



	Experiment title: Investigation of the Electronic Topological Transition on Multiferroic CuO under pressure by X-ray Absorption Spectroscopy.	Experiment number: HC3339
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Shifts:	Local contact(s): Vera Cuartero	<i>Received at ESRF:</i>
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Report:

CuO has renewed the interest of condensed matter community in the last years due to the recent discovery of multiferroicity (MF) at room temperature (RT) and high pressure (~4 GPa). [1] The origin of MF under these conditions is proposed to be the large super-exchange correlations, J , specially the second-neighbour interaction of the edge-sharing chains. [2] An anomaly on the dielectric constant is found around 4.4 GPa and ferroelectricity is proposed to be correlated with strong dynamic O-ion displacements. The macroscopic response of the system appears then to be closely linked to its local structural and electronic properties. However, there is still a great controversy, as recent calculations estimate that the multiferroic state would be fulfilled at 38 GPa and 260K [3].

X-ray absorption spectroscopy (XAS) measurements at Cu K edge were undertaken on CuO powders at high pressure up to 17 GPa. The experiment was performed at BM23 beamline at the ESRF, with a double crystal Si (111) monochromator and Kirkpatrick-Baez mirrors to focus the monochromatic x-ray beam down to $5 \times 5 \mu\text{m}^2$, with a Pt coating and set at an angle of 6 mrad to reject high order harmonics. The powdered sample was charged on a nano-polycrystalline diamond anvil cell (to avoid glitches from the anvils), with ruby chips as pressure markers. Neon gas was used as pressure transmitting medium.

The Cu K-edge X-ray absorption near edge structure (XANES) spectra are showing two clear features on the pre-edge region (A, at 8978 eV at ambient pressure) and at the edge (B, at 8986 eV at ambient pressure), as can be seen in figure 1 (a). A peak is normally ascribed to quadrupole transitions to empty d states [4], and it does not show any evolution along the whole pressure range; however B structure mean position changes with P as the chemical shift of the edge does. B feature is normally ascribed to electronic $1s \rightarrow 4p_{xy}$ transitions accompanied by charge transfer effects from the ligand (O) to the metal. The evolution of the Cu-O distances was obtained from the analysis of the extended X-ray absorption fine structure (EXAFS) spectra. There local environment of Cu consists of square-planar CuO_4 units, and 2 O atoms further away (2.72 Å), followed by Cu next-nearest-neighbours. The Cu-O shorter distances barely change below 6 GPa, but a contraction of the

Cu-O distances takes place above 6 GPa, concomitant to a change on the tendency on the chemical shift evolution on the XANES region of the spectra, as shown in figures 1 (b) and (c). The Cu-O long distance is highly reduced along the whole pressure range, from 2.72 down to 2.4 Å. The Debye-Waller factors barely change along the whole pressure range. Furthermore, multiple scattering calculations have been performed to simulate the XANES under the Green formalism in the muffin-tin approach, considering the Hedin Lundqvist exchange correlation potential and including the Hubbard correction. The dipole approximation on a 6 Å cluster is enough to nicely reproduce the low and high pressure spectra.

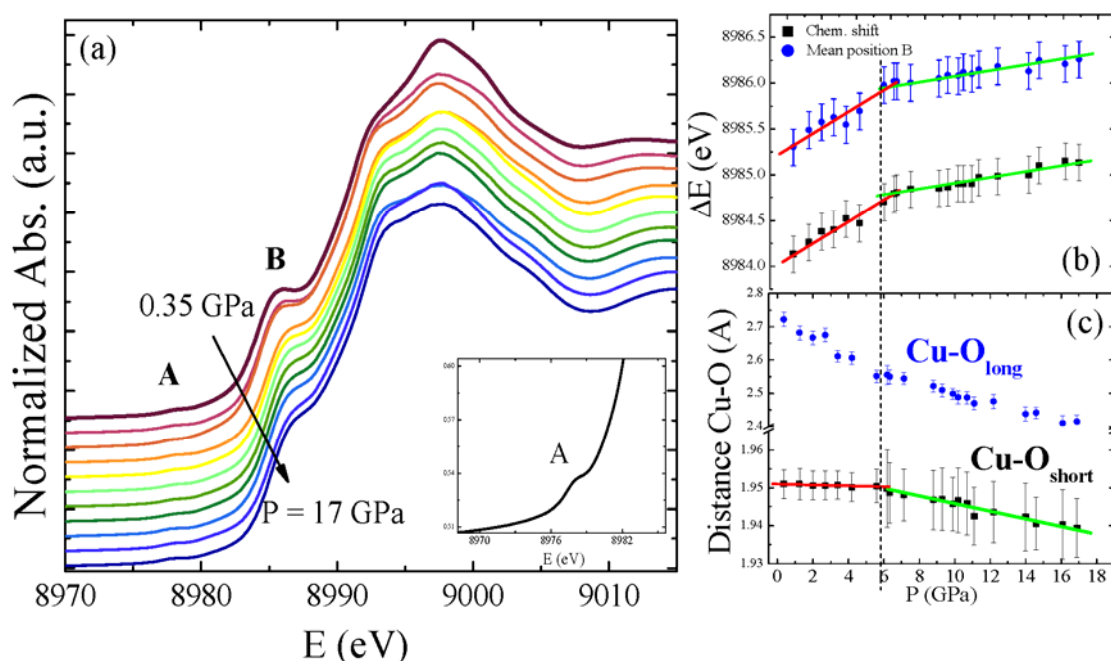


Figure 1: (a) XANES spectra shifted in vertical scale normalized to the jump at different pressure points. (b) Pressure evolution of the chemical shift and (c) Cu-O distances.

Our results from XANES and EXAFS analysis indicate that above the critical pressure of 6 GPa there is a strong effect of first neighbours distances contraction, that favours charge transfer in between the metal and the ligand, whose dynamics could potentially enhance electric polarization. [5]

- [1] R. Jana et al., *Sci. Rep.* **6**, 31610 (2016).
- [2] X. Rocquefelte et al., *Nat. Commun.* **4**, 2511 (2013).
- [3] D.P. Kozlenko, *Phys. Rev. B* **95**, 054115 (2017).
- [4] O. Sivr et al., *J. Synchrotron Rad.* **8**, 235 (2001).
- [5] A. S. Tayi et al., *Nature* **488**, 485 (2012)