

## O K and Cu L<sub>III</sub> edge study of itinerant holes in I<sub>2</sub>-, HgI<sub>2</sub>- and HgBr<sub>2</sub>- intercalated BSCCO(2212) single crystals

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Intercalation effect on BSCCO (2212) system, although it increases the interlayer distance and the c-axis remarkably, produces only a small change in the transition temperature. Thus, amongst other things, intercalation provides an effective method to investigate the influence of the inter-block coupling. Electrons are transferred from the host Cu-O<sub>2</sub> layers to the guest molecules I<sub>2</sub>, HgBr<sub>2</sub>, HgI<sub>2</sub> leading to evolution of the T<sub>c</sub>. For this we have made high resolution XANES study on the O K and Cu L<sub>3</sub> edges to estimate the density of the doping holes. We attempt on basis of our and earlier results the evolution of T<sub>c</sub> in these as also the much larger decrease produced in T<sub>c</sub> for I<sub>2</sub>-intercalation for which the increase in basal spacing is the smallest of the three halides.

### 1. Introduction

The idea of introducing foreign atoms or molecules into two dimensional solid lattice started a new field, intercalation chemistry. It was extended to the high T<sub>c</sub> superconducting materials as it may provide some understanding of the mechanism of the superconductivity. In an intercalate the guest and the host layers influence each other's physical and chemical properties. Although hole density is now regarded as the most important parameter for superconductivity in these materials, the inter-block electronic coupling between the next nearest CuO<sub>2</sub> layers via the Bi<sub>2</sub>O<sub>2</sub> layer has also been considered to be an important factor. Intercalation of molecules between the adjacent Bi<sub>2</sub>O<sub>2</sub> layers resulting into lengthening of the c-axis may also consequently lead to weakening of the coupling between the consecutive Cu-O<sub>2</sub> layers. It is therefore a handy tool to explore the importance of inter-block coupling to superconductivity. Intercalation of I<sub>2</sub> into BSCCO (2212) was found to cause a significant

depression in T<sub>c</sub> raising question if the T<sub>c</sub> evolution is dependent on the hole concentration or the inter-block coupling or both [Xiang et al (1990,1992), J. Ma et al (1994), D. Pooke et al (1992)]. However, Wheatley et al (1988) ascribed the superconductivity in these to the coherent hopping of valence bond pairs between the Cu-O<sub>2</sub> planes with the phase coherence between the valence bond being achieved by pairing of the holons rather than the inter-block Josephson coupling.

Later on, Choy et al (1997), for example, were able to intercalate much larger HgBr<sub>2</sub> and HgI<sub>2</sub> molecules between the Bi<sub>2</sub>O<sub>2</sub> bilayer resulting into a basal increment of nearly 7.2 Å— almost twice that caused by I<sub>2</sub> (3.6 Å). The decrease in T<sub>c</sub> was however found to be only about 5-7 K in comparison to decrease of more than 13 K in case of the I<sub>2</sub> intercalate and thereby concluded that it is mainly the doping holes generated via charge transfer from host layer to the guest molecule that are responsible for evolution of T<sub>c</sub>. Lack of direct evidence in support of this as well as the anomalous depression of T instead of such Josephson coupling in the I<sub>2</sub> intercalate provided the motivation for the present study.

### 2. Experimental

First, a single crystal of pristine BSCCO (2212) was synthesized by the travelling-solvent floating-zone method. Intercalation of the halides into the BSCCO (2212) single crystal was then performed by using the vapor transport reaction between the guest and the host. Further details are described in Choy et al (1997). The O K- and Cu L<sub>III</sub>-edge measurements were performed at the HGSM beamline at SRRC, Taiwan using an array of nine fluorescence detectors with the ring operating at 1.5 GeV and 130-200 mA. The spectra were measured for .05 sec at each point, with the separation of consecutive points being 0.1 eV. A number of scans, varying from 10 to 20, were taken for each spectrum. The energy resolution was estimated to be better than 0.2 eV at the Cu L<sub>III</sub> edge.

