

Local structures of the amorphous chromium sulfide, CrS₃, and selenide, CrSe₃, from X-ray absorption studies†

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Extended X-ray absorption fine structure (EXAFS) studies of the amorphous chromium sulfide, CrS₃, the amorphous chromium selenide, CrSe₃, and the crystalline vanadium sulfide model compound, VS₄, have been carried out at both the metal and chalcogen K edges. Structural models based on the distances and co-ordination numbers obtained from the analysis of these data are presented for CrS₃ and CrSe₃. In CrS₃, chromium is surrounded by an average of six sulfurs at 2.35 Å. The sulfur-edge data can be fitted by two shells containing two chromium neighbours at 2.34 Å and one sulfur neighbour at 2.03 Å. The results of sulfur K-edge absorption spectroscopy of CrS₃, Cr₂S₃, VS₄ and α -S suggest that all the sulfur is found in one oxidation state, S⁻¹, and we formulate CrS₃ as Cr^{III}(S⁻¹)_{1.5}. The edge shift, ΔE , of the chromium K edge of CrS₃ ($\Delta E = 6.37$ eV) relative to chromium metal, is close to that of Cr₂S₃ ($\Delta E = 6.88$ eV), supporting the assignment of the oxidation state of chromium as III. In CrSe₃, chromium is surrounded by an average of six seleniums at a distance of 2.50 Å. Each selenium has an average of two chromium neighbours at 2.45 Å, and 0.67 of a selenium neighbour at 2.34 Å. We formulate CrSe₃ as Cr^{IV}(Se⁻¹)₂Se^{-II}. The chromium K-edge shift of CrSe₃ ($\Delta E = 5.79$ eV) is large for a chromium selenide and provides further evidence for the assignment of the oxidation state of chromium in CrSe₃ as IV. The magnetic moments per chromium measured at room temperature were 1.74(3) μ_B for CrS₃ and 2.62(3) μ_B for CrSe₃, supporting the assignment of different oxidation states to chromium in the two materials.

We have recently prepared a number of new transition-metal chalcogenides with high chalcogen to metal ratios. The new sulfides include compounds of approximate composition CrS₃, MoS_{4.5} and WS₅,¹ and the new selenides CrSe₃, MoSe₅ and WSe₆.² These materials are amorphous and to obtain structural information we have embarked on a series of extended X-ray absorption fine structure (EXAFS) spectroscopic,³ X-ray and neutron diffraction studies.⁴ In this paper we report the results of X-ray absorption studies at the Cr, S and Se K edges on the two new chalcogenides, CrS₃ and CrSe₃.

The only well characterised binary sulfides and selenides of the first-row-transition metals with chalcogen to metal ratios greater than two are the crystalline compounds TiS₃,⁵ TiSe₃,⁵ VS₄,⁶ and V₂Se₉.⁷ The evidence for the existence of the sulfur-rich materials Cr₂S₅,⁸ V₂S₅,^{9,10} and VS₅¹¹ is not compelling, and the reports of these materials have not been confirmed. The chalcogenide TiS₃ contains Ti^{IV}, S₂²⁻ and S²⁻, with metal atoms in eight-co-ordinate sites; TiSe₃ is isostructural. The vanadium sulfide, VS₄ contains V^{IV} with all the sulfur in S₂²⁻ groups, again with the metal in an eight-co-ordinate site. In VS₄, the co-ordination around sulfur is simple, with each S₂²⁻ unit bridging two vanadium atoms. The VS₈ units share rectangular faces to form infinite chains with alternate long and short V...V distances, Fig. 1. The structure of V₂Se₉⁷ is related to that of VS₄, with selenium replacing sulfur and the two S₂²⁻ groups bridging the long V...V distance replaced by a Se₅⁴⁻ group. We have considered these materials as possible model compounds. Since our preliminary work on CrS₃ had suggested that the compound could be formulated as Cr^{III}-(S₂²⁻)_{1.5}, with all the sulfur present as disulfide groups, we decided to collect EXAFS data on VS₄, at both the vanadium and sulfur K edges, for comparison.

