XAFS on Exfoliated Single-Layer WS_2, MoS_2 and $MoSe_2$

R.A. Gordon, D. Yang, E.D. Crozier, D.T. Jiang and R.F. Frindt
Simon Fraser University, Burnaby, BC, Canada V5A 1S6

Introduction

Many transition metal dichalcogenide materials form with layered structures [1]. Most adopt a structure related to the CdI_2 structure type, where the transition metal is octahedrally coordinated by the chalcogen. Some few others though, adopt a structure, for which MoS_2 is the parent example, where the coordination is trigonal prismatic. In this type, the title compounds MoS_2, $MoSe_2$ and WS_2 are particularly remarkable in that the layers can be, after lithium intercalation, separated (exfoliated) [2, 3] and subsequently restacked with other materials incorporated between the layers [4, 5]. This provides a new approach for the synthesis of new materials: layered nanocomposites.

Knowledge of the structure of these single layer systems is vital to the understanding of the properties of both the single layers and the layered nanocomposites but is incomplete. Both electron and X-ray diffraction studies [6, 3] indicate that the coordination of the transition metal transforms to octahedral during lithiation/exfoliation. Recent electron crystallography work [6] has indicated an orthorhombic unit cell for MoS_2 and WS_2, with a proposed two-dimensional structural model related to WTe_2 [7]. XAFS studies performed on MoS_2 and derivative materials [8, 9] have revealed a contracted nearest Mo-Mo distance consistent with a WTe_2 - related structure but no analysis has been done on this or the other systems in the context of a WTe_2 model. By combining diffraction results with XAFS on exfoliated layers of WS_2, MoS_2 and $MoSe_2$, and some elementary geometry, we obtain three-dimensional models of the structures.

Experimental

Exfoliated samples were prepared by lithium intercalation and extraction as per the literature [2, 3]. Powder X-ray diffraction measurements were made on moist exfoliated slurry sealed under plastic using a Siemens model D500 diffractometer. X-ray absorption measurements were made at the PNC-CAT beamline, Sector 20, Advanced Photon Source [10]. Distilled, de-ionised water was added to moist paste of the exfoliated materials and sealed in plastic bags. The material was allowed to settle in the bag and the bag clamped to give a region of uniform thickness when viewed in transmission on to a phosphor crystal. Powdered binary dichalcogenide samples were prepared on tape and examined as well by XAFS for reference. Sample containers (tape or bag) were oriented at an angle between 30 and 45 degrees to the polarisation vector of the synchrotron beam in case of preferred orientation of the samples relative to the container surfaces. XAFS data were collected in fluorescence and transmission modes using helium (transmission) or argon (fluorescence) filled ionisation chambers.

Results and Discussion

XAFS interference functions, $\chi(k)$ (Figure 1), were extracted from the absorption data using polynomial background removal, normalisation to edge jump and a McMaster correction. Fourier transforms to R-space were done using k^2 weighting and 10% Gaussian window over a range using zero-crossings of $\chi(k)$ between $3Å^{-1}$ to $4Å^{-1}$ and $13.5Å^{-1}$ to $15Å^{-1}$, depending on sample. Data were fit in R-

