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# Polarized XANES study of the importance of inter-block *vis-à-vis* intra-block coupling in evolution of $T_c$ in halide-molecule-intercalated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$ single crystals

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## Abstract

In addition to doping in the lattice that affects the intra-block coupling, intercalated molecules sit in between the consecutive basal planes, thereby increasing the effective length of the  $c$ -axis. This, in turn, must lead to a decrease in inter-block coupling. Both the doping and intercalation have been reported to affect the evolution of  $T_c$  in a system, implying the inherent importance of both types of coupling. In the latter case, the resulting depression of  $T_c$  is ascribed to transfer of charge between the intercalate and the host  $\text{CuO}_2$  plane. Most interesting studies in this regard pertain to use of  $\text{I}_2$ ,  $\text{HgI}_2$  and  $\text{HgBr}_2$  molecules as intercalates for the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  system. Earlier reports mostly claim that the host  $\text{CuO}_2$  plane in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  invariably becomes overdoped whichever the intercalate, thereby leading to a fall in  $T_c$ . In this paper, we examine these claims in the case of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  single crystals by measuring the number of itinerant holes before and after intercalation by making polarization-dependent soft-x-ray absorption measurements at the O K and the Cu  $L_3$  edges. Our results do support the earlier claims on overdoing of the  $\text{CuO}_2$  plane in the case of iodine intercalate but are not in agreement with those in the case of the  $\text{HgI}_2$  intercalate.

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## 1. Introduction

One of the most interesting aspects of the high- $T_c$  superconducting oxides is that even subtle changes in their crystal structure can also have dramatic effects on their  $T_c$  [1, 2]. It was believed that electrical transport anisotropy in these derives from their structural anisotropy [1–5]. An important issue was whether these anisotropies form the intrinsic nature of the  $\text{CuO}_2$  network and are intimately related to  $T_c$  or are of no consequence to it [6]. The earliest studies showed how replacing one of the cations in the unit cell by another—similar or dissimilar in terms of valence, magnetic nature, ionic radii or atomic number—always led to a change in the value of the  $T_c$  of the system [6–11]. Of all the high- $T_c$  cuprates discovered so far,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  is markedly anisotropic and hence quite interesting. The coupling between the consecutive Bi–O bilayers of the adjacent blocks happens to be rather weak [12]. This led to the idea of introducing foreign atoms or molecules between the consecutive Bi–O bilayers and gave rise to the use of the intercalation chemistry in this field. Intercalation of alien atoms/molecules usually leads to a drastic expansion of the inter-block separation and consequently changes in the strength of the inter-block coupling. In many cases intercalation is found to also lead to charge transfer between the intercalant and the  $\text{CuO}_2$  layers of the host [15, 16, 18]. Physical properties of the host materials can thus be tuned over a wide range through intercalation. It therefore became a powerful means of investigating the dependence of the superconducting properties of the intercalated system on the inter-block coupling.

Xiang *et al* [12–14] have demonstrated how intercalation can induce well defined structural changes in the cuprate superconductors. Intercalation of an iodine molecule in  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  yielded a new stage-I superconducting compound  $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  with a 23% expansion of the  $c$ -axis and a suppression of  $T_c$  by  $> 10$  K. XRD studies [12] showed that iodine intercalates between all the Bi–O bilayers, thereby affecting the inter-block coupling but leaving the intrinsic  $\text{CuO}_2$  plane structure intact. Xiang *et al* [14] also synthesized a stage-II  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  intercalate in which iodine intercalates into every other Bi–O bilayer, and the depression in  $T_c$  this case was found to be only  $\sim 5$  K. They also reported a ‘metallization’ of the  $c$ -axis direction [13] and worsening of the in-plane normal state conductivity.

Choy *et al* [15] have done a tremendous amount of work on this subject. Apart from the iodine molecule they have also studied the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  system intercalated with other much larger mercury halides,  $\text{HgI}_2$  and  $\text{HgBr}_2$ . These result in a basal increment of nearly  $7.2 \text{ \AA}$ —almost twice that caused by  $\text{I}_2$  ( $3.6 \text{ \AA}$ ). This was done with an implicit intention to study the importance of the inter-block coupling to the evolution of the  $T_c$ . However, the decrease in  $T_c$  was found to be only about  $5\text{--}7$  K, much less than that found ( $13$  K) in the case of  $\text{I}_2$ . Choy *et al* concluded that intercalation of mercury halide molecules also leads to a charge transfer from the host  $\text{CuO}_2$  plane to the intercalated molecule. This results in overdoping of the  $\text{CuO}_2$  plane and the consequent decrease in  $T_c$ , just as in the case of the  $\text{I}_2$  molecule.

Although the iodine intercalation appeared to have been thoroughly studied [16–19], we felt incontrovertible evidence in favour of conclusions drawn in the case of the mercury-halide-doped systems was lacking. Polarized x-ray absorption spectroscopy at the O K and Cu  $L_3$  edges has proved to be a powerful tool for probing the nature and symmetry of the hole states in the superconducting cuprate perovskites [20–33]. This motivated the present study, in which we make use of the polarized XANES measurements at the O K and the Cu  $L_3$  absorption edges. As is well known, polarization-dependent  $E \parallel (a, b)$  and  $E \sim \parallel c$  measurements on well characterized single crystals yield quite reliable estimates of the itinerant hole density in the  $\text{CuO}_2$  plane and that along the  $c$ -direction [20–26, 30–33]. Our preliminary results in this regard have been reported earlier [34]. In the present contribution, we report the results of our carefully carried out  $E \parallel (a, b)$  and  $E \sim \parallel c$  high-resolution x-ray absorption measurements.