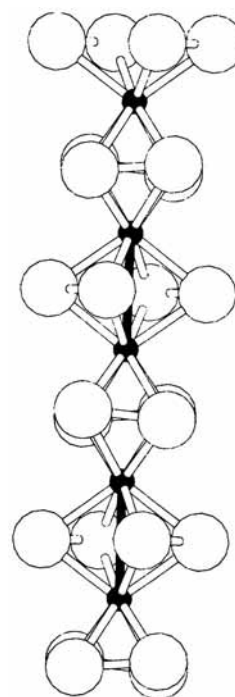


Fig. 1 Structure of a single chain found in crystalline VS₄ (black spheres, V; white spheres, S)

Experimental

Sample preparation and characterisation

(a) VS₄. A sample of VS₄ was prepared using the method described by Brauer.¹² The sulfide V₂S₃ (ca. 0.5 g, Alfa) was finely ground with a large excess of sulfur (BDH). This mixture, of approximate composition V:S 1:20, was heated in an evacuated Pyrex tube at 400 °C for 3 d, followed by a further

† Supplementary data available (No. SUP 57137, 6 pp.): EXAFS spectra and their corresponding Fourier transform for the metal and chalcogen K edges of VS₄ and CrSe₃. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

Non-SI unit employed: eV $\approx 1.60 \times 10^{-19}$ J; $\mu_B \approx 9.274 \times 10^{-24}$ J T⁻¹.

period of heating at 90 °C, in order to convert the unreacted sulfur to the α (orthorhombic) modification. The excess sulfur was removed from the product by thorough washing with carbon disulfide. Comparison of the X-ray powder diffraction pattern, recorded on a Spectrolab Series 3000 CPS-120 diffractometer equipped with an Inel multichannel detector, with the literature data¹³ confirmed the identity of the monophasic product. An infrared spectrum of the material, recorded in a KBr pellet in the region 4000–350 cm⁻¹ using a Perkin-Elmer 1720X infrared Fourier-transform spectrometer, showed absorptions only around 545 and 370 cm⁻¹, corresponding to sulfur–sulfur stretches of the disulfide groups and vanadium–sulfur stretches respectively.

(b) CrS₃. This was prepared by the reaction of Cr(CO)₆ (Aldrich, 99%) with sulfur (BDH) in boiling 1,2-dichlorobenzene (Aldrich).¹ The sulfur to chromium ratio was varied by carrying out reactions in solutions of different sulfur molarity, but always with an excess of sulfur. Unreacted sulfur remaining in the solid product was removed by washing with CS₂.

Energy-dispersive X-ray microanalysis was carried out with a Philips CM20 electron microscope fitted with an EDAX PV9900 analysis system. Small quantities, *ca.* 25 mg, of the chromium sulfides were dispersed in chloroform (*ca.* 2 cm³) by an ultrasonic bath. A drop of this dispersion was placed on a 3 mm carbon-coated copper grid and the solvent allowed to evaporate. A sample of VS₄ was similarly examined after first finely grinding the material in an agate mortar. The Cliff–Lorimer method,¹⁴ which is appropriate for thin samples, was used to determine compositions. The ratio of the intensities of the S K to V K emission lines in VS₄ was used to derive a calibration constant for the determination of the sulfur to metal ratio in the chromium sulfides from the relative intensities of the S K and Cr K emission lines. Ten particles were analysed to determine the average composition of the products from each preparation. The upper limit in the sulfur to chromium ratio appeared to be 3.9. Electron microscopy showed that all the chromium sulfides prepared were amorphous.

In this paper we report the results of our experiments on materials with sulfur to chromium ratios close to three. The material used in the EXAFS experiments had the composition CrS_{3,1(1)}. It was prepared using a S:Cr(CO)₆ ratio of 23:1 in a 0.51 mol dm⁻³ solution of sulfur in 1,2-dichlorobenzene.

