Simultaneous measurement of XANES in halide-intercalated BSCCO(2212) using electron and fluorescence yield to compare their performance

S.G. Saxena[1], B. Dalela[2], S. Dalela[2], D. Chaturvedi[2], R.K. Singhal[2] , P. Parikh[2] , D.C. Jain[2] and K.B. Garg[2*]

[1]*Vanasthali Vidyapeeth, Vanasthali , Rajasthan, India*
[2]*Department of Physics, University of Rajasthan, Jaipur-302004, India*
*e-mail: krishna@jp1.dot.net.in Fax: +91-141-511912.

Total Yield with an escape depth of ~100-200 Å is known to be rather surface sensitive. Fluorescence Yield, on the other hand, with an escape depth of ~1000-2000 Å is relatively less prone to surface effects but necessitates some corrections to obtain the true signal. Both have their plus and minus points and, if used with care, yield reliable data. In the present experiment both the techniques have been simultaneously employed for measuring orientation dependent O K and the Cu L_3 edges from an uncleaved surface of I(2)BSCCO(2212) single crystal to compare the performance of the two modes of detection. Despite glaring differences in intensities the results from the two appear to show reasonable agreement in respect of relative intensities of the spectral features.

Keywords: Total yield, Fluorescence yield, XANES, BSCCO(2212)

1. Introduction

XAFS has emerged as a powerful and versatile technique in study of electronic structure and near-neighbor environment around a given cation, particularly since the advent of synchrotron radiation sources that not only give high flux and brightness but also a very high degree of polarization and resolution. XAFS has also been widely employed to probe the local orbital character of the carriers in doped cuprates and the short-range order around various cations. The high degree of polarisation in the incident beam enable orientation dependent measurements on single crystals to be made. However, the geometry of the experiment as also the mode of detection have to change when it comes to making measurements on single crystals, thin films or thick samples or for measurements in the soft X-ray region.

The latter measurements have to be done under UHV conditions and one has to, in general, use Total Yield (TY) or Fluorescence Yield (FY) modes of detection. With the advent of high performance soft X-ray monochromators, it has become possible to obtain high intensity and high resolution- resolving power of the order of 10,000 can be routinely produced (P. A. Heimann et al (1990))-alongwith a very high degree >99% of linear polarization or a circular polarization of the order of 90%(C.T. Chen et al (1990)). These advances have helped reveal valuable information on the electronic and magnetic structure of matter, including isolated molecules, transition metal compounds, magnetic trilayers, biological samples and high T_c superconducting cuprates. Some of the applications of soft XAS is to study the Oxidation State, Spin State, crystal field and phase transition of transition metal compounds (C.T.Chen and F. Sette (1990)).

The TY and FY modes of detection have been frequently employed in case of the high T_c superconductors for probing the in-plane Cu $3d_{x2-y2}$ and O $2p_{x,y}$ orbitals and the out-of-plane Cu $3d_{z2-r2}$ and O $2p_z$ states. However, to obtain reliable data from the two techniques one has to exercise care and caution. Total yield is dominated by low energy electrons, for which the mean free path is only ~50-100 Å, although it will potentially carry bulk information, it tends to be surface sensitive resulting in impure data particularly if the surface is dirty. This is more often true when one is measuring the O K edge. TY offers a higher count rate and is easier to measure but gives a poorer signal to background ratio. FY, on the other hand, has a probing depth of ~ 2000 Å and is thus less sensitive to surface but its yield is low and the signal is not proportional to the absorption coefficient for light atoms although the signal to background ratio is high. It is less of a problem when using it for high Z atoms. A number of corrections have to be applied to the FY signal for obtaining the true value of absorption coefficient from it (E. Pellegrin et al(1993), L. Troger et al(1993)).

2. Experimental

The Cu L-III and O K edge have been recorded on intercalated Bi-2212 superconducting single crystal at the HSGM beamline (SRRC, Taiwan) in both fluorescence and total yield modes. Details on preparation and characterization of the samples are given elsewhere (S.-J. Hwang et al (1998)). Using linearly polarized synchrotron radiation light, the polarized spectra of the intercalated single crystal have been recorded with various incidence angles between the electric field of the photon beam E and the sample surface. The crystal was not cleaved in situ for the measurements for the lack of such facility at the experimental station. It may, however be stressed that the aim of the experiment was to compare the performance of the TY and FY modes of detection rather than study the properties of the intercalated crystal albeit intercalation of the halide molecule I_2 does lead to a lowering of the T_c. For enabling a more reliable comparison of their performance the Cu L_{III} and the O K edge spectra in our experiment were measured with the TY and FY modes simultaneously in order to eliminate any change in the spectra creeping in owing to possible change in the condition of the crystal surface.

