X-Ray absorption studies of amorphous Re_2S_7

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Amorphous Re_2S_7 is formulated as $Re^{3.5}_2S^{-1}_7$ and a rhomboidal metal–metal bonded Re_4S_{16} unit proposed as the basic structural building block.

The amorphous rhenium sulfide Re_2S_7 and its hydrate are used as catalysts in a number of hydrogenation reactions.[1–3] The structure of this material is significant both because of these uses and as part of the wider interest in the structure of amorphous transition-metal chalcogenides.[4–7] The only direct structural information about the material is from an X-ray diffraction study by Diemann which showed the presence of short rhenium–rhenium distances of *ca.* 2.7 Å.[8]

Recently Müller *et al.* used chemical extrusion to gain information on the structural building blocks present in Re_2S_7.[9] They concluded that Re_2S_7 contained two types of Re_4 cluster, rhomboidal and tetrahedral clusters, and contained sulfur in polysulfide groups and as S^{2-}. We have attempted to gain information directly from the solid state to determine if these conclusions are justified. We have carried out EXAFS (extended X-ray absorption fine structure) studies at the rhenium L_{III}-edge to gain information on the local coordination around rhenium and X-ray absorption studies at the sulfur K-edge to give information on the oxidation state of sulfur in Re_2S_7.† Unfortunately EXAFS studies at the sulfur K-edge are complicated by the close proximity of the Re M_{II}-edge at 2682 eV. Experiments on the model compounds ReS_2, VS_4 and S were carried out at the same time.

The Re L_{III}-edge EXAFS study of ReS_2 gave coordination numbers and distances around rhenium in excellent agreement with the crystallographic values[10] (see Table 1). The Fourier transform of the Re L_{III}-edge EXAFS data for Re_2S_7 clearly showed two shells and the refined values for a rhenium and sulfur shell are shown in Table 1. Fig. 1(*a*) shows the k^3-weighted EXAFS data for Re_2S_7 and the theoretical curve for our model. Fig. 1(*b*) shows the Fourier transform. The refined Re–Re coordination number of 2.82 is consistent with the presence in Re_2S_7 of rhomboidal Re_4 units with an average Re–Re coordination number of 2.5, tetrahedral Re_4 units with an Re–Re coordination number of 3 or a mixture of these species. These experiments support the conclusions of Müller as to the identity of the metal clusters in amorphous Re_2S_7.

X-Ray absorption at the S K-edge was measured for Re_2S_7 and the model compounds α-S, VS_4 and ReS_2, which contain