Further characterisation was carried out to confirm that these materials did not contain free sulfur. X-Ray powder diffraction showed all the materials were amorphous and confirmed the absence of crystalline sulfur. Differential scanning calorimetry experiments, carried out using a Perkin-Elmer DSC7 instrument, showed no elemental sulfur in any of the samples. Infrared spectra of the materials show absorptions in the region 500–550 cm⁻¹, indicative of sulfur–sulfur bonding in disulfide groups (*cf.* VS₄), but there are not any indications of elemental sulfur (S–S stretch in α -S occurs at 464 cm⁻¹) in the samples. Weak infrared absorptions at 659, 750 and 1452 cm⁻¹, corresponding to the most intense infrared absorption bands of 1,2-dichlorobenzene, showed that a small amount of solvent remained trapped in the amorphous product.

An estimate of the amount of trapped solvent was obtained by comparing the formula weights derived by oxidising the product to Cr₂O₃ with those derived from electron microscopy. These results showed that the amorphous chromium sulfides contain approximately 7 mass % 1,2-dichlorobenzene.

Magnetic susceptibilities of the materials were measured at room temperature using a Sherwood Scientific magnetic susceptibility balance. These values were converted to an effective magnetic moment using formula weights derived from oxidation to Cr₂O₃. The average magnetic moment was found to be 1.74(3) μ_B per chromium. The pycnometric density was determined as 3.1(1) g cm⁻³ by liquid displacement.

(c) Cr₂S₃. This was used as supplied (Alfa, 99%) for the X-ray absorption study.

(d) CrSe₃. This was prepared by the reaction of Cr(CO)₆ (Aldrich, 99%) with selenium powder (Aldrich, >99.5% 100 mesh) in boiling 1,2-dichlorobenzene (Aldrich).² A 1:2 molar ratio of Cr(CO)₆ to Se was employed to prevent unreacted selenium remaining in the solid product. The product was washed with hexane. Infrared spectroscopy showed no carbonyl or 1,2-dichlorobenzene remained in the solid product.

Chromium selenide, CrSe (Alfa, 99.5%), was employed as the calibration standard in the analytical electron microscopy, and the ratio of the Se L to Cr K emission lines was used to determine the composition of the amorphous chromium selenide. Analysis of ten particles gave the composition, CrSe_{2.8(1)}. Electron microscopy and powder X-ray diffraction confirmed the product was amorphous and did not contain any unreacted selenium.

The average magnetic moment per chromium in CrSe₃ at room temperature was found to be 2.62(3) μ_B (no diamagnetic correction was applied). The pycnometric density was determined as 4.9(1) g cm⁻³ by liquid displacement.

X-Ray absorption experiments

Chromium K-edge, vanadium K-edge and selenium K-edge EXAFS data were collected in transmission mode on station 7.1 at the Daresbury Laboratory SRS, with an electron-beam energy of 2 GeV and an average beam current of 200 mA. The silicon(111) double-crystal order sorter monochromator was adjusted to give 50% harmonic rejection. An unfocused beam of size 0.8 mm vertically and 10 mm horizontally was employed. Finely ground samples were diluted in boron nitride to give a satisfactory edge jump and absorption and around 2 mm thickness of the mixture held in an aluminium holder between sheets of Sellotape™.

Separate experiments were carried out to measure accurately the shift in the chromium K edge of CrS₃, Cr₂S₃ and CrSe₃ with respect to chromium metal. The edge was scanned in steps of 0.295 eV with a count time of 2 s per point and the absorption spectrum of a chromium foil was monitored simultaneously with each sample. The edge shift, ΔE , relative to chromium metal was determined by measuring the difference between the maxima of the first derivatives of the sample data and of the corresponding chromium-foil data.

Sulfur K-edge EXAFS data were measured by total electron yield on station 3.4 at the Daresbury Laboratory SRS.^{15,16} A double germanium(111) straight-cut type monochromator was used. No harmonic rejection was necessary, since a grazing incidence pre-mirror acted as a high energy filter; this mirror also gave a 2:1 vertical focusing of the beam. Samples were mixed with about 30% of graphite by volume, to increase their electrical conductivity, dispersed in chloroform, and painted onto stainless-steel stubs to produce a continuous film. The samples were placed in a vacuum chamber and data were collected under ultra-high-vacuum conditions by drain-current detection. Four scans were recorded from each sample and these were normalised and summed using the data-analysis programs described below. The sulfur K-edge absorption spectra were calibrated with respect to α -S (2472 eV), which was run repeatedly to ensure that no shift in energy scale occurred between measurements on the different samples. One set of data, for CrSe₃ at the chromium K edge, was collected at 90 K; all other experiments were carried out at room temperature.

