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AND LOCAL REAL STRUCTURE OF SOME ANTIMONY  
CALCHOGENIDES

XANES STUDIES OF UNOCCUPIED ELECTRONIC STATES AND LOCAL REAL  
STRUCTURE OF SOME ANTIMONY CALCHOGENIDES(\*)

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ABSTRACT

The X-ray absorption edges of antimony and iodine in  $SbSI$ ,  $Sb_2S_3$ ,  $Sb_2S_5$  have been measured at high resolution with synchrotron radiation. It is shown that the density of unoccupied levels in the conduction band is adequate to interpret the edge structures between 0 and 10 eV. The structures between 0 and 10 eV and the chemical shifts of the three compounds are compared: original information is obtained about the ionicity of the chemical bond. The structures between 10 and 50 eV are analyzed and interpreted in terms of stereochemical coordination. The non-existence of  $Sb_2S_5$  as a stoichiometric compound is confirmed.

1.- INTRODUCTION

The fine structures within the first 10 eV above the X-ray absorption edges of solid state samples reflect the local partial density of unoccupied states of the conduction band, with the possible influence of final state effects like excitons, multi-electron contributions, relaxation effects<sup>(1)</sup>.

It is still controversial which partial density of states has to be compared with the experimental spectra in the single electron configuration: the density of states of the final system with the core hole excited or more simply the density of the unperturbed states<sup>(2-4)</sup>.

Recently a comparison between the X-ray absorption spectra of some rare-earth metals and the calculated single electron band structure over an energy range of about 100 eV showed that the single electron theory can well describe the white peak and the near-edge structures of those compounds<sup>(5)</sup>.

Within the single electron approximation the absorption coefficient is proportional both to the projected density of states (DOS) and to the energy-dependent matrix element. The experimental spectra are often qualitatively compared only with the DOS, although the influence of the matrix element is widely recognized. Due to the lack of a direct knowledge of the matrix element as a function of energy, one takes advantage, as a first approximation, of the hypothesis that the matrix element varies smoothly within the first 10 eV above the edge.

The fine structures between 10 and 50 eV above the edge, when interpreted in terms of multiple scattering of the photoelectron by the atoms surrounding the absorber, contain information about bond angles and distances<sup>(6)</sup>.

SbSI and  $Sb_2S_3$ , representative compounds of the  $A^V B^VI C^VII$  and  $A_2^V B_3^VI$  groups respectively, have aroused much interest for their peculiar mechanical and electronic properties deriving from the low-dimensional structure<sup>(7,8)</sup>. Both these compounds, whose structure is characterized by a double ribbon parallel to the crystallographic direction [001], are ferroelectric and photoconductive semiconductors.

Few calculations of the electronic band structure of these crystals have been performed up to now due to the complexity of the geometrical structure and to the insufficiency of available experimental data.

Experimental information concerning the occupied electronic states of SbSI,  $Sb_2S_3$  and other compounds of the  $A^V B^VI C^VII$  and  $A_2^V B_3^VI$  groups have been obtained from photoemission spectra<sup>(9)</sup>. Transmission and reflectivity measurements provided information about the joined density of conduction and valence states<sup>(10)</sup>. A direct experimental investigation of the unoccupied electronic states is still almost completely lacking.

$Sb_2S_5$  has been little studied up to now for what concerns physical properties<sup>(11,12)</sup>. Actually it is a non-stoichiometric compound: composition and structure can differ in different samples. The short-range order around the antimony atom looks in any case similar to that in  $Sb_2S_3$ .

In this work the absorption spectra within the first 50 eV at the L edges of antimony and iodine are studied for the three compounds: SbSI,  $Sb_2S_3$ ,  $Sb_2S_5$ .

The interpretation of the edge structures within the first 10 eV is carried out in terms of density of the lowest unoccupied states in the conduction band. At first the absorption spectra of the three compounds are analyzed separately. In particular the structures at the edges  $L_1$  and  $L_3$  of antimony and iodine in SbSI are compared to the total DOS calculated for the conduction band. A comparative analysis of the three compounds is then performed for what concerns both the shape of the spectra and the energy shift of the edge. Finally the analysis of the structures between 10 and 50 eV is utilized to obtain information about the stereochemical coordination.

## 2.- EXPERIMENTAL DETAILS

The X-ray absorption measurements have been performed with synchrotron radiation at the wiggler source of the Frascati National Laboratories<sup>(13)</sup>.

To reduce the harmonics content of the beam the storage ring was operated at an electron energy of 1.2 GeV and a wiggler magnetic field of 1.6 T. The critical energy of the photon beam was consequently 1.7 keV.

