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Sulfur–sulfur bonding in the amorphous sulfides WS_3, WS_5, and Re_2S_7 from sulfur K-edge EXAFS studies

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The measurement of extended X-ray absorption fine structure (EXAFS) using energy-selective fluorescence detection in the soft X-ray region has enabled sulfur K-edge EXAFS studies of the amorphous sulfides WS_3, WS_5 and Re_2S_7, to be carried out for the first time. Quantitative information about the local environment of sulfur in these highly structurally disordered sulfides has been obtained and is compared with that obtained by previous EXAFS studies at the metal L_{III} edges. The average oxidation state of sulfur and hence the metals in these amorphous sulfides is derived from S–S co-ordination numbers. Results from the crystalline model compound $[NH_4]_2[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]$ are also presented to give an indication of the reliability of the results. In all the amorphous compounds studied S–S bonds with bond lengths close to 2.0 Å are found. In WS_3 each sulfur has on average 0.5 sulfur near neighbours and close to 2 tungsten near neighbours at 2.43 Å. In WS_5 each sulfur has on average 1 sulfur near neighbour and ≈1.2 tungsten near neighbours at 2.46 Å, consistent with the material being formulated as $W^{V}(S_2^{2-})_{2.5}$. Amorphous Re_2S_7 also contains sulfur with an average sulfur co-ordination number of 1 and the compound is thus formulated as $Re^{3.5}{}_2(S_2^{2-})_{3.5}$. The S–Re bond distance is found to be 2.32 Å. All the S-M distances found are in excellent agreement with those found from previous metal L_{III}-edge EXAFS studies. Possible structural models for the amorphous materials are discussed.

Introduction

Extended X-ray absorption fine structure (EXAFS) spectroscopy has become an important technique in the study of amorphous materials, since it allows the local environment of individual elements to be probed selectively, and structural parameters (interatomic distances, co-ordination number, and displacement parameters) can be extracted.[1,2] It is particularly useful when EXAFS studies can be carried out for all the different elements contained in the materials. For example in the study of amorphous CrS_3 we were able to obtain both chromium and sulfur K-edge EXAFS data and hence show that the compound could be formulated as $Cr^{III}(S_2^{2-})_{1.5}$.[3] In certain cases EXAFS studies may be complicated by closely lying absorption edges of two elements, making isolation of the X-ray absorption fine structure from one or more of the elements in a compound by conventional X-ray absorption measurements impossible. For example, Wittnebden *et al.*,[4] in their X-ray absorption study of thiometalates of molybdenum and tungsten, were only able to study the near edge region (XANES) of the sulfur K-edge because of overlap of structure from the molybdenum L-edges and tungsten M-edge in the EXAFS region. In our studies of amorphous transition-metal chalcogenides of Groups 6 and 7 we have encountered this problem with the tungsten sulfides, WS_3 and WS_5,[5] and the rhenium sulfide Re_2S_7:[6] the metal M_{II}-edges (at 2575 and 2682 eV, respectively) lie only slightly higher than the sulfur K-edge (at 2472 eV). In our previous work we had to rely on vibrational spectroscopy, and shifts and structure of the sulfur X-ray absorption edge for information on S–S bonding and hence the oxidation state of the transition metal in these amorphous sulfides.[5,6]

For many years energy-selective fluorescence detection of EXAFS has been possible in the hard X-ray region, whereby the intensity of emission of one element is followed as a function of incident X-ray intensity, avoiding any other elements with closely lying absorption edges, but until recently this has not proved possible in the soft X-ray region. In this paper we describe the first sulfur K-edge EXAFS studies of the amorphous sulfides WS_3, WS_5 and Re_2S_7 using a new high-resolution fluorescence detector.[7] We have also collected EXAFS data from a crystalline compound containing the complex anion $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]^{2-}$, at both the sulfur K-edge and tungsten L_{III}-edge, to give a measure of the accuracy of our results on the amorphous sulfides. The compound $[NH_4]_2[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]$ contains sulfur in a number of different environments and oxidation states (0, −1 and −2) and a range of W–S bonding distances. This material provides an interesting model for materials of unknown structure that may contain sulfur in a similar variety of oxidation states.

We have been studying the structure of amorphous transition-metal chalcogenides since the discovery by our group of the new sulfides CrS_3, $MoS_{4.7}$ and WS_5, and selenides $CrSe_3$, $MoSe_5$ and WSe_6.[8,9] The three amorphous sulfides we investigate here, WS_3, WS_5 and Re_2S_7, are of particular interest because they are more sulfur-rich than the highest known crystalline sulfides of tungsten and rhenium.[10] The amorphous tungsten sulfide WS_3 has been known for over 150 years[11] and has been the subject of numerous structural studies, including tungsten L_{III}-edge EXAFS experiments and X-ray diffraction.[5,12–16] As a result of these studies a number of different structural models have been presented. One fundamental area of conflict is the problem in determining whether WS_3 is best formulated as containing W^{IV} or W^{V}. The synthesis of the amorphous rhenium sulfide Re_2S_7 was reported over 60 years ago[17] and the material has more recently found use as a catalyst in certain hydrogenation reactions.[18,19] Müller *et al.*[20] proposed a structural model for Re_2S_7 based on a chemical degradation study and examination of the crystalline products for characterisation. However, our recent rhenium L_{III}-edge EXAFS and sulfur K-edge XANES study was the first that extracted meaningful structural information directly from the solid state and we concluded that Re_2S_7 could

