

## Empty states in cuprous halides studied with bremsstrahlung isochromat spectroscopy

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(Received 2 July 1993)

The conduction bands of cuprous halides are studied through bremsstrahlung-isochromat-spectroscopy (BIS) experiments. These results are compared with the densities of states calculated by the linear-muffin-tin-orbital (LMTO) method. The good agreement in the low-energy range permits us to determine the contributions of the different symmetries on the two sites of the three halides. On the higher-energy side BIS, as well as x-ray-absorption spectra, show that the LMTO gives better agreement when they are compared with the *p* states on copper in CuI than in CuCl.

### I. INTRODUCTION

In this paper we study the empty states in cuprous halides through BIS (bremsstrahlung isochromat spectroscopy) experiments. The photoemission,<sup>1,2</sup> optical spectroscopy,<sup>3</sup> and energy-band calculations<sup>4,5</sup> have already given a clear structure of the valence bands. For the empty bands some partial information is available through secondary photoemission data<sup>2,6</sup> and in a more general manner, through x-ray-absorption measurements. Presently we have performed BIS experiments for the following reasons.

We have already measured the Cu *K* and Cu *L*<sub>3</sub> edges on the three halides (CuX, X = Cl, Br, I).<sup>7,8</sup> According to the dipole selection rules these spectra give formally the partial densities of states (DOS) localized on the copper atom. However, the very different resolution due to core hole widths (respectively, 1.55 and 0.56 eV), makes the correlation of the two types of spectra quite difficult. The comparison with theoretical band schemes, through critical point considerations as attempted up to now, becomes still more hazardous when the optical spectra<sup>3</sup> are also taken into account. It is also not easy, if not impossible, to refer all these spectra to the valence-band maximum (VBM) with a precision compatible with the characterization of core excitons through the evaluation of the binding energy.

At the halogen site, due to the increase of the hole width from Cl to I, it becomes impossible to track the evolution of the partial DOS in the CuX sequence. Even when we refer to the *L*<sub>1</sub> of iodine, the hole width increases from 0.64 to 3.08 eV when going from CuCl to CuI. The instrumental resolution for BIS experiments is of the same order of magnitude as that of the overall resolution of the Cl *K* and Cu *L*<sub>3</sub> spectra.

Up to now the BIS technique has been mainly used for the study of the electronic properties of narrow-band metallic materials<sup>9</sup> or oxides.<sup>10,11</sup> In a more general manner it is interesting to look about the opportunity of BIS experiments on semiconductor materials, other than oxides,

in regard to their thermal and electrical behavior when interacting with the impinging intense electron beam.

For the understanding of the x-ray-absorption spectra, usually two models are used to describe the electronic structure of a material: (1) the band-structure model and (2) the multiple-scattering model. In the band-structure model, the DOS are considered. The BIS technique gives a direct image of the total DOS as far as the transition matrix elements may be neglected. Hence, BIS is the natural partner of the band-structure problem via the DOS. In the present paper the partial DOS are calculated by the linear-muffin-tin-orbital (LMTO) method.

In the multiple-scattering model, one supposes the creation, on a central atom, of a photoelectron which is scattered by the neighboring atoms.<sup>12</sup> This model involves directly the x-ray absorption and works in the real space. The confrontation of the experimental x-ray-absorption spectra with theoretical calculations shows that the agreement is generally good with the two models for about 15 eV above the edge. For higher energies, the experimental broadbands, predicted in the multiple-scattering model are often considered as resonant structures, involving characteristic interatomic distances.<sup>13</sup> In the present work, the comparison of the Cl *K* edge with the BIS spectra shows that a broadband, as reproduced by multiple-scattering model for the isoelectronic compound ZnS,<sup>14</sup> appears also in the DOS as probed by BIS.

In Sec. II we recall some experimental details principally in regard to the compounds to be studied. In Sec. III some theoretical points are summarized, in particular the local and partial DOS on the two atoms are displayed. The essential features and their behaviors in the CuX sequence are outlined. In Sec. IV the experimental results are presented and discussed in terms of partial DOS. The tentative conclusions to bring the experimental data in better agreement with DOS give some indications about the cross section of the different orbitals on the two sites. We show also briefly how the BIS spectra, and their interpretation with the help of the LMTO, are useful for the understanding of x-ray-absorption spectra.

