

## The orientation dependence of the Cu L loss as assessed by PEELS for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$

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**ABSTRACT:** The changes in form of the Cu L edge for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , as examined using PEELS in the TEM, are described for varying oxygen contents. These changes were assessed using an approach which has the potential to allow the losses associated with the nature of the Cu-O bonding in the c direction to be distinguished from those in the a-b plane. The degree to which this momentum resolved technique can be used successfully is discussed.

### 1. PEELS FINGER PRINTING

Changes in the position, form and intensity of an EELS edge for a given element reflect changes in the nature of the bonding. Furthermore, the electron promotions that occur under the dipole approximation for transitions from the s to p states, if less strictly for transitions to the d states, are for orientations of the final state ligand which have the same direction as the momentum transfer occurring in the loss event. Thus, if losses can be assessed which are associated with a specific final energy loss electron direction (and thus momentum transfer) then the near edge data obtained should provide useful information about the bonding in this specific direction. If, for example, we are interested in differences in the Cu-O bonding in the sheets on the a-b planes and in the c direction for a material such as  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (and such differences could point to requirements for high  $T_c$  superconductivity) then we need to obtain momentum resolved energy loss data.

It is often difficult to predict the precise changes in the form of the losses to be expected for a given change in the band structure. This has led to the use of a more general approach in which the characteristic near edge losses for an unknown state, as usually obtained non specifically with respect to the bonding directions, are compared with those seen for related compounds with well determined valence states for the element of interest. The approach, which is known as "finger printing", has general application in the characterisation of the bonding in mixed state Cu based oxides as can be judged by the comparison of the near edge L losses for Cu at different valencies (figs. 1a, b and c for the metal, CuO and  $\text{Cu}_2\text{O}$  respectively). The losses were obtained using a Gatan PEELS on a Philips CM30 operated at 100kV and are shown after diode gain variation reduction using the approach described by Boothroyd et al (1990) and deconvolution of the low loss spectrum. For typical acquisition conditions (30 sec for each spectrum) the full width at half maximum (FWHM) of the zero loss peak was  $\leq 1.2$  eV. In the electronic configuration of metallic Cu all the d bands are fully occupied so the white lines arising from transitions from  $2p_{3/2}$  ( $L_3$ ) and  $2p_{1/2}$  ( $L_2$ ) to unoccupied d states are not observed (fig. 1a). For  $\text{Cu}_2\text{O}$  and CuO ( $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  ions respectively) the d bands are not full (holes being created in the d bands by the ligand orbitals) and transitions from  $2p_{3/2}$  and  $2p_{1/2}$  to empty d final states can occur but do so differently as a function of the oxidation state. It is important to note however that because of the strong Coulomb interaction between the 2p core hole and the excited final state an important

redistribution of intensity is observed and the spectra do not reflect the detailed density distribution of the unoccupied states. The intensity of the white lines is therefore related to the number of holes in the d bands. An energy shift of the  $L_3$  and  $L_2$  lines ( $\cong 3\text{eV}$ ) was measured between  $\text{Cu}^{\text{I}}$  and  $\text{Cu}^{\text{II}}$  and a significant tail is present on the  $\text{Cu}^{\text{I}}$   $L_3$  edge. These results (which are significant given that the spectra were calibrated using a multimeter and a sample of NiO as a standard ( $L_3$  at  $856\text{eV}$ )) agree with the x-ray absorption spectroscopy literature.