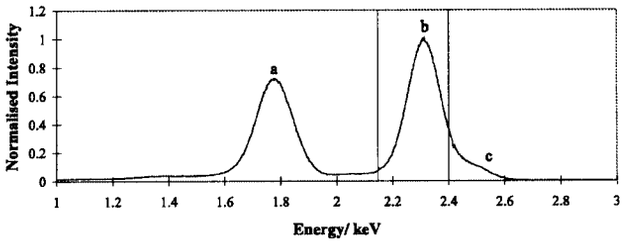

Fig. 1 The energy-dispersive fluorescence spectrum of WS_3 obtained at 2930 eV. The window used to isolate the sulfur K emission (b) is indicated by vertical lines. Peak a is due to tungsten M emissions and c due to directly scattered incident X-rays.

be formulated as $Re^{3.5}{}_2(S_2{}^{2-})_{3.5}$.[6] Amorphous WS_5 has been less extensively studied because it has been known only for six years. We used tungsten L_{III}-edge EXAFS and neutron diffraction to investigate its structure and suggested possible simple structural building blocks.[5,21] Clearly information on S–S and S–M bonding in these amorphous sulfides obtained using sulfur K-edge EXAFS studies should help in discriminating between the different structural models proposed for WS_3 and Re_2S_7, and confirming if our model for WS_5 correctly describes the bonding around sulfur in this compound. For the transition-metal sulfides here sulfur K-edge EXAFS studies are especially useful, because determination of accurate co-ordination numbers and bonding distances around sulfur using X-ray or neutron diffraction techniques is difficult. This is because the metal atoms have much higher X-ray form factors and neutron scattering lengths than sulfur and the derived correlation functions are dominated by M–M and M–S correlations.

Results and discussion

Fig. 1 shows the window (260 eV) used to separate the sulfur fluorescence from the M emissions of W and Re and from X-rays directly scattered into the solid-state detector, superimposed on the emission spectrum from WS_3 obtained with an incident X-ray energy of 2930 eV. It is clear that the detector has sufficient resolution to exclude tungsten and rhenium M emission lines. Fig. 2(a) shows the k^3-weighted tungsten L_{III}-edge EXAFS spectrum and the Fourier transform for the model compound $[NH_4]_2[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]$ and Fig. 2(b) the equivalent plots for the sulfur K-edge EXAFS. The modelling of the tungsten L_{III}-edge EXAFS was straightforward: radial distances and shell occupation numbers were initially set at those values previously determined crystallographically and then varied in least-squares refinements until the fit index was minimised. It was found that two near sulfur shells could be resolved (at ≈2.3 and ≈2.5 Å) and a further tungsten shell at 2.75 Å, corresponding to the short W–W bond in the compound (Fig. 3). The refined interatomic distances show excellent agreement with those determined crystallographically (Table 1). The sulfur K-edge EXAFS data were first modelled by fixing the co-ordination numbers of two atomic shells at the values expected from the crystal structure of the compound; a shell of 1.1 sulfur atoms at an average distance of 2.06 Å and a shell of 0.94 tungsten atoms at an average distance of ≈2.31 Å (see Fig. 3).[22] Radial distances and Debye–Waller factors of these two shells were varied in least-squares refinements with the threshold energy until the fit index was minimised, Table 1. The interatomic distances obtained again agree very well with those previously obtained crystallographically for the compound by Fedin *et al.*[22] Although it is expected that a range of W–S distances occur in the complex it is not possible to divide the tungsten shells into sub-shells because of the relatively short k range of the sulfur K-edge data (*cf.* the tungsten L_{III}-edge data above). In order to probe the accuracy of the sulfur shell parameters, and to test the validity of methodology later applied to the data from the amorphous compounds, the occupation number of the tungsten shell was fixed at 0.94, and that of the sulfur shell (N_S) varied in steps of 0.1 between 0 and 2, and all other parameters varied at each step to minimise the fit