Data analysis

The basic equation for the interpretation of EXAFS data is (1),

$$\chi(k) = \sum_j \frac{N_j}{kR_j^2} |f_j(\pi)| e^{-2R_j/\lambda} e^{-2\sigma_j^2 k^2} \sin(2kR_j + 2\delta + \psi_j) \quad (1)$$

Table 1 Distances (R) and Debye–Waller factors (A) obtained from the EXAFS studies of VS_4 , CrS_3 and CrSe_3 (crystallographically derived distances for VS_4 are shown in italics)

	K Edge	Shell	N^a	$R/\text{\AA}$	$A/\text{\AA}^2$	Number of parameters refined
VS_4	V	S	8	2.406(4)	0.0144(6)	5
		V	1	<i>2.434^b</i>	0.0053(18)	
					2.848(8)	
	S	S	1	2.002(7)	0.0022(7)	5
		V	2	<i>2.036^b</i>	0.0099(7)	
					2.402(4)	
CrS_3	Cr	S	6	2.351(2)	0.0140(3)	3
		S	1	2.03(9)	0.006(2)	5
		Cr	2	2.34(9)	0.010(1)	
CrSe_3	Cr ($T = 90$ K)	Se	6	2.495(4)	0.015(1)	3
		Se	6	2.495(4)	0.017(1)	3
	Se ($T = 300$ K)	Cr	2	2.49(1)	0.007(2)	5
		Se	0.67	2.32(1)	0.004(1)	

^a The absolute accuracy of the co-ordination numbers derived from the EXAFS data is 10–20%, see text for the discussion of the relative values for these materials, which were fixed after preliminary data analysis. ^b Average distance.

where $\chi(k)$ is the magnitude of the X-ray absorption fine structure as a function of the photoelectron wave-vector k , N_j is the co-ordination number and R_j the interatomic distance for the j th shell. The terms δ and ψ_j are phase shifts experienced by the photoelectron, $f_j(\pi)$ is the amplitude of the photoelectron backscattering and λ is the electron mean free path; these are calculated within the program EXCURV 92,¹⁷ using spherical-wave theory and a single scattering model. The Debye–Waller factor is represented by $A = 2\sigma^2$ in EXCURV 92.¹⁷

We used the programs EXCALIB, EXBACK and EXCURV 92¹⁷ to extract the EXAFS signal and analyse the data. Least-squares refinements of the structural parameters of the compounds were carried out against the k^3 -weighted EXAFS signal to minimise the fit index, f.i. [equation (2)], where $\chi_i^{\text{theor}}(k)$

$$\text{f.i.} = \sum_i \{k^3[\chi_i^{\text{theor}}(k) - \chi_i^{\text{exp}}(k)]\}^2 \quad (2)$$

and $\chi_i^{\text{exp}}(k)$ are the theoretical and experimental EXAFS respectively. In all cases, the number of independent parameters was significantly fewer than the theoretical number of independent data points given by $N_{\text{idp}} = 2\Delta k\Delta r/\pi$, assuming the EXAFS data are significant over the distance range 1–4 Å. Co-ordination numbers were fixed after preliminary data analysis, thus reducing the total number of parameters varied. This has the effect of reducing the estimated standard deviations of the refined parameters. The results of refinements are also reported in terms of the discrepancy index R [equation (3)].

$$R = \left\{ \int |\chi_i^{\text{theor}}(k) - \chi_i^{\text{exp}}(k)|k^3 dk / \int |\chi_i^{\text{exp}}(k)|k^3 dk \right\} \times 100\% \quad (3)$$

