Evidence of Ion Diffusion at Room Temperature in Microcrystals of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductor

Single crystals of the $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi-2212) high-*T*c superconductor can be grown in samples whose length (≥ 500 µm) 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 [1].

Bi-2212 whiskers undergo a significant increase in the in-plane resistivity when aged at room temperature, most likely because of the oxygen loss [2]. Variations in the O non-stoichiometry of Bi-2212 whiskers must be accompanied by a change of the Cu oxidation state to guarantee the electrostatic neutrality. To verify whether the variation of the local Cu oxidation state, induced by O diffusion, is accompanied by a cation migration or not, we have combined µ-XANES and µ-XRF experiments at beamline ID22. Also the *c*-axis value has been monitored by µ-XRD. A laboratory AFM study supports the ID22 data.

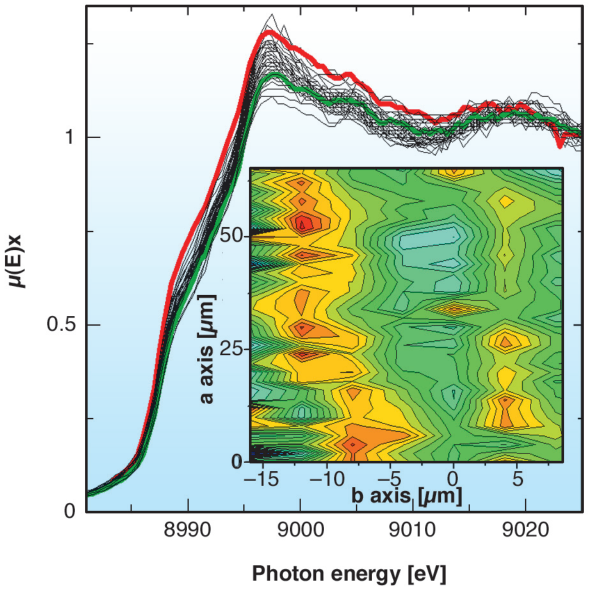

Fig. 1: Normalised XANES spectra collected on different positions of the Bi-2212 whisker. A shift of the edge up to 2.5 eV, accompanied by a modification of the white line intensity, which clearly displays an important modification of both the oxidation and the coordination state of Cu along the crystal. Bold curves represent spectra collected in central (green) and in near-edge (red) positions along the b direction, the others representing intermediate positions.
The inset shows the map (resolution 1 x 4 µm) reporting the ratio between the Cu(Kα) and Bi(Lβ) XRF counts on the same portion of the Bi-2212 sample used for the XANES study (color scale: red = 0.24; green = 0.22; blue = 0.20). The red regions correspond to the edge of the crystal, where a Cu enrichment has been observed. Beam energy = 17.3 keV).

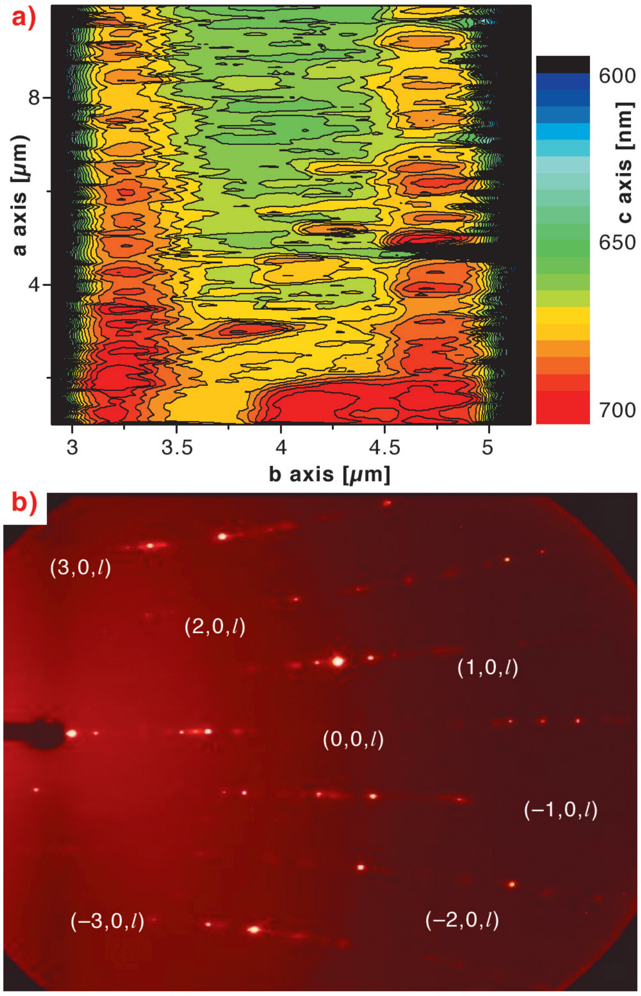

Fig. 2: (a) Colour scale AFM map of the Bi-2212 sample. The red regions correspond to the edge of the crystal, where a higher thickness has been observed.
(b) (h, 0, l) reflections (h = -3, -2, -1, 0, 1, 2 and 3) collected at ID22 in transmission mode with an image plate sampling a point in the border region along the b axis. Beam energy = 17.3 keV.