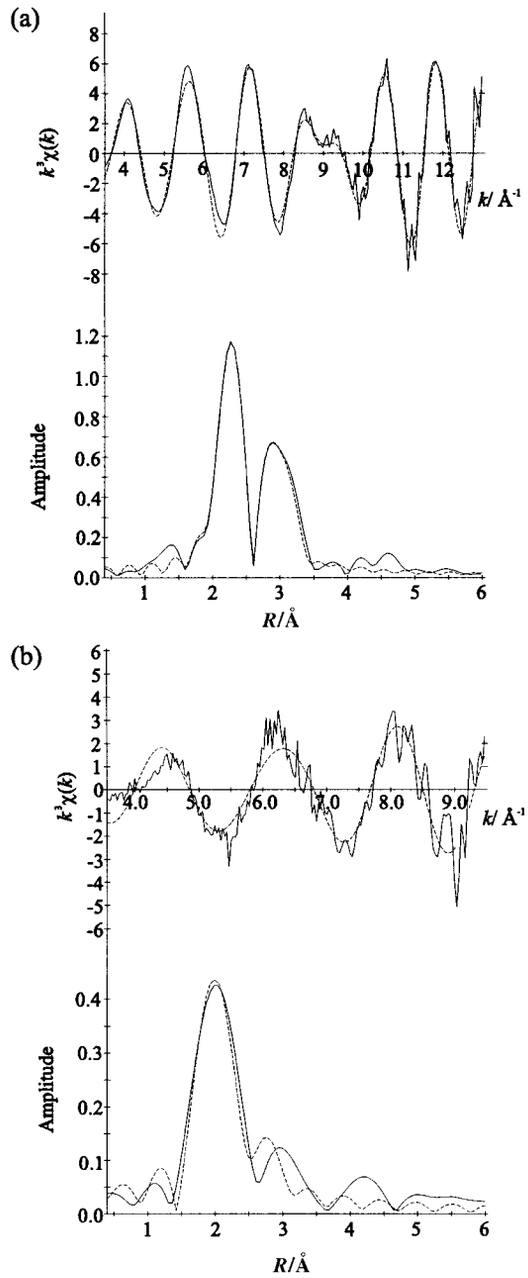

Fig. 2 EXAFS Spectra of $[NH_4]_2[W_3S_{16}(NH_3)_3]$ from (a) the tungsten L_{III}-edge and (b) the sulfur K-edge (top k^3-weighted EXAFS and bottom its Fourier transform; (———) experimental and (– – – –) theoretical).

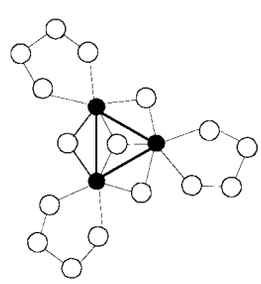

Fig. 3 A sketch of the $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]^{2-}$ anion found in $[NH_4]_2[W_3S_{16}(NH_3)_3]$, used as a model compound in the EXAFS experiments. Unfilled circles represent sulfur atoms and filled circles, tungsten. Co-ordinated ammonia molecules (one per tungsten atom) are omitted for clarity.

Table 1 Comparison between crystallographic and EXAFS structural parameters for $[NH_4]_2[W_3S_{16}(NH_3)_3]$

Edge	Shell	Occupation number[a]	Crystallographic distance [ref. 22]	EXAFS Radial distance[b]/Å	EXAFS Debye–Waller factor[b]/Å^2	EXAFS Fit index/10^{-4}
W L_{III}	S	3	2.338[c]	2.322(3)	0.0076(7)	
	S	2	2.504[c]	2.467(16)	0.0204(69)	3.5
	W	2	2.784	2.757(3)	0.0070(3)	
S K	S	1.1	2.066[c]	2.063(8)	0.0086(11)	18.9
	W	0.94	2.404[c]	2.313(9)	0.0167(23)	

[a] Fixed at these values after preliminary EXAFS data analysis (see text). [b] Errors in distances and Debye–Waller factors are those derived from least-squares refinements and take no account of systematic errors in the EXAFS experiment and data analysis which limit the true accuracy of the distances to ±0.02 Å and Debye–Waller factors to ±20%. [c] Average crystallographic distance.

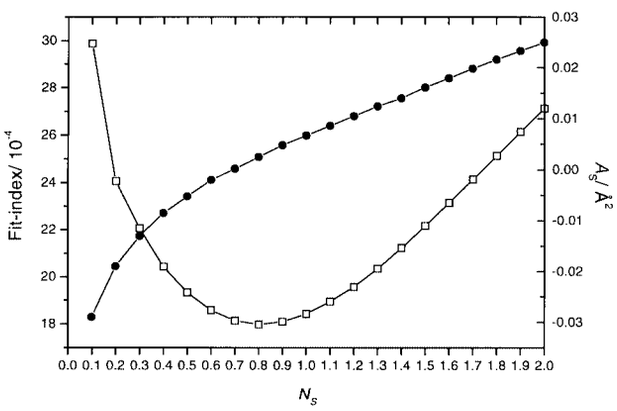

Fig. 4 The effect on sulfur K-edge EXAFS fit index (unfilled squares) and Debye–Waller factor (filled circles) of the occupation number of the sulfur shell at 2.06 Å for $[NH_4]_2[W_3S_{16}(NH_3)_3]$.