The measurements were made on the O K and Cu  $L_3$  edges in three  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  single crystals, one pristine and the other two  $\text{HgI}_2$  and  $\text{I}_2$  intercalated. We reaffirm that while  $\text{I}_2$  intercalation leads to overdoping of the host  $\text{CuO}_2$  plane, in the case of  $\text{HgI}_2$  the host plane becomes underdoped.

## 2. Experimental details

Three well characterized  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  single crystals, pristine  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ , iodine-intercalated  $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$  and  $\text{HgI}_2$ -intercalated  $(\text{HgI}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+y}$ , were synthesized by the travelling-solvent floating zone method and chemical composition confirmed by Fourier transform infrared (FTIR) spectroscopy as described elsewhere [15]. The x-ray absorption measurements on the three crystals were carried out on the DRAGON beamline 11 A at the Synchrotron Radiation Research Centre (SRRC), Hsinchu, Taiwan, using a bending magnet and cylindrical element monochromator (CEM), a horizontal focusing mirror (HFM) and a vertical focusing mirror (VFM) with four gratings of different grating elements to focus and monochromatize the photon beam in different energy regions. The incident photon flux was of the order of  $1.1 \times 10^{11}$ . The experimental set-up yields a maximum resolving power of  $\sim 10\,000$  at the O K edge but the actual requirements in our case were not so demanding. A high-sensitivity nine-element Ge detector was used to record the spectra in the fluorescence yield (FY) mode. The Cu  $L_3$  and O K x-ray absorption edges were recorded at room temperature while the pressure at the end station was measured as  $\sim 5 \times 10^{-10}$  mbar. Primary photon intensity  $I_0$  is recorded by measuring the photocurrent from a clean gold mesh to normalize the intensity in the measured spectra. The samples were mounted on a sample holder which could be rotated in the azimuthal plane, which enabled us to record the  $E \parallel (a, b)$  an  $E \sim \parallel c$  polarized spectra.

Although the FY mode has the advantage that it gives spectra predominantly from the bulk, it suffers from the disadvantage of self-absorption. A self-absorption correction (SAC) is therefore essential to obtain the real signal from the measured FY signal. On their way to the sample surface the fluorescent x-rays are attenuated by the total absorption coefficient  $\mu_{tot}(E_f) = \mu_{abs}(E_f) + \mu_{bac}(E_f)$  at the energy of fluorescence radiation,  $E_f$  for the absorber atom A. The normalized fluorescence intensity  $\mu_{FY}$  is given by the relation [20, 35]

$$\mu_{FY} \equiv \frac{I_f(E)}{I_0(E)} \alpha \frac{\mu_{abs}(E)}{\mu_{tot}(E)/\cos\alpha + \mu_{tot}(E_f)/\cos\beta}$$

wherein  $I_f(E)$  is the intensity of the measured fluorescence signal,  $I_0(E)$  the intensity of the incident beam,  $\alpha$  the angle between the incoming beam and the sample normal and  $\beta$  the angle between the sample normal and the outgoing beam.  $\mu_{abs}(E_f)$  and  $\mu_{bac}(E_f)$  are the absorption coefficients of the absorbing atoms and the back-scattering atoms respectively. We have applied SAC to both the Cu  $L_3$  and the O K spectra. However, before applying the SAC the fluorescence intensity was first normalized with respect to the intensity variations in the monochromatic incident beam to obtain  $(I/I_0)$  followed by pre-peak background subtraction. The spectra were then normalized to the known absorption cross-sections at 600 eV for the O K and 1000 eV for the Cu  $L_3$  cases respectively where the absorption cross sections become purely atomic in nature.