The monochromator was a silicon channel-cut crystal with reflecting (111) planes. The energy resolution of the experimental apparatus was estimated to be 0.5 eV at 5 keV, mainly determined by the intrinsic resolution of the crystal. The experimental points were spaced 0.3 eV at the lowest energies (edge  $L_3$  of antimony), 0.4 eV at the highest (edge  $L_1$  of iodine).

Two ionisation chambers filled with krypton were used as detectors, one before and one after the sample. The pressures of the gas were calibrated to obtain a 30% absorption in the first ion chamber, the maximum absorption in the second one.

Typical acquisition time was 30 minutes per spectrum.

The samples of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$  (nominal composition) were powders purchased from Merck. The crystalline structure of the two compounds was checked by means of an X-ray powder diffractometer. The samples of SbSI had been obtained by fine pulverisation of monocystals<sup>(14)</sup>.

The powders were deposited on filter paper by a sonication technique to obtain a uniform thickness<sup>(15)</sup>.

The thickness of the samples was carefully calibrated to get the same value of total absorbance  $\mu x$  at a given wavelength for the different compound. For what concerns SbSI, the same sample was used in measuring the edge of both antimony and iodine since the thicknesses best suited for the analysis of the two groups of L edges are nearly identical.

The measurements were performed at a temperature of about 300 K for all the samples. For SbSI some measurements were performed at liquid nitrogen temperature as well, to monitor possible differences between the paraelectric and ferroelectric phases.

The pre-edge region of each experimental spectrum has been extrapolated to the higher energies by means of a Victoreen-like fit. The fitting curve has then been subtracted from the experimental spectrum to obtain the elemental absorption coefficient.

### 3.- RESULTS AND DISCUSSION

#### 3.1.- SbSI

SbSI is a semiconducting compound, with an optical gap of 2 eV<sup>(7)</sup>. A para-ferroelectric phase transition has been observed at 295 K<sup>(16)</sup>.

The SbSI crystal has orthorhombic symmetry. The spatial group is  $D_{2h}^{16}$  in paraelectric phase,  $C_{2v}^9$  in ferroelectric phase. In both phases each antimony atom is surrounded by three sulphur and two iodine atoms placed at the vertices of a slightly distorted pyramid with square basis<sup>(17)</sup>. In paraelectric phase the mean Sb-S distance is 2.62 Å, the Sb-I distance 3.12 Å.

The atomic arrangement has been considered almost consistent with the ionic model  $\text{Sb}^{3+}\text{S}^{2-}\text{I}^-$ . The rather short distances between negative ions on the other hand suggest a partial covalency of the bond<sup>(18)</sup>.

In paraelectric phase we performed X-ray absorption measurements at the  $L_1, L_2$  and  $L_3$  edges of both antimony and iodine.

The edge  $L_1$  of antimony is characterized by a strong white peak. The FWHM of the peak, calculated as twice the left halfwidth, is  $3.2 \pm 0.3$  eV (Fig. 1). In a previous paper<sup>(19)</sup> the white peak was interpreted in terms of high density of unoccupied states of p symmetry in the bottom of the conduction band.

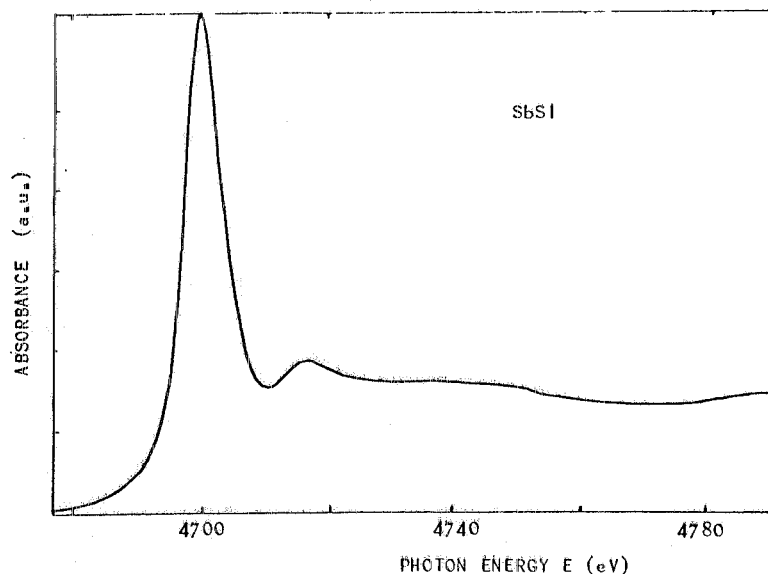


FIG. 1 - XANES at the edge  $L_1$  of antimony in SbSI.