index. The results of this data analysis are shown on Fig. 4, which illustrates that a shallow minimum in fit index is observed at $N_S = 0.6$–1.1. This is reasonably consistent with the fact that sulfur has on average 1.1 near neighbours in the $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]^{2-}$ ion (Fig. 3). If N_S was set to be zero the fit index was considerably higher (81.15) clearly illustrating that two atomic shells are responsible for the broad peak of the EXAFS Fourier transform. Also shown on Fig. 4 is the value of the sulfur Debye–Waller factor derived by least-squares refinement for each co-ordination number, and this is a second measure of how appropriate a co-ordination number is to model the data. Co-ordination numbers of 0.7 or less give zero or negative Debye–Waller factors for the sulfur shell, which are physically impossible. Our previous sulfur EXAFS studies of disulfide-containing materials, both crystalline and amorphous, showed that $A_S = 0.005(1)$ Å^2 for a disulfide bond at room temperature,[3] and it is reasonable to assume that in the S_4^{2-} similar bonding, and therefore Debye–Waller factors, will be expected (infrared spectroscopy shows that S–S stretching freqencies are very similar for S_n^{2-} anions of different chain lengths, suggesting thermal displacement parameters will also be similar[23]). It should be noted that the spread of S–S bonding distances in the tetrasulfide anion in $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]^{2-}$ (2.036–2.096 Å) gives rise to a small amount of static disorder in the average sulfur shell and thus the average sulfur–sulfur Debye–Waller factor might be expected to be at least 0.005 Å^2. Fig. 4 shows that appropriate Debye–Waller factors are produced when N_S is between 0.9 and 1.2; higher values of N_S give physically unlikely values for A_S. Thus by considering the behaviour of *both* fit index and Debye–Waller factor with N_S, the sulfur K-edge EXAFS data enable the correct co-ordination number of sulfur in $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]^{2-}$ to be estimated to within ±0.2.

The Fourier transform of the sulfur K-edge data of amorphous WS_3, Fig. 5(a), shows one major broad feature which indicates atomic correlations between 2 and 2.5 Å. Since previous EXAFS studies of WS_3 at the tungsten L_{III}-edge find W–S distances at ≈2.4 Å[5,13–16] these must contribute to the EXAFS signal, and at least in part account for the main feature of Fourier transform. However, it was found that a single tungsten shell could not produce a reasonable fit to the data, even if Debye–Waller factors were increased to simulate a large spread of S–W distances. Including a sulfur shell with $d_{S\text{–}S} \approx 2$ Å gave a much more satisfactory fit. Such short S–S distances imply the presence of polysulfide groups (S_n^{2-}, $n = 2,3,4\ldots$) in WS_3, since sulfur–sulfur bonding distances in polysulfide anions are generally between 2 and 2.1 Å and are independent of the chain length[24] (*cf.* the model complex we described above). It is not unexpected that the average oxidation state of sulfur in WS_3 is greater than −2 since it is well established that the compound contains W–W bonds, and that tungsten cannot therefore be in oxidation state VI with all the sulfur occurring as S^{2-}.[5] The question of interest is to determine the extent of S–S bonding, and hence to resolve whether tungsten is in oxidation state IV or V. The relatively short k range of our data means that it would not be meaningful to refine the Fermi energy and interatomic distances, occupation numbers and thermal factors for each shell. Previous structural studies of WS_3 all find tungsten to have ≈6 sulfur near neighbours[5,13–16] and therefore sulfur must on average have 2 tungsten near neighbours, to be consistent with the composition of the material. We therefore fixed the occupation number of the tungsten shell at ≈2.4 Å at 2, and investigated the effect on fit index of varying the occupation number of the sulfur shell at ≈2.0 Å; N_S was varied in steps of 0.1 and for each value the radial distances and the Debye–Waller factors of both atomic shells varied in least-squares refinements to minimise the fit index. Fig. 6(a) shows these data and a significant minimum in fit index is observed when N_S is approximately 0.5. Calculation of a contour map showing the combined effect of shell occupation number and Debye–Waller factor on fit index gave agreement with these results. The refined S–W distance of 2.43 Å is in agreement with that deduced from our tungsten L_{III}-edge study of 2.40 Å,[5] and the S–S distance of 2.07 Å is similar to that observed in crystalline disulfide-containing materials, for example in VS_4 ($V^{IV}(S_2^{2-})_2$), $d_{S\text{–}S} = 2.04$ Å,[25] in TiS_3 ($Ti^{IV}(S_2^{2-})S^{2-}$), $d_{S\text{–}S} = 2.04$ Å,[26] and in NbS_3 ($Nb^{IV}(S_2^{2-})S^{2-}$), $d_{S\text{–}S} = 2.05$ Å.[27] An important point to note is that the Debye–Waller factor of the sulfur shell (A_S) at the point where the fit index is at its minimum has a physically reasonable value and is close to values previously observed for disulfide anions (see above). Models with higher S–S co-ordination numbers (>0.7) give considerably higher values for A_S whilst those with lower (<0.4) give negative values for A_S which are physically impossible. Fig. 5(a) also shows how a model that does not include sulfur–sulfur bonding ($N_S = 0$) is not adequate to model the sulfur EXAFS data for WS_3. This is the first direct structural evidence for sulfur–sulfur bonding in WS_3 and strongly suggests the presence of disulfide anions in the material. Bearing in mind the associated inaccuracy of EXAFS-derived co-ordination numbers the refined S–S co-ordination number of 0.5 is consistent with the two most commonly postulated formulations of the compound: $W^{IV}(S_2^{2-})(S^{2-})$, where 2/3 of sulfur is bonded directly to another sulfur atom, or $W^V(S_2^{2-})_{0.5}(S^{2-})_2$, where 1/3 of the sulfur atoms

