Journal of Non-Crystalline Solids 42 (1980) 345-356

AMORPHOUS MoS_3 AND WS_3

K. S. Liang, S. P. Cramer, D. C. Johnston, C. H. Chang, A. J. Jacobson, J. P. deNeufville and R. R. Chianelli

Corporate Research Laboratories
Exxon Research and Engineering Company
Linden, New Jersey 07036, USA

MoS_3 and WS_3 are examples of a group of transition metal chalcogenides which have only been prepared in amorphous form. Recently these compounds have been found to show interesting properties as cathode materials in ambient temperature alkali metal batteries. In particular, MoS_3 reacts readily and reversibly with lithium, giving a battery system with a high theoretical energy density. In this paper, we report results of structural studies of amorphous MoS_3 and WS_3 using x-ray radial distribution analysis, EXAFS, X-ray photoelectron spectroscopy, magnetic susceptibility measurements and vibrational spectroscopies. The results reveal that these amorphous compounds have a chain-like structure similar to that of the crystalline trichalcogenides of the neighboring IVB and VB elements. However, the combined formations of the metal dimers and polysulfide bonds along the chains are structural features unique to these amorphous compounds. The possible implications of this structure to the observed electrochemical behavior will be discussed.

INTRODUCTION

The structure of amorphous trichalcogenides of Mo and W of Group VIB have been the subject of several studies[1-5]. The earliest results of these studies suggested that amorphous (a-) MoS_3 was not an independent compound but a mixture of MoS_2 and non-crystalline sulfur[1-3]. Later, from analysis of the x-ray radial distribution functions (RDF), Diemann[4] concluded that these amorphous trichalcogenides were genuine compounds, although ambiguities remained concerning their detailed structure. The most recent structural studies on a-MoS_3 and a-WS_3 using high resolution RDF and XPS (x-ray photoelectron spectroscopy) revealed the unique structural features of these compounds. A chain-like structure similar to that of the crystalline trichalcogenides of the neighboring IVB and VB elements was proposed[5]. Along the chain, adjacent metal atoms are bridged with three S atoms. The results also showed dimerization of the metal atoms along the chain and the presence of polysulfide bonds. A formal charge state, $M^{V}(S_2^{=})_{1/2}$ $S_2^{=}$, for these amorphous trichalcogenides was therefore proposed.

It is interesting to note that the trichalcogenides of Mo and W can only be prepared in amorphous form. These amorphous compounds were reported to have special catalytic properties[6]. More recently, amorphous MoS_3 was found to have interesting electrochemical properties[7]. a-MoS_3 can react readily and reversibly with more than three lithium atoms per MoS_3 unit at room temperature. Therefore, a-MoS_3 has potential application as an electrode material for secondary lithium batteries in energy storage. In fact, the electrochemical properties of a-MoS_3 are better than those of the crystalline trisulfides. This study is part of our continuing work aimed at understanding the origin of the unusual electrochemical and catalytic properties of these amorphous compounds.

In this paper, the previously proposed structural model[5] of a-MoS_3 and a-WS_3 will be further refined using EXAFS. The results of magnetic susceptibility measurements and IR and Raman vibrational spectroscopies provide further support of the structural model.

The paper is organized in the following order. Procedures of sample preparation are first presented. The structures of a-MoS_3 and a-WS_3 are then discussed in the next two sections in terms of the local atomic arrangements and the charge states. The former contains the results of RDF and EXAFS analyses and the latter reviews the results of XPS, magnetic susceptibility and vibrational spectroscopic measurements. The paper concludes with a discussion of the structural model and its possible implications with regard to the electrochemical properties of a-MoS_3.