### 3. Results

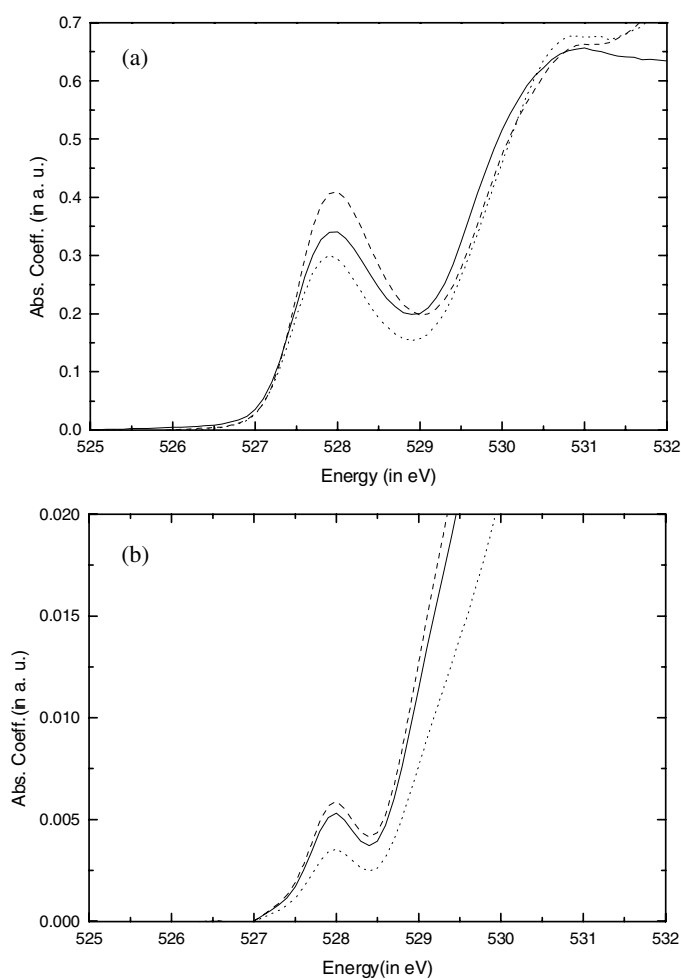
#### 3.1. The O K edge

The  $E \parallel ab$  and  $E \parallel c$  polarized O K-edge spectra for the three single crystals are shown in figure 1. The former probes the O  $2p_{x,y}$  symmetric hole states and the latter the states with O  $2p_z$  character. As is well known, the presence of itinerant holes is clearly indicated by the presence of the pre-edge peak  $\sim 528$  eV, which is conspicuously missing in the absence of these holes, e.g. in the spectrum for CuO and undoped cuprates [33]. The pre-peak is ascribed to the transition  $1s \rightarrow 2p$  Zhang–Rice impurity states formed in the correlation gap as known from the Hubbard model of doped charge transfer insulators [30]. This feature arises due to a doping-induced shift of the Fermi level into the valence band, the creation or transfer of holes in the valence band and a transfer of spectral weight from states in the upper Hubbard band (UHB) to the upper edge of the valence band. Neglecting the excitonic effects, one can conclude that these oxygen-derived  $2p$  final states are located at the Fermi level [31, 32]. The intensity of this pre-peak is known to be directly proportional to the amount of hole doping and is known to be a direct measure of density of the itinerant/doping holes [20–26, 30–32] in these systems but not their  $T_c$  [36].

Figures 1(a) and (b) show this pre-peak at  $\sim 528$  eV for all the three  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  single crystals for the  $E \parallel (a, b)$  and  $E \sim \parallel c$  plane in the corrected spectra. One can clearly see that intensity of this peak in the case of  $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  is higher than the pristine  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$ , while in the case of  $(\text{HgI}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  it turns out to be lower than that in the pristine sample. Comparing the intensities of the pre-peak from the  $E \sim \parallel c$  ( $75^\circ$ ) spectra we see similar albeit smaller changes with intercalation. This implies that intercalation of  $\text{I}_2$  leads to further doping of  $2p_{x,y}$  holes in the  $ab$  plane as well as  $2p_z$  holes along the  $c$ -axis, but hereafter we shall confine our attention solely to the  $E \parallel ab$  spectra as it is these in-plane holes that are intrinsic to their superconductivity.

Gaussians, four in each case, were fitted to these corrected O K spectra for all the three crystals to obtain a relative quantitative estimate of the itinerant holes (figures 2(a)–(c)). The first Gaussian represents the pre-peak at  $\sim 528$  eV, which represents the itinerant holes. The next two Gaussians beyond 530 eV appear due to the localized holes and arise from the transition in the UHB. This band is associated with intrinsic holes due to charge transfer from O to Cu described as covalent or localized holes [20, 29]. The spectral weight of these peaks is caused by O  $2p$  states covalently mixed with Cu  $3d$ , Cu  $4s$ , Cu  $4p$ , Ca  $3d$  and Sr  $4d$  states [26, 29]. The intensity of the first representing holes and the composite intensity of the next two Gaussians is shown in table 1. The percentage error was estimated by repeating the fitting process with the Gaussian representing covalent holes a number of times. The background correction, normalization and SACs were also repeated, followed by fitting of Gaussians again. The value shown in table 1 represents the maximum error in the measured area of the Gaussians.

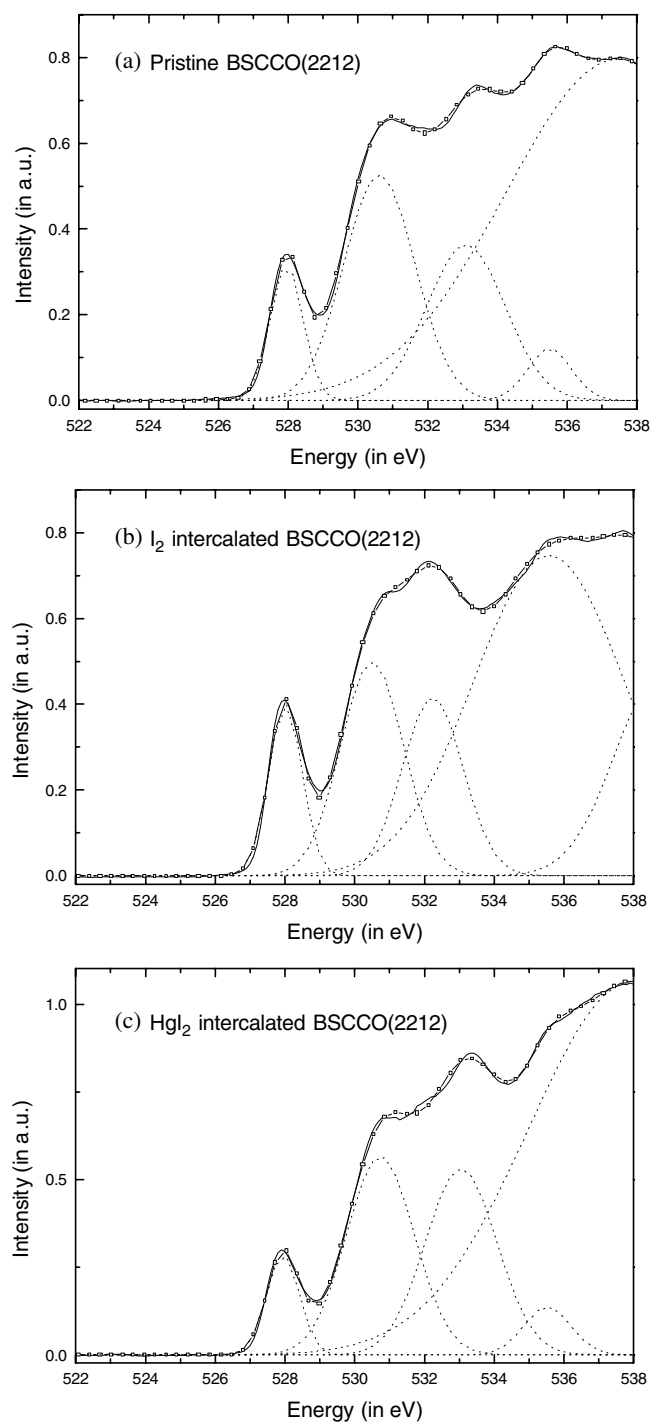
Confining our attention to the O  $2p_{x,y}$  symmetric holes we look at table 1. It can be clearly seen that for the  $E \parallel (a, b)$  polarization the area of the first Gaussian, i.e. the number of O  $2p_{x,y}$  symmetric hole states, increases on intercalation of the  $\text{I}_2$  compared with that in the  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  pristine crystal. This clearly indicates that the intercalation of  $\text{I}_2$  has resulted in further doping of holes in the  $\text{CuO}_2$  plane, which thus becomes overdoped and hence shows a depression in  $T_c$ . This result is in complete agreement with all the earlier studies [15]. However, the crystal intercalated with  $\text{HgI}_2$  molecules appears to tell an entirely different story. In this case, it can be clearly seen that the number of O  $2p_{x,y}$  symmetric doping holes (first Gaussian) is unambiguously smaller than that in the case of the pristine crystal. Evidently, in contrast to the intercalation of  $\text{I}_2$ , the intercalation of the  $\text{HgI}_2$  molecule quenches