Results

EXAFS data

VS_4 . The vanadium K-edge EXAFS data (SUP 57137) were analysed over the range $k_{\text{min}} = 3$ to $k_{\text{max}} = 12.4 \text{ \AA}^{-1}$. The bond distances from the single-crystal X-ray structural determination⁶ were used as a starting point for fitting the EXAFS signal, and co-ordination numbers fixed at the crystallographic values. A single sulfur shell containing eight sulfur atoms at 2.41 Å and a vanadium shell containing one vanadium atom at 2.85 Å were used to model the data. No information on the longer non-bonded intrachain $\text{V} \cdots \text{V}$ distance of ca. 3.2 Å is contained in

the EXAFS signal. Table 1 shows the refined structural parameters obtained from vanadium K-edge EXAFS on VS_4 , together with crystallographically determined interatomic distances⁶ for comparison. The large A factor of the sulfur shell reflects the variation in the V–S distances found in the single-crystal study.

The sulfur K-edge EXAFS data (SUP 57137) were analysed over the range $k_{\text{min}} = 3$ to $k_{\text{max}} = 11.9 \text{ \AA}^{-1}$. The co-ordination numbers were fixed at the crystallographically determined values of one sulfur and two vanadium atoms. The refinement of the sulfur–sulfur and sulfur–vanadium distances, Debye–Waller factors and the Fermi energy (E_F) simultaneously yielded interatomic distances in close agreement with those from the single-crystal study and physically reasonable thermal parameters. The refined structural parameters are given in Table 1.

CrS_3 . The chromium K-edge EXAFS data were analysed over the range $k_{\text{min}} = 3$ to $k_{\text{max}} = 13 \text{ \AA}^{-1}$. A satisfactory fit to the data was obtained using a single sulfur shell and refining the four parameters, E_F , A , R and N for the shell. This gave a value of 5.9(2) for N . Changing N in steps of 0.5 between 3 and 9 and allowing the other parameters to vary produced a deep minimum in the fit index corresponding to co-ordination by six sulfurs. The co-ordination number of chromium was thus fixed at six and the three parameters A , R and E_F allowed to vary in least-squares refinements. The Fourier transform showed that the EXAFS signal did not contain information beyond this single shell. Fig. 2(a) shows the k^3 -weighted chromium K-edge EXAFS data for CrS_3 and the theoretical curve produced from our model; Fig. 2(b) shows the Fourier transform. In all the data analysis described, a Gaussian window was used in the calculation of the Fourier transforms. Table 1 contains the refined structural parameters obtained.

The sulfur K-edge EXAFS data were analysed over the range $k_{\text{min}} = 3$ to $k_{\text{max}} = 9.6 \text{ \AA}^{-1}$. The upper limit was determined by absorption by the chlorine of the occluded solvent at 2822 eV. Although only one peak can be seen in the Fourier transform, two shells are required to give a satisfactory fit to the observed EXAFS signal and its transform. Least-squares refinements of a sulfur shell at ca. 2 Å and of a chromium shell at ca. 2.3 Å were carried out. The number of chromium neighbours was fixed at two, to be consistent with the chromium K-edge data and the stoichiometry, and the number of sulfurs fixed at one, in agreement with the sulfur K-edge X-ray absorption near-edge