Data of the high quality exhibited by these spectra have prompted us to re-examine approaches in which the "finger printing method" might be extended, using momentum resolved techniques, to allow directionally related differences in bonding behaviour to be examined. Batson and Chisholm (1988) were the first to show that energy loss spectra could be obtained exhibiting at least the effects of anisotropy in the transferred wave vector using a VG STEM and Wien filter electron spectroscopy. They compared the  $L_3$  edge of Cu for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for orientations with the c axis parallel to the beam and in the a-b plane, tuning the axial collection angle to promote the contribution from losses associated with momentum transfer perpendicular to the beam. The Cu  $L_3$  edges they reported for these two orientations are sufficiently different to suggest that differences respectively in the sheet and ribbon CuO bonding were being probed. Nücker et al (1989) used the  $45^\circ$  technique (e.g. Leapman et al 1983) which apparently allowed very good momentum resolution for their dedicated EELS spectrometer. Their Cu  $L_3$  results for  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_6$  are startlingly different for momentum transfer parallel and perpendicular to c. We accordingly investigate here the application of this method using a conventional CM30 TEM for a range of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  states, investigating too the effects of beam damage at, in this case,  $100\text{kV}$ . If the approach can be made to work on a TEM then we would have the advantage that changes in the bonding in areas exhibiting different forms of defect structure could be easily compared.

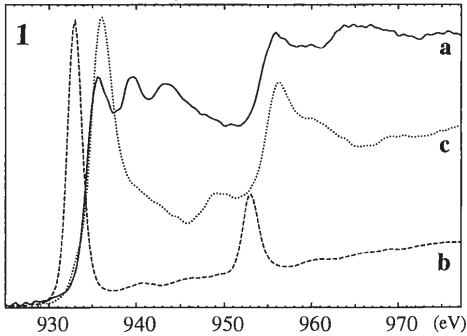
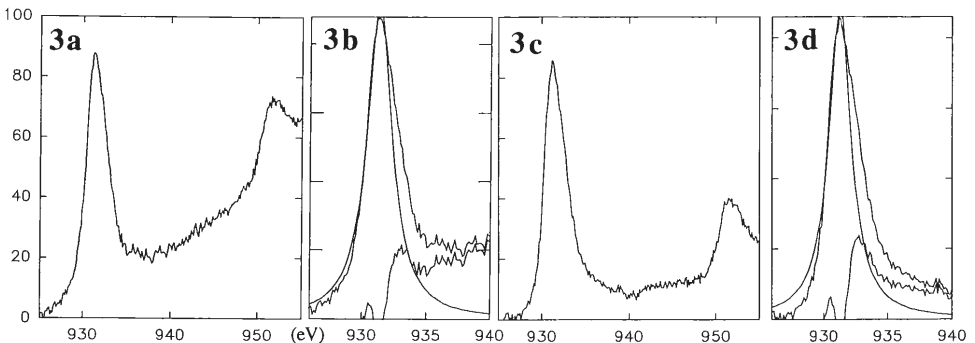
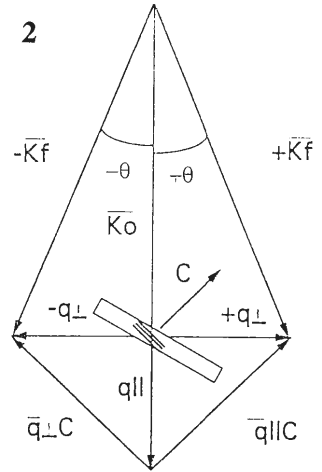


Fig. 1 Cu L edges for a) Cu metal, b) CuO and c)  $\text{Cu}_2\text{O}$

Fig. 2 Schematics of scattering

Fig. 3 Momentum resolved data for  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .  
a)  $q_{\parallel}c$  b) fit to a), c)  $q_{\perp}c$  and d) fit to c)



2. RESULTS OBTAINED USING A MOMENTUM RESOLVED METHOD

Both  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  were examined as crushed in pure alcohol and dispersed on a holey carbon film, the latter sample, with  $\delta=0.48$  being prepared by reduction of an  $\text{YBa}_2\text{Cu}_3\text{O}_7$  sample at  $525^\circ\text{C}$  for 13hrs in an atmosphere of  $\text{N}_2-0.2\%\text{O}_2$ . Typical maximum values for the relative thickness examined for the superconducting samples were less than half the relevant inelastic mean free path.