SAMPLE PREPARATION

Amorphous MoS_3 and WS_3 used in this study were prepared by thermal decomposition of the ammonium tetrathio compounds[8], $(NH_4)_2MoS_4$ and $(NH_4)_2WS_4$, respectively. These tetrathio compounds were prepared by passing H_2S through a solution of ammonium paramolybdate or paratungsdate in aqueous ammonia at ambient temperature. Crystals of these salts separated during the reaction. The crystals were removed by vacuum filtration, washed and dried. Compositions of representative batches were checked by chemical analysis. Their x-ray diffraction patterns agreed well with the literature data. The samples were also checked with IR transmission spectra to ensure negligible contamination by oxygen impurities.

The thermal decomposition behavior of the ammonium tetrathio salts is illustrated by a typical thermogravimetric curve in Figure 1. The curve shows a plateau region of temperature near 325°C, which corresponds to a weight loss of 26.24% from $(NH_4)_2MoS_4$. This value is close to the theoretical weight loss of 26.16% for the formation of MoS_3. The compositions of the amorphous compounds typically obtained are very close to MX_3 stoichiometry.

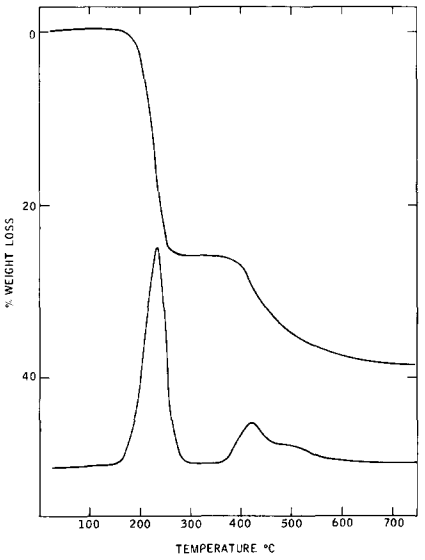

Figure 1

Thermogravimetric decomposition of $(NH_4)_2MoS_4$, top. thermogram; bottom, differential thermogram

LOCAL ATOMIC ARRANGEMENTS

The local atomic arrangements of a-MoS_3 and a-WS_3 were studied using x-ray RDF and EXAFS. The experimental details of x-ray RDF have been discussed previously[5]. A detailed description of the EXAFS study will be published separately[9].

The radial distribution function of a-WS_3 obtained from the x-ray diffraction measurements using Mo$K\alpha$ radiation is shown in Figure 2. For the following discussion, we are particularly interested in the first three peaks of the RDF which are closely related to the EXAFS results. Using curve fitting with Gaussian peaks the positions, widths and areas of these peaks are obtained (Table 1). As pointed out in our previous paper[5], the presence of a strong peak at 2.8 Å and only a weak peak at 3.2 Å indicates that a-WS_3 is not a mixture of WS_2 and S. The proposed structure from our previous work is shown in Figure 3.

We first comment briefly about the interpretation of RDF peaks. Based on a given structure, the theoretical values of the areas of RDF peaks can be calculated from the relation,[10]

$$\rho_{ab}(d) = X_a N_{ab}(d) Z_a Z_b \qquad (1)$$

where $\rho_{ab}(d)$ is the calculated area due to type a atoms coordinated by N_{ab} type b atoms at a distance d, X_a is the atomic percent of type a atoms, and Z_a is the electron density of a type a atom which can be approximated by the atomic number. The calculated values of different atomic pairs are given separately in the Table so that comparisons with the EXAFS results can be easily made later. The S-S pairs are not included because of their small contribution to the RDF areas due to the low Z value of S in comparison with W.

The proposed structure of a-MoS_3 and a-WS_3 is a chain-like structure. This structure in fact is similar to that of the crystalline trichalcogenides of the neighboring groups IVB (Ti, Zr, Hf) and VB (Nb, Ta)[11]. Along the chains, there are alternate short (2.8 Å) and long (3.2 Å) metal-metal distances corresponding to the ρ_{W-W} values shown on Table 1. Each metal-metal pair is bridged with three S atoms with a metal-sulfur distance of 2.4 Å (ρ_{W-S} and ρ_{S-W} on Table 1). The metal-sulfur distance at 2.4 Å and metal-metal distance at 3.2 Å are close to the corresponding interatomic distances in crystalline WS_2. However, the short W-W distance of 2.8 Å reveals the formation of metal-metal bonds due to strong metal-metal interaction.