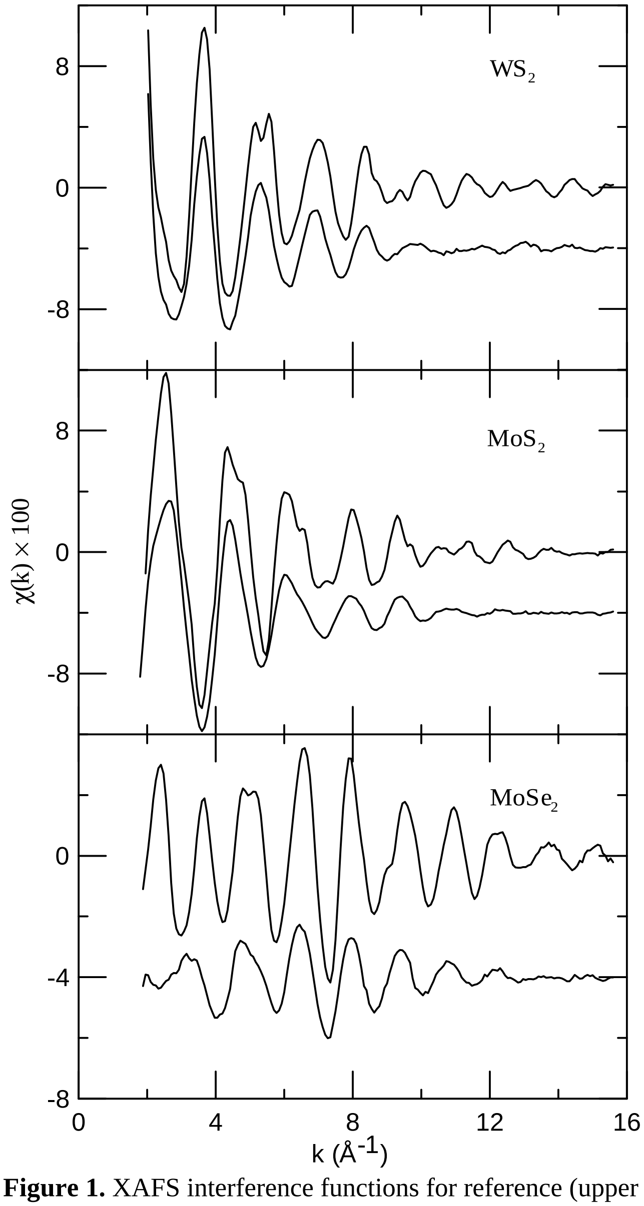

Figure 1. XAFS interference functions for reference (upper curve) and exfoliated (lower) WS_2, MoS_2 and $MoSe_2$.

space between 1.6Å and approximately 4Å using models generated by FEFF7 [11] in WinXAS [12] with no polarisation dependence. Coordination numbers were fixed according to the WTe_2-based models used and shifts in edge energy (ΔE_0) were fixed for the samples to the values obtained from fitting the reference compound data. Separate ΔE_0 values were used for M-M and M-X interactions. All other parameters (S_0^2, $\{R_j\}$ and $\{\sigma_j^2\}$) were allowed to vary when fitting the sample data.

Table 1 summarises the metal-scatterer distances obtained from the fits for the nearest metal-chalcogen and metal-metal distances. The values for MoS_2 are in good agreement with published values. By combining these distances with the lattice constants from diffraction, the out-of-plane puckering is obtained. By locating the chalcogens within the average M-X distance, atomic positions can be modeled. Figure 2 shows the model for WS_2.