**Figure 1.** (a), (b) Intensity of the O K pre-peak at  $\sim 528$  eV in (a) the  $E \parallel (a, b)$  polarization and (b) the  $E \sim \parallel c$  polarization. Pristine  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  spectra, solid curve;  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}\text{-I}_2$ , dots;  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}\text{-Hg}_{0.5}\text{I}$ , dashes.

**Table 1.** Intensity of the O K-edge pre-peak at  $\sim 528$  eV from our corrected spectra shown in figures 1(a) and (b).

Compound (pristine as well as intercalated)	$T_c$ (K)	Length of $c$ -axis ( $\text{\AA}$ )	Area below O K pre-peak and the second + third peaks for $E \parallel (a, b)$ ( $\times 10^{-3}$ ) $\pm 0.2\%$	
			Area of pre-peak	Area of II + III peaks
Pristine	78	30.6	386	2368
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$				
$\text{I}_2$ intercalated	63	37.8	434	2043
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$				
$\text{HgI}_2$ intercalated	68	44.9	344	2748
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$				



**Figure 2.** (a)–(c) The corrected O K spectra for  $E \parallel (a, b)$  orientation for the pristine and  $I_2$ - and  $HgI_2$ -intercalated  $Bi_2Sr_2CaCu_2O_{8-\delta}$  single crystals with the Gaussian fits. The first peak indicates the itinerant holes while the second and the third peaks correspond to the localized/covalent holes.

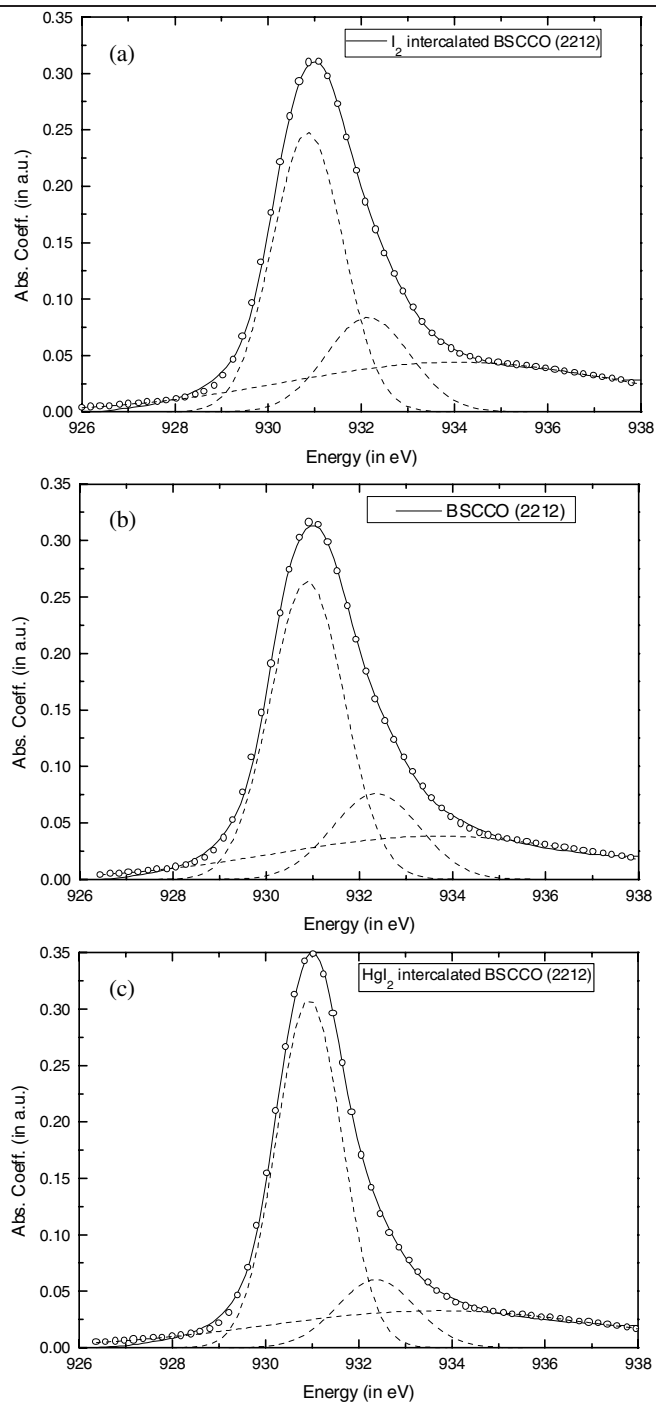
the hole density, indicating a charge transfer in the opposite direction, reducing the system to an underdoped state. This is substantiated by the fact that the area of the next two Gaussians turns out to be larger in this as compared with that in the case of the pristine crystal, clear evidence for transfer of itinerant holes to the localized/covalent holes or the UHB. Such transfer of weight was reported by Merz *et al* [20] in the case of Pr-doped detwinned  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  single crystals, Nucker *et al* [32] in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  upon doping and Chen *et al* [31] in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system upon cooling. It is also of interest to note that the composite area of the two Gaussians in the  $\text{I}_2$  intercalated crystal is lesser than that in the pristine sample. Thus, taking these facts into account, it is easy to conclude that while  $\text{I}_2$  intercalation leads to transfer of spectral weight from the covalent to the valence band region, the intercalation of  $\text{HgI}_2$  leads to transfer of spectral weight in the opposite direction, i.e. from valence band to covalent region. Our results in the case of  $\text{HgI}_2$  are thus in complete contradiction to the assertions made earlier [15] that in this case also the depression in  $T_c$  results from overdoping.

