	Experiment title: Electronic Inhomogeneity and Competition of the La and Bi Dopants for the A-Site in the Superconductor $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+\delta}$	Experiment number: HE 3233
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Report: We have recorded the Bi- L_{III} (13418 eV) EXAFS of superconducting $\text{Bi}_2\text{Sr}_{2-x}\text{La}_x\text{CuO}_{6+x}$ from an overdoped (OD, $x = 0.22$, $T_c=15$ K, 85% orthorhombic superstructure), a weakly overdoped (OD/OPT, $x = 0.31$, $T_c=13$ K, 80% orthorhombic superstructure), and two strongly underdoped (UD, $x=0.8$, $T_c= 5$ K, 100% monoclinic superstructure) single crystals (typical size $\approx 2 \times 2 \times 0.1\text{mm}^3$). The scans were performed in the transmission and total electron yield (TEY) modes with the polarization vector $\mathbf{E} \parallel \mathbf{a}, \mathbf{b}$. Beam harmonics could be eliminated by a double Si-mirror in the non focussing set-up. A Motor Controlled (MOCO) feedback system stabilized the operation of the double crystal monochromator at the maximum of the rocking curve. The absorption contrast at the Bi- L_{III} edge was adjusted to typically $\Delta\mu d \approx 0.45$. We obtained usable data between $T = 30$ and 300 K almost only in the transmission geometry up to $k = 12.5 \text{ \AA}^{-1}$. The limit of the usable k -range was mainly due to low frequency modulations in the energy dependence of the absorption background at high k , not to counting statistics. The data analysis was carried out using the IFeffit and FeffFit v.8 software.

We find no sizable occupation of the crystallographic Sr site (in the “A-site” doping layer) by Bi^{3+} in La^{3+} -doped $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$, neither in the OD, nor in the UD regimes. Sr^{2+} is exclusively substituted by La^{3+} . Within the accuracy of our data ($< 5\%$) Bi^{3+} is found *not* to compete with the La^{3+} dopants for the crystallographic Sr site, although their ionic radii are nearly identical. In the entire doping range Bi^{3+} resides at the nominal “B-site” layer which may be directly verified by inspection of the first peak (Bi- m O) in the Fourier transform (FT) spectra (Fig. 1). The experimental Bi- m O peak corresponds to the one calculated from the average crystallographic data, but indicating a central symmetric position of Bi^{3+} in the distorted oxygen polyhedron. The second peak in the FT spectra is nominally dominated by the planar 1-leg Bi-Bi ($R_{eff} \approx 3.4 \text{ \AA}^{-1}$) scattering in the “B-site” layer, nearly degenerate with much weaker 1-leg Bi-Sr scattering connecting the “B-site” and “A-site” layers. Since La substitutes Sr, this peak is expected to be strongly doping dependent. We observe at high concentrations of La ($x=0.8$, UD) a strong reduction of the peak

height, quite unexpected since La ($Z=57$) is a much better photoelectron scatterer than Sr ($Z=38$). Preliminary modelling shows that accidental extinction of the Bi-Bi and Bi-La/Sr scattering can be most likely excluded.