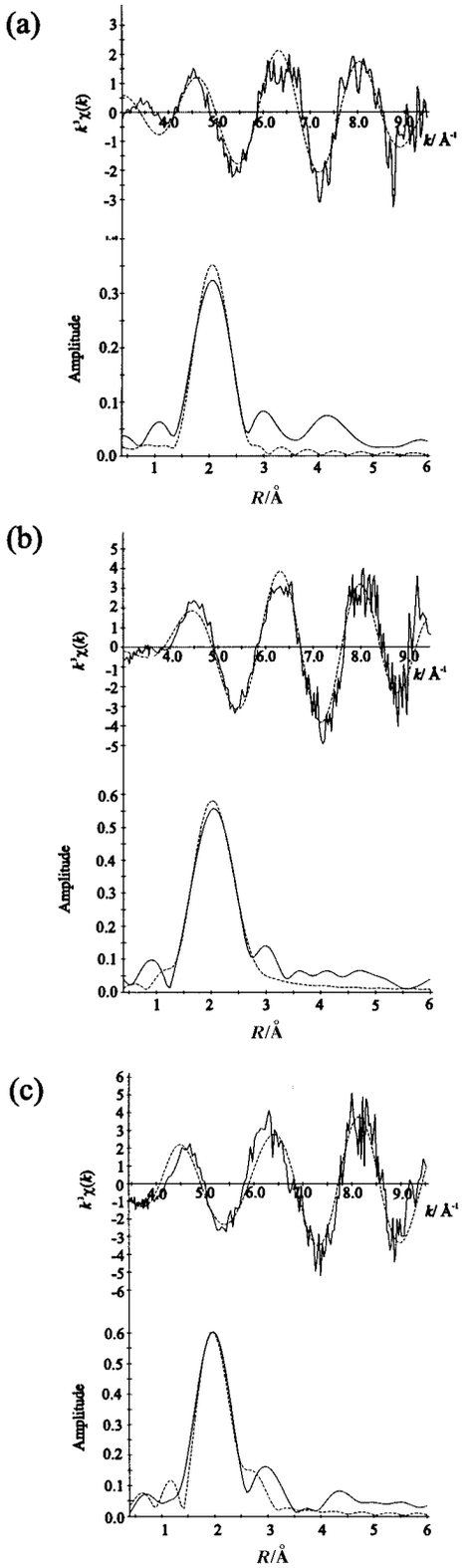

Fig. 5 Sulfur K-edge EXAFS for (a) WS_3 (b) WS_5 and (c) Re_2S_7: top k^3-weighted EXAFS (———) experimental and (– – – –) theoretical and bottom the Fourier transform.

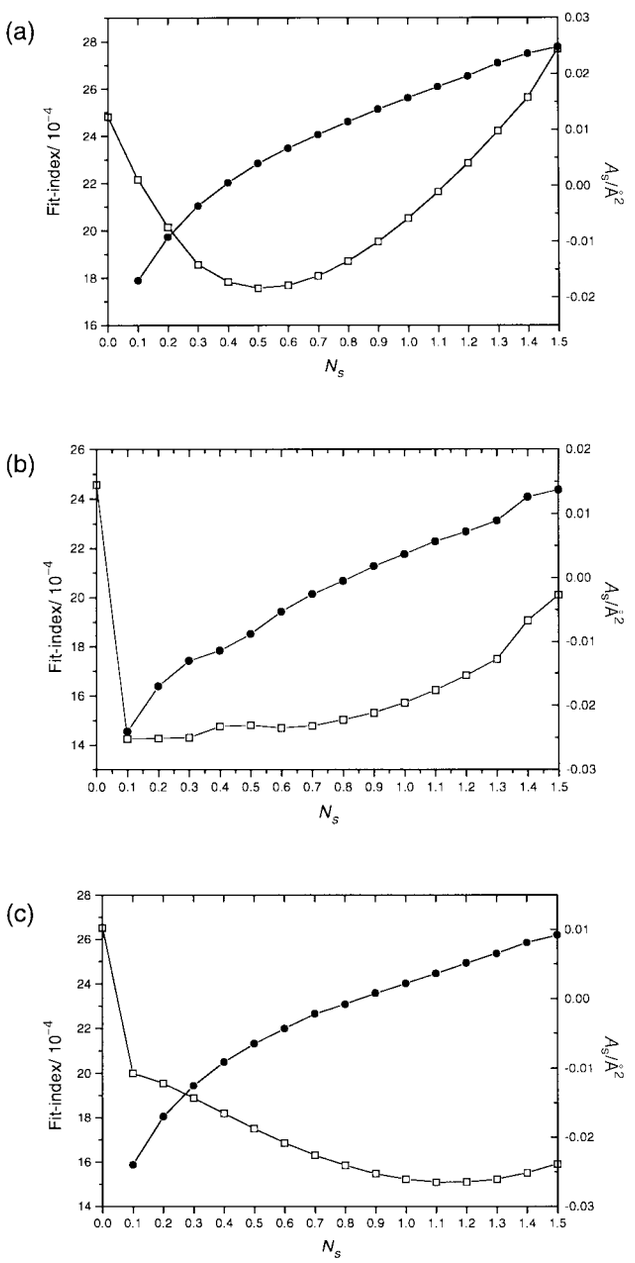

Fig. 6 The effect on EXAFS fit index (unfilled squares) and sulfur shell Debye–Waller factor, A_S (filled circles), of the occupation number of the bonded sulfur shell for (a) WS_3, (b) WS_5 and (c) Re_2S_7. Lines are for guidance only and have no mathematical significance.