Before proceeding further it is important to note that the approach we have applied to probing the orientation dependence of the final states in the crystals is dependent on the assumption that the loss can be referred to the primary beam incident on the crystal. On this basis we can attempt to tune the momentum transfer vector  $\mathbf{q}$  (fig. 2) towards a particular crystallographic direction by changing geometrical parameters. Transitions will thus be observed for orbitals in the direction of the  $\mathbf{q}$  vector. For a particular small angle  $+\theta$ , selected by displacing the diffraction pattern relative to the spectrometer entrance aperture, we can equate the perpendicular components of the momentum transfer  $\mathbf{q}$  ( $q_{\perp} = q \sin \theta$ ) and thus obtain a  $\mathbf{q}$  vector lying at  $45^\circ$  with respect to the incident beam momentum direction  $\mathbf{K}_0$  (fig. 2). Therefore, by tilting the sample, so that the  $c$  zone axis is at  $45^\circ$  with respect to  $\mathbf{K}_0$ ,  $\mathbf{q}$  will be parallel to this axis. Similarly, we can displace the diffraction pattern by an angle  $-\theta$  to obtain  $\mathbf{q}_{\perp c}$ . The magnitude of  $q_{\parallel}$  (and thus  $q_{\perp}$ ) is dependent upon the energy loss  $E$  and can be calculated as  $q_{\parallel} = K_0 E / (2E_0)$  where  $E_0$  is the incident electron energy (e.g. Leapman et al 1983). For the selected conditions and given the small scattering angles,  $q_{\perp} = q_{\parallel} = K_0 \theta$ . In our experiments ( $E=931\text{eV}$  for the  $\text{Cu } L_{2,3}$  edge and for 100 KeV electrons)  $\theta=4.7\text{mrad}$ . If tilting is carried out about the  $\mathbf{b}$  or  $\mathbf{a}$  axis,  $\mathbf{q}$  will be parallel to the  $\mathbf{a}$  or  $\mathbf{b}$  directions respectively. With this approach, momentum resolved spectra can be obtained with the same energy resolution and from the same area. As the momentum resolution is affected by a combination of the convergence and collection angles, in terms of directions of the selected scattering vectors, we will generate a cone of  $\mathbf{q}$  vectors around the direction selected by geometry (fig. 2).

The  $\text{Cu } L_3$  line in the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  is asymmetric and has a FWHM of  $2.5\text{eV}$ . Our measurements indicate that its maximum intensity is situated  $1.3\text{eV}$  below the  $L_3$  line in the  $\text{Cu}^{\text{II}}$  oxide. We have not observed significant anisotropy in intensity and shapes of the  $L_3$  line

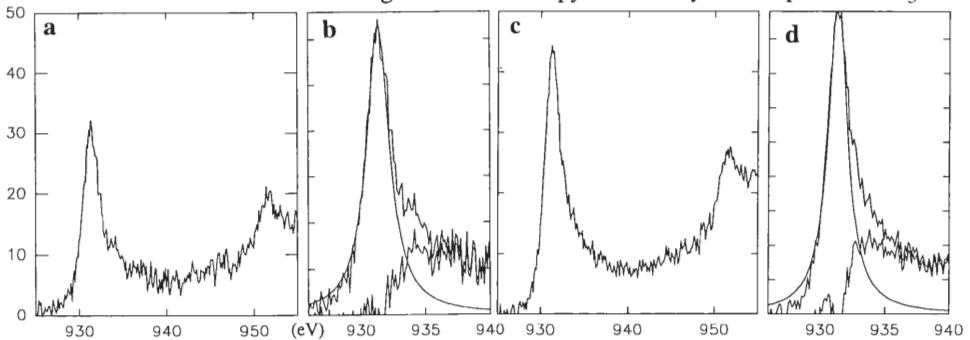


Fig. 4 Momentum resolved data for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . a)  $\mathbf{q} \parallel \mathbf{c}$  b) fit to a), c)  $\mathbf{q} \perp \mathbf{c}$  and d) fit to c)