The edge  $L_1$  of iodine also shows a white peak, much less pronounced however than that at the edge  $L_1$  of antimony (Fig. 2). The FWHM of the

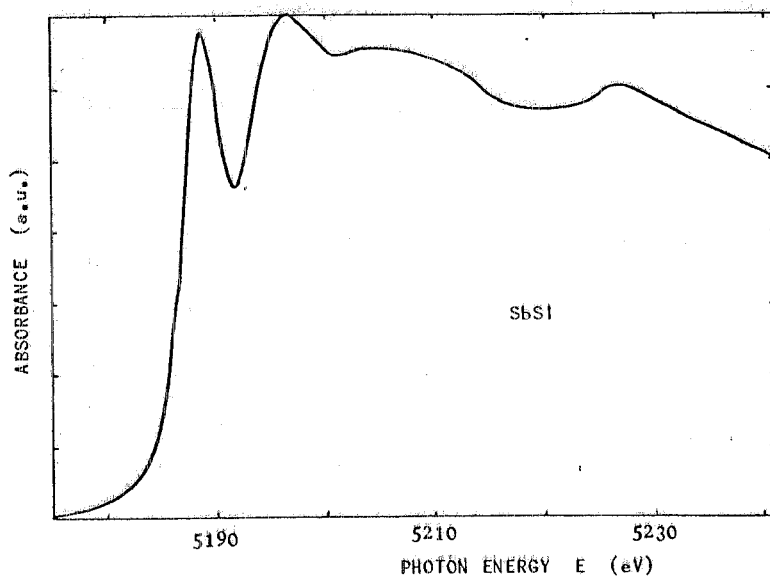


FIG. 2 - XANES at the edge  $L_1$  of iodine in SbSI.

peak, calculated as twice the left halfwidth, is  $2.3 \pm 0.3$  eV, the same as that of the antimony peak.

The band structure of SbSI has been calculated for the unidimensional model by Yamada and Chihara<sup>(20)</sup> and by Khasabov and Nikiforov<sup>(21)</sup>. More recent calculations have been performed by the empirical potential method by Nakao and Balkanski in both phases<sup>(22)</sup> and by Fong only in the paraelectric phase.

In the paper by Nakao and Balkanski the total DOS are also shown. Calculations of partial DOS are on the contrary not yet available in literature.

The structures at the absorption edges have to be correlated to the partial DOS. Nevertheless in the present case the comparison of the experimental data with the total DOS has provided some useful and original information.

The structures at the edges  $L_1$  of antimony and iodine are compared in Fig. 3 with the total DOS calculated for the conduction band.

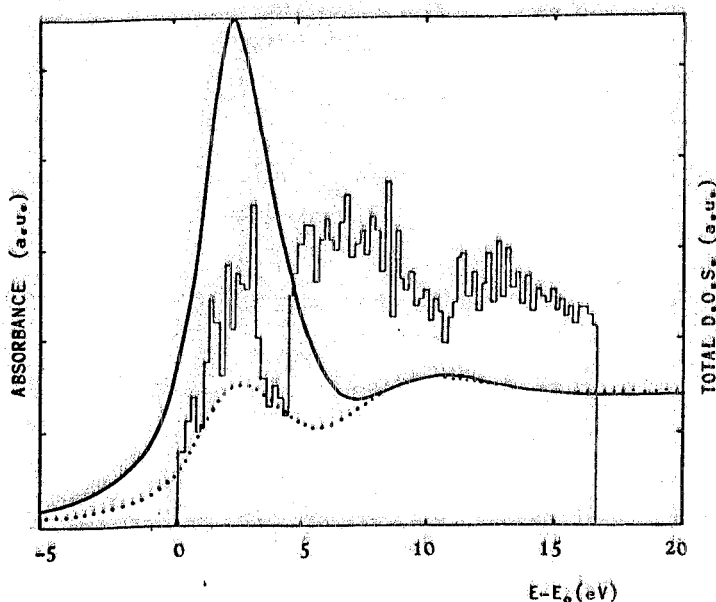


FIG. 3 - Comparison between the fine structures at the edges  $L_1$  of antimony (thick continuous line) and iodine (dotted line) in SbSI with the total DOS of the conduction band calculated by Nakao and Balkanski (narrow continuous line).

A low-lying group is evident in the calculated DOS between 0 and 4.5 eV, clearly separated from the remaining part of the conduction band and

attributed to levels of p symmetry of the antimony atoms<sup>(22)</sup>. The energy scales of the two experimental spectra have been shifted to put in correspondence the maximum of the white peaks with the center of gravity of the low-lying group of the calculated DOS. Moreover the intensities of the experimental spectra have been normalized by equalizing the mean absorption coefficient beyond 15 eV above the absorption limit (defined as the energy of first maximum in the first derivative).