## II. EXPERIMENT

The experimental device is a classical one working at a base pressure in the  $10^{-10}$ -torr range.<sup>15</sup> The monochromator is Johann's type with a quartz crystal of 100 mm diameter. The Rowland circle has a diameter of 1 m. The quartz plane is (10 $\bar{1}$ 0) which selects the Al  $K\alpha$  line (1486.6 eV) with a Bragg angle of 78°32'. The monochromatized electrons, impinging normally on the sample, are delivered by a cylindrical Pierce gun designed with indirect heated BaO impregnated cathodes. To sweep the acceleration voltage we use the retarding potential ramp from the electron spectrometer (CLAM 100 from VG) which also equips the UHV chamber to perform Auger spectroscopy. The selected energy range is swept repetitively in order to minimize the effect of the instabilities of the emission current. This current is typically 0.5 mA. The x-ray photons are intercepted by a stainless-steel cathode, recovered by CsI, placed at the focusing point of the monochromator. This cathode acts as the exit slit of the monochromator and as a photoconverter. The resulting secondary electrons are focused onto the entrance cone of a channeltron, which is also monitored by the counting system of the CLAM 100.

The sample holder is at liquid-nitrogen temperature. The samples are thin layers of about 1000 Å evaporated onto molybdenum sheets. This configuration avoids electrical charging effects even in the case of CuCl for which the resistivity is the highest. Before the transfer in the measuring chamber the samples are heated in the preparation chamber at a temperature where the sublimation starts. This procedure leads not only to an outgasing but also to a regeneration of the surfaces of the microcrystallites. This regeneration will probably also act during the measurement when the thin layers are exposed to the electron beam of about 0.75 W. The energy is swept by steps of 0.1 or 0.2 eV. The whole resolution of the apparatus is estimated to 0.7±0.1 eV. The spectra are not deteriorated during the accumulation time which may be about several hours. The stability of the spectra on long time range, within the precision of 0.3 eV, also shows that charging effects may be neglected. Nevertheless the spectra reported here are registered within typically 1 h.

## III. THE PARTIAL DENSITIES OF STATES BY LMTO

To compare the experimental spectra with band-structure calculations, we presume that the bremsstrahlung transition has the same probability near the core of the copper or the halogen atom. Hence, the transition rate on each atom results from a band-structure effect taking into account the local and partial DOS modulated by an atomic cross section  $\sigma$ .

The partial densities for the three halides are deduced for the band structure calculated by the method of LMTO in atomic-sphere-approximation where the combined correction is properly included.<sup>16</sup> The Hedin-Lundqvist local-density approximation is used for exchange correlation.<sup>17</sup>

The CuX compound is a I-VII zinc-blende (ZB) structure where one chemical specie forms a face-centered-cubic structure while the other occupies the four alternate corners ( $a/4, a/4, a/4$ ), ( $3a/4, 3a/4, a/4$ ), ( $3a/4, a/4, 3a/4$ ), and ( $a/4, 3a/4, 3a/4$ ). The remaining four corners ( $3a/4, 3a/4, 3a/4$ ), ( $a/4, a/4, 3a/4$ ), ( $a/4, 3a/4, a/4$ ), and ( $3a/4, a/4, a/4$ ) are empty. Here  $a$  is the lattice constant. Due to these four empty corners the ZB structure is not compact. To make it compact, the common procedure is to put empty spheres (Es) in these corners.<sup>18</sup> Now, instead of two atoms per unit cell we have three atoms per unit cell and the chemical formula becomes CuXE<sub>s</sub>.

The starting potential is constructed with the electronic charge of Cu and X atoms calculated for their proper electronic configurations. For the Es the starting charge is zero. For Cu we consider  $3d^{10}4s^14p^0$  and for X  $ns^2np^5nd^0$  as valence electrons. Here,  $n=3, 4$ , and  $5$  for Cl, Br, and I, respectively. For the Brillouin zone (BZ) integration we used tetrahedron method<sup>19</sup> with 95  $k$  points in the irreducible BZ. The self-consistency in all three cases was attained with less than 30 iterations.