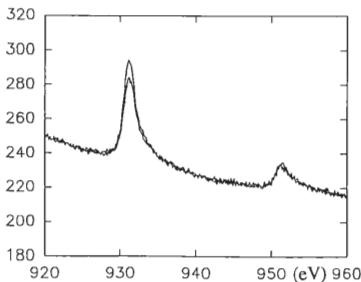


Fig. 5. Scattering dependence for  $\mathbf{q}$  components along  $\mathbf{a}$  and  $\mathbf{b}$

from spectra obtained with  $q_{\parallel c}$  and  $q_{\perp c}$  (figs. 3a and c) as is demonstrated by the Lorentzian fitted profiles for these two orientations shown in figs. 3b and d. For  $YBa_2Cu_3O_{6.52}$ , the  $L_3$  white line has a FWHM of 1.8eV and there is a small reduction in intensity of the line when  $q$  is oriented parallel, rather than perpendicular, to  $c$  (parallel to  $b$  or  $a$ ). Fitting Lorentzian profiles for these peaks indicates the emergence more strongly for  $q_{\parallel c}$  than for  $q_{\perp c}$  (compare fig. 4b,  $q_{\parallel c}$  and fig 4d,  $q_{\perp c}$ ) of a high energy shoulder at about 934eV. The anisotropic behaviour for the  $YBa_2Cu_3O_7$  loss is consistent with the higher energy loss resolution data of Batson and Chisholm (1988) as well as with XAS results reported by Fink et al (1993). However, the magnitude of the change in intensity of the  $L_3$  peak relative to that of its shoulder for  $YBa_2Cu_3O_{6.52}$ , as a function of direction, is far less than was observed by Nücker et al (1989) at 170keV. Furthermore they showed data for  $YBa_2Cu_3O_6$  indicating that the peak at 934 eV is for this composition some 3 times larger than that at 931eV as momentum resolved with  $q_{\parallel c}$ , with the reverse tendency for  $q_{\perp c}$ . We have not been able to observe such a change for material irradiated in the column for a period (3hrs) giving a substantial (~30%) further reduction in the O content (as determined from the O K edge). However, as damaged, the ratio of the pre-peak to the peak height for the O K edge remained constant and this indicates that the damage process was such as to redistribute the O content generally rather than just to remove the O in the chains.

The orientation dependence of the Cu L edge was also examined, probing neighbouring twins in  $YBa_2Cu_3O_7$ , with the sample on the  $c$  zone axis and collecting the spectra by shifting the diffraction pattern so that the component  $q_{\perp}$  of the scattering vector is parallel to the  $b$  axis or  $a$  axis ( $\theta=4\theta_{\text{Bragg}(010)}$  or  $\theta=4\theta_{\text{Bragg}(100)}$  respectively) i.e.  $q$  has a component towards the  $b$  or  $a$  directions respectively. The results show that a strong electronic anisotropy is present along these directions, changes of intensity in the order of 30% being observed (figs. 5a and b). This would indicate a possible increase in the number of empty states along one of the basal directions. The result is as expected but, we believe, demonstrated here for the first time using EELS. In the orthorhombic structure of  $YBa_2Cu_3O_7$  the Cu coordination is fourfold planar (with CuO bonds along the  $c$  and  $b$  directions) so the hybridisation with the ligand must involve, preferentially, orbitals along the  $b$  rather than in the  $a$  direction and thus more holes in the former orbitals. It is important to note that we did not see similar changes in the  $L_2$  white line so it is not clear whether or not there is also preferential redistribution of the orbitals in the ground state.

### 3. IS THE DATA MOMENTUM RESOLVED ?

In summary we have demonstrated that the approach described to obtaining momentum resolved EELS data yields spectra which exhibit consistent orientation related changes as a function of changes in composition. However, whether one thinks in terms of the inelastic scattering process from a Bloch wave approach or in terms of the way elastic scattering leads to secondary sources as Bragg beams, it is surprising if truly momentum resolved data can be obtained by the technique we, like Nücker et al (1989), have used. We would not expect substantial differences in the momentum resolution obtainable as a function either of the primary beam energy or the use of a dedicated EELS spectrometer rather than a TEM. There are thus no obvious reasons for the poorer momentum resolution of our data relative to that obtained by Nücker et al (1989).

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