



Experiment title: Space resolved Cu-K edge XANES, chemical analysis and lattice parameter determination of micrometric Bi-2212 whiskers: an attempt to correlate local structure, composition and Cu oxidation state with long range superconductivity

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Single crystals of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ (Bi-2212) high- T_c superconductor can be grown in samples whose lengths ($\geq 500 \mu\text{m}$) is much greater than both their width and their thickness (whiskers). These kinds of samples have recently attracted remarkable interest from the point of view of both basic and applied physics. In fact, they have proved to be suitable systems for the study of the excess conductivity above T_c and of the transport properties along the c axis because of their high quality and small sizes.

It is known that that Bi-2212 whiskers can undergo a significant increase in the in-plane resistivity when aged at RT on a two-year time scale, most likely because of the oxygen loss. Variations in the O non-stoichiometry of Bi-2212 whiskers must be accompanied by a change of the Cu oxidation state in order to guarantee the electrostatic neutrality of the crystal. With this aim we have performed μ -XANES experiments at ID22. To verify whether the variation of the local Cu oxidation state, induced by O diffusion, is accompanied by a cation migration or not, x-ray fluorescence (XRF) has also been measured with the same spatial resolution of $1 \mu\text{m}$ (vertical) x $4 \mu\text{m}$ (horizontal).

In order to better appreciate the expected variation of the Cu oxidation state induced by O migration, samples were grown 40 days before the synchrotron measurements and aged at ambient conditions. High quality single crystals were selected at the optical microscope and either mounted on a glass capillary, for synchrotron measurements, or electrically contacted by Ag thermal evaporation and diffusion. The single-phase character of the samples was checked by standard electrical resistance R vs. the temperature T . The typical $R(T)$ behavior is reported in the inset of Fig. 1, which shows $T_c=79.1 \text{ K}$.

Fig. 1 reports the normalized XANES spectra, collected in fluorescence mode with a sampling step of 0.5 eV across the Cu K edge. By moving from the central position to the crystal edge, we observe an increase of the white line intensity of 10% and a red shift of the edge higher than 2 eV. This indicates an important gradient of the oxidation state of Cu along the b direction. At the crystal edges, where the atomic O^{2-} anions are supposed to recombine to give O_2 molecules leaving the samples (and their 4 electrons), a significant Cu^+ enrichment has been observed. As the energy shift between the K edge of pure Cu^+ and Cu^{2+} Model compounds is typically 5.0–6.5 eV, assuming that in the central position of the crystal we still have a homogeneous population of Cu^{2+} cations, a fraction of about 30% of Cu^+ is estimated at the edges. This experimental evidence suggests that, in the O loss process, the rate-determining step is the O^{2-} migration to the crystal surface and not the O_2 recombination at the surface.

To verify whether the combined O migration and Cu^{2+} reduction has any effect on the local cation distribution, we have collected a $90\text{-}\mu\text{m}$ (vertical) x $32\text{-}\mu\text{m}$ (horizontal) two-dimensional XRF map by a spatial sampling of $2 \mu\text{m}$ (vertical) x $4 \mu\text{m}$ (horizontal). To avoid any systematic error related to the XRF

counts to chemical stoichiometry conversion, we decided to analyze the $r(\text{Cu,Bi}) = \text{Cu}(\text{K}\alpha)/\text{Bi}(\text{L}\beta)$, $r(\text{Cu,Sr}) = \text{Cu}(\text{K}\alpha)/\text{Sr}(\text{K}\alpha)$ and $r(\text{Bi,Sr}) = \text{Bi}(\text{L}\beta)/\text{Sr}(\text{K}\alpha)$ count ratios. See Fig. 2 for the $\text{Cu}(\text{K}\alpha)/\text{Bi}(\text{L}\beta)$ ratio, where a lateral Cu enrichment is apparent. To quantify this enrichment we have averaged these ratios in central and in lateral positions, defining $\langle r_c(\text{A,B}) \rangle$ and $\langle r_l(\text{A,B}) \rangle$ (A, B = Cu, Bi, and Sr), respectively. Being $\langle r(\text{A,B}) \rangle$ the value of the ratio averaged over the whole map, the following three inhomogeneity factors $f(\text{A,B}) = [\langle r_l(\text{A,B}) \rangle - \langle r_c(\text{A,B}) \rangle] / \langle r(\text{A,B}) \rangle$, were obtained: $f(\text{Cu,Bi}) = 0.10$, $f(\text{Cu,Sr}) = 0.07$ and $f(\text{Bi,Sr}) = -0.05$.

