CuO$_4$. This is a very stringent test of the ground-state structure of the LTO phase, since in La$_2$CuO$_4$ there are no impurities and therefore no extrinsic driving force for disorder or tilting behavior.

2. EXPERIMENTAL

The sample was prepared by solid state reaction from La$_2$O$_3$ and CuO and annealed in a reducing atmosphere of Ar. The resulting sample had a Néel temperature of 305K indicating that it is very close to being perfectly stoichiometric. Neutron powder diffraction data were collected from the same sample using the Spedal Environmental Powder Diffractometer (SEPD) at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory and using the High Intensity Powder Diffractometer on the Manuel Lujan Jr. Neutron Scattering Center (LANSCE) at Los Alamos National Laboratory. Data were collected at 10K in each case. Pair distribution functions (PDF), G(r), were obtained from the data using a standard procedure [4]. Local structural information is obtained from the PDF by refining structural parameters in direct analogy with the Rietveld method for powder diffraction data [4].

3. RESULTS

The PDFs from the La$_2$CuO$_4$ data are shown in Fig. 1 as dashed lines. The upper curve is the data from the SEPD; the lower curve is the PDF from the identical sample measured using the SEPD. Both sets of data were measured at 10K. Peaks in G(r) correspond to atom-atom pair correlations in the sample; for example, the first physically allowed peak is from the copper to copper oxygen (O1) nearest-neighbor correlation at 0.19 nm which can be seen clearly in the models and in the data of Fig. 1. The structure which can be seen in the region of the PDF below 0.19 nm is an experimental artefact. It originates primarily...
from imperfect spectral and background corrections to the data. This systematic noise dies out quickly with increasing $r$ and at higher $r$ values $(r > 0.8 \text{nm})$ the main uncertainty in the data comes from random errors [5]. The source of these systematic errors are different between the two diffractometers we used since details of the source spectrum and instrument background differ. This is evident in Fig. 1 where the structure in the unphysical region of the PDF is different between the data-sets. Nonetheless, the data in the physical region of the PDF, which is dominated by the signal from the sample, is highly reproducible between the data-sets as it should be.

Structural models have been refined to the data to understand the local structure of the LTO phase. The structural parameters which were allowed to vary were lattice parameters, isotropic thermal factors and atom positions. Atom shifts were constrained by the Abrikos space-group symmetry of the LTO crystallographic model. There were a total of 18 independent variables; the data were refined over a range from 0.1 to 1.0 nm. Details of the refinement will be published elsewhere [6]. The structural parameters obtained from the fully converged fits to the two data-sets reproduced each other very well [6]. However, the overall fit to the data is inadequate in a number of places in the PDF, for example, around 0.25, 0.45, 0.65 and 0.75 nm. It can be seen in the difference curves shown in Fig. 1 that the discrepancy, seen as features in the difference curves, reproduce very well between the two data sets. This indicates that the discrepancy between the model and the data in these regions originates from the signal from the sample and is not an experimental artefact. There are real discrepancies between the fully ordered LTO model and the real local structure of La$_2$CuO$_4$ in the LTO phase at low temperature. The nature of these differences are being investigated and will be reported in the future but there is good evidence that the orthorhombic tilts are not fully ordered LTO-like tilts.

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REFERENCES