Although the pre-peak in the O K spectra represents the doping holes in O  $2p_{x,y}$ , it must be made clear that the  $T_c$  is not directly proportional to the intensity of this pre-peak [36]. Earlier studies on the relative importance of the in-plane and out-of-plane holes have clearly demonstrated the predominant importance of the former to superconductivity in all the cuprate systems [22]. In fact, some measurements [26] have even served to show an anomalous temperature dependence of the hole concentration in the  $\text{CuO}_2$  plane, i.e. the O  $2p_{x,y}$ -symmetric hole states, while no such behaviour has been reported for the out-of-plane  $E \parallel c$  O  $2p_z$ -symmetric holes.

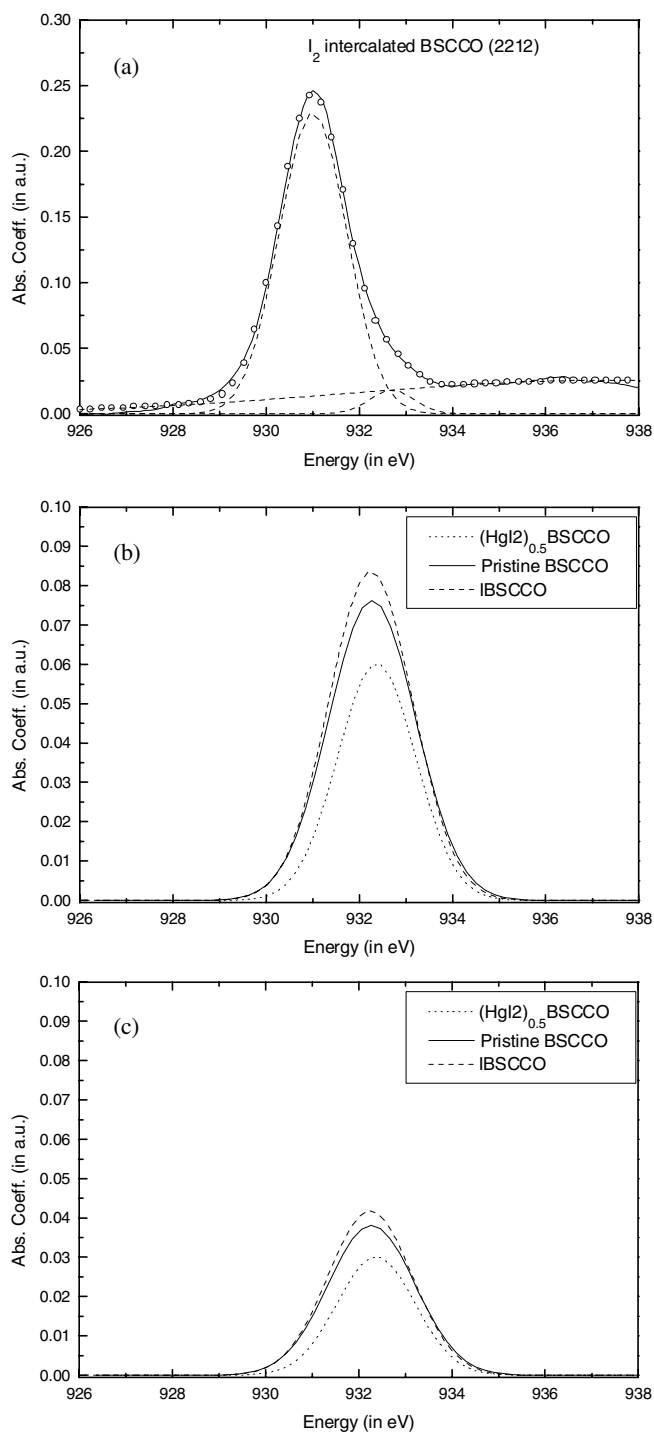
### 3.2. The Cu $L_3$ edge

Our corrected  $E \parallel (a, b)$  and  $E \sim \parallel c$  polarized Cu  $L_3$ -edge spectra recorded under identical conditions for all three  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  single crystals show a shoulder on the high-energy wing of the so-called white line. It is well established that the shoulder on the high-energy side of the main peak signifies the presence of itinerant holes [20–33] and does not appear in the absence of these holes, e.g. in undoped systems [33]. This shoulder ( $2p^63d^9\bar{\underline{L}} \rightarrow 2p^53d^{10}\bar{\underline{L}}$ ) following the main peak ( $2p^63d^9 \rightarrow 2p^53d^{10}$ ) grows proportionately to the number of itinerant holes in the superconducting systems, as does the intensity of the pre-peak in the O K edge XAS. In fact, it has been clearly shown [33] that the Cu  $L_3$  spectra of the undoped samples (having no itinerant holes) are beautifully fitted by a single Gaussian corresponding to  $|3d^9\rangle$  states. On the other hand, in the case of the doped systems having mobile holes one always has to fit two Gaussians separated by  $\sim 1.4$  eV [33]. The area of the second Gaussian can be reliably used for the estimation of the doped hole density [20–33]. We have first taken the second derivative of these Cu  $L_3$  spectra to correctly mark the positions of the main peak and the shoulder and then fitted the Gaussians to these. Then the error estimation in the area of the Gaussians was performed just as in the case of O K edge; this represents the maximum error value in our experiment. Figures 3(a)–(c) show the three Gaussians fitted to the Cu  $L_3$ -edge spectra for all the intercalated and pristine  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  single crystals for the  $E \parallel (a, b)$  polarization. The first Gaussian represents the Cu  $|3d^9\rangle$  states, the second the Cu  $|3d^9\bar{\underline{L}}\rangle$  states and the third Gaussian represents the inelastic scattering of photons from the crystal surface. Figure 4(b) shows the relative intensities of the doping hole states (represented by the second Gaussian) and clearly indicates that it is a maximum in the case of the  $\text{I}_2$ -intercalated crystal followed by that in the pristine crystal and then lowest in the  $\text{HgI}_2$ -intercalated crystal. This, in turn, means that while intercalation of iodine renders the system overdoped, the intercalation of  $\text{HgI}_2$  makes it underdoped. In either case, overdoping or underdoping, the  $T_c$  will be depressed.