The partial and local DOS have been calculated for the three compounds. In the LMTO method the potential of the muffin-tin spheres is of spherical symmetry and is the function of the absolute value of the distance, whereas the potential in the interstitial space is put to zero. In Fig. 1 we represent those corresponding to the interstitial spaces. The forbidden gaps are about half as compared to those measured experimentally which are 3.4, 3.1, and 3.1 eV, respectively, for CuCl, CuBr, and CuI.<sup>3</sup> This is a common feature in all self-consistent energy bands of semiconductors obtained in local-density approximation. The maxima of the valence band has 74%, 63%, and 42% of Cu  $d$  orbitals for CuCl, CuBr, and CuI according to the present calculation. This is in excellent agreement with experimental observations.<sup>20</sup> We limit ourselves to about 20 eV which corresponds to the limit where experimental features are still observed with an accuracy of 1 eV in regard to the signal-to-noise ratio which becomes very small. In order to compare the experimental BIS data to the DOS, these last are convoluted with a Lorentzian with a width at half maximum of 0.6 eV. The convolution is done only for nonzero DOS, so that the forbidden gaps before convolution are conserved. This is the reason that one notices an abrupt change in the convoluted DOS when one reaches the forbidden gap.

The BIS spectra will be dominated by the  $B$  peak (Fig. 1) which appears with a pronounced shape for  $p$  states on copper as well as for  $d$  states on the halogen for the three halides. This peak delimits two ranges: in the lower part, the contribution of  $s$  states on the copper is predominant; on the high-energy side, the  $d$  states on the halogen are important.

About the low-energy side, all the partial DOS on copper suggest that the  $B$  peak will be preceded by two structures,  $A$  and  $A'$  (Fig. 1). The intensity of  $A$  will be highly affected by the cross section of  $s$  states on copper, which appears as a well-defined peak which narrows from CuCl to CuI. The  $A'$  structure corresponds principally to a step on the low-energy side of the  $B$  maximum in the

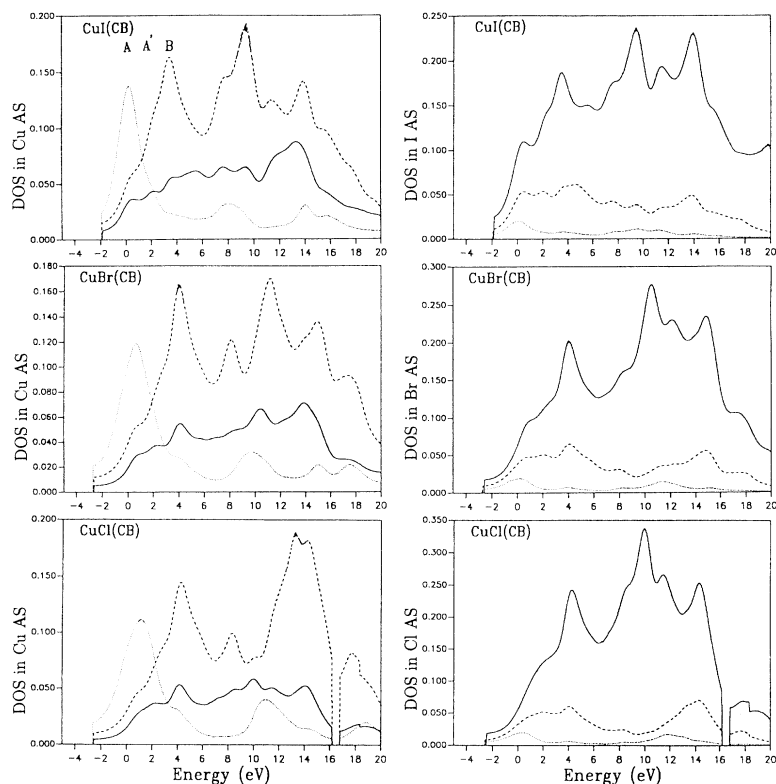


FIG. 1. The convoluted partial DOS ( $\text{eV}^{-1}$ ) as given by LMTO in the atomic spheres of copper (CuAS) and halogen (XAS).  $\cdots$ ,  $s$  states;  $---$ ,  $p$  states;  $—$ ,  $d$  states.