are bound to other sulfurs. However, the latter formulation appears to be ruled out on the basis of the negative Debye–Waller factor it produces. Another possibility is that the material contains a mixture of W^{IV} and W^{V} and has an average composition $W^{IV}W^{V}(S_2^{2-})_{1.5}(S^{2-})_3$. In the final refinement the S–S co-ordination number was fixed at 0.5, and S–W co-ordination number at 2 and all other parameters for both shells allowed to vary in least-squares refinements, the results are shown in Table 2. Fig. 7(a) shows a possible structural model for WS_3. A chain-like structure is formed by face sharing of approximate trigonal prisms of sulfur atoms with tungsten atoms at their centre, and tungsten–tungsten bonding between every other pair of metal atoms gives alternating long and short W–W distances along a chain. Sulfur–sulfur bonding is introduced by distorting the trigonal prisms. In the sketch shown 2/3 of sulfur is found as disulfide anions, but the amount of sulfur bonding can be reduced by removing sulfur pairing among the sulfurs bridging the non-bonded W_2 pair and oxidising some W^{IV} to W^{V}. Disorder could be introduced into the model by the flexibility of the sulfurs bridging the non-bonded W···W pairs, indeed the large value of the S–W Debye–Waller factor (≈0.03 Å^2) (which matches closely that found by tungsten L_{III}-edge EXAFS studies studies[5]) suggests a large amount of static disorder in W–S distances is present in WS_3. Another means of introducing disorder would be randomness in occurrence of disulfide anions along a chain and in their relative position on the chain and this in turn would create disorder in packing

Table 2 Structural parameters derived from the sulfur K-edge EXAFS study of WS_3, WS_5 and Re_2S_7. Legend as for Table 1

Compound	Shell	Occupation number	Radial distance/Å	Debye–Waller factor/Å²	Fit index/ 10^{-4}
WS_3	S	0.5	2.066(70)	0.004(9)	17.58
	W	2	2.432(12)	0.035(3)	
WS_5	S	1.0	2.071(8)	0.002(1)	15.72
	W	1.2	2.456(14)	0.019(3)	
Re_2S_7	S	1.0	2.037(8)	0.0036(1)	15.09
	Re	1.57	2.317(11)	0.025(4)	

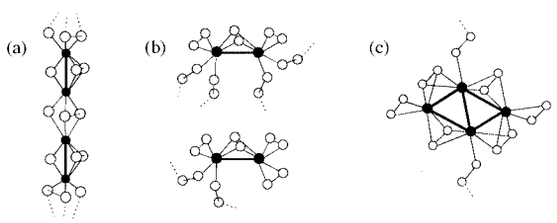

Fig. 7 Possible structural models for (a) WS_3, (b) WS_5 and (c) Re_2S_7. Filled circles represent metal atoms, and unfilled circles sulfur atoms. Bold lines represent metal–metal bonds, and dotted lines sulfur–metal bonds to other similar structural units.

chains to give an extended structure, and explain why the material is amorphous.

The sulfur K-edge EXAFS data for WS_5, Fig. 5(b), were analysed using a similar approach to that adopted for WS_3. Once again the single broad feature in the Fourier transform of the EXAFS data could not be modelled by a single shell of W atoms, and a sulfur shell had to be included. For WS_5 we knew from our previous tungsten L_{III}-edge EXAFS and neutron diffraction studies[5,21] that the W–S co-ordination number was six and hence the average S–W co-ordination number was 1.2. We therefore fixed the occupation number of the tungsten shell and followed the behaviour of the fit index as we varied the occupation number of the sulfur shell. Fig. 6(b) shows the effect of varying the occupation number of the sulfur shell in steps of 0.1 on the fit index and sulfur Debye–Waller factor. In this case the minimum in fit index is not as distinct as for WS_3. Clearly a sulfur shell is necessary to model the data since the model with $N_S = 0$ has a considerably poorer fit than others. Consideration of the behaviour of A_S as N_S is varied shows that $N_S = 1$ gives the most reasonable fit to the data; values of N_S lower than this give negative Debye–Waller factors or values close to zero and those with N_S higher the fit index is higher, and A_S increased from what we expect for a disulfide bond. In the final refinement N_S was fixed at 1, N_W at 1.2 and radial distance and Debye–Waller factors allowed to vary, Table 2. The refined S–W distance of 2.46 Å is in good agreement with that of 2.44 Å determined by tungsten L_{III}-edge EXAFS,[5] and as before the S–S distance agrees well with that seen in other disulfide-containing materials. Fig. 7(b) shows a sketch of possible structural units for WS_5 based on its formulation as $W^V(S_2^{2-})_{2.5}$. This is consistent with all experimental evidence available on the compound. The potential flexibility of the inter-unit S_2^{2-} linkages might explain how an amorphous network can be generated if an extended structure is created.

