ESRF	Experiment title: Hole Saturation and Structural Phase Segregation in Overdoped $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$	**Experiment number:** **HE 2955**
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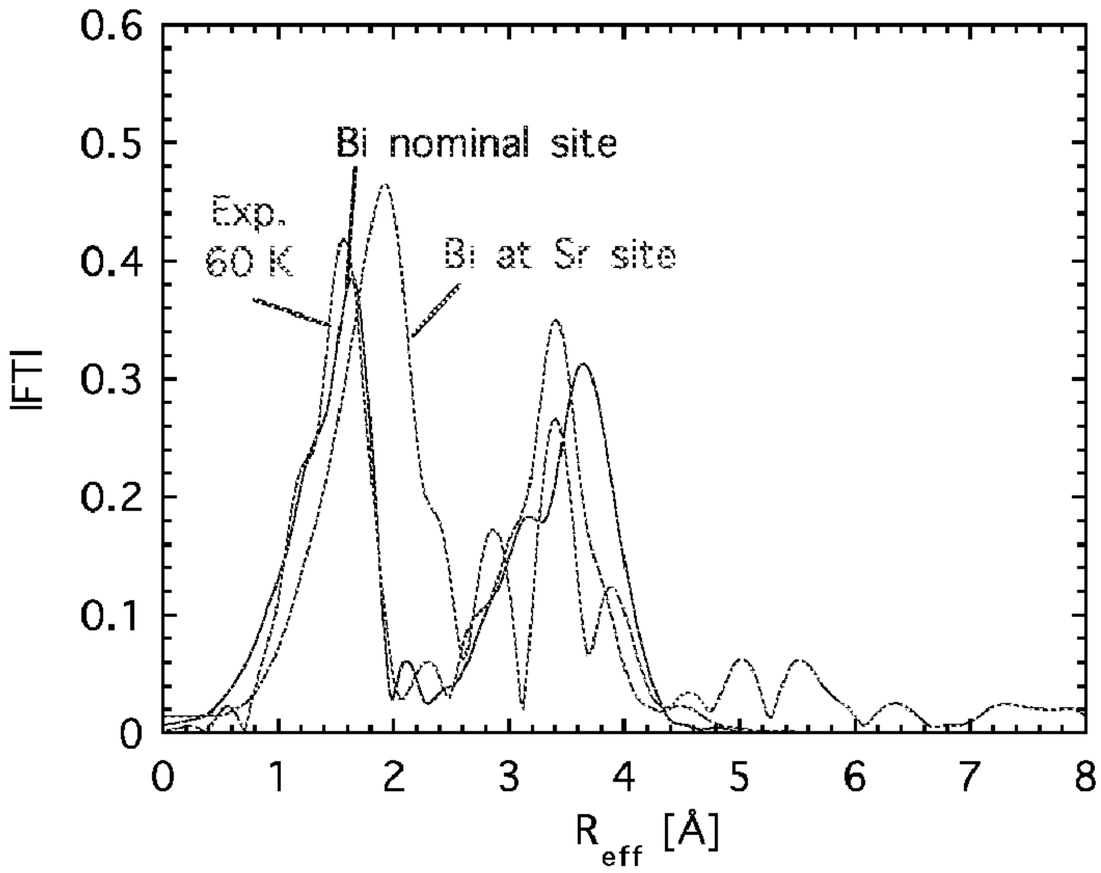
Report: We have measured the Sr -K (16105 eV) and Bi-L_{III} (13418 eV) EXAFS of three overdoped $Bi_2Sr_{2-x}La_xCuO_{6+\delta}$ (x = 0.22 -0.26) single crystals (size ≈ 2 x 2 x 0.1mm^3) in transmission geometry with the polarization vector **E** || **a, b**. Although the usable k -range of the Sr-K EXAFS is restricted to about only k = 8 Å^{-1} by the Bi-L_I edge (16387 eV) , simulations of the Radial Distribution Functions (RDF) had indicated sufficient resolution to extract the expected structural effects from hole saturation in the Sr-O1(planar), Sr-O2(apical), and Sr-Cu coordination shells. In the experiment we found that about 600 eV beyond the Bi-L_{II} edge (15710 eV) the Sr-K EXAFS are still strongly affected by Bi EXAFS. A monochromator glitch in the middle of the limited k-range added a further experimental constraint to the data quality.