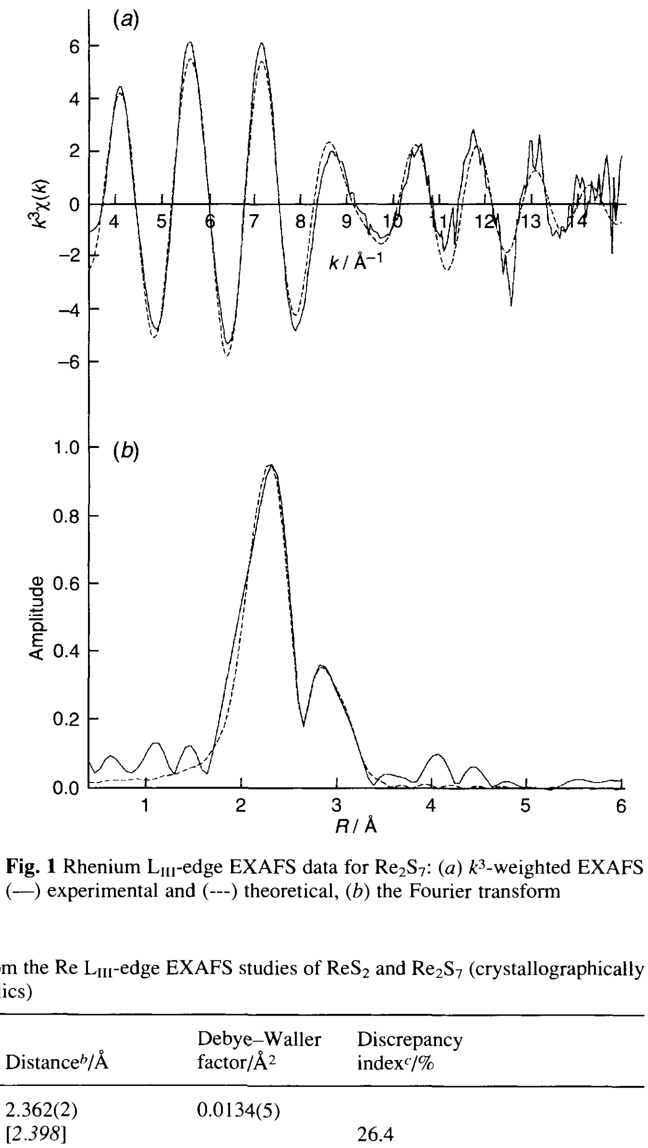

Fig. 1 Rhenium L_{III}-edge EXAFS data for Re_2S_7: (*a*) k^3-weighted EXAFS (—) experimental and (---) theoretical, (*b*) the Fourier transform

Table 1 Coordination numbers, distances and Debye–Waller factors derived from the Re L_{III}-edge EXAFS studies of ReS_2 and Re_2S_7 (crystallographically derived average distances and coordination numbers for ReS_2 are shown in italics)

	Shell	Occupation number[a]	Distance[b]/Å	Debye–Waller factor/Å^2	Discrepancy index[c]/%
ReS_2	S	5.96(22)	2.362(2)	0.0134(5)	26.4
		[6]	*[2.398]*		
$\Delta k = 15$ Å^{-1}	Re	3.18(46)	2.759(3)	0.0154(11)	
$N_{ind} = 7$[d]		*[3]*	*[2.803]*		
Re_2S_7	S	5.02(20)	2.325(2)	0.0182(7)	24.9
$\Delta k = 15$ Å^{-1}	Re	2.82(37)	2.739(3)	0.0156(1)	
$N_{ind} = 7$					

Errors quoted are statistical errors from the least-squares refinement. [a] From the ReS_2 data and consideration of the behaviour of the fit-index with coordination number, we estimate the relative confidence limits for refined occupation numbers are ±10–15% for the sulfur shell and ±20% for the rhenium shell. [b] *Errors in distances arise from systematic errors in the EXAFS experiment and data analysis, and limit the true accuracy of the distances to* ±0.02 Å. [c] $R = \{\int|[\chi_i^T(k) - \chi_i^E(k)]|k^3dk/\int|\chi_i^E(k)|k^3dk\} \times 100\%$ where $\chi_i^T(k)$ and $\chi_i^E(k)$ are the theoretical and experimental EXAFS respectively. [d] Δk is the k-range used in the EXAFS analysis and N_{ind} the number of independent parameters refined.

only S^0, S^{-I} and S^{-II} respectively. The results are shown in Fig. 2. The position of the S K-edge shows that the lowest oxidation state of sulfur in Re_2S_7 is S^{-I}. We suggest all sulfur is present as $(S_2)^{2-}$ groups; this is consistent with our observation of an absorption band in the IR at 521 cm^{-1}, which can be assigned as an S–S stretching mode of this group, and the absence of bands due to polysulfide groups {for example, in the complex $[NH_4]_4[Re_4(S^{2-})_4(S_3{}^{2-})_6]$, the S–S stretch occurs at 465 cm^{-1} (ref. 11)}.

The simplest model for the structure of Re_2S_7 would assume that all sulfur is found as S^{-1} and would result in the formulation $Re^{3.5}{}_2S^{-1}{}_7$. This would produce an electron count of 14, which is appropriate for the electron-rich Re_4 rhombus of Müller and the results of our rhenium L_{III}-edge EXAFS experiment. In Fig. 3 an Re_4S_{16} unit is shown; this contains 4 μ-η^2-S_2, 2 η^2-S_2 and 2 μ-S_2 groups. The 2 μ-S_2 are shared between similar units and this model therefore produces the correct stoichiometry and fits all our experimental data. The average Re–S coordination number of 5.5 is closer to that found from our EXAFS study than the value of 6 produced by Müller's models.