partial  $p$  contribution of copper. It is also in the energy range where  $s$  states are still present. Accordingly, not only its shape, but also its energy position will strongly depend upon the cross section of  $s$  states. We retain of these considerations that in all cases the BIS spectra will start with a triplet structure whose shape depends on the weight of the  $s$  states.

For CuCl, on the high-energy side of  $B$ , the dominant contribution of  $p$  states on copper will be a well-defined peak at about 4 eV from  $B$  and then a more or less structured, but intense, band will be centered at about 10 eV from  $B$ . This configuration is only weakly affected when  $s$  or  $d$  states on copper are considered together. However, this overall shape may be strongly affected when  $d$  states on chlorine, with their very different shapes are taken into consideration. This last point will be discussed in the frame of the whole sequence. Coming back to the copper site, for CuBr and CuI the situation is somewhat different: four well-separated  $p$  peaks are observed in CuBr on the high-energy side of  $B$ . The Cu  $p$  DOS in CuI is almost the same but somewhat narrowed as compared to the corresponding DOS in CuBr. Hence, when considering only the partial  $p$  DOS on the copper, CuCl appears different as compared to CuBr and CuI. This particularity, accompanied by a gap following the broadband at about 10 eV from  $B$ , is probably related with the already well-known evolution of the mixing rate in the valence band when going from CuCl to CuBr,<sup>20</sup> the contribution of  $d$  copper states being maximum in the highest valence band of CuCl.

In regard to these differences it is interesting to note that the shapes of  $d$  states are very similar on the halogen sites. It is also surprising that the width of this spectrum

increases from CuCl to CuBr and decreases only slightly from CuBr to CuI. This observation is apparently not in agreement with the increase of the lattice parameter from CuCl to CuI. Finally it is very important to note that in the particular case of CuI, the shape of  $d$  DOS on I is quite similar to that of  $p$  DOS on Cu.

To improve the comparison of these data with the experiment we have to take into account the matrix elements of transitions between the incident free electrons described as plane waves and the final Bloch states in the different symmetry configurations. The cross sections of these transitions, for copper, are known.<sup>21</sup> Up to an energy of about 8 eV above the Fermi level, corresponding to the energy range where the most significant structures in BIS appear, the matrix elements per electron are of the same magnitude for  $s$  and  $p$  states, whereas they are about two times higher for  $d$  states.

The considerations apply only to the nonionized monoatomic copper, with its own muffin-tin radius. They are not representative for configurations involving two atoms and the accompanying charge transfer. In spite of these restrictions, we retain that in the concerned energy range the variation of the different cross sections is small but their relative values are unknown.

On the other hand, when dealing with two different chemical species of atoms, the comparison between BIS and partial DOS may give an insight to this problem. To reproduce a theoretical shape, as close as possible to the BIS, we try to modulate the contribution of  $s$  states on Cu in the lower part of the spectra. On the higher part the relative weight of  $p$  and  $d$  states on the halogen, from CuCl to CuI, is the origin of characteristic features in BIS as well as in x-ray absorption.

#### IV. THE BIS SPECTRA COMPARED TO DOS

The BIS spectra are displayed in Figs. 2(a) and 2(b). In regard to the high noise level two sets of curves are given. In Fig. 2(a), the recording of the spectra with an increased energy resolution shows some structures which are not observed in Fig. 2(b). The measurements performed in a more extended energy range, but with a loss of energy resolution, confirm the overall shape as already shown in Fig. 2(a) and give some information about the energy range extending up to 12 eV above the *B* peak.