In order to account for the strong RDF peak at 2.8 Å, the proposed structure also includes inter-chain correlations at this distance (ρ_{W-S} and ρ_{S-W} at 2.8 Å in Table 1 and Figure 3). Each W would be coordinated with 2 S and one third of the S with 2 W in the adjacent chains to form a super layered structure.

The agreement between the experimental values and the calculated areas of RDF peaks of a-WS_3 based on the above proposed model is reasonably good. The calculated values are larger than the experimental values by ~10% for the 2.4 Å and 3.2 Å peaks. This may partly be due to a density deficiency arising from the porous nature of the thermally decomposed samples. Very intense x-ray scattering at low angles was recently observed on these amoprhous samples. Since the small-angle scattering has not been included in our RDF analysis, its effect on the RDF peak area has to be studied[12]. The larger discrepancy shown on the 2.8 Å peak could be due to the disorder of the inter-chain correlation, since the calculation is based on an ordered structure.

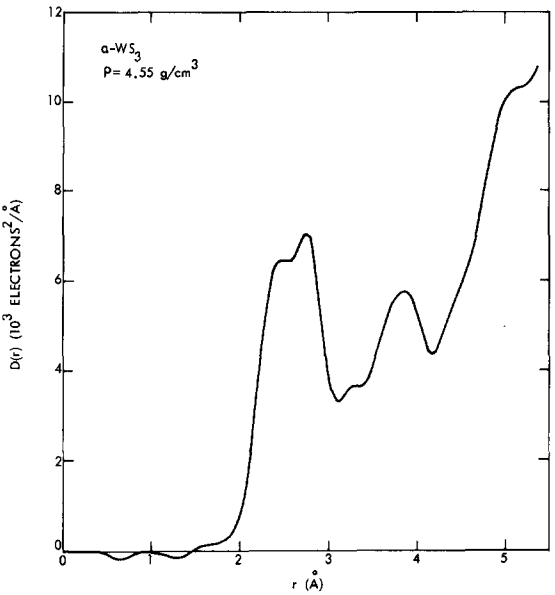

Figure 2

Radial distribution function, $4\pi r^2\rho(r)$, for a-WS_3 obtained from Fourier inversion of the MoKα x-ray diffraction data

Table 1

Coordination Numbers for the Proposed Structure of a-WS_3

Partial RDF	2.46 Å	2.83 Å	3.24 Å
ρ_{W-W}	0	1	1
ρ_{W-S}	6	2	0
ρ_{S-W}	2	2/3	0
Cal. Area	3552	2580	1369
Exp. Area	3261	2029	1237
% Difference	-8.2%	-21.3%	-9.6%

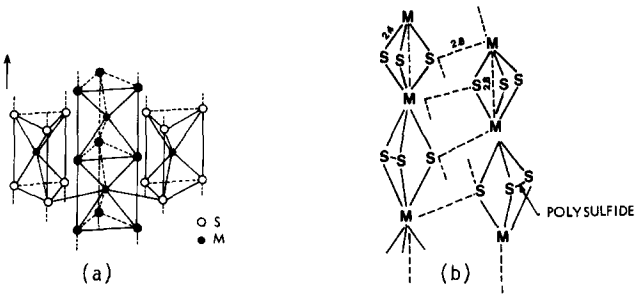

Figure 3

Schematics of (a) the structure of crystalline transition-metal trisulfides and (b) the proposed structure of amorphous WS_3 and MoS_3

Due to the fluorescence problem using MoKα radiation, the RDF for a-MoS_3 was only obtained using CuKα radiation. A broad peak corresponding to the sum of the 2.4 Å and 2.8 Å peaks in the a-WS_3 case was observed at 2.45 Å with a peak area of 2953 electrons^2 (using a density value of 3.04 g/cm^3). This value is quite close to the calculated value of 3129 electrons^2 based on the above proposed structure.