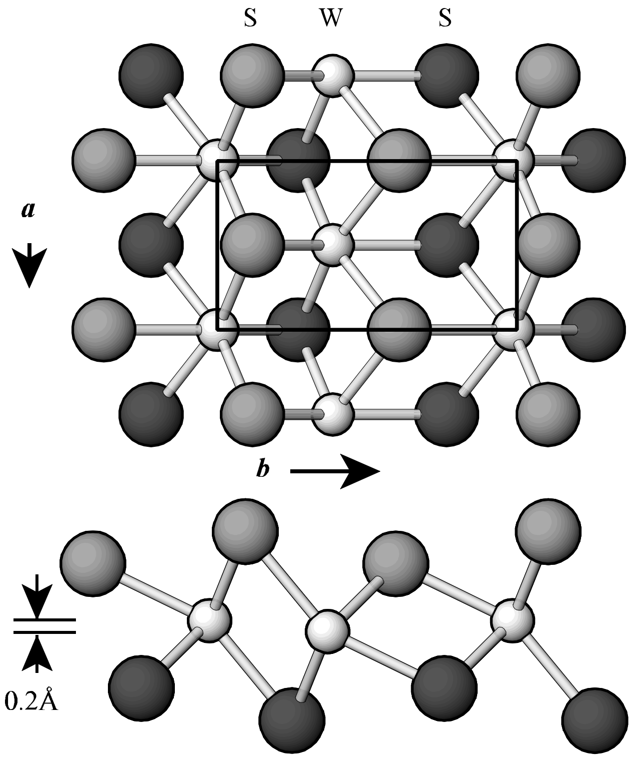

Figure 2. Model structure of an exfoliated WS_2 layer. The 0.2Å layer puckering is indicated in the lower, edge-on view along **a**.

Table 1. Summary of absorber-scatterer distances for exfoliated single layers of WS_2, MoS_2 and $MoSe_2$.

R(Å)\MX_2	WS_2	MoS_2	$MoSe_2$
M-X	2.42(1)	2.41(1)	2.54(1)
M-M_1	2.74(1)	2.75(1)	2.74(2)
M-M_2	3.24(2)	3.15(1)	3.20(1)
M-M_3	3.82(2)	3.78(2)	4.07(3)

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada provided funding for this project through operating grants and a Major Facility Access Grant. Funding and support were also provided by the US Department of Energy, Basic Energy Sciences, under contracts W-31-109-Eng-38 (APS) and DE-FG03-97ER45628 (PNC-CAT).

References

[1] A.A. Balchin, in "Crystallography and Crystal Chemistry of Materials with Layered Structures", F. Levy (Ed.), Chapter 1, D. Reidel Publishing, Dordrecht, Holland (1976).
[2] P. Joensen, R.F. Frindt and S.R. Morrison, “Single Layer MoS_2” Mat. Res. Bull. 21, 457-461 (1986).
[3] D. Yang and R.F. Frindt, "Li-Intercalation and Exfoliation of WS_2", J. Phys. Chem. Solids 57(6), 1113-1116 (1996).
[4] W.M.R. Divigalpitiya, R.F. Frindt and S.R. Morrison, “Inclusion System of Organic Molecules in Restacked Single-layer Molybdenum Disulfide” Science 246, 369-371 (1989).
[5] R. Bissessur et al., “Nanocomposites Formed by Encapsulation of Polymer in MoS_2” Mol. Cryst. Liq. Cryst. 245, 651-656 (1994).
[6] J. Heising and M.G. Kanatzidis, "Structure of Restacked MoS_2 and WS_2 Elucidated by Electron Crystallography," J. Am. Chem. Soc. 121, 638-643 (1999).
[7] A. Mar, S. Jobic and J.A. Ibers, "Metal-Metal vs Tellurium-Tellurium Bonding in WTe_2 and its Ternary Variants $TaIrTe_4$ and $NbIrTe_4$," J. Am. Chem. Soc. 114, 8963-8971 (1992).
[8] P. Joensen, E.D. Crozier, N. Alberding and R.F. Frindt, "A Study of Single-Layer and Restacked MoS_2 by X-ray Diffraction and X-ray Absorption Spectroscopy," J. Phys. C:Solid State Phys. 20, 4043-4053 (1987).
[9] K.E. Dungey, M.D. Curtis and J.E. Penner-Hahn, "Structural Characterization and Thermal Stability of MoS_2 Intercalation Compounds," Chem. Mater. 10, 2152-2161 (1998).
[10] S.M. Heald et al., "XAFS and Micro-XAFS at the PNC-CAT Beamline," J. Synch. Rad. 6, 347 (1999).
[11] S.I. Zabinsky et al., "Multiple Scattering Calculations of X-ray Absorption Spectra," Phys. Rev. B. 52, 2995 (1995).
[12] T. Ressler, "WinXAS: A New Software Package not only for the Analysis of Energy-Dispersive XAS Date," J. Phys IV France 7, 269-270 (1997).