The good correspondance between the experimental spectra and the calculated DOS allows to attribute both white peaks to dipole transitions to levels of p symmetry in the bottom of the conduction band.

For what concerns the edges  $L_2$  and  $L_3$  no considerable differences have been remarked in the shape of the spectra between the edge  $L_2$  and the edge  $L_3$  for both antimony and iodine. The intensity of the edge  $L_3$  is twice the intensity of the edge  $L_2$  within the experimental accuracy.

In Fig. 4 the structures at the edges  $L_3$  of antimony and iodine are compared with the total DOS calculated for the conduction band. The two experimental spectra have been normalized by equalizing the mean absorp-

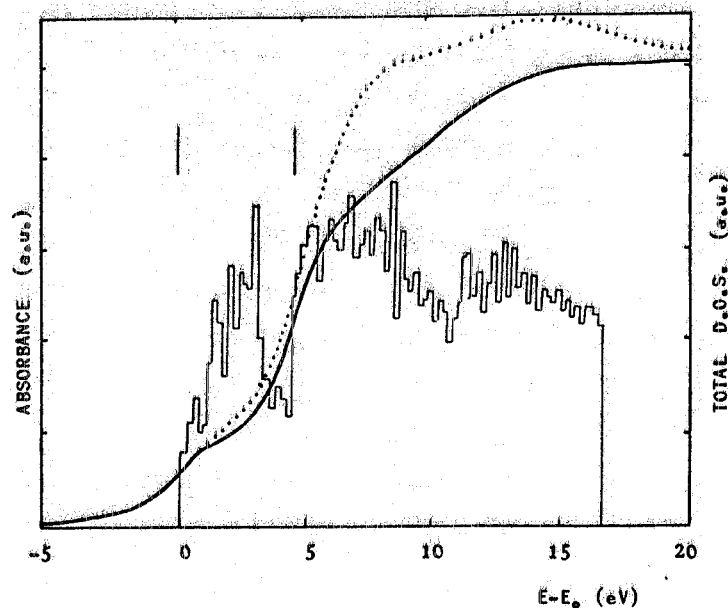


FIG. 4 - Comparison between the fine structures at the edges  $L_3$  of antimony (thick continuous line) and iodine (dotted line) in SbSI with the total DOS of the conduction band calculated by Nakao and Balkanski (narrow continuous line). The vertical bars show the positions of the first two maxima of the first derivatives of the experimental spectra.



tion coefficients beyond 15 eV above the absorption limit. For what concerns the energy scales, the absorption limits of the experimental spectra have been put in correspondence with the onset of the low-lying group of the conduction band.

The experimental spectra, characterized by two humps, are very similar. The distances between the first and the second maximum of the first derivative is  $4.5 \pm 0.3$  eV for both spectra. One can reasonably attribute the first hump to transitions to unoccupied states of s symmetry, the second hump to unoccupied states of mixed s and d symmetry.

Correspondingly the low-lying group between 0 and 4.5 eV in the calculated DOS is followed, at 4.8 eV, by the onset of a wide band.

The comparative analysis of the edges  $L_1$  and  $L_3$  of antimony and iodine allows to state that the low-lying group of the conduction band is a mixing of states of s and p symmetry, in agreement with theoretical expectations<sup>(23)</sup>.

While however the structures at the edges  $L_3$  are very similar, the white peak of the edge  $L_1$  of antimony is much stronger than the peak at the edge  $L_1$  of iodine (Fig. 3). This can be attributed to a strong localization of the free 5p orbitals near the antimony atom. As a matter of fact the ionicity of SbSI is related to the depletion of 5p levels of antimony when the compound is formed. The similarity between the spectra at the edges  $L_3$  within the first 5 eV allows to suppose that the s free orbitals, unlike the 5p, are delocalized.

The spectra at the edges  $L_1$  and  $L_3$  of antimony have been measured in the ferroelectric phase as well. No difference has been noticed with respect to the paraelectric phase for what concerns both the shape of the spectra and the energy position of the absorption limit (within the 0.3 eV step of the monochromator). According to theoretical calculations no significant variations in the band structure are expected at the phase transition<sup>(7,22)</sup>.

### 3.21- $Sb_2S_3$

$Sb_2S_3$  is a semiconducting compound with an optical gap of 2.2 eV<sup>(24)</sup>. A para-ferroelectric phase transition has been observed at 290.5 K<sup>(25)</sup>.