The sulfur K-edge EXAFS data for Re_2S_7 (Fig. 5(c)) can only be satisfactorily fitted by a two shell model with a rhenium shell at ≈2.3 Å and a sulfur shell ≈2.0 Å. Data analysis was approached as above, in this case the S–Re co-ordination number was fixed at 1.57 using the result from our rhenium L_{III}-edge study that each rhenium has on average ≈5.5 sulfur neighbours.[6] Fig. 6(c) shows the effect of varying the occupation number of the sulfur shell in steps of 0.1 on the fit index and sulfur Debye–Waller factor, with all other parameters allowed to vary in the least squares refinement. A minimum in fit index is observed at $N_S = 1.0$–1.2, and at this point the sulfur Debye–Waller factor has a value appropriate for a disulfide-containing compound (0.004–0.006 Å²). For the final refinement N_S was fixed at 1.0 and N_{Re} at 1.57 and all other parameters varied in least squares refinements, Table 2. The S–Re distance of 2.32 Å agrees with our distance of 2.33 Å,[6] within experimental error, and the S–S distance is typical of the disulfide anion. The features in the Fourier transform of the EXAFS signal at around 3 Å may be fitted as non-bonded sulfur distances, but this offers no statistical improvement of the fit to the data and increases the number of independent variables in least-squares refinements to an inappropriately high value. In our rhenium L_{III}-edge study we found that Re–Re bonded clusters make up the structure of Re_2S_7 and by considering the electron counts of various clusters we deduced that formulating the compound as $Re^{3.5}{}_2(S^{-1})_7$ was the most satisfactory model.[6] The new results provide clear evidence that in Re_2S_7 sulfur is found solely as disulfide. Fig. 7(c) shows a metal–metal bonded $Re^{3.5}{}_4$ rhombic cluster that might make up the structure of Re_2S_7. This is consistent with available structural data on the compound, satisfies electron counting and produces a model with correct composition when linked with other such units to give an extended structure.

The amorphous sulfur-rich sulfides we have studied here all contain appreciable sulfur–sulfur bonding in the form of disulfide anions. This was previously predicted on the basis of sulfur K-edge XANES studies and infrared spectroscopy, but the sulfur K-edge EXAFS results we have described provide the first direct evidence for the nature of the S–S bonding in the materials. The EXAFS results are far more conclusive, and by comparison of the structural parameters we have obtained (bonding distances and displacement parameters) with crystalline disulfide-containing materials we can show that the models we propose are chemically reasonable. Clearly much further work is necessary for detailed structural models for the amorphous compounds to be produced, in particular information on non-bonded distances is necessary to describe how the units shown in Fig. 7 are linked to form extended structures. Such medium-range order is very difficult to determine in an EXAFS experiment, but diffraction methods can be used and this is an area of our current research.

Conclusions

The experiments performed in this work have demonstrated that energy-selective fluorescence detection is, with the development of new detectors, now a useful tool for collecting EXAFS data for soft X-ray absorption edges even when a sample contains elements with closely lying emission lines. This situation is extremely common at low X-ray energies. This development has enabled us to gain important new structural information on amorphous WS_3, WS_5 and Re_2S_7. Previously sulfur K-edge EXAFS studies of amorphous tungsten and rhenium sulfides would have been impossible because of the occurrence of metal M absorption edges and emission lines close to the sulfur K-edge and emission lines.

Experimental

Sample preparation

The compound WS_3 was prepared by thermal decomposition of

ammonium tetrathiotungstate. The salt $[NH_4]_2[WS_4]$ was used as supplied by Aldrich, finely ground and placed in a Pyrex tube under dynamic vacuum. This was heated at 200 °C for 10 h, in which time gas evolution ceased and the yellow starting material had decomposed into a black powder. The compound WS_5 was prepared by the reaction between tungsten hexacarbonyl (Aldrich) and sulfur (BDH) in boiling 1,2-dichlorobenzene as described previously.[8] The mixture $[W(CO)_6 : 7S]$ was heated under nitrogen for 2 h and the brown-black precipitate formed recovered by suction and washed using carbon disulfide (to remove unchanged sulfur). The compound Re_2S_7 was prepared by reaction between potassium perrhenate (Aldrich) and sodium thiosulfate (Aldrich) in boiling dilute hydrochloric acid (BDH).[17] A boiling solution of ≈0.25 M $Na_2S_2O_3$ was added to a boiling solution of 0.25 g of $KReO_4$ in 20 cm^3 of 2 M HCl. A black precipitate of the rhenium sulfide formed immediately on mixing the chemicals. The mixture was heated for five minutes and the solid recovered by suction filtration, washed with 2 M HCl and carbon disulfide, and dried over silica gel under vacuum. X-Ray powder diffraction patterns of the tungsten and rhenium sulfides confirmed them to be amorphous and to contain no crystalline impurities. A Philips CM20 transmission electron microscope fitted with an EDAX PV9900 system was used to perform X-ray microanalysis. Crystalline WS_2 (Aldrich) and ReS_2 (Alfa) were employed as standards and calibration constants were determined to convert the metal M to sulfur K X-ray emission ratios into metal : sulfur ratios. Ten particles each of the amorphous sulfides were analysed and found to have the compositions $WS_{3.1(1)}$, $WS_{5.0(2)}$ and $ReS_{3.4(2)}$.

