An XAS Study of the Semi-Conducting Sulfides M_2S_3 ($M = As, Sb, Bi$)

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Abstract. XANES has been used to probe the low-lying vacant states in the Period 15 sulfide semi-conductors M_2S_3 ($M = As, Sb, Bi$). The As K- and L_{3-} , Sb K- and L_{3-} , and Bi L_{3-} and L_{1-} edges are related to the S K-edge XANES in terms of bands of mixed orbital character. In the K-edge spectra transitions from the 1s state to states of some p character can be seen in the region between 5 eV before the edge and 15 eV after it. The S spectra are alike showing the similar nature of the electronic structure of these compounds. The white line intensity decreases down the period showing the density of empty S 2p states at the Fermi level is also decreasing. The Period 15 spectra are related to theoretical band structure calculations for As_2S_3 .

1. INTRODUCTION

The sulfide minerals exhibit an intriguing diversity in their structural chemistry and electrical, magnetic and other physical properties. The understanding of the electronic properties has been aided by band-structure and MO calculations. The period 15 M_2S_3 ($M = As, Sb, Bi$) minerals are all semi-conductors; this results in their band structure around the Fermi level being of interest. Watanabe [1] calculated the DOS structure of crystalline As_2S_3 using a tight binding method with a basis set consisting of only s and p orbitals of the constituent atoms. Thus their representation of the lowest empty bands ignores the contribution from higher d orbitals. Modelling the near-edge XANES region is difficult [2] as there are several different physical phenomena which may contribute to its shape. Interpreting XANES spectra in terms of the density of empty states just above the Fermi level ignores the perturbations in these states caused by the core-hole; however, a relaxation of the valence electrons does occur after the ejection of the core-electron. This relaxation occurs because of the attractive potential of the core-hole. The binding energies of these orbitals relative to zero energy are different from their ground state values; thus a one-electron model may fail to predict the near-edge features correctly. It has succeeded for metals as core-hole relaxation and screening effects have been shown to be negligible [3]. In insulators however the one-electron approach is less fruitful, as other important effects have been seen such as core excitons in NiO. For semi-conductors the situation is intermediate; the core-hole relaxation and screening are probably more efficiently ensured for the atomic species of anionic rather than cationic character, because of the large valence electron content of the anions. However, the metals studied here also have valence electrons, and the experimental spectra are interpreted in terms of the ground state electronic structure while the near-edge features are explained in terms of electronic transitions to empty states.

2. EXPERIMENTAL

Using the SRS, Daresbury Laboratory XANES spectra of the S K-edge (Station 3.4), As K- (9.2) and L_{3-} edge (3.4), Sb K- (9.3) and L_{3-} edge (8.1) and Bi L_{3-} (9.2) and L_{1-} edge (9.2) spectra of As_2S_3 , Sb_2S_3 and Bi_2S_3 have been obtained in the normal manner [4]. The samples were natural minerals from the Harwood collection of the Department of Earth Sciences, University of Manchester. The spectra were calibrated, normalized and have been aligned to zero by the subtraction of the energy of the appropriate X-ray line and the X.P.S. binding energy where required (see the figure captions for details).

3. DISCUSSION

The spectra are displayed in Figure 1a, b and c; assignments of the peaks are made in Table 1. The S K-edge spectra are alike showing that the three minerals have similar electronic structures. They all show 3 peaks in the near-edge region. These peaks are assigned to transitions to S 3p states mixed with M states in some cases. This matches Watanabe's calculation which shows three bands of S 3p character in the 0–20 eV region. The different core-hole lifetimes and calibration errors are probably the causes of the inexact matches of the peak positions. The principal difference between the spectra is in the relative intensity of these peaks. The size of the white line decreases down the group from As to Bi. This indicates that the density of empty S p states at the Fermi level is also decreasing down the group. This may be a result of better overlap between the S and M orbitals as the size of the M atom increases. These S spectra show more detail than the M spectra as the intrinsic line width of the S K-edge (0.59 eV) is lower than that of the As K (2.14), L_3 (0.94), Sb K (9.16), L_3 (2.87), and Bi L_3 (5.98) and L_1 (12.4) edges [5].

Figure 1a: As K, L_3 and S K XANES spectra for As_2S_3 . The As K-edge has the energy of the As $K\alpha_1$ line (10 543.7 eV) and the As $2p_{3/2}$ B.E. (11 325.5 eV) subtracted; the As L_3 -edge has the energy of the As $2p_{3/2}$ B.E. subtracted and the S K-edge has the energy of S $K\alpha_1$ line (2 307.8 eV) and the S $2p_{3/2}$ B.E. (162.6 eV) subtracted. **Figure 1b:** Sb K, L_3 and S K XANES spectra for Sb_2S_3 . The Sb K-edge has the energy of the Sb $K\beta_{5/1}$ (29 963.2 eV) and the Sb $3d_{5/2}$ B.E. (529.4 eV) subtracted; the Sb L_3 -edge has the energy of the $L\alpha_1$ line (3 604.7 eV) and of the Sb $3d_{5/2}$ B.E. subtracted and the S K-edge has the energy of S $K\alpha_1$ line and the S $2p_{3/2}$ B.E. (161.1 eV) subtracted. **Figure 1c:** Bi L_1 and L_3 and S K XANES spectra for Bi_2S_3 . The Bi L_1 and L_3 spectra were aligned by subtracting the energy of the L_1-N_{VII} line (16 217 eV) and L_{α} line (13 259.3 eV) respectively and the Bi $4f_{7/2}$ B.E. (158.2 eV). The S spectrum was aligned by subtracting the energy of the S $K\alpha_1$ line and the S $2p_{3/2}$ B.E. (161.1 eV)

The smaller white line in the Sb K-edge spectra compared to the As K-edge may not be as significant, as the large line width at this edge wipes out detailed information. The presence of peaks b and c in both the As K-edge and S K-edge spectra show the mixing between As 4p and S 3p states. Watanabe's calculations [1] show that the lowest empty states are mainly of As 4s and S 3p character. No peaks near the Fermi level are seen in the As K-edge spectra which agrees with this. Mixing of S and Sb states is shown by the match in the S K and Sb L_3 spectra. The latter has the same pattern of peaks as the As L_3 spectra indicating a close similarity in electronic structure. In the Bi L-edge spectra, transitions from the 2s (L_1) and $2p^{3/2}$ (L_3) to states of 6p (L_1) and 6s/5d (L_3) character are seen. Hence the similarity between the Bi L_1 -edge and the Sb K-edge spectra is expected. The large line width washes out detail in these spectra.

Table 1: The assignments and energy values for the peaks in the near-edge XANES

Material	Peak label	S K-edge	M K-edge	M L_3 -edge	M L_1 -edge	Assignment of transition
As_2S_3	a	1.7		2.6		to S 3p/ As 4s/ 3d states
	b	8.8	8.6	9.1		to S 3p/ As 4s/ 4p/ 3d states
	c	16.2	17.0	17.2		to S 3p/ As 4s/ 4p/ 3d states and multiple scattering resonances
Sb_2S_3	a	1.9		2.5		to S 3p/ Sb 5s/ 4d states
	b	9.2	10.3	9.6		to S 3p/ Sb 5s/ 5p/ 4d states
	c	17.4		16.8		to S 3p/ Sb 5s/ 4d states and multiple scattering resonances
Bi_2S_3	a	2.2				to S 3p states
	b	9.5			10.2	to S 3p/ Bi 6p states
	c			15.5		to Bi 6s/ 5d states and multiple scattering resonances
	d	19.3				to S 3p states and multiple scattering resonances

References

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