The energies of the main structures are listed in Table I where they are referred to the *B* peak. First we observe, in the low-energy range in the three compounds, the three features *A*, *A'*, and *B*, as predicted in the partial DOS taking into account independently, the *s* and *p* states on copper as given by the LMTO calculation. This comparison gives the first indication about the agreement of BIS and LMTO. In Fig. 3, we give the convoluted theoretical total densities of states. In Table I, we also give the beginning energy of the BIS spectra (*S*, i.e., the Fermi level). It is not possible to relate *S* with the band structure without complementary data given by other experiments or by theoretical approaches. We have already seen that LMTO underestimates the gap, moreover its zero is not formally related to the vacuum level, so its contribution is not useful for an accurate location of VBM or conduction-band minimum (CBM) with respect to *S*. However in CuCl, the optical spectra as measured at room temperature by the reflection<sup>22</sup> reproduce quite well the *A*, *A'*, and *B* of the BIS spectra within  $\pm 0.3$  eV. So the position of the *B* peak is known with respect to the localized 3*d* Cu orbital which is well defined in the band scheme.<sup>23</sup> Combining these data with the gap, we may conclude that the *B* in BIS is at 6.8 eV from CBM. In other words *S*, within the experimental errors of about  $\pm 0.6$  eV, corresponds to the CBM. This will be extensively discussed in the work devoted to core excitons.<sup>8</sup>

Focusing our attention first to the low-energy side of the spectra we note that for CuCl the experimental triplet structure is not well reproduced by the total DOS (Fig. 3). The agreement is improved when going from CuCl to CuI. For CuBr the energy positions are reproduced by this configuration but the intensities of *A* and *A'* are inverted as compared to the calculated DOS. For CuI the agreement is quite good for the overall shape except that the experimental width of the triplet is about 2.6 eV whereas the theoretical value is 3.2 eV. In a more general manner, the intensity of *A* increases while that of *A'* decreases from CuCl to CuI. It is also noticeable that the width of the *s* band, which may be approximated by the

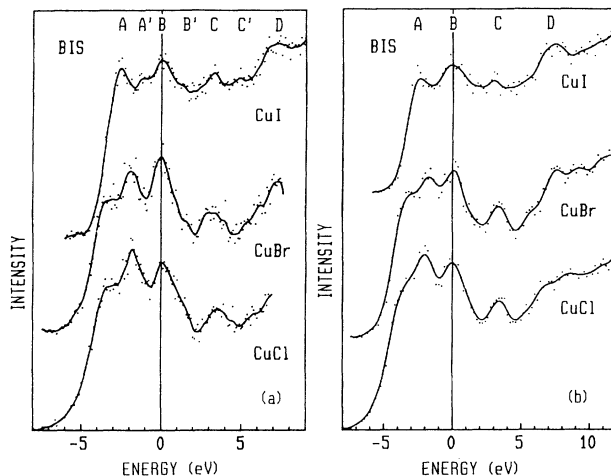


FIG. 2. BIS results for the three halides. The energy range of the electron gun is swept by steps of 0.1 eV in (a) and 0.2 eV in (b). The peak labels, with their true positions, apply to CuI. For the correspondence in the other compounds see Table I and Fig. 4(a) for CuCl.

separation between the beginning of the BIS and the first structure, respectively, 3.6, 3.2, and 2.3 eV in CuCl, CuBr, and CuI, is quite satisfactorily reproduced by the half width of the partial *s* peak in DOS, 3.8, 3.4, and 2.3 eV. These values correspond to the respective widths of the lowest conduction bands.

To improve the agreement between DOS and BIS, we take into account the cross section of the different symmetries, knowing that this procedure leads to the modification of the whole spectrum including the high-energy part, if we postulate that the matrix elements vary slowly as stated above in regard to the small-energy range. The comparable intensities of *A* and *A'* component in total DOS in CuCl result from the overestimated weight of *s* orbitals on copper [Fig. 3(c)]. The best correspondence between DOS and BIS is obtained when the *s* contribution on copper is reduced to about 30%. Even in this configuration the relative intensities of *A'* and *B* are not reproduced by LMTO. *A'* is always less intense as compared to *B*, whereas experimentally the situation is reversed.