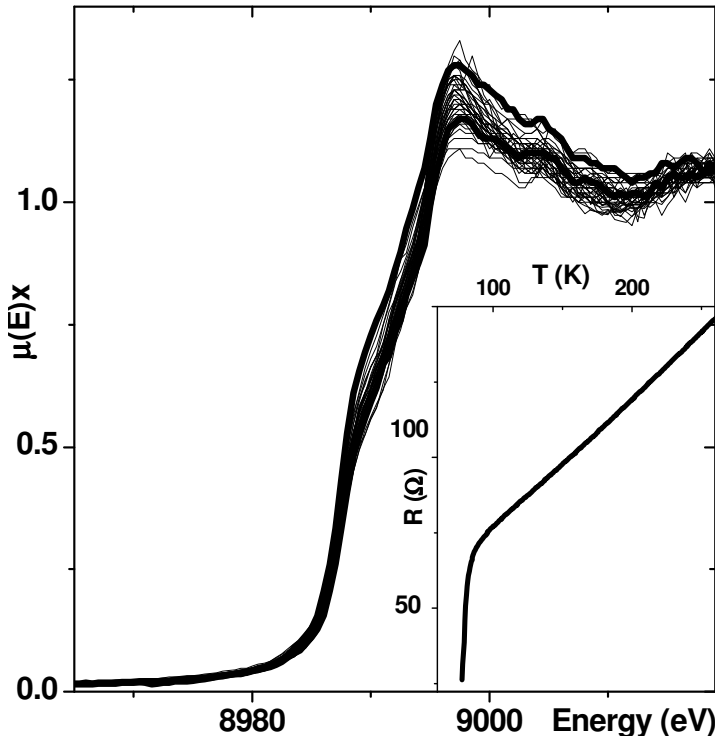


FIG. 1. Normalized XANES spectra collected on different positions of the Bi-2212 whisker. A shift of the edge up to 2.5 eV, accompanied by a modification of the white line intensity, clearly testifies an important modification of both the oxidation and the coordination state of Cu along the crystal. Bold curves represent spectra collected in central and in near-edge positions along the b direction, the others representing intermediate positions. The inset reports the R vs T curve showing $T_c = 79.1$ K.

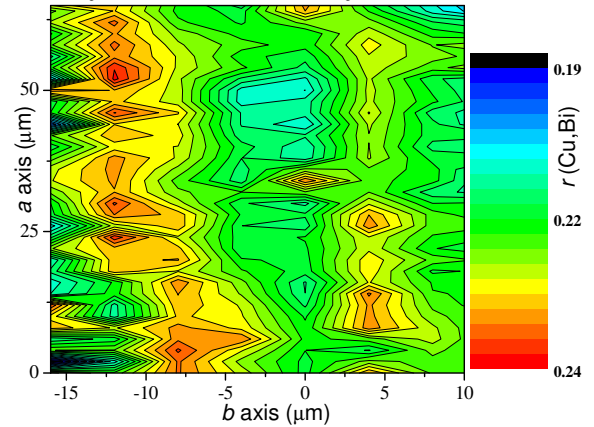


FIG. 2. XRF map reporting the $r(\text{Cu,Bi}) = \text{Cu}(\text{K}\alpha)/\text{Bi}(\text{L}\beta)$ ratio on a portion of the same aged Bi-2212 sample used for the XANES study. The red regions correspond to the edge of the crystal.

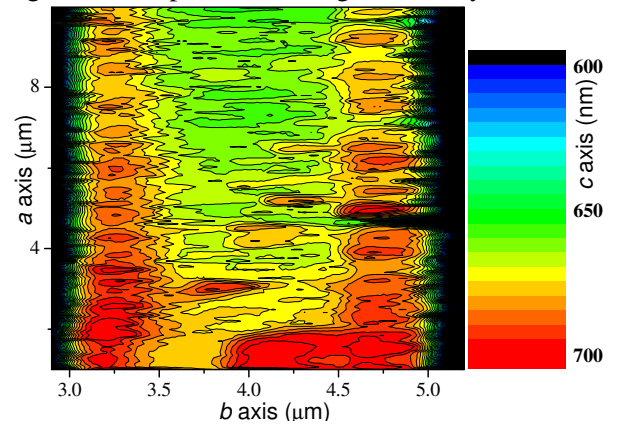


FIG. 3. AFM map of the Bi-2212 sample used for the electrical measurements at the end of the 40-day aging process. The red regions correspond to the edge of the crystal.

The whisker used for the electrical characterization was mapped by atomic force microscopy (AFM) at the end of the 40 days aging process and the result is shown in Fig. 3. The crystal, exhibiting an almost flat a - b surface in the as-grown condition, clearly shows an increased thickness Δz at the borders along the b direction. This is the consequence of the O depletion, which is known to induce an increase of the c axis lattice parameter whose average over the crystal size along the c -axis direction (≈ 200 unit cells) has been clearly detected by AFM. The c -axis increase, located at the border of the crystal along the b direction, well correlates with the higher fraction of Cu^+ singled out in the same region by μ -XANES (Fig. 1). These independent evidences agree well with the anisotropy in the in-plane O diffusion coefficients for Bi-2212 that testifies a slower migration process along the b direction and therefore enhances the possibility to evidence a compositional gradient. On a quantitative ground, the measured $\Delta z/z$ (corresponding to $\Delta c/c$) is 4%, indicating that the average c value on the b borders is around 32 Å. μ -XRD measurements, collected in transmission mode with an image plate, resulted in a c -axis value of 32.2 Å for the b border region. More details can be found in a recent publication [1].

[1] M. Truccato, C. Lamberti, C. Prestipino and A. Agostino, “Evidence of ion diffusion at room temperature in micro-sized crystals of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ superconductor”, *Appl. Phys. Lett.*, **86** (2005) 213116