We therefore focussed on scans of the Bi-L_{III} EXAFS. Spectra up to k = 16 Å^{-1} were recorded at low temperatures, T = 30 - 300 K. Usable data were obtained from one crystal with x = 0.22 (#2, previously investigated at the La-K edge). From EDX this crystal was found to exhibit a Bi : Sr nonstoichiometry of 0.15 and a hole concentration of 0.18 like optimum doped crystals. Nominally 15% of the Sr sites should be substituted by Bi, competeing with about the same fraction of La dopants at this site.

Surprisingly the measured RDF does not coincide with that from a weighted superposition of RDFs at its nominal crystallographic Bi B-site and the Sr A-site. Within the accuracy of the data Bi does not occupy the Sr-site. Fig. 1 compares the experimental Fourier spectrum (60 K) with model calculations using the FEFF code. The left peak in the experimental Fourier spectrum (green) is found to correspond to the Bi-O cluster at the Bi B-site. Here Bi exhibits an almost central position in its nearest oxygen environment deviating strongly the average crystallographic structure - where the Bi-O3 bond lengths range from 2.2 - 3.3 Å. The right peak in the experimental Fourier spectrum contains most of the Bi-metals (Bi, Sr) bonds. It seems that the Bi-Bi bonds are significantly shorter than to be expected from the average crystallographic structure.



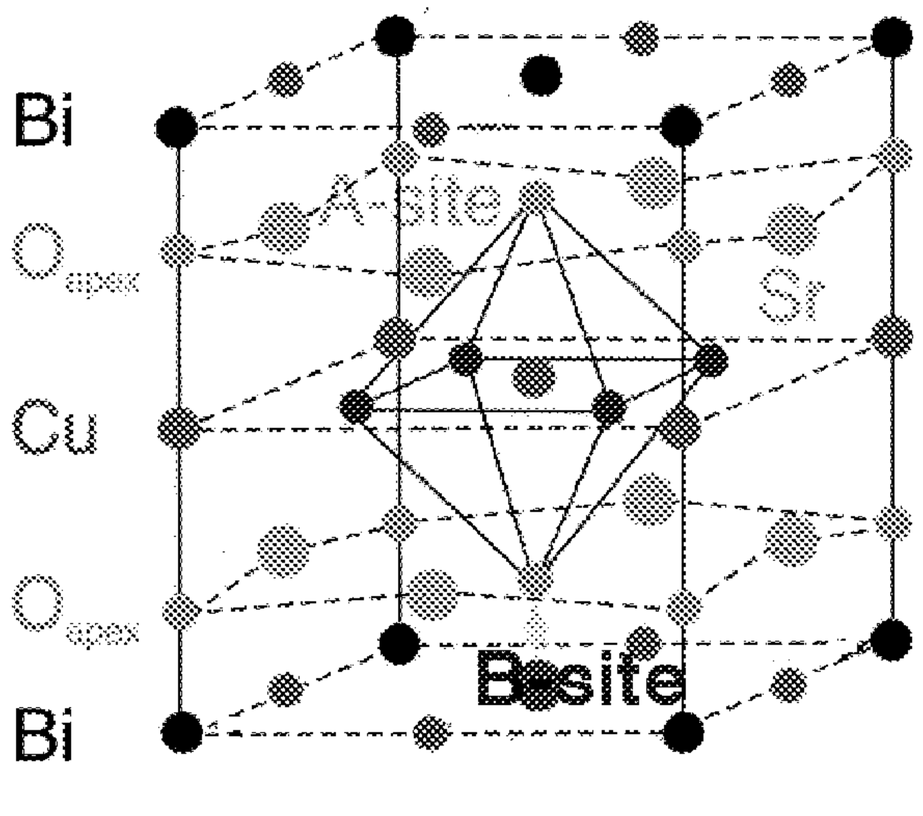
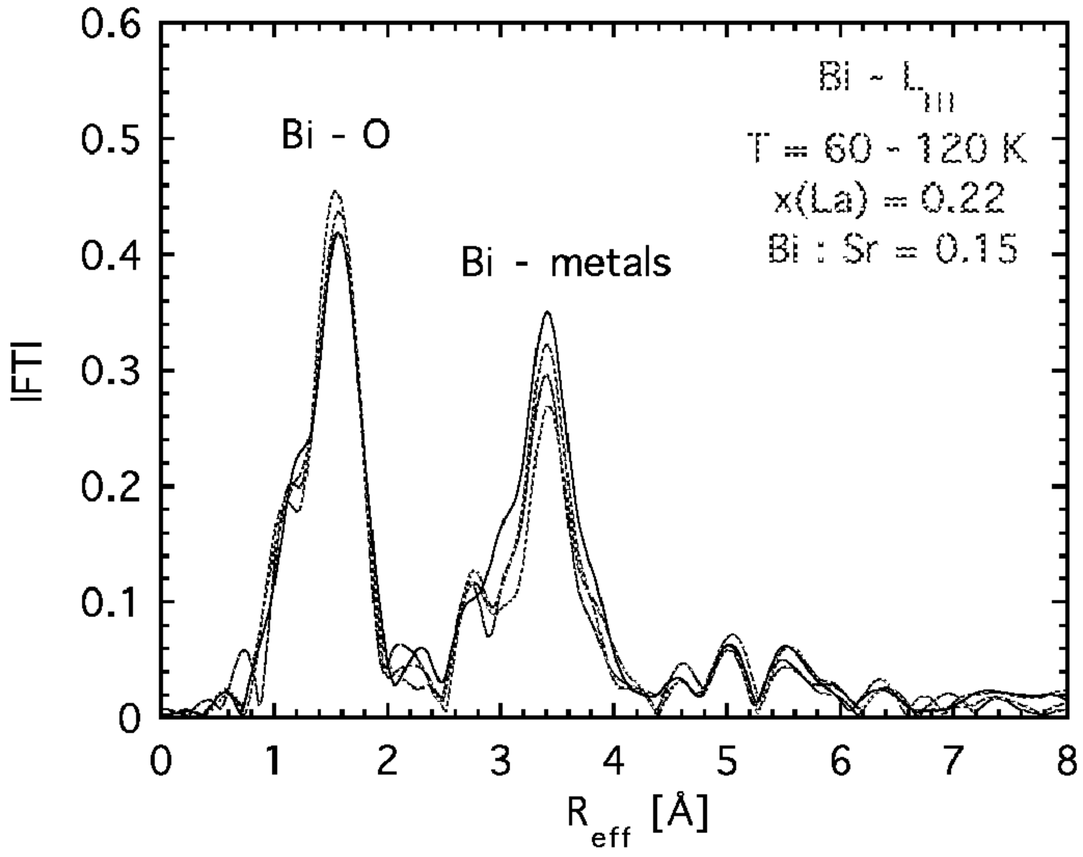


Fig. 1 *Left*: Fourier transform spectrum spectrum of Bi-L_{III} recorded from an overdoped x=0.22 crystal (**E || a, b**) compared with two simulations: Bi at the nominal site, and Bi at the Sr site. The first peak (Bi-planar oxygen and copper, ...) is shifted to higher *R* and cannot be adjusted to the experimental data. A fraction > 5% Bi at the Sr site must be excluded, which is in conclict with the 15% Bi : Sr nonstoichiometry. *Right*: Schematic structure with the two possible sites of Bi. At the A-site Bi competes with the La dopant.