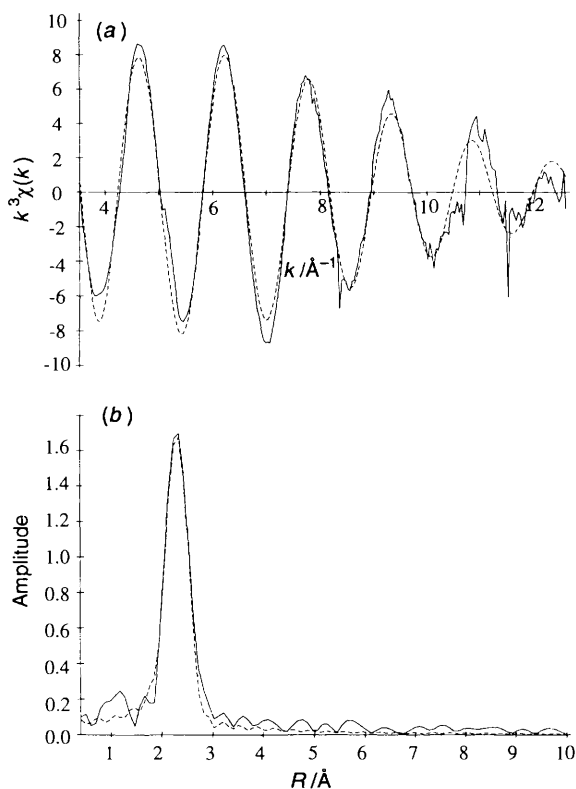


Fig. 2 Chromium K-edge EXAFS data for CrS_3 : (a) k^3 -weighted EXAFS (—) experimental and (---) theoretical, $R = 21.82\%$ and (b) the Fourier transform

structure (XANES) results described below. All other parameters were allowed to vary in least-squares refinements. This procedure gave physically reasonable distances, and Debye–Waller factors for the S shell and values for the Cr shell in good agreement with those obtained from chromium K-edge data (Table 1). Fig. 3(a) shows the k^3 -weighted sulfur K-edge EXAFS data for CrS_3 and the theoretical curve produced from our model; Fig. 3(b) shows the Fourier transform.

CrSe₃. The chromium K-edge EXAFS data (SUP 57137) were analysed over the range $k_{\min} = 4.5$ to $k_{\max} = 10 \text{ \AA}^{-1}$, giving information on only a single shell of *ca.* 6 selenium atoms at $2.50(1) \text{ \AA}$. Refining N using the highest quality, 90 K, data set, gave a value of $5.8(4)$. Taking account of the uncertainties in coordination numbers derived from EXAFS data, we fixed N at 6 in further data analysis and all other parameters were allowed to vary in the least-squares refinements. The relatively high Debye–Waller factor of the Se shell suggested that there might be different Cr–Se bond lengths present, but these could not be resolved. The expected resolution in distance ($\pi/2\Delta k$) is *ca.* 0.17 \AA in this EXAFS study. Table 1 contains the refined structural parameters obtained.

The selenium K-edge EXAFS data (SUP 57137) were analysed over the range $k_{\min} = 3$ to $k_{\max} = 14 \text{ \AA}^{-1}$. Two shells were required to model the EXAFS signal satisfactorily, a selenium shell at 2.32 \AA and a chromium shell at 2.49 \AA . Varying distances, Debye–Waller factors and the numbers of atoms of the two shells, simultaneously, gave N values of 0.8 and 1.9 for the selenium and chromium shells respectively. Fixing the number of chromiums at two, the value required by the stoichiometry, CrSe_3 , and the number of seleniums found bonded to each chromium from the chromium K-edge EXAFS results, resulted in a refined value of $0.7(2)$ for the number of seleniums in the Se shell. This value was close to two-thirds, the value we would expect if we formulate CrSe_3 as $\text{Cr}^{\text{IV}}(\text{Se}^{-1}_2)\text{Se}^{-\text{II}}$. Fixing the number of seleniums in this shell at 0.67 , to agree with this formulation, resulted in a physically reason-