To produce an electron count of 12, which is appropriate for the Re_4 tetrahedon, some sulfur would have to be in the −II oxidation state. This is ruled out by the S K-edge absorption data. We therefore believe structural models for Re_2S_7 based on Re_4 tetrahedra to be less plausible than those based on Re_4 rhombi.

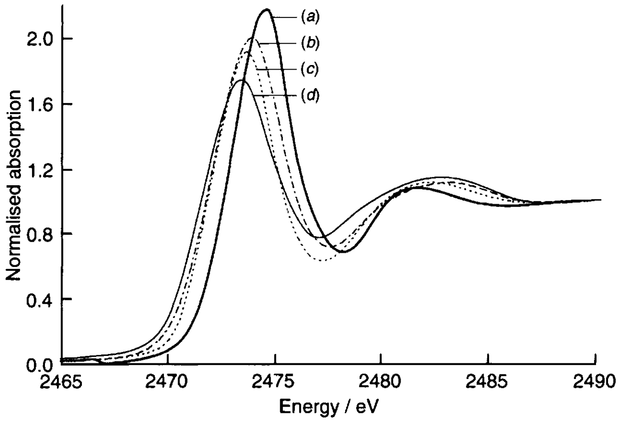

Fig. 2 Normalised sulfur K-edge absorption spectra: (*a*) α-S, (*b*) VS_4, (*c*) Re_2S_7, (*d*) ReS_2

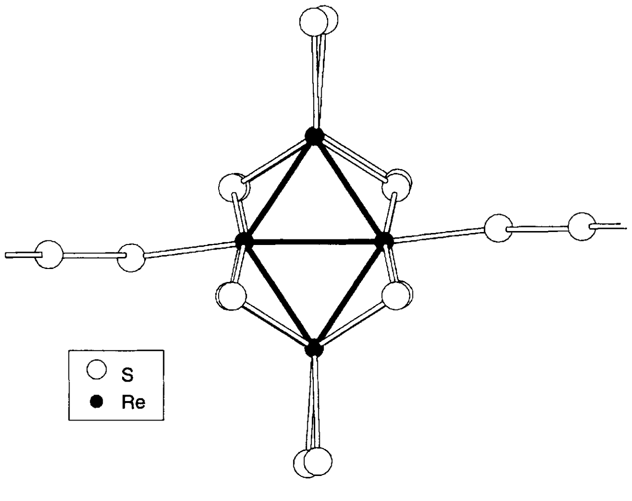

Fig. 3 Proposed Re_4 rhomboidal structural building block for Re_2S_7

The results of our X-ray absorption study suggest that amorphous Re_2S_7 contains Re_4 rhomboidal clusters which is in agreement with the chemical extrusion studies of Müller *et al.* The results of the sulfur K-edge absorption studies provide more direct information about the mode of bonding of sulfur than those obtained by chemical degradation. Although in the case of amorphous Re_2S_7 there is some agreement between the results of EXAFS measurements carried out on the solid-state sample and the conclusions reached from chemical extrusion studies, this is not always the case. For example, in our EXAFS studies of amorphous MoS_3[12] we found no evidence for the Mo_3 triangles that Müller *et al.* postulate from their extrusion studies on this material.[13] We suggest that chemical extrusion might be a useful tool in investigating the structure of amorphous materials and may complement other techniques, but that it should be used with caution.

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Footnote

† Re_2S_7 was prepared by one of the methods described by Briscoe *et al.*, namely the reaction between potassium perrhenate and sodium thiosulfate in an acidic solution.[14]

Rhenium L_{III}-edge EXAFS data and sulfur K-edge X-ray absorption spectra were recorded at the Daresbury SRS on stations 7.1 and 3.4, respectively, at room temperature with an electron-beam energy of 2 GeV and average beam current of 200 mA, as described in our previous work.[15] The programs EXCALIB, EXBACK, and EXCURV92 were used to extract the EXAFS signal and analyse the data.[16] Least-squares refinements of the structural parameters of the compounds were carried out against the k^3-weighted EXAFS to minimise the discrepancy index.

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