CuBr is an intermediate case. The *A* peak is observed as a step on *d* states on bromine. The total DOS [Fig. 3(b)] already gives three components predicted by the experiment. However, to reproduce the "plateau"-like shape of the first component the *s* contribution has to be limited to about 30% as already stated for CuCl. In this

TABLE I. The structures of the three halides are given as observed in BIS. Their positions are given, in eV, with respect to the main peak *B*. The *S* denotes the beginning of the BIS spectra. In regard to the high noise level, the precision of the data is about 0.3 eV. The labeling of the structures is the same as those already used in our x-ray-absorption spectra (Ref. 7).

	<i>S</i>	<i>A</i>	<i>A'</i>	<i>B</i>	<i>B'</i>	<i>C</i>	<i>C'</i>	<i>D</i>	<i>E</i>
CuI	-4.9	-2.6	-1.2	0	1.3	3.2	4.8	7.2	
CuBr	-6.4	-3.2	-1.9	0	1.5	3.3			
CuCl	-6.8	-3.2	-1.8	0	1.5	3.5		7.5	8.7

way the complementarity of BIS and DOS permits us to propose cross-section values for  $s$  orbitals which are about 30%.

The surprising good agreement between BIS and LMTO for CuI results probably from the combination of two factors. The  $A$  feature appears now as a peak in the  $d$  states on the halogen and the  $s$  peak is narrowed in regard to what arises for the two other compounds. Accordingly, we retain a comparable cross section for  $s$  and  $p$  states on copper in BIS or at least compensated by an increasing contribution of  $d$  feature on the halogen.

The particular behavior of CuCl and CuBr in comparison to CuI is also found in the high-energy part of the BIS. In this range, the behavior of the  $C$  peak gives some indications about the contribution of  $d$  states on halogen. The well-separated  $C$  peak in the BIS of CuCl and CuBr

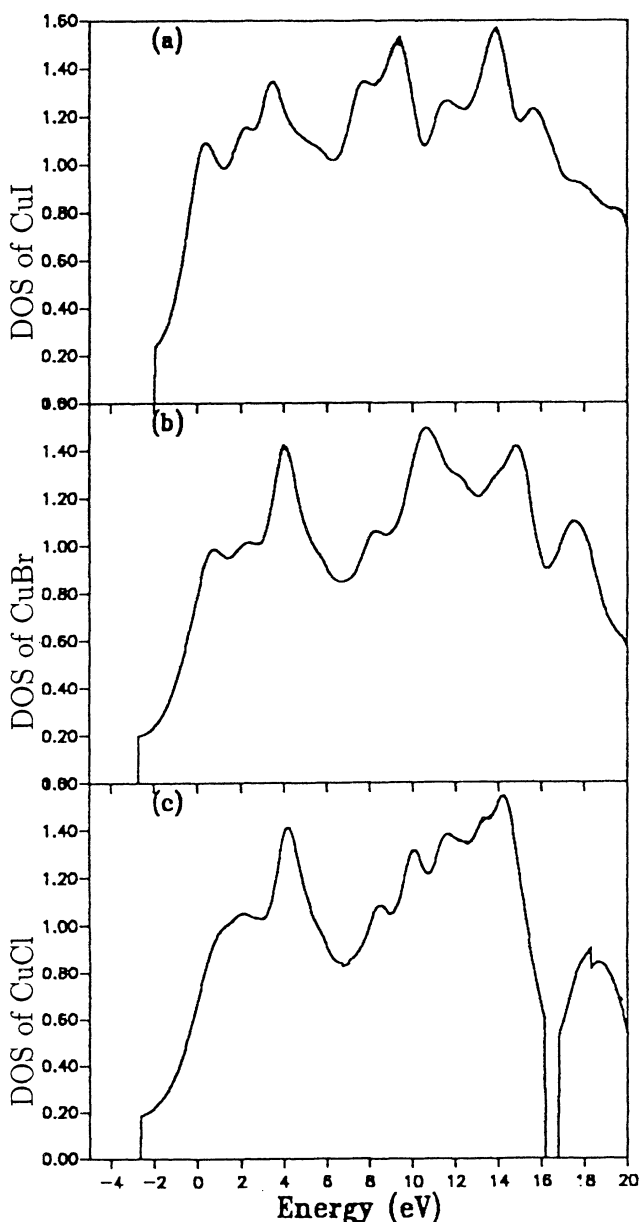


FIG. 3. The convolved total DOS ( $\text{eV}^{-1}$ ) in the three cuprous halides. CuI (a), CuBr (b), and CuCl (c).