### 3. Results and Discussion

Figs. 1 and 2 represent the results of our polarised XAFS measurements on the O K-edge and the Cu L<sub>III</sub> edge in the orientation E//ab for the pristine, I<sub>2</sub>-, HgI<sub>2</sub>- and HgBr<sub>2</sub>-intercalated BSCCO (2212) single crystals. Fig 1 compares the O K-edge pre-peak at ~528 eV, that characterises the density of the doping holes. Fig 2 represents the E//ab spectra of the Cu L<sub>III</sub> edge measured by us on all the intercalated systems. As shown earlier by Saini et al (1996) the Cu L<sub>III</sub> edge in these systems depicts a shoulder on the high-energy side signifying the presence of the itinerant holes. This Cu L<sub>III</sub> white line when fitted with gaussians and lorentzians yields two components resulting from transitions to the final states Cu 3d<sup>9</sup> and Cu 3d<sup>9</sup>L. The T<sub>c</sub>, the c-axis, and the estimated density of the doping holes in all the above cases are given in the table 1. The density was estimated as described by Saini et al (1996).

**Table 1** Measured values of  $T_c$ , increase in the basal spacing and the density of doping holes ( $\pm 5\%$ ) for the intercalated & pristine BSCCO.

Compound (pristine as well as intercalated)	$T_c$	Hole conc. per Cu-O <sub>2</sub> plane	Increase in basal spacing
Pristine BSCCO(2212)	78 K	0.19	-
I <sub>2</sub> intercalated BSCCO(2212)	63 K	0.28	3.60
HgBr <sub>2</sub> intercalated BSCCO(2212)	71 K	0.11	6.30
HgI <sub>2</sub> intercalated BSCCO(2212)	68 K	0.16	7.15

As can be seen from these, the intensity of the pre-peak is the highest for the I<sub>2</sub> intercalate compared even to that for the pristine case. Though the increase in its basal spacing is only  $\sim 3.6$  Å its  $T_c$  (63K) turns out to be the lowest of all. This is followed by the pristine BSCCO (78 K). The intensity of the O pre-peak for HgI<sub>2</sub> is found to be larger than that for the HgBr<sub>2</sub> intercalate even though the increase in basal spacing for HgI<sub>2</sub> ( $\sim 7.2$  Å) is larger than that for HgBr<sub>2</sub> ( $\sim 6.3$  Å). There is thus an anomalous situation here. The  $T_c$  is the lowest for the I<sub>2</sub> case which has the largest intensity in the pre-peak and the smallest increase in basal spacing. On the other hand, the HgBr<sub>2</sub> system with a lower intensity of pre-peak and a smaller increase in basal spacing shows a higher  $T_c$  than the HgI<sub>2</sub> that has a larger density of holes.

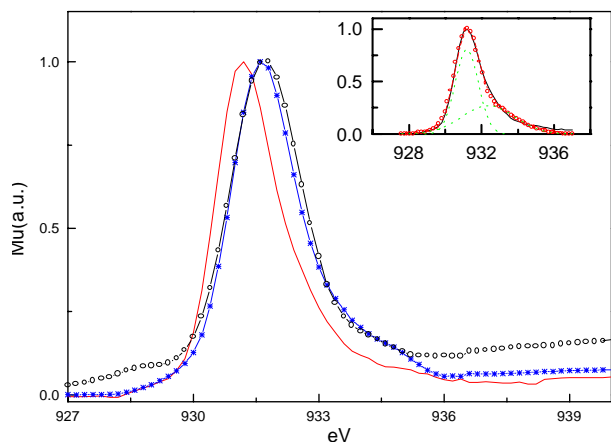


Fig. 1. Polarised Cu L<sub>III</sub> absorption edge E//ab in BSCCO(2212) intercalated with I<sub>2</sub> [solid line], HgI<sub>2</sub> [\*\*\*\*], and HgBr<sub>2</sub> [ooo]. Inset shows two Gaussians fit to the white line of the I<sub>2</sub> intercalated system.

Xiang et al (1990, 1992) and some others have expounded that the decrease in their  $T_c$  is due to weakening of the interblock coupling between adjacent Cu-O<sub>2</sub> planes across the Bi<sub>2</sub>O<sub>2</sub> layer owing to the increase in the length of the basal spacing. Choy et al (1993, 1994, 1996, 1997, 1998) have argued that since even such large enhancement of the basal spacing in the HgBr<sub>2</sub> and HgI<sub>2</sub> reduces the  $T_c$  only marginally the inter-block coupling may not be all that important to the evolution of the  $T_c$  and observed changes in  $T_c$  may instead be due to a change in the density of the itinerant holes. Thus, if the interblock coupling were the sole criterion for evolution of the  $T_c$  then the order should have been the pristine, I<sub>2</sub>,

HgBr<sub>2</sub> and HgI<sub>2</sub> systems. On the other hand, if the criterion were simply the density of the doping holes the order should have been I<sub>2</sub>, Pristine, HgI<sub>2</sub> and HgBr<sub>2</sub>. In reality, it is found to be neither.