Like SbSI,  $Sb_2S_3$  in paraelectric phase has orthorhombic symmetry with space group  $D_{2h}^{16}$ . Two different coordinations are possible for the antimony

atoms. The  $Sb_I$  atom has three sulphur atoms as nearest neighbours at a mean distance of 2.57 Å: they form the basis of a trigonal pyramid of which the  $Sb_I$  atom is the vertex. The  $Sb_{II}$  atom is surrounded by five sulphur atoms (one at 2.49 Å, two at 2.68 Å, two at 2.82 Å) placed at the vertices of a slightly distorted pyramid with square basis<sup>(17)</sup>. The coordination of the  $Sb_{II}$  atom is similar to that of the Sb atom in SbSI, but for the substitution of the two iodine atoms with two sulphur atoms.

It has been stated that the antimony atoms are trivalent in  $Sb_2S_3$ <sup>(26)</sup> and that the compound is mainly covalent: the Pauling ionicity of the bond has been estimated to be about 12%<sup>(24)</sup>.

The edge  $L_1$  of antimony in  $Sb_2S_3$  shows a white peak (Fig. 5). The FWHM of the peak, calculated as twice the left halfwidth, is  $3.6 \pm 0.3$  eV.

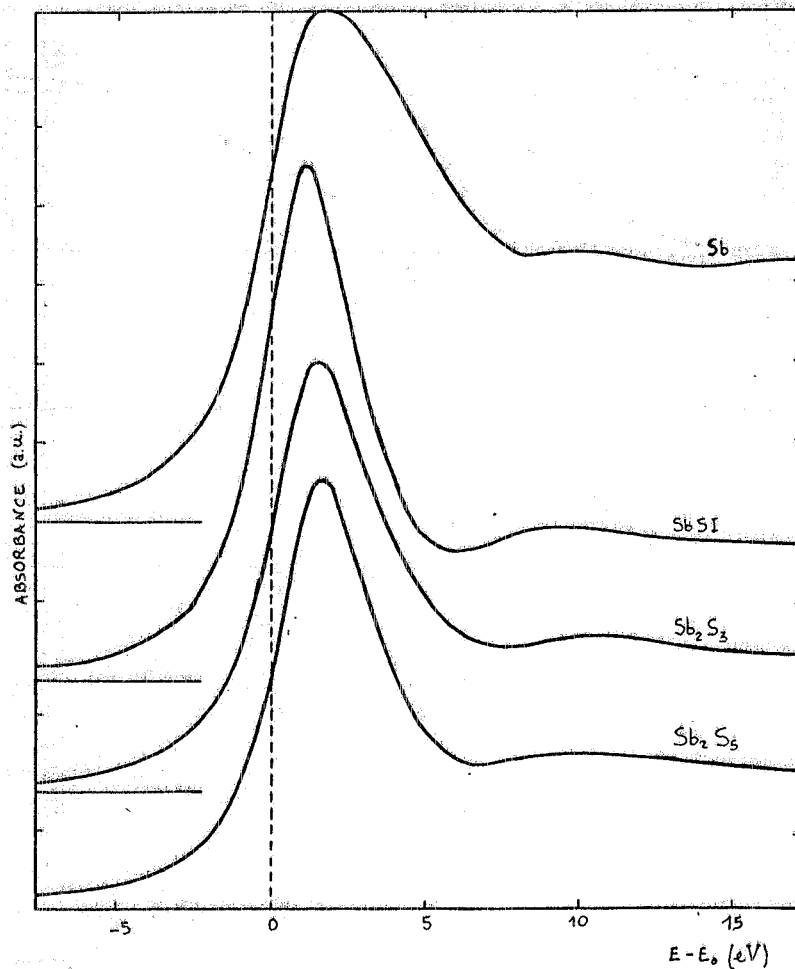


FIG. 5 - Comparison between the fine structures at the edge  $L_1$  of antimony in pure crystalline Sb and in the compounds SbSI,  $Sb_2S_3$ ,  $Sb_2S_5$ . The absorption limits  $E_0$  of the experimental spectra have been put in coincidence with the zero of the energy scale.

The edges  $L_2$  and  $L_3$  (Fig. 6) present two humps at a distance of  $5.2 \pm 0.3$  eV. The intensity of the edge  $L_3$  is twice that of the edge  $L_2$  within the experimental accuracy.