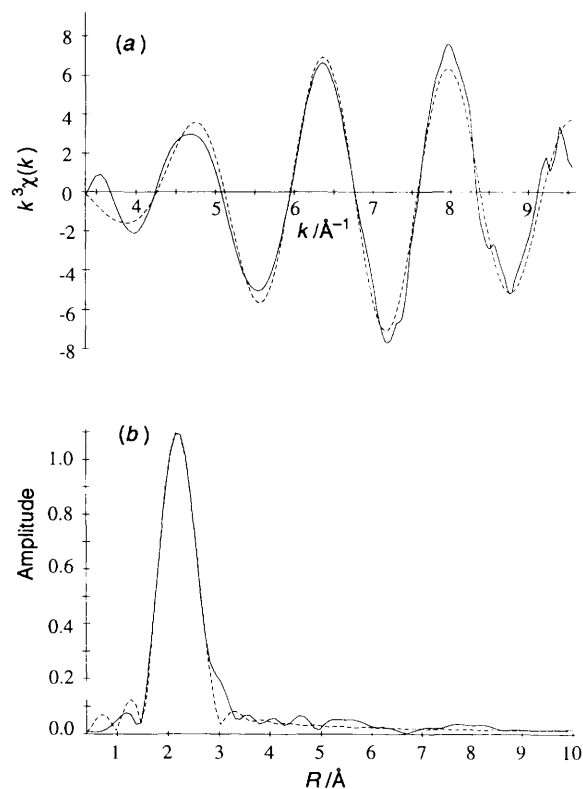


Fig. 3 Sulfur K-edge EXAFS data for CrS_3 : (a) k^3 -weighted EXAFS (—) experimental and (---) theoretical, $R = 18.78\%$ and (b) the Fourier transform

able Debye–Waller factor and a Se–Se distance of 2.32 \AA (Table 1). This is close to the values found in the literature for Se–Se distances in diselenide groups, for example, in ZrSe_3 where the Se–Se distance in the Se_2^{2-} group is 2.33 \AA .⁵

XANES data

Sulfur K-edge absorption spectra. The normalised sulfur K-edge absorption spectra for CrS_3 , Cr_2S_3 , VS_4 and $\alpha\text{-S}$ are shown superimposed on each other in Fig. 4. Significant changes in both the position of the absorption edges and in the peak shapes for the different compounds can be seen. The simplest interpretation is that the absorption edge shifts to higher energies as the oxidation state of sulfur increases.

Chromium K-edge absorption spectra. The normalised chromium K-edge absorption spectra for CrS_3 , Cr_2S_3 and CrSe_3 are shown superimposed on each other in Fig. 5. The edge shifts, ΔE , relative to chromium metal are 6.37, 6.88 and 5.79 eV for CrS_3 , Cr_2S_3 and CrSe_3 , respectively.

Discussion

CrS₃

The results of the sulfur K-edge EXAFS study, the sulfur K-edge absorption spectra and the IR spectra support the conclusion that all the sulfur is found as disulfide in this compound. Comparisons with the results from the model compound, VS_4 , are especially revealing. The close similarity in the S–S bond lengths and in the position of the sulfur K edge suggest that there must be strong structural similarities in the bonding of the disulfide ion in the two materials. The width of the sulfur K-edge absorption is only slightly larger than that for VS_4 , suggesting that all the disulfide groups in CrS_3 are found in similar chemical environments, as they are in VS_4 . The IR spectra show that the disulfide stretching frequency is similar in the two compounds, which also supports the conclusion that the structures contain similarly bonded disulfide units. We

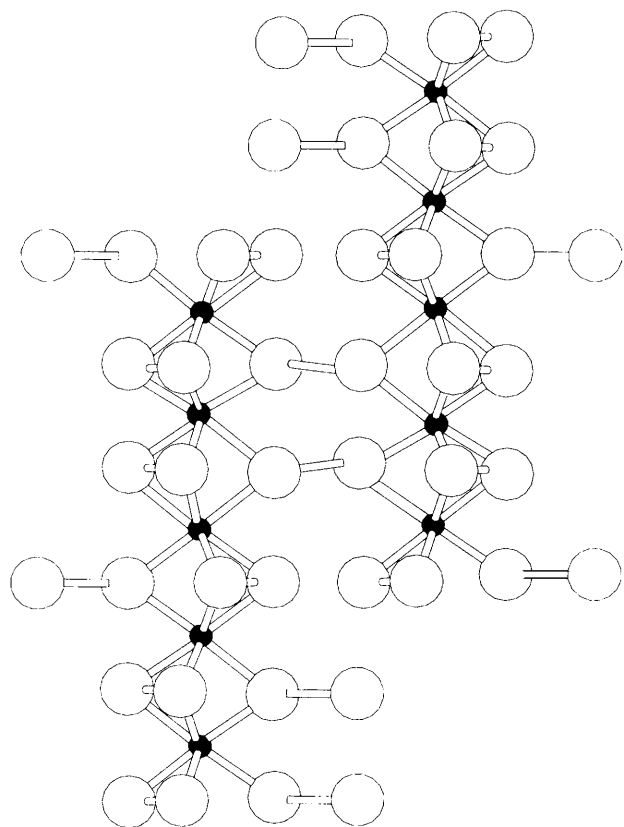


Fig. 7 Possible structure for CrSe_3 including interchain bonding (black spheres, Cr; white spheres, Se)