**Figure 3.** (a)–(c) Background-subtracted and normalized Cu  $L_3$ -edge  $E \parallel a, b$  polarized spectra for the three single crystals (solid curve) with three Gaussians fitted to each of them: (a) the  $I_2$ -intercalated  $Bi_2Sr_2CaCu_2O_{8-\delta}$ , (b) the pristine  $Bi_2Sr_2CaCu_2O_{8-\delta}$  and (c) the  $HgI_2$ -intercalated  $Bi_2Sr_2CaCu_2O_{8-\delta}$  single-crystal spectra. The Gaussians fitted to them are shown as dashed curves and open circles represent the total contribution from the three Gaussians. The agreement between the experimental spectra (solid curves) and the curve obtained from the sum of the three Gaussians (open circles) is rather good.



**Figure 4.** (a) The Gaussian fits in the case of the out-of-plane  $E \sim (c)$  spectra for the  $\text{I}_2$ -intercalated crystal. (b) The relative intensities of the second Gaussian for the in-plane  $E \parallel (a, b)$  polarization in the three crystals, which represents the  $3d^9 \underline{L}$  doping hole states and (c) the relative intensities of the Gaussian representing the doping hole states in the  $E \sim (c)$  polarization in the cases of the three crystals.

**Table 2.** Intensity of the shoulder and the itinerant hole density from the Cu L<sub>3</sub> spectra.

Single crystal	$E \parallel (a, b) (0^\circ)$		$E \sim \parallel c (75^\circ)$	
	Area ( $10^{-3}$ ) $\pm$ 0.3%	$n_h$	Area ( $10^{-3}$ ) $\pm$ 0.3%	$n_h$
Pristine	184	0.26	45	0.05
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8-<math>\delta</math></sub>				
I <sub>2</sub> intercalated	188	0.28	48	0.05
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8-<math>\delta</math></sub>				
HgI <sub>2</sub> intercalated	131	0.18	34	0.04
Bi <sub>2</sub> Sr <sub>2</sub> CaCu <sub>2</sub> O <sub>8-<math>\delta</math></sub>				

Figure 4(b) show three Gaussians fitted to the Cu L<sub>3</sub>-edge spectra for the I<sub>2</sub>-intercalated Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8- $\delta$</sub>  single crystal for the  $E \parallel c$  polarization. Similar fits were made in the case of the spectra from the pristine and the HgI<sub>2</sub> intercalated crystals (not shown).

Figure 4(c) shows the relative intensities of the second Gaussian for the out-of-plane  $E \parallel \sim (c)$  for the three crystals. It can be clearly seen that compared with the intensity in the case of the pristine crystal that for the I<sub>2</sub>-intercalated crystal is higher but that in the HgI<sub>2</sub> intercalated system is lower.

The results from the Cu L<sub>3</sub> edge are thus in complete agreement with the results obtained from the O K-edge spectra earlier. These results are summarized in table 2. Further, the density of doping holes for various orientations in all the three crystals were calculated quantitatively in the usual way with the help of the relation  $n_h = I(3d^9\bar{L}) / \{I(3d^9) + I(3d^9\bar{L})\}$  [23–29] where  $n_h$  is the number of doping holes as a fraction of total number of holes (doping and covalent i.e. density of doping holes per CuO<sub>2</sub> plane) present in that particular orientation. These results are also given in table 2 and are in agreement with our earlier results [37].