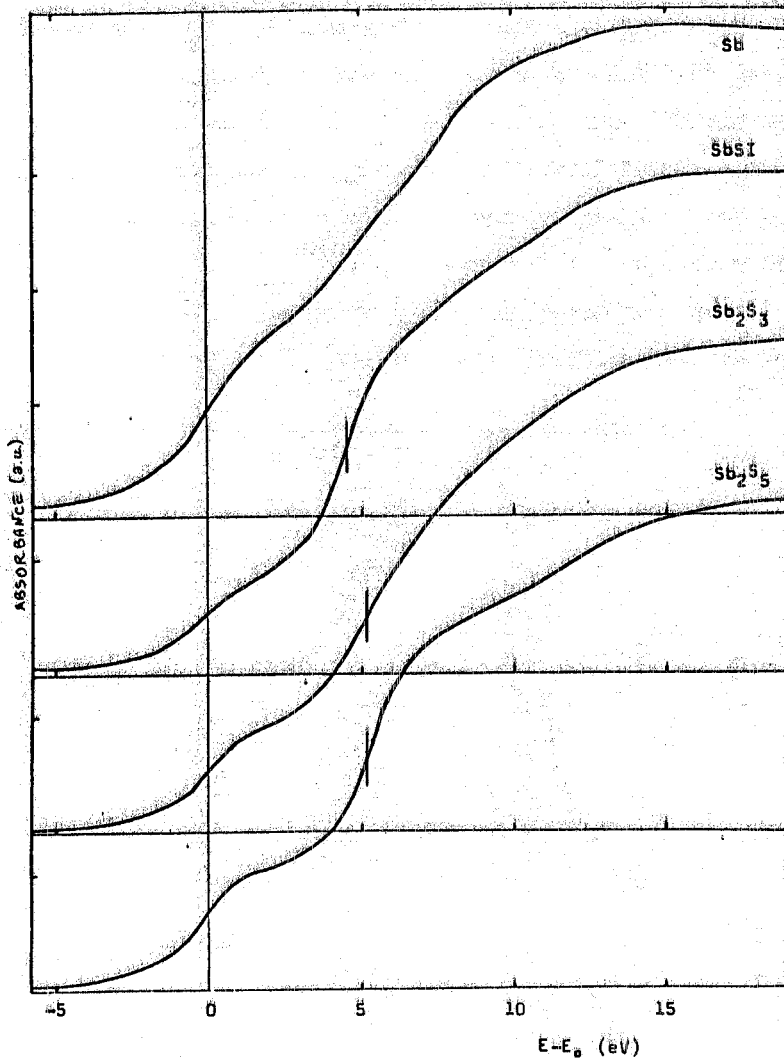


FIG. 6 - Comparison between the fine structures at the edge  $L_3$  of antimony in pure crystalline Sb and in the compounds SbSI,  $Sb_2S_3$ ,  $Sb_2S_5$ . The absorption limits  $E_0$  of the experimental spectra have been put in coincidence with the zero of the energy scale. The vertical bars at about 5 eV show the position of the second maximum of the first derivative.

Calculations of the band structure of  $Sb_2S_3$  have been performed only for the unidimensional model in paraelectric phase utilizing the LCA method<sup>(24)</sup>. The analysis of the calculated wavefunctions has shown that the electrons of p symmetry predominate within the first 5 eV above the onset of the conduction band. Total or partial DOS for tridimensional models of

$\text{Sb}_2\text{S}_3$  have not yet been calculated.

The partial DOS have been calculated for the chalcogenide compound  $\text{As}_2\text{S}_3$  (27).

It has been observed that the chalcogenide compounds  $\text{A}_2\text{B}_2^{\text{VVI}}$  of antimony and arsenic exhibit similar photoelectric spectra, which sample the density of the valence states, in spite of the rather differing crystal structure (28). This supports the hypothesis that the density of the conduction states within the first eV are also similar in the chalcogenide compounds of antimony and arsenic.

The partial DOS calculated for  $\text{As}_2\text{S}_3$  shows that the bottom of the conduction band (within the first 5 eV) is mainly formed by levels of p symmetry of sulphur and arsenic with a insignificant contribution from the s levels of arsenic (27).

The theoretical band calculations for  $\text{Sb}_2\text{S}_3$  and  $\text{As}_2\text{S}_3$  support the attribution of the white peak at the edge  $L_1$  of antimony in  $\text{Sb}_2\text{S}_3$  to dipole transitions to levels of p symmetry in the bottom of the conduction band. The first hump in the  $L_2$  and  $L_3$  spectra has to be ascribed to transitions to levels of s symmetry.

### 3.3.- $\text{Sb}_2\text{S}_5$

The so-called "antimony pentasulphide" actually is a non stoichiometric compound: different samples can exhibit different compositions and structures (11).

The Mössbauer analysis has shown that the oxidation number of antimony is +3 in  $\text{Sb}_2\text{S}_5$ , like in  $\text{Sb}_2\text{S}_3$ , both in crystalline and amorphous phase: the sulphur atoms exceeding the stoichiometric needs are probably organized in polysulphide linkages randomly located (12).