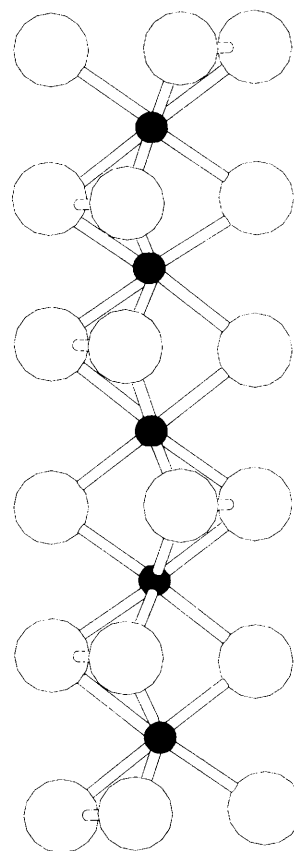


Fig. 8 Chain model for the structure of CrSe_3 (black spheres, Cr; white spheres, Se)

in the shell at 2.35 Å refines to a value close to 0.67, which is the value expected if two-thirds of the selenium atoms occur as Se^{-1} in diselenide groups and one-third as Se^{-II} . The larger Debye–Waller factor found for the selenium shell around chromium in CrSe_3 , compared to the sulfur shell in CrS_3 , is also in agreement with this conclusion, since we would expect this value to be lower for Cr–Se, because the thermal disorder will be less for the heavier chalcogen. The higher A value is thus a reflection of the larger static disorder present in the chalcogen shell resulting from differences in the Cr–Se bond lengths. We would expect Cr– Se^{-1} bonds to be longer than Cr– Se^{-II} bonds. Further support for the formulation of CrSe_3 as a Cr^{IV} compound comes from the measured chromium K-edge shift of 5.79 eV in this compound. The edge shift is much larger than those found by Manthiram *et al.*¹⁸ for Cr^{II}Se ($\Delta E = 2.52$ eV) and $\text{Cu}(\text{Cr}^{III})_2\text{Se}_4$ ($\Delta E = 1.70$ eV).

The results of this EXAFS study on CrSe_3 can be compared to the results we obtained using neutron scattering.⁴ In that study we were able to account for the first peak in the radial-distribution function as arising from the sum of contributions from the first co-ordination spheres of Cr–Se (5.4) and Se–Se (0.67). We have been unable to obtain information on Cr–Cr distances from EXAFS or neutron-scattering data, where Se–Se and Cr–Se correlations dominate the scattering, and this makes it difficult to distinguish between structural models.

Fig. 8 shows a possible structural model for CrSe_3 , which incorporates the information on the CrSe_6 units we have derived from the EXAFS study. Three selenium atoms are shared between neighbouring chromium atoms in a chain, two of these are bonded together to form a bridging diselenide and the remaining selenium is a Se^{-II} unit. This model is derived from the second model we presented for CrS_3 (Fig. 7), by reducing the interchain dichalcogenide links to produce two Se^{-II} units. Confirmation of this single-chain model requires information on the Cr–Cr distances.

Conclusion

The two new chromium chalcogenides, CrS_3 and CrSe_3 , although of identical stoichiometry, have different structures and contain chromium in different oxidation states. We formulate CrS_3 as $\text{Cr}^{III}(\text{S}^{-1})_{1.5}$ and CrSe_3 as $\text{Cr}^{IV}(\text{Se}^{-1})_2\text{Se}^{-II}$ on the basis of the arguments presented above. It is surprising, and notable, that the more weakly oxidising chalcogen, selenium, gives the chromium compound with chromium in the higher formal oxidation state. The co-ordination number of the metal, six, in both of the amorphous materials, CrS_3 and CrSe_3 , is lower than that observed in the closest known crystalline analogues, TiS_3 , TiSe_3 and VS_4 , which all contain eight-co-ordinate metal centres.

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