3. Result and Discussion

Fig.1 & 2 respectively represents the measurements on the O K-edge performed using the TY and FY techniques and Fig. 3 and 4 similarly our data on Cu L_{III}-edge. All the spectra have been

corrected for background and normalized at a point away from the XANES part. Because of this shortcoming one can presume that the measurements were done on a dirty surface and consequently the data from the TY more is likely to be contaminated with the signal from the dirty surface also. A glance at fig. 1 and 2 is enough to show that the data on the O K-edge pre-peak which represents the itinerant holes, is of much better quality and intensity than the one recorded using the TY mode which is not surprising as the crystal surface was not cleaved.

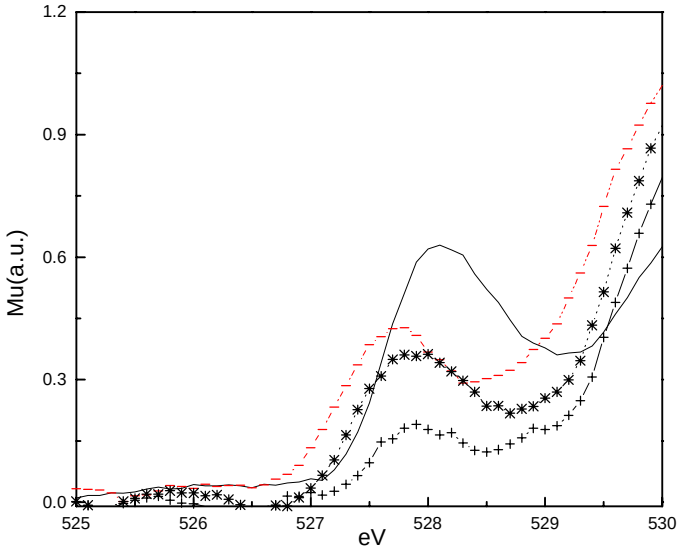

Fig. 1
Comparison of the O K-edge in the I2 intercalated BSCCO (2212) system using FY mode of detection with 0 deg. [solid line], 45 deg.[bar], 60 deg. [****] and 75 deg. [++++] angle of polarisation.

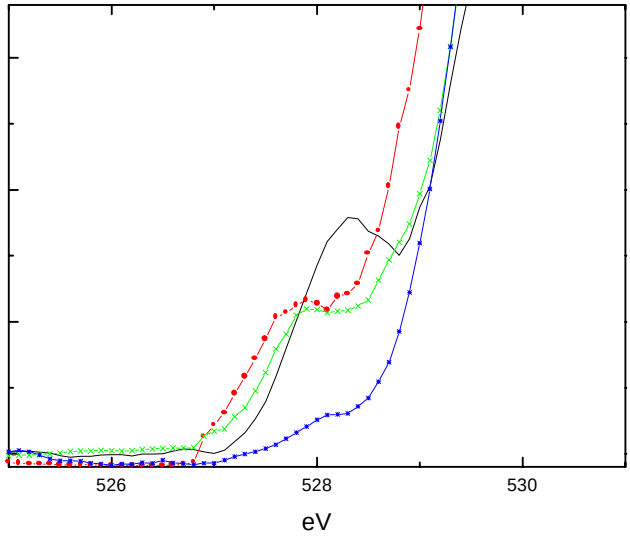

Fig. 2
Comparison of the O K-edge in the I2 intercalated BSCCO (2212) system using TY mode of detection with 0 deg. [solid line], 45 deg.[ooo], 60 deg. [xxxx] and 75 deg. [****] angle of polarisation.

The four spectra in each of these figures correspond to different orientation of the polarization vector **E**, (0, 45, 60 and 75 degrees) with respect to the ab plane of the crystal. As expected the intensity is maximum for 0 degree (**E**//ab) case indicating that a large fraction of the itinerant holes reside in the CuO_2 plane and only a small fraction in the **E**//c direction. Although this peak is visible in TY recorded figure 2 case also for all the four angles but with much poorer relative intensity. This implies that the surface of the crystal must have been contaminated with dirty oxygen and other impurities that tend to mask the genuine oxygen signal from the superconducting crystal. Also, as stated earlier, the yield is greater in the TY mode but the signal to noise ratio is poorer compared to that in the FY mode. Table one below incorporates the relative intensities of the peak at the four angles in each case. It is interesting to see from the table that the relative intensities of the peak at various angles are very similar except for the 75° case. This may probably be due to fact that at grazing incidence the penetration of the incident beam is rendered smaller thereby enhancing the contribution coming from the dirty surface.

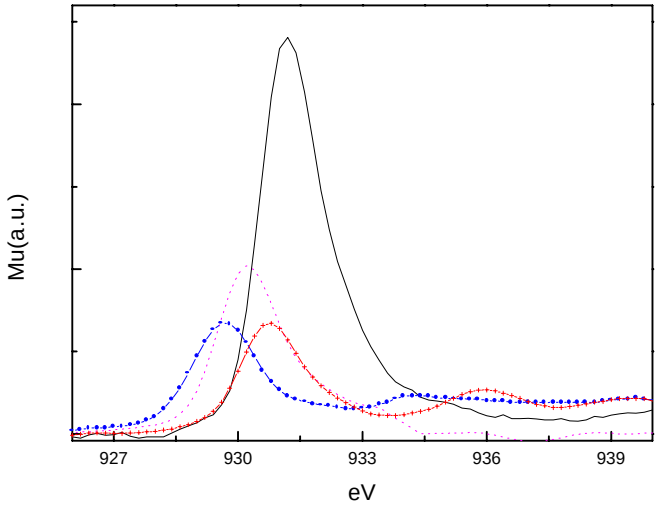

Fig. 3
Comparison of the Cu L_{III}- edge in the I2 intercalated BSCCO (2212) system using FY mode of detection with 0 deg.[solid line], 45 deg.[……], 60 deg.[ooo] and 75 deg.[++] angle of polarization.