To characterize the particular sample of  $\text{Sb}_2\text{S}_5$  under study we analyzed it by an X-ray powder diffractometer. The spectrum of the  $\text{Sb}_2\text{S}_3$  sample, measured for comparison, is in good agreement with the ASTM tables. The spectrum obtained for the  $\text{Sb}_2\text{S}_5$  sample reveals on the contrary a very poor degree of crystallinity: only two peaks are visible corresponding to interplanar spacings differing from those of  $\text{Sb}_2\text{S}_3$ .

The edge  $L_1$  of antimony in  $\text{Sb}_2\text{S}_5$  shows a white peak, as was the case for SbSI and  $\text{Sb}_2\text{S}_3$  (Fig. 5). The FWHM of the peak is  $3.6 \pm 0.3$  eV.

The edges  $L_2$  and  $L_3$  have a very similar shape, characterized by two humps at a distance of  $5.2 \pm 0.3$  eV (Fig. 6).

### 3.4.- Comparative analysis

The structures within the first 10 eV above the Sb L<sub>1</sub> absorption edge for pure crystalline antimony and for the three compounds SbSI, Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>5</sub> are compared in Fig. 5. The absorption limit of each spectrum has been put in coincidence with the zero of the energy scale. The spectra of the three chalcogenide compounds are very similar. In particular the white peaks of Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>5</sub> are almost identical. The white peak of SbSI is 17% higher and slightly narrower.

The structures within the first 10 eV above the Sb L<sub>3</sub> absorption edges are compared in Fig. 6. They are characterized by two humps, at the same distance in Sb<sub>2</sub>S<sub>3</sub> and in Sb<sub>2</sub>S<sub>5</sub>, slightly closer in SbSI. Minor differences are also noticeable in the shape of the spectra.

The similarity of the structure at both the L<sub>1</sub> and L<sub>3</sub> edges suggests the similarity of the projected DOS at the bottom of the conduction bands. The bottom of the conduction band for the three compounds is a mixing of s and p levels of sulphur and antimony, the p levels prevailing within the first 5 eV.

The similarity of the spectra reveals not only the same oxidation state of antimony in the three compounds, but a striking similarity of the electronic structure close to the antimony atom as well. In particular, for what concerns the oxidation state of antimony in Sb<sub>2</sub>S<sub>5</sub>, X-ray absorption measurements confirm the analogous results obtained by Mössbauer isomeric shift measurements<sup>(12)</sup>.

An independent test of the similarity of the chemical bond of antimony in the three compounds can be obtained by studying the energy position of the absorption edges. It is well known that the chemical shift is related to the kind of chemical bond and varies depending on the ionicity<sup>(29)</sup>.

In Table I the shifts of the L<sub>1</sub> and L<sub>3</sub> absorption limits with respect to pure antimony are listed. For comparison the shifts of the levels 3d<sub>3/2</sub> and 3d<sub>5/2</sub> are listed as well. The latter have been calculated by comparing the binding energies measured by XPS<sup>(9)</sup> with the corresponding binding energies of pure antimony tabulated by Bearden and Burr<sup>(30)</sup>.

The shifts obtained by XAS and by XPS are different due to the different influence of multielectronic effects in the process of photoelectron extraction.

Table I clearly shows that the shifts of the same level, when measur-

ed by the same technique, are identical for the three compounds, within the experimental accuracy.

TABLE I - Chemical shifts of the core levels 2s, 2p<sub>3/2</sub> measured by X-ray absorption experiments (XAS, present work), and 3d<sub>3/2</sub>, 3d<sub>5/2</sub>, obtained from XPS results<sup>(9)</sup>. The shifts are measured in eV.

	XAS		XPS	
	2s	2p <sub>3/2</sub>	3d <sub>3/2</sub>	3d <sub>5/2</sub>
SbSI	1.4 ± 0.3	1.3 ± 0.3	2.0 ± 0.3	2.0 ± 0.3
Sb <sub>2</sub> S <sub>3</sub>	1.4 ± 0.3	1.3 ± 0.3	2.1 ± 0.3	2.2 ± 0.3
Sb <sub>2</sub> S <sub>5</sub>			1.8 ± 0.3	1.9 ± 0.3

SbSI has been quoted as a compound mainly ionic with partial covalency<sup>(18)</sup>, Sb<sub>2</sub>S<sub>3</sub> has been considered covalent with a 12% ionicity<sup>(24)</sup>. The results presented in this work concerning the chemical shift and the shape of the spectra show that the effective charge of the antimony ion is the same in both compounds.

The information obtained from the structures within 10 eV above the edge can be completed by the analysis of the structures between 10 and 50 eV which test the stereochemical coordination.

These structures, obtained by calculating the variations relative to the atomic absorption coefficients for the L<sub>1</sub> edges, are shown in Fig. 7. The three spectra present the common structures labelled A, B, C, D.