is also well reproduced by DOS for  $p$  states on copper. However, it will be smoothed when  $d$  states on halogen are also considered (Fig. 3). This observation is another indication that BIS spectra suggest a negligible contribution of  $d$  final states located on the halogen for CuCl and CuBr.

The situation becomes more complicated when we compare all the high-energy features in the three compounds. There is not a direct correspondence between DOS and BIS when we compare the peak positions and their relative intensities on the three compounds. In the particular case of CuI [Fig. 4(b)], the  $B'$ ,  $C$ ,  $C'$ , and  $D$  features may have their equivalent in the partial DOS belonging either to  $d$  states on iodine or  $p$  states on copper since LMTO gives the similar shape for the two orbitals. About the apparent discrepancy concerning the peak positions in CuI, we have already noted that on the low-energy side of  $B$ , LMTO gives an enlarged picture when compared to BIS (respectively, 3.2 and 2.7 eV). Further information is necessary to comment on the interpretation given above. Some helpful data are available, either through secondary photoelectrons in photoemission or through x-ray absorption. However, we limit ourselves to report here some partial features of x-ray absorption. The comparison with the whole x-ray-absorption spectra on the two sites, in the different symmetry configurations, will be presented in a future paper.<sup>8</sup> In Fig. 4(a), we display the Cu  $K$  and Cl  $K$  edges, the BIS, and the partial  $p$  DOS on copper and chlorine. In Fig. 4(b) the Cu  $K$  and the I  $L_3$  edges, the BIS, the partial  $p$  DOS on copper, and the partial  $d$  DOS on iodine are shown.

At first, the presence of  $C$  in BIS and Cu  $K$  edges confirms the contribution of  $p$  orbitals, not only in CuCl but also in CuI even if in this case LMTO does not give a well-marked contribution. In CuCl, the very small  $D$  structure in Cu  $K$  and the intense  $E$  peak in Cl  $K$  are observed. These structures are also observed in BIS. This

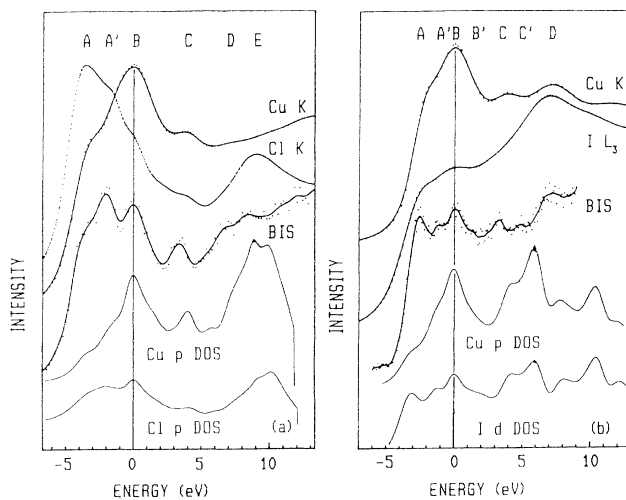


FIG. 4. The BIS experiments are compared with x-ray absorption and DOS. In (a) we show the Cu  $K$  and Cl  $K$  edges,  $p$  states on copper, and  $p$  states on chlorine. In (b), the Cu  $K$ , the I  $L_3$  edges, the BIS, the  $p$  states on copper, and the  $d$  states on iodine are displayed.