Turning our attention to fig. 3 and 4 we find that the intensities of the Cu L_{III} white line in the two cases are very much comparable. This is not surprising as the impurities on the crystal surface would largely comprise of oxygen and other low Z components which would not be quite as detrimental to the quality of the Cu L_{III} spectrum as in the case of the O K edge. No corrections have been applied to FY spectra for self absorption etc. as these do not make a substantial difference to the spectra in the near edge region. C.T. Chen et al (1992), while investigating the in-plane and out-of-plane density in the LSCO single crystal, had reported an intensity of less than 3% in the E//c direction and had ascribed it to possible lack of polarisation in the incident beam. They ascribed the high intensities, ~20% in the **E**//c direction, observed earlier in BSCCO (2212) and other crystals to the vagaries of the TY mode of detection which tends to have a strong contribution from the surface. Saini et al (1994, 1995) have demonstrated that the spectra from a BSCCO (2212) single crystal using both the TY and FY modes of detection turned out to be identical after the crystal was repeatedly cleaved *in situ* before making the measurements. This served to show that the difference in the

spectra from the two techniques perhaps mainly arises from the condition of the surface. An earlier report by S. Venkatesh et al(1995) wherein they report a larger intensity the for the Cu L_{III} edge in the FY mode compared to that from the TY mode from a crystal not cleaved *in situ* also tends to confirm this. Pellegrin et al(1993) have indicated how an alignment error of up to $\pm$5% may also contribute to the discrepancies in the measured intensities. They emphasise the need for another correction in the FY case to account for the lack of proportionality of the FY signal to the true absorption coefficient, particularly in the Cu L_{III} absorption edge, wherein the true absorption at the edge becomes of the same order as the total absorption coefficient and consequently much greater than the absorption coefficient due to all the other atoms in the sample.

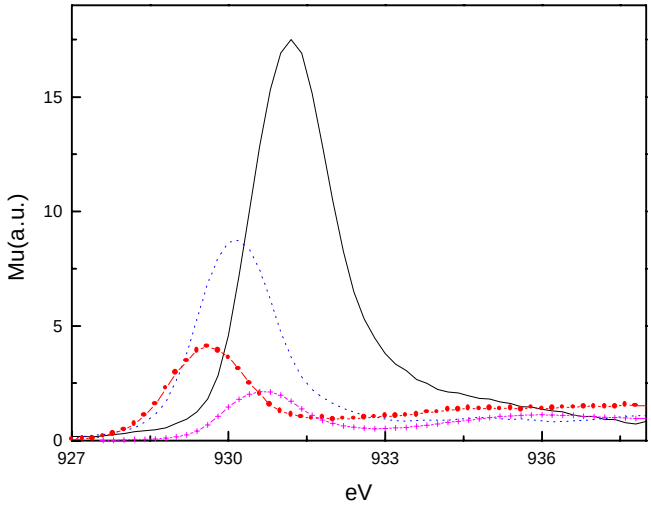

Fig. 4
Comparison of the Cu L_{III}- edge in the I2 intercalated BSCCO (2212) system using TY mode of detection with 0 deg.[solid line], 45 deg.[…...], 60 deg.[ooo] and 75 deg.[+++] angle of polarization.

Table 1: Relative intensities of the O K-edge pre-peak and the Cu LIII-white line measured using TY and FY modes of detection

R. intensities of the O K-edge pre-peak			R. intensities of the Cu LIII-edge white line	
TY (%)	FY (%)	Angles	TY (%)	FY (%)
100	100	0	100	100
65	67	45	50	43
61	59	60	24	28
15	32	75	12	27

4. Conclusion

The performance of the FY and the TY modes of detection has been compared measuring the intensities of the O K edge pre-peak and the Cu L_{III} white line from an I_2 intercalated BSCCO (2212) single crystal. The relative intensities in case of the O K-edge turn out to be much higher in the FY mode as the TY signal tends to get masked by the large contribution from the dirty surface. It is however interesting to note that except in the 75° orientation case the relative intensities from the two techniques turn out to be quite similar. The relative intensities for the Cu L_{III} white line from the TY and FY measurements, on the other hand, do not are quite similar as the contamination on the surface mainly comprises of oxygen and other low Z elements. Various corrections must be made and a great deal of caution exercised in order to get reliable and identical data from the two techniques.

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