It has been shown that, in principle, the structures between 10 and 50 eV contain information about the site symmetry as far as beyond the third coordination shell<sup>(31,32)</sup>.

The spectra of Sb<sub>2</sub>S<sub>3</sub> and Sb<sub>2</sub>S<sub>5</sub> are very similar: only the structure C is smoother in Sb<sub>2</sub>S<sub>5</sub>. This suggests that the geometrical structure surrounding the antimony atom is almost the same in both compounds at least within the third coordination shell. X-ray diffraction measurements show on the other hand that the similarity lacks for what concerns the long-range order.

The spectrum of SbSI differs from the two other particularly for what concerns amplitude and shape of the structures A and C. A possible explanation is that two types of coordination exist in Sb<sub>2</sub>S<sub>3</sub> for the antimony atom (Sb<sub>I</sub> and Sb<sub>II</sub>) while in SbSI the antimony atom has only one coordi-

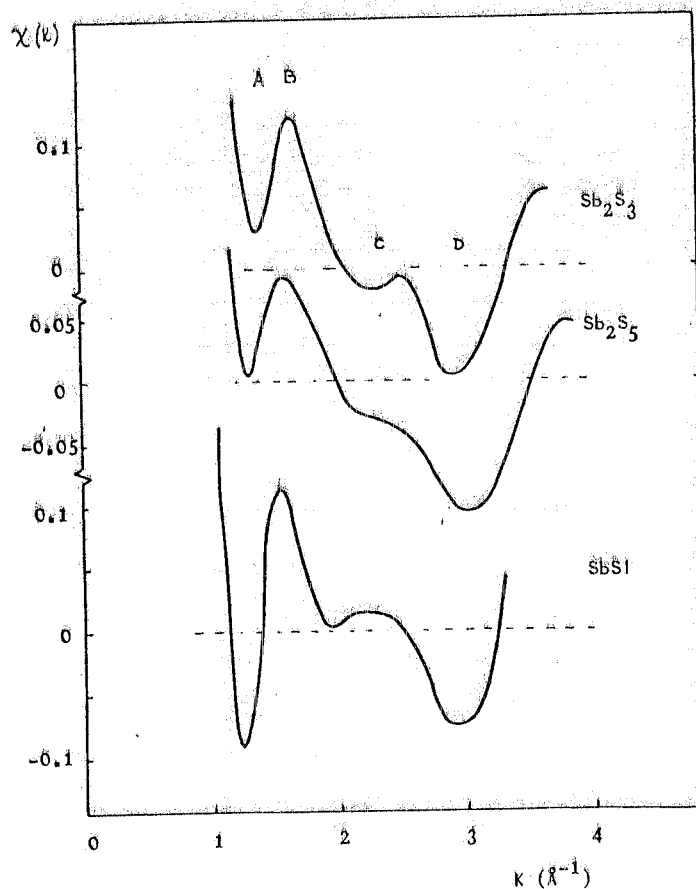


FIG. 7 - Fine structures between 10 and 50 eV above the edge  $L_1$  of antimony in  $SbSI$ ,  $Sb_2S_3$ ,  $Sb_2S_5$ . On the horizontal axis  $k$  is the wavevector of the photoelectron emitted by the absorbing atom.

nation, similar to that of  $Sb_{II}$ . Moreover, two sulphur atoms nearest neighbours of  $Sb_{II}$  in  $Sb_2S_3$  are substituted by two iodine atoms in  $SbSI$ : back-scattering amplitudes and phases of iodine differ considerably from those of sulphur.

#### 4.- CONCLUSIONS

In this work the structures at the L absorption edges of antimony and iodine have been analyzed in the XANES region (0 to 50 eV above the edge) for the three chalcogenide compounds  $SbSI$ ,  $Sb_2S_3$ ,  $Sb_2S_5$ .

The XANES between 0 and 10 eV have been correlated to the structure of the conduction band.

The comparison of the XANES at the edges of antimony and iodine in  $SbSI$

with the calculated total DOS has shown that the edge structures can be satisfactorily interpreted, for this case, in terms of density of unoccupied levels of the conduction band according to the independent electron model.

The striking similarity of the edge structures of SbSI,  $Sb_2S_3$ ,  $Sb_2S_5$  and the identity of the chemical shifts allow the state that the chemical bond of antimony with its nearest neighbours doesn't differ in a sensible way in the three compounds.

The XANES between 10 and 50 eV have been correlated to the stereochemical coordination.

In particular this analysis allows to strengthen the hypothesis already made on the ground of Mössbauer isomeric shift measurements - that the short-range coordination of antimony is the same in  $Sb_2S_5$  as in  $Sb_2S_3$ , thus confirming the non-existence of  $Sb_2S_5$  as a stoichiometric compound.

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