First of all, it can be easily seen from table 2 that the area of the  $|3d^9\bar{L}\rangle$  peak and the doping hole density is not only non-zero but is significant in the  $E \sim \parallel c$  case, which establishes beyond any doubt that some Cu 3d <sub>$z^2-r^2$</sub>  doping holes are also present. This is quite in agreement with our earlier report [24]. We have already seen the same behaviour in the case of the O 2p <sub>$z$</sub>  holes. Taken together, this implies that there are holes at the apical oxygen too, albeit less in magnitude as compared with the in-plane hole concentration.

Since the differences in the intensities of the shoulder ( $|3d^9\bar{L}\rangle$  doping holes) from one crystal to another are far beyond the maximum error limit there is no cause for doubting the reliability of these numbers. However, to further rule out any chance of errors creeping into the above numbers we have subtracted spectra for both the I<sub>2</sub>-intercalated and the HgI<sub>2</sub>-intercalated crystals from that of the pristine crystal (not shown). This shows a positive residual spectrum at the Cu 3d<sup>9</sup> position and a negative residue at the position of the  $|3d^9\bar{L}\rangle$  shoulder. This leaves no doubt whatever about I<sub>2</sub> intercalation resulting in overdoping of the CuO<sub>2</sub> planes. The results in the case of the HgI<sub>2</sub> intercalation are exactly opposite, with the residual spectrum at the Cu 3d<sup>9</sup> position turning out negative and a positive residue at the position of the  $|3d^9\bar{L}\rangle$  shoulder. In short, one can conclude that, contrary to the results reported earlier [15], HgI<sub>2</sub> intercalation in the case of the Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8- $\delta$</sub>  crystal results in underdoping of the CuO<sub>2</sub> host planes.

#### 4. Discussion

From the above results one can unhesitatingly support the conclusion drawn earlier [14, 15, 17–19] and say that the depression of  $T_c$  on I<sub>2</sub> intercalation results from the CuO<sub>2</sub> plane becoming overdoped; that in the case of HgI<sub>2</sub> intercalation is due to the host plane becoming underdoped.

This is also quite understandable in view of the great affinity of iodine for electrons. In  $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$ , the  $\text{I}_2$  molecule is intercalated between Bi–O bilayers. In the  $\text{I}_2$  molecule the electron affinities of the two atoms will be the same; both will be neutral and their electron affinity is greater than Bi, hence the I atom will act as an acceptor of electrons, leaving the  $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  system overdoped. Meanwhile, in  $(\text{HgI}_2)_{0.5}\text{-Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$ , the  $\text{HgI}_2$  molecule will be in the opposite situation, i.e.  $\text{I}^{\delta-}\text{-Hg}^{2\delta+}\text{-I}^{\delta-}$ , hence there will be some negative charge on the I, and now sitting in the lattice between the Bi–O bilayers it will act as a donor of electrons, leaving the system underdoped.

From a critical study of the literature we find that the conclusion drawn earlier on hole density in the case of the  $\text{I}_2$ -intercalated system is derived from the Hall coefficient measurements [19]. However, the conclusion in the case of the  $\text{HgI}_2$  intercalation [15] appears to have been drawn on basis of indirect conjectures rather than on the basis of any such direct experimental evidence. This should also be clear from the argument about the relative affinity of the  $\text{I}_2$  and the  $\text{HgI}_2$  molecules for electrons discussed above. In fact, Garg *et al* [34] have, from their preliminary measurements, reported underdoping resulting not only from the intercalation of  $\text{HgI}_2$  molecule but also the  $\text{HgBr}_2$  molecule. On the other hand, an earlier report [19] shows the existence of an asymmetrical negative tri-iodide ion weakly interacting with the adjacent Bi–O layer. It is believed that the Bi–O layers act as charge reservoirs for electrons, which create holes in the Cu– $\text{O}_2$  planes. Therefore, they suggest that the major contribution to the change in  $T_c$  on iodine intercalation could be due mainly to suppression of the staggered configuration of the layers with all getting aligned along the  $c$ -axis. This results in the interlayer expansion within a block rather than the charge transfer between iodine and the host layers. However, our results show very clear evidence of change in the hole density, leading to the system becoming overdoped. Further, from table 1 it is easy to see that there is no direct relationship between the length of the  $c$ -axis and  $T_c$ . The length of the  $c$ -axis in the three systems happens to be in the order pristine  $< \text{I}_2 < \text{HgI}_2$ ; the  $T_c$  turns out to be in the order pristine  $> \text{HgI}_2 > \text{I}_2$ . Huang *et al* [19] have studied the pressure dependence of  $T_c$  and the Hall coefficient in  $\text{I-Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  crystals and found the  $T_c$  to decrease at the rate  $dT_c/dp \sim -3.5 \text{ K GPa}^{-1}$  because of further doping of holes in the Cu– $\text{O}_2$  planes. They also observed an improved conductivity along the  $c$ -direction, reinforcing their conclusion. This can also be seen in the increase of hole density in  $\text{I}_2$ -intercalated  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  with a smaller increase in the  $c$ -axis compared with that in the  $\text{HgI}_2$ -intercalated crystal, in which the  $c$ -axis is becoming larger. This clearly means that the smaller the distance between the intercalant and the host layer the larger would be the hole transfer from the intercalant molecule to the host layer. As a corollary of this and on the basis of our observed results we dare predict that the pressure dependence of the  $\text{HgI}_2\text{-Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  system, when measured, is likely to also yield a negative value of  $dT_c/dp$ , for the decrease of the distance between the intercalant on applying pressure ought to lead to a larger hole transfer in the opposite direction, i.e. a large transfer of electrons from the intercalant to the host layer, rendering the system further underdoped. It would also be negative in the  $\text{I}_2$ -intercalated  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  System, as this would make the system more overdoped. Also, it has been reported [15] that a shortening of the Cu– $\text{O}_{\text{Sr}}$  bond implies the broadening of the valence band, which, in turn, is known to induce different  $T_c$  changes depending on the hole concentration of the Cu– $\text{O}_2$  layer [19]; the  $T_c$  is enhanced in the case of an underdoped system and depressed in an overdoped system. This would imply that the  $dT_c/dp$  should be positive in the case of the  $\text{HgI}_2$ -intercalated  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  system and negative in the case of the  $\text{I}_2$ -intercalated  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  system, which contradicts the above results [19].

