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NEAR EDGE STRUCTURE AND EXAFS OF ANTIMONY L_I AND L_{III} EDGES OF SbSI

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Abstract The fine structures at the L absorption edges of antimony in SbSI have been observed in the paraelectric and ferroelectric phases using synchrotron radiation. The near edge structure (NES) has been analysed and compared with the theoretical density of states of the conduction bands. The analysis of the extended x-ray absorption fine structure(EXAFS) allows to discriminate the first three coordination shells of antimony, and to determine the value of the Sb-S mean distance both in the paraelectric and in the ferroelectric phase.

INTRODUCTION

In order to try to define the dynamics of the change of SbSI crystal structure across the Curie temperature,we analyzed the fine structures at the L_I and L_{III} x-ray absorption edges of the antimony ion. These measurements have indeed become a useful research tool in the study of condensed matter, since x-ray structures contain information about the electronic properties and the geometrical structure of the environment of the absorbing atom.

The absorption spectroscopy measurements have been performed at the Wiggler facility of Adone storage ring in Frascati, using the synchrotron radiation beam emit-

ted by a wiggler magnet inserted in the electrons path. The experimental set-up is described in details elsewhere[1].

NEAR EDGE STRUCTURE(NES) RESULTS

In the single-particle approximation the absorption coefficient $\mu(E)$, where E is the energy of the incident photon, depends on both the density N(E) of the available states and the transition probability P(E), i.e. $\mu(E) \propto N(E)P(E)$. Within a few electronvolts above the absorption edge, P(E) varies slowly as a function of energy[2] so $\mu(E)$ directly reflects the distribution N(E) of the available states. This allows a correlation between x-ray absorption spectra and partial density of states(DOS) curves.

The x-ray photoelectric absorption is mainly due to electric dipole transitions. For a given transition, P(E) depends on the symmetry of the wave functions of both the initial and final states. The L_I edge is adscribed to $2s \rightarrow np$ transitions; it thus probes the density of states with p symmetry above the Fermi level. The L_{II} and L_{III} edges depend on transitions from the core states $2p_{1/2}$ and $2p_{3/2}$, respectively, to unoccupied states of both s and d symmetries, the $2p \rightarrow nd$ transitions being by far the most favored.

The 300 K NES spectra at the L_I and L_{III} edges of antimony in SbSI are shown in Figs. 1 and 2, respectively. The "white peak" at the L_I edge ($\sim$4.7 keV) is due to a high density of final states of predominant p character. The high density of 5p states shown by the experimental spectrum is in agreement with the total DOS calculations performed by Nakao and Balkanski[3] by the pseudopotential method, whose results are shown for comparison in Fig.1. Nakao and Balkanski, identifying qualitatively the character of the bands from the chemical point of view, state that the low-lying group of the conduction bands,between O and 5 eV, corresponds to the 5p-like bands of the Sb atoms.The zero of energy has been put at the bottom E_O of the conduction bands.

The peak energy of the white-line is associated in Fig.1 with the center of gravity of the low-lying group of the conduction bands;its FWHM is 3.2 eV. By subtracting from this value the core level width, 2.4 eV, and the instrumental broadening, 0.5 eV, a value less than 1 eV is obtained for the width of the p band. The low-lying group of the theoretical bands is clearly broader than 1 eV.This discrepancy could be attributed

to a broadening of the low-lying group of the conduction bands due to the overlapping of non p-symmetry states.

This hypothesis is supported by the analysis of the Sb L_{III} edge in SbSI, and by its comparison with the calculated DOS(Fig.2). Here the absorption limit is associated with the bottom E_o of the conduction bands. The experimental spectrum exhibits two humps, the first one at the absorption limit, the second at about 5 eV. It is reasonable to attribute the first hump to a transition $2p \rightarrow 5s$. This indicates the presence of partially unoccupied states of s symmetry mixed to the prevailing p states.

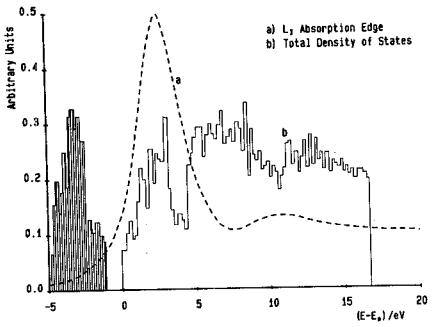

FIGURE 1 L_I absorption edge of antimony in SbSI(a) compared with the total DOS(b) calculated by Nakao and Balkanski[3].The dashed area is the highest valence band.

The second hump corresponds to the onset of the transition $2p \rightarrow 5d$.

The comparison between the experimental spectra and the available DOS looks rather satisfactory. The x-ray absorption spectra are selective in angular momentum: a more profitable comparison should then be made with the partial, rather than the total,DOS.This could allow a more accurate interpretation of the absorption spectra and could show, in addition, the possible contributions to the NES arising from multielectronic transitions, excitonic transitions, and many-body effects.

The weak structures observable in both the L_I and L_{III} spectra between about 10 and 50 eV from the edge are currently interpreted as due to multiple scattering of the photoelectron inside the first coordination shells. This effect becomes negligible at higher photon energies, where the single-scattering theory of EXAFS is adequate.

The NES observed in samples at 300 K(paraelectric phase) and at 275 K(ferroelectric phase) did not show any valuable difference in the shape of the structures nor any shift of the edge energies(within the angular step of the monochromator,i.e. 0.3 eV). This can depend

on the relatively small variations of the electronic structure, the coordination symmetry, and the Sb ion charge connected to the phase transition.

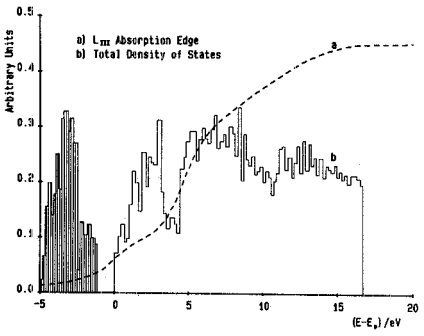

FIGURE 2 L_{III} absorption edge of antimony in SbSI(a) compared with the total DOS(b) calculated by Nakao and Balkanski[3].

EXAFS RESULTS

The EXAFS spectra of samples in the paraelectric phase (300 K) have been compared with those of samples in the ferroelectric phase (275 K). The homogeneity in the data processing and the identity of the phase-shifts due to the chemical identity of the samples allows an accuracy in the EXAFS determination of distance variations greater than that attainable from measurements of absolute distances[4].

The analysis of the EXAFS allowed us to discriminate the first three coordination shells of antimony, and to determine the difference between the values of the Sb-S mean distance in the paraelectric and in the ferroelectric phase. This difference corresponds to a relative shift of the Sb-S ions along the c-axis of 28 ± 9 pm crossing the transition temperature, a result somewhat larger than the values of 15 pm reported by Kikuchi et al.[5] and of 8.4 pm measured by Itoh et al.[6] by x-ray diffraction techniques.

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