The crystalline model compound $[NH_4]_2[W_3S_{16}(NH_3)_3]$ was synthesized by a route not previously described. The complex $K_5[W_3S_4(CN)_9]\cdot nH_2O\cdot mKCN$ (0.5 g) was dissolved in 20 ml of water in a 100 ml conical flask. Ammonium polysulfide solution (20 ml, ≈10 M) was added and the resulting dark brown solution kept at 60 °C for 48 h. Small black crystals and a grey yellow solid (impure sulfur) were removed by filtration. The black crystals were isolated by washing the bulk material successively with water, ethanol, carbon disulfide (to remove sulfur), and diethyl ether and then dried in air. Infrared spectroscopy and X-ray powder diffraction confirmed the identity of the product by comparison with the literature data.[22] All materials were stored in a vacuum desiccator before EXAFS measurements were performed.

EXAFS experiments

Sulfur K-edge (2471 eV) EXAFS experiments were performed on Station 3.4 of the Daresbury synchrotron radiation source (SRS). The source operates with an electron-beam energy of 2 GeV and average beam current of 200 mA. Station 3.4 receives X-rays in the energy range 800–3500 eV and in our experiments the incident X-ray energy was selected using a Ge(111) double crystal monochromator.[28,29] No adjustment of the monochromator was necessary to provide harmonic rejection since a chromium pre-mirror provides a high energy cut-off. An EG&G germanium solid state detector was used for fluorescence detection.[7] The high resolution of this detector (≈125 eV full width at half maximum, FWHM) allowed collection of only the sulfur K fluorescence without interference from either the tungsten M (1775 eV) or rhenium M (1843 eV) emissions. A window of 0.26 keV was used to select the sulfur K fluorescence from the total fluorescence spectrum, rejecting primary scatter as well as metal M emissions. The detector and the sample were both situated at close to 90° to the incident X-ray beam to minimise direct scatter of X-rays into the detector, and to obtain accurate EXAFS amplitudes beyond the metal M_{II}-edge.[30] Data were collected from samples of the sulfides diluted in graphite (≈60% by mass) and pressed into 13 mm pellets at room temperature, and under high vacuum conditions. 5–10 Scans were recorded from each sample, and later normalised and summed. At present only one detector element is available and so the data that may be collected in a reasonable period of time (5–10 h) are of lower quality than those obtained by conventional methods. This limited the maximum k value we could use in data analysis. Thus, we analysed the sulfur EXAFS data in each case over the range $k = 3$–10 Å^{-1}. This range is sufficient to allow structural parameters for various models to be varied in least-squares refinements. The number of independent parameters, N_{ind}, that may be varied in EXAFS data analysis to give meaningful results is given by $\approx 2\Delta k \Delta R/\pi$, and the smallest separation of shells that can be resolved, Δr, by $\pi/2\Delta k$, where Δk is the extent of data in k-space, and ΔR the range of distance over which EXAFS data are being modelled (usually determined by inspection of the Fourier transform).[31] For the sulfur k-edge EXAFS data $N_{ind} \approx 5$ and $\Delta r = 0.22$ Å, since $\Delta k = 7$ Å^{-1} and taking ΔR to be 1 Å, since atomic shells between 2 and 3 Å are being considered. In all cases the number of independent parameters was fewer than the calculated value and the distances refined differed by more than ΔR.

The tungsten L_{III} EXAFS data was collected on Station 7.1 at Daresbury. Data were collected in transmission mode at room temperature from a powdered sample of $[NH_4]_2[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(S_4)_3(NH_3)_3]$ finely ground with boron nitride and pressed into a 13 mm diameter pellet. The boron nitride acted as a diluent to ensure $\mu d \approx 2.5$ with $\Delta\mu d \approx 1.1$. The variation of X-ray absorption with energy was measured using a Si[111] double-crystal monochromator and X-ray intensity measured before and after the sample using ionisation chambers filled with appropriate quantities of inert gases to optimise detector sensitivity. The monochromator was calibrated by scanning the tungsten L_{III} absorption edge of a tungsten foil, and harmonic rejection set at 50%. Data were collected to $k = 13$ Å^{-1}.

The programs EXCALIB, EXBROOK, and EXCURV 92 were used to extract the EXAFS signal from raw X-ray absorption data and to analyse the data.[32] Phase shifts were calculated within EXCURV 92 using the Hedin–Lundqvist method for determining ground state potentials and exchange potentials calculated using the von Barth method. EXAFS Spectra were Fourier transformed to produce a one-dimensional radial distribution function, using phase shifts calculated for the first atomic shell.

Least-squares refinements of the structural parameters of the compounds were performed within EXCURV 92 against the k^3-weighted EXAFS to minimise the fit index (F.I.). The fit index is defined as: $\Sigma_i(k^3(\chi_i^{calc}(k) - \chi_i^{exp}(k)))^2$ where χ_i^{calc} and χ_i^{exp} are the ith data point of the calculated and experimental X-ray absorption coefficient, respectively.

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