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XANES IN  $SbS_1$ ,  $Sb_2S_3$ ,  $Sb_2S_5$

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# XANES in SbSI, Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>5</sub>

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## 1. Introduction

SbSI and Sb<sub>2</sub>S<sub>3</sub>, representative compounds of the  $A^V B^VI C^{VII}$  and  $A_2^V B_3^{VI}$  groups respectively, have awakened a remarkable interest for their physical and mechanical properties related to the low dimensional structure.

Both these compounds, which have a double ribbon structure parallel to the [001] crystallographic direction, are ferroelectric and semiconducting materials with high photoconductivity [1]. Moreover, the optical properties of the  $V_2VI_3$  compounds change considerably from the crystalline to the amorphous state.

There are few calculations of the electronic band structure of these crystals owing to their very complex geometrical structure and to the lack of a sufficient amount of experimental data.

Sb<sub>2</sub>S<sub>5</sub> has not yet been much studied; it is a non-stoichiometric compound with variable composition and structure.

In this work we analyse the X-ray absorption spectra at the L edges of antimony and iodine in SbSI, Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>5</sub>, measured at high resolution with synchrotron radiation.

The interpretation of the edge structure within the first 10 eV has been carried out in terms of density of the unoccupied levels in the conduction band. By analysing the structure between 10 and 50 eV some stereochemical information has been obtained.

## 2. Results and discussion

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

In Fig.2 the structure within the first 10 eV above the Sb L<sub>3</sub> edges are compared; they are characterized by two humps which are equidistant in Sb<sub>2</sub>S<sub>3</sub> and in Sb<sub>2</sub>S<sub>5</sub> and slightly closer in SbSI.

In a previous work the white peak at the Sb L<sub>1</sub> edge in SbSI has been interpreted in terms of a high density of unoccupied states of p symmetry in the bottom of the conduction band [2]. The comparative analysis of the edges L<sub>1</sub> and L<sub>3</sub> of antimony and iodine in SbSI and the available calculated DOS sug-

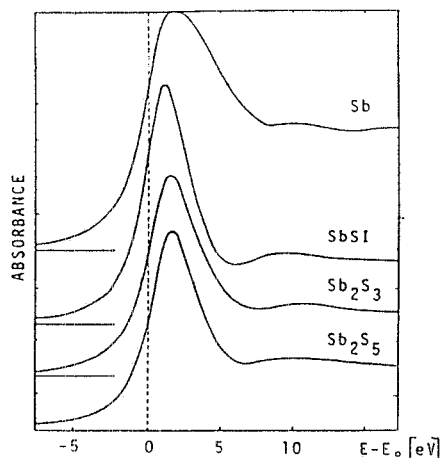


Fig.1. Edges  $L_1$  of antimony.

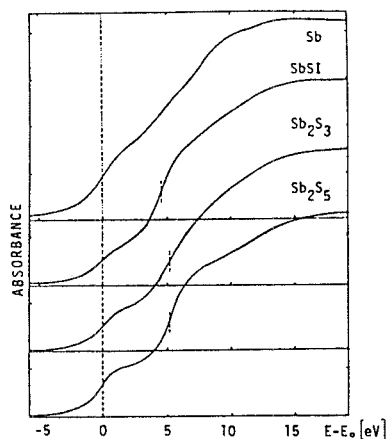


Fig.2. Edges  $L_3$  of antimony.

gests that the low-lying group of the conduction band is formed by a mixing of states of  $s$  and  $p$  symmetry, in agreement with theoretical calculations.

Moreover the white peak at the  $L_1$  edge of antimony in SbSI is much more pronounced than the white peak at the  $L_1$  edge of iodine. This has been related to a partial localization of the unoccupied orbitals of  $p$  symmetry near the antimony atoms [3].