Very recently, intercalation has also been performed in fullerenes [38], as the molecular structure of fullerenes facilitates intercalation. It is believed that the superconducting state of

fullerides is caused by the coupling of the carriers with intra-molecular vibrations of the  $C_{60}$  unit [39]. With the field effect technique it is possible to dope the parent compound with either electrons or holes [40]. In the latter case, the critical temperature of the fullerides is higher than that for usual n-doped materials, because the doping hole band has a larger density of states. Intercalation of  $CHCl_3$  and  $CHBr_3$  into the hole-doped  $C_{60}$  fullerides leads to a drastic increase in  $T_c$  ( $52 \rightarrow 80 \rightarrow 117$  K). This increase in  $T_c$  is caused by the softening mechanism, i.e. by the decrease in the characteristic vibrational frequencies and corresponding increase in the coupling constant. For the same reason the authors of [41] predict the coupling constant to be larger for the  $C_{60}/CHI_3$  compound, and as a result of this we should obtain an even larger  $T_c$  of 140 K. This is just the opposite of the results in the cuprates. However, one must take into account that intercalation in the fullerides leads to a structural change too, while in cuprates it is only the length of the  $c$ -axis that changes. In fullerides on doping of holes the  $T_c$  is increasing due to change in the structure as a whole and to softening of the molecular vibrations. However, in the  $Bi_2Sr_2CaCu_2O_{8-\delta}$  system only the  $c$ -axis length is increasing and superconductivity is not subject to any such molecular vibrations. Also, the parabola of  $T_c$  versus hole density has not been found to be applicable to the fullerides.

It is thus amply clear that the inter-block coupling is of importance to the evolution of the  $T_c$  as it affects the charge transfer between the intercalant and the host layer, thereby affecting the hole density. As far as the intra-block coupling is concerned, we have more than adequate evidence that it usually plays havoc with the  $T_c$ , e.g. on substitution of Y in  $YBa_2Cu_3O_7$  (123) or Ca in  $Bi_2Sr_2CaCu_2O_{8-\delta}$  by Pr or non-magnetic Zn or any magnetic cation in place of Cu in any of the cuprates. Successful synthesis of a pure  $PrBa_2Cu_3O_7$  (123) single crystal [11] has been reported, but the evolution of superconductivity in this system has been ascribed to some Ba and Pr interchanging sites [11]. All said and done, the importance of coupling between different layers of the same block to  $T_c$  is beyond any realm of doubt. In this regard it would be interesting to find out whether the exchange of Ba and Pr cations takes place only when all Y has been replaced by Pr, which would be rather strange, or also when it is partially replaced, as in  $Y_{(1-x)}Pr_xBa_2Cu_3O_7$ . If the latter is found to be true it would imply that a fraction of Y smaller than that reported in the  $YBa_2Cu_3O_7$  (123) system,  $x \sim 0.5$ , would be enough to quench the superconductivity if there were to be no exchange of sites between Ba and Pr. It would be interesting to test the above results and predictions by having a  $Bi_2Sr_2CaCu_2O_{8-\delta}$  single crystal with a small fraction of its Ca replaced by Pr, resulting in depression of  $T_c$ , and intercalating iodine in it, which is expected to dope additional holes in the  $CuO_2$  layer and thus push the  $T_c$  up, compensating for the earlier depression in  $T_c$  due to Pr doping.

## 5. Conclusion

From our polarization-dependent Cu  $L_3$ - and O K-edge XAS measurements in the superconducting pristine  $Bi_2Sr_2CaCu_2O_{8-\delta}$ , and two other single crystals intercalated with  $HgI_2$  and  $I_2$  molecules, it is clear that the interblock coupling does lead to a charge transfer between the intercalated molecule and the host  $Cu-O_2$  layer. Contrary to conclusions drawn in earlier reports, while intercalation of  $I_2$  in the crystal leads to overdoping, intercalation of  $HgI_2$  leads to underdoping. Of course, as expected, the  $T_c$  in both cases is depressed, albeit by different amounts. As far as comparison of interblock and intrablock coupling is concerned, it is quite apparent that both are important to the evolution of  $T_c$  in a system. We also predict that application of pressure on the  $HgI_2$  intercalate ought to lead to further depression of  $T_c$ , although in this case it would be due to further quenching of holes due to decrease of distance between the intercalant and the host layer; on the other hand, in the  $I_2$  intercalate the  $T_c$  will decrease because the shortening of the basal distance would render the system more overdoped.

We also suggest study of a  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8-\delta}$  single crystal with a small fraction, say 10–20%, of Ca replaced by Pr and an  $\text{I}_2$  molecule intercalated, and find out whether the former, which reduces the hole density, can be compensated by the latter, which should dope additional holes. This happens to be the subject of our study under progress.

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