The under-doped nature of the HgI<sub>2</sub> and HgBr<sub>2</sub> crystals and the over-doped nature of the I<sub>2</sub> intercalated crystal - which is even larger than that in the pristine crystal - is a rather curious result. Choy et al (1997, 1998) have shown on the basis of their XAFS measurements on the I L<sub>I</sub> and Br K absorption edges that there is a charge transfer from the host Cu-O<sub>2</sub> layer to the guest intercalated layer and that such a charge transfer is greater for I<sub>2</sub> than for HgI<sub>2</sub> intercalation. This is probably why the I<sub>2</sub> intercalate becomes an overdoped system. They also conclude from their Hg L<sub>III</sub> XAFS that the bond distance Hg-I decreases remarkably in comparison to Hg-Br on intercalation. Also, they find that HgBr<sub>2</sub> molecule stays tilted at 65° to the c-axis in the Bi-O bilayer.

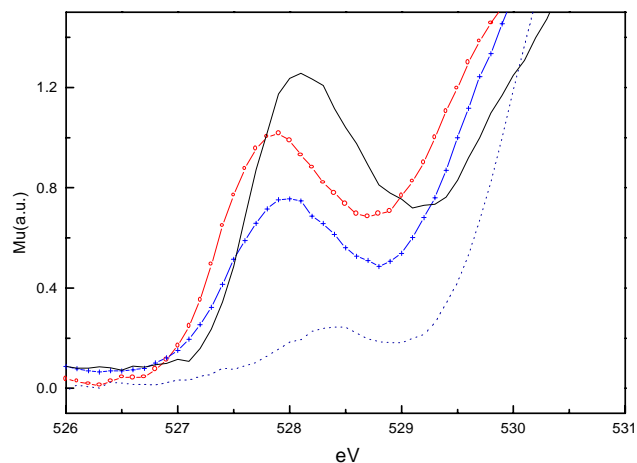


Fig. 2. The pre-peak intensities of the O K-edge, E//ab spectra from I<sub>2</sub> [solid line], HgI<sub>2</sub> [\*\*\*], HgBr<sub>2</sub> [.....] intercalated and the pristine BSCCO(2212) [oooo].

Hwang et al (1998) have partially substituted La for Sr in the HgBr<sub>2</sub> intercalated system and come to the conclusion that Cu-O<sub>Sr</sub> bond gets shortened resulting into the broadening of the valence band, which in turn is known to induce different  $T_c$  changes depending on the hole concentration of the CuO<sub>2</sub> layer. It enhances  $T_c$  in case of the under-doped systems and depresses it in the over-doped systems. Choy et al (1997) have further reported observing a shortening of the Cu-O<sub>Sr</sub> bond distance while the in-plane Cu-O is not found to change significantly from Cu K-edge EXAFS. It is thus possible that the  $T_c$  of the overdoped I<sub>2</sub> system gets depressed and those of the underdoped HgI<sub>2</sub> and HgBr<sub>2</sub> systems get enhanced due to shortening of the above bond. However, it is still not clear why the  $T_c$  of the HgBr<sub>2</sub> system with a smaller concentration of the doping holes should turn out to be greater than that of the HgI<sub>2</sub> system that has a higher density of the holes unless the smaller increase in the basal plane in case of the former is in some way responsible for it. This would be tantamount to admitting that it may be the interplay between the density of holes and the inter-block coupling that may be responsible for the evolution of the  $T_c$  rather than one or the other of them. Sun et al (1999) have from their study of Pr-doped

BSCCO(2212) single crystals while affirming that the main reason for destruction of superconductivity derives from the hole quenching by Pr concluded that the Pr ion also strongly affects the coupling of the two Cu-O<sub>2</sub> planes on either side of the Ca, Pr layer.

#### 4. Conclusion

The evolution of  $T_c$  in the above halide intercalates can thus not be fully understood on the basis of only the density of the doping holes or only the strength of the inter-block coupling. The above facts therefore underscore the need for further careful investigation on the effect of local substitution on all the present chemical bonds to understand the behaviour of the intercalated perovskite superconductors.

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