The similarity of the structures at the edges  $L_1$  and  $L_3$  of antimony in  $Sb_2S_3$  and  $Sb_2S_5$  suggests a substantial equality of the projected DOS at the bottom of the conduction band. Also for  $Sb_2S_3$  and  $Sb_2S_5$ , like for SbSI, the bottom of the conduction band is thus formed by a mixing of  $s$  and  $p$  levels of sulphur and antimony; the  $p$  levels prevail within the first 5 eV.

The similarity of the spectra has to be related to an equal oxidation state of the antimony atoms in SbSI,  $Sb_2S_3$ ,  $Sb_2S_5$ . In particular, for what concerns  $Sb_2S_5$ , the X-ray absorption measurements strengthen the analogous results obtained by Mössbauer isomeric shift [4].

A confirmation of the similarity of the antimony chemical bond for the three compounds has been obtained by analyzing the energy position of the absorption edges. It is well known that the edge shift is related to the nature of the chemical bond and changes with its ionicity.

In Table I the XAS and XPS energy shifts are compared; the shifts of the same core level measured with the same technique are equal for all the compounds.

	XAS		XPS [5]	
	2 s	2 $p_{3/2}$	3 $d_{3/2}$	3 $d_{5/2}$
SbSI	$1.4 \pm 0.3$	$1.3 \pm 0.3$	$2.0 \pm 0.3$	$2.0 \pm 0.3$
$Sb_2S_3$	$1.4 \pm 0.3$	$1.3 \pm 0.3$	$2.1 \pm 0.3$	$2.2 \pm 0.3$
$Sb_2S_5$			$1.8 \pm 0.3$	$1.9 \pm 0.3$

Table I: Energy shifts (eV) of core levels measured by XAS and XPS.

The information given by the structure within the first 10 eV above the edge can be completed by the study of the structure between 10 and 50 eV which is sensitive to the stereochemical coordination.

The spectra obtained for SbSI, Sb<sub>2</sub>S<sub>3</sub>, Sb<sub>2</sub>S<sub>5</sub> by calculating the relative variation with respect to the atomic absorption coefficient are shown in Fig.3. They present common features labelled A,B,C,D.

The structure between 10 and 50 eV contains information about the geometrical symmetry around the absorbing atom till the third shell. The SbSI spectrum differs from the other spectra for what concerns the amplitude and the shape of the features A and C. The difference can be due to the fact that two crystallographic sites for the Sb atoms exist in Sb<sub>2</sub>S<sub>3</sub> (Sb<sub>I</sub> and Sb<sub>II</sub>) while in SbSI the Sb atom has a coordination like that of Sb<sub>II</sub>. Moreover, it has to be remarked that, under the same geometrical coordination, two sulphur near neighbours of Sb<sub>II</sub> in Sb<sub>2</sub>S<sub>3</sub> are substituted by two iodine atoms in SbSI and that the backscattering amplitudes and phases of iodine and sulphur are considerably different.

The analysis of XANES structure strengthens the hypothesis, already put forward on the grounds of Mössbauer isomeric shift, that the short range coordination of antimony in Sb<sub>2</sub>S<sub>5</sub> is nearly equal to that in Sb<sub>2</sub>S<sub>3</sub>. This confirms the non-existence of Sb<sub>2</sub>S<sub>5</sub> as a stoichiometric compound.

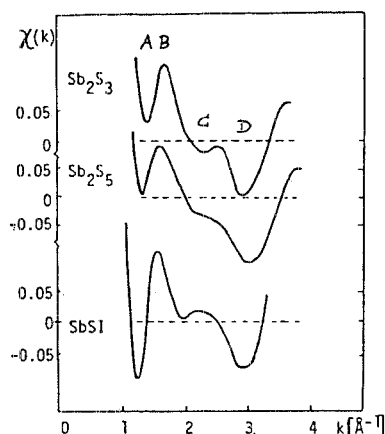


Fig. 3. Structure between 10 and 50 eV at the Sb L<sub>1</sub> edge. On the horizontal axis K is the wavevector of the emitted photoelectron.

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