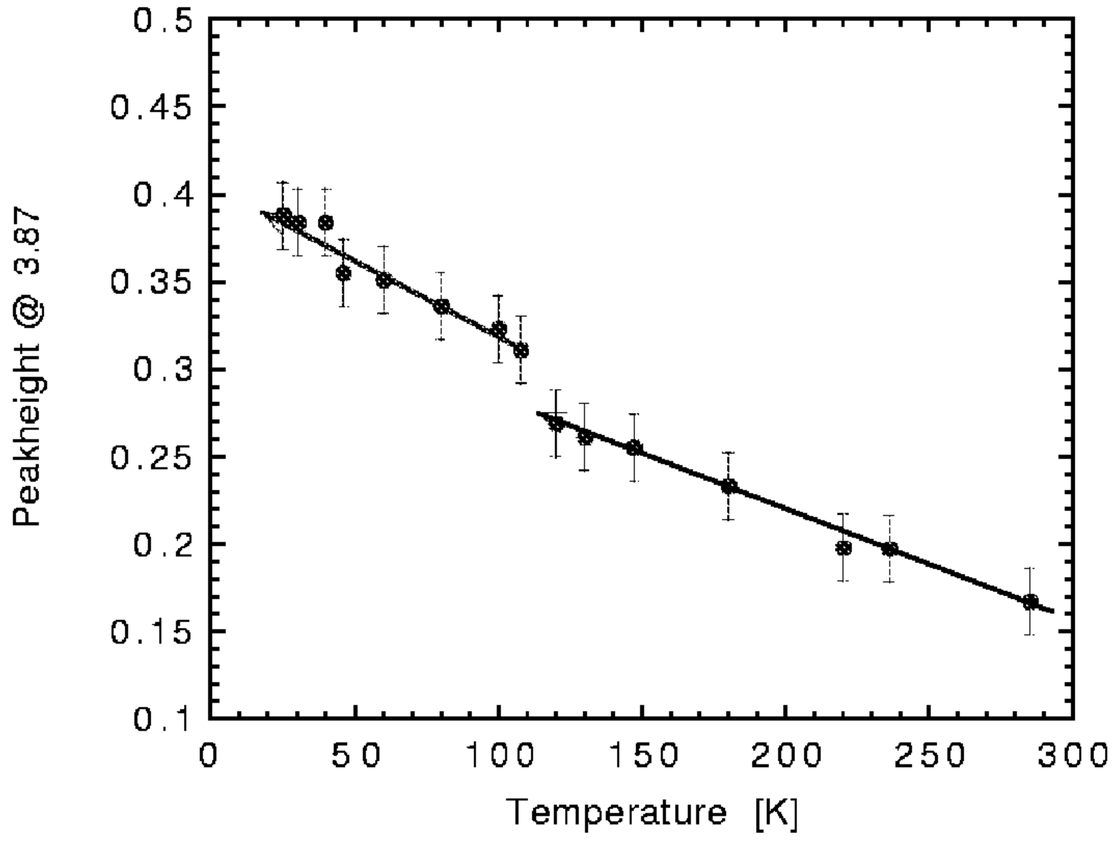


Fig. 2 *Left:* Fourier transform spectra from Bi-L_{III} (overdoped x=0.22 crystal) at different temperatures between 60 and 120 K. Note the temperature effects in the Bi-metals (Bi, Sr) peak. *Right:*. The temperature dependence of the peak height at 3,87 Å. At 112 K occurs a discontinuity and a change of slope in the Bi-metals environment of Bi at its nominal B-site.

The Bi excess of typically 15% systematically found in overdoped BSLC seems to form a different phase than simply BLSC with a fraction of Bi at the Sr A-site. If Bi does not compete with La at the A-site, the Bi-excess most likely forms another Bi-containing phase. Measurements from the Bi : Sr stoichiometric optimum doped regime and the Bi deficient underdoped regime will answer this question. Advantageously by a differential analyis. Doping of BLSC is a complex multiparameter problem; Bi deserves special attention as a dopant competeing with La and oxygen.