comparison confirms that the BIS spectra reproduces the contribution of partial DOS, as given experimentally by x-ray absorption, on the copper and the chlorine atoms. In this energy range, the LMTO model is not in agreement with the experiments because the partial  $p$  DOS on copper shows a strong contribution after the  $C$  peak which is not observed in the Cu  $K$  edge [Fig. 4(a)]. The agreement is better for the  $p$  orbitals on chlorine. The very pronounced  $E$  peak of Cl  $K$  is reproduced by  $p$  DOS on chlorine as given by LMTO. However the small intensity of  $E$  in BIS suggests another contribution when x-ray absorption is considered. The study by Saintavit *et al.* on the S  $K$  edge of the isoelectron ZnS shows that the  $E$  peak is very sensitive to the first neighboring S atoms when the theoretical spectra are calculated in the multiple-scattering scheme on small particles.<sup>14</sup> This confirms the importance of  $p$  DOS on chlorine when applying this model to CuCl. This also shows the resonant nature of the  $E$  when the photoelectron in x-ray absorption, instead of the free electron in BIS is considered. Coming back to the low-energy range in regard to  $B$ , it is also noteworthy that the Cl  $K$  reproduces quite well the BIS spectrum when we look for the energy positions only.

For CuI the situation is somewhat different. Even in the  $p$  DOS on copper the  $C$  peak appears only as a step. Moreover, the shape of  $p$  states on copper and  $d$  states on iodine are very similar in opposition to those for CuBr and CuCl, except that a new structure  $B'$  appears between  $B$  and  $C$  in  $d$  states on iodine. This last structure is well defined in BIS [Fig. 4(b)]. Hence, at least qualitatively, these considerations involve that  $d$  states on halogen are also probed by BIS in CuI. To confirm this point and also to see the correspondence between BIS and LMTO as suggested above, the x-ray-absorption spectra will be considered. Assuming that the core hole width of 1.5 eV will smooth out the  $B'$  and that the  $C$  and  $C'$  in BIS will form a single structure in Cu  $K$  for the same reason, the agreement between Cu  $K$  and BIS will be considered as very good. Especially it should be noticed that the  $D$  structure now appears as an intense and well-resolved peak not only in BIS and Cu  $K$  but also in I  $L_3$ . This means that the  $p$  states on copper and the  $d$  states on iodine have comparable shapes. This is exactly what we have already pointed out while discussing the partial density of states as given by LMTO for CuI. However, the exact shape is another question: the comparison with

BIS, as suggested in Fig. 4(b), shows that LMTO does not reproduce the relative intensities.

We have already observed the  $D$  peak in angle-resolved secondary photoemission spectroscopy.<sup>2</sup> There, it was attributed to the beginning of a dispersive final state in the  $\Gamma$ - $K$ - $X$  direction. Hence, the correspondence between BIS and LMTO, as suggested in Fig. 4(b), becomes still more plausible. This means that the LMTO model, in this energy range, is qualitatively appropriate for CuI, but it presents some difficulties for CuCl especially to describe the orbitals located on the copper.

## V. CONCLUSION

In this paper the empty bands in the cuprous halides are studied through BIS measurements and compared with LMTO calculations.

In the first 10 eV there is a good agreement between the experimental data and the theoretical calculations. The complementarity of these two gives some information about the partial density of states on the two types of atoms. In CuCl and CuBr the agreement about the peak energies is good, but the relative intensities are not reproduced by LMTO, even when weight factors for the different orbitals are taken into account. In CuI the agreement about the shape is very good but the LMTO gives somewhat wider spectra as compared to BIS. In any case, this study gives an important contribution to the understanding of the empty states in the cuprous halides in this energy range.

On the higher-energy side the correspondence between experiment and theory is less evident, especially, for CuCl. Further information is necessary. It is found in x-ray-absorption spectra. Once more the difference between CuCl and CuI is apparent. This is probably due to the increasing contribution of  $d$  orbitals on the halogen when going from CuCl to CuI.

The BIS experiments are also very useful to improve the interpretation of optical and Cu  $L_3$  spectra essential in the evaluation of the binding energy of core excitons. This will be reported in a future paper.<sup>8</sup>

## ACKNOWLEDGMENT

Institut de Physique et Chimie des Matériaux de Strasbourg is 'Unité Mixte 380046-CNRS-ULP-EHICS.'

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