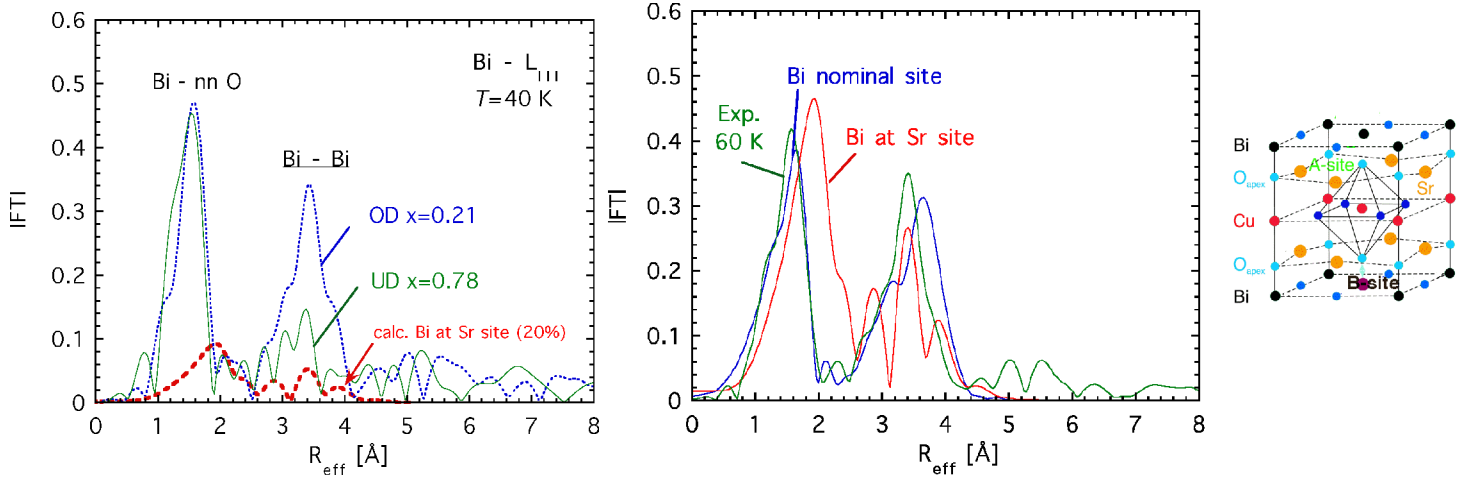


Fig. 1 *Left*: Bi- L_{III} FT spectra recorded ($\mathbf{E} \parallel \mathbf{a}, \mathbf{b}$) from OD ($x=0.21$, dotted blue) and an UD ($x=0.78$, drawn out green) crystals. Partial occupation of the Sr site by Bi (shown for 20%, thick red dashes) would bulge the first peak around $R_{eff} \approx 1.9 \text{ \AA}$, which is not observed. *Middle*: Comparison of calculated FT spectra with Bi at the nominal La/Sr sites with a 60 K OD experimental spectrum *Right*: CuO_6 octahedron sandwiched between the “A-site” and “B-site” doping layers.

Alltogether these findings point towards a crucial role of the defect oxygen atoms being on track of the heterovalent cation ($\text{La}^{3+}/\text{Sr}^{2+}$) substitution. A possible mechanism for doping by interstitial oxygen atoms in the track of the $\text{Sr}^{2+}/\text{La}^{3+}$ heterovalency is summarized in Fig. 2. Charge neutrality for fixed Cu^{II} oxidation requires incorporation of $0 < \delta < 0.5$ oxygen atoms for $0 < x(\text{La}) < 1$ (non oxidizing O^B), far apart from the CuO_2 layers in the Bi “B-site” doping layer. Doping and metallicity of nominally Cu^{III} requires additional oxygen defect atoms (oxidizing O^A), close to the faces of the CuO_6 octahedra, that is in the Sr “A-site” doping layer. As a result in the UD regime the Bi “B-site” doping layer gets rich of *interstitial* oxygen atoms (most likely forming a ion complex with La), but poor of them in the La-poor OD regime. We propose the thus formed La-O ion complexes as possible source for the apparent structural disorder in the Bi “B-site”.

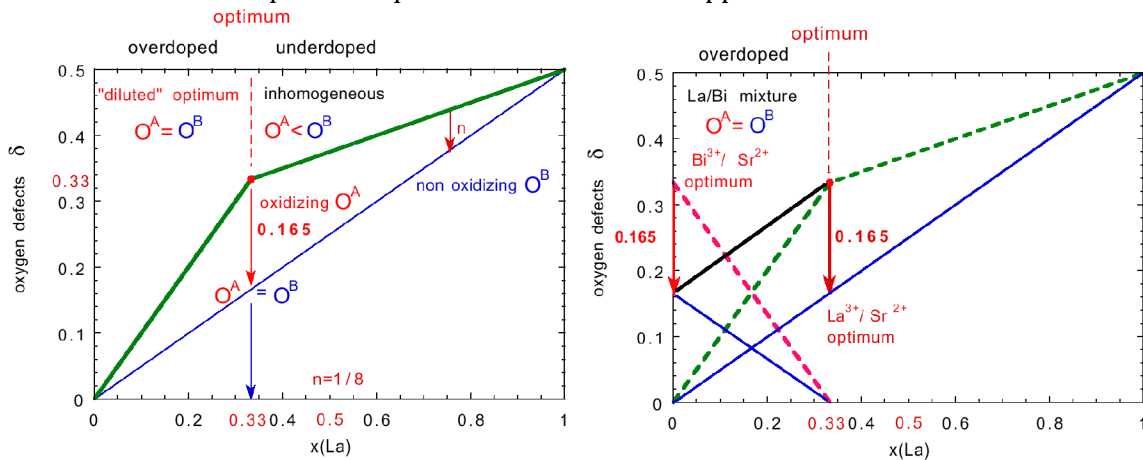


Fig. 2 *Left*: Partition of the oxygen defect atoms between the Bi “B-site” (O^B) and Sr “A-site” (O^A) doping layers dependent $x(\text{La})$. *Right*: Number of holes saturates at 0.165 through chemical phase separation in the La-poor ($x < 0.33$) OD regime. Transition to purely oxygen doped $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ without La-O ion complexes.