Figure 1 presents the Cu K edge fluorescence µ-XANES spectra. Moving from the central position (green spectrum) to the crystal edge (red spectrum), we observe an increase in the white line intensity of ≈ 10% and a red shift of the edge of 2.5 eV. This indicates an important gradient of local structure and in the oxidation state of Cu along the *b* direction. At the crystal edges a significant Cu^+ enrichment is observed (Figure 1). This is where the atomic O^{2-} anions are supposed to recombine to give O_2 molecules, which then leave the crystal (leaving behind their 4 electrons). According to previous XANES studies we evaluated that a fraction of about 30% of Cu^+ is estimated at the edges [3]. This suggests that the rate-determining step of the O loss process, the is the O^{2-} migration to the crystal surface and not the O_2

recombination at the surface. From the μ-XRF study (Figure 1 inset) a Cu enrichment at the crystal edges along the *b* direction is found.

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, as determined by AFM (**Figure 2a**). 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). 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 (Figure 1). These independent pieces of evidence agree with the anisotropy in the in-plane O diffusion coefficients for Bi-2212 that indicates a slower migration process along the *b* direction. Therefore, the possibility of identifying a compositional gradient is enhanced. Quantitatively, 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 at ID22 in transmission mode with an image plate, resulted in c = 32.2 Å for the *b* border region (Figure 2b).

References

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Principal publication and Authors

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Scaling in the Time Domain - Universal Dynamics of Order Fluctuations in Fe_3Al

Solid state theory predicts that a material should respond ultra-sensitively to external perturbations (temperature, pressure, magnetic or electric fields), when it is close to a phase transition. This response is governed by microscopic fluctuations in the system: quantities like volume, entropy or sub-lattice order are strongly fluctuating for temperatures near the critical temperature T_C. For continuous phase transitions, the correlation length (ξ) in the system is diverging [1] when T_C is approached. The mesoscopic size of fluctuating domains leads to universal macroscopic response functions – power laws involving critical exponents that depend only on the dimensionality and symmetry of the system. X-ray and neutron scattering experiments have led to a consistent picture of the static critical behaviour. However, since fluctuations exhibit a time structure, our picture of phase transformations is incomplete without understanding the microscopic fluctuations in the time domain.

Recently the technique of X-ray intensity fluctuation spectroscopy has been developed, using coherent synchrotron X-ray beams: the diffracted intensity is a time-dependent "speckle pattern", uniquely related to the spatial arrangement of the ordered domains in the sample [2]. This approach is strongly limited today by the low intensity in the coherent beam. In order to observe dynamic fluctuations on a microscopic scale we used a partially coherent focused X-ray beam (**Figure 1**) illuminating the sample which is kept close to T_C. We record in real time intensity fluctuations of the diffracted beam, which are associated with the order fluctuations in the sample. Since a fully coherent beam is not required in this approach, the whole X-ray beam can be focused to a micrometre spot on the micrometre-thick sample. Thus, we reduce the probed volume to a few μm^3 and also preserve the high number of incident photons.

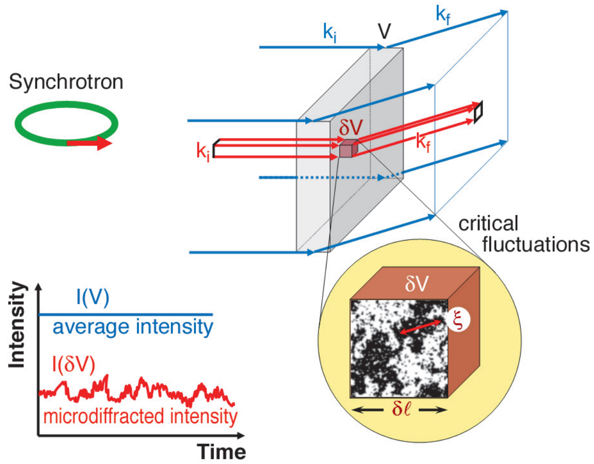

Fig. 1: Principle for a diffraction "microscope": In a conventional diffraction experiment (large probed volume compared to ξ) an ensamble average is performed, the diffracted intensity is constant (blue curve). When the probed volume in the sample δV is small enough to contain only a few fluctuating domains (each of size ξ), the diffraction experiment no longer performs an ensamble average; the diffracted intensity fluctuates and directly reflects the dynamics of thermal fluctuations (red curve).

The experiment was carried out at the ID22 beamline using a focused beam slightly smaller than 2 x 2 μm^2. The sample was a Fe_3Al single crystal, in which the Fe and Al atoms order on a cubic lattice (chemical order).