We now turn our discussion to the EXAFS results. The principle of EXAFS and its application to the study of the local atomic arrangement of amorphous materials have been extensively discussed in the literature[13]. EXAFS can yield accurate interatomic distances (≲0.02 A). If the amplitude functions and the Debye-Waller factors are known, the coordination numbers and mean relative displacements may also be obtained.

For a-MoS_3 and a-WS_3, EXAFS data using Mo K edge (∼20,000 eV) and W L_{III} edge (∼10,205 eV) were obtained at Stanford Synchrotron Radiation Laboratory. Figure 4 shows the Fourier transform of the Mo K edge EXAFS of a-MoS_3. The three peaks assigned on the figure were determined through a curve fitting procedure. It should be noted that the positions and origins of these peaks agree with the results of our x-ray RDF analysis.

A simplified version of the curve fitting routine can be described briefly as follows[14]. The fitting is performed with three floating parameters for each shell of the assumed atomic pairs, the coordination number N, the interatomic distance R, and the disorder parameter $\Delta\sigma^2$, by the following relation

$$\frac{N}{R^2} \; e^{-\Delta\sigma^2/k^2} \; A(k)F(k) \qquad (2)$$

where A(k) and F(k) are the amplitude and phase shift of M-S or M-M pair expressed in functional forms, and k (= $[2m(E-E_0)/\hbar^2]^{1/2}$) is the photoelectron wave vector. In this study, A(k) and F(k) are obtained from the corresponding crystalline disulfides, MoS_2 and WS_2. Since both A(k) and F(k) are quite different for M-S and M-M pairs[14], the peaks in the Fourier transformed EXAFS can be identified quite unambiguously (Figure 4). The results of the fit based on a three-shell model are summarized in Table 2 with the quality of the fit shown in Figures 5 and 6 for a-MoS_3 and a-WS_3, respectively.

The EXAFS results for a-MoS_3 show that the Mo atoms are coordinated with approximately 5.9 S atoms at 2.41 Å, 0.9 Mo atoms at 2.74 Å and 1.6 Mo atoms at 3.15 Å. This agrees very well with our earlier model. For a-WS_3, the quality of the curve fit is less satisfactory (Figure 6). This is partly due to the limited k range accessible for curve fitting. The experimental k range is limited by the W L_{II} edge at 11542 eV.

An interesting feature of the $\Delta\sigma^2$ values shown in Table 2 is their negative sign for the M-M shell at 2.74 Å. This sign is consistent with the formation of metal-metal bonds and consequently the reduction of the mean displacements of the metal-metal pairs relative to the crystalline MS_2 standard.

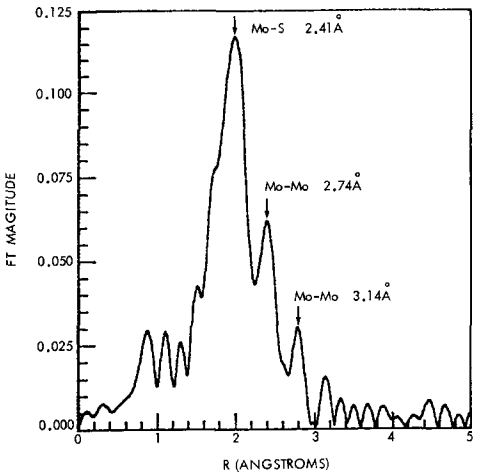

Figure 4

Fourier transform MoS_3 EXAFS, over k = 4-23 $Å^{-1}$ with k^3 weighting. All peaks appear shifted from the true distances because of phase shifts.

Table 2

EXAFS Fitting Parameters

	M-S		M-M(1)		M-M(2)	
SAMPLE	N	$\Delta\sigma^2$	N	$\Delta\sigma^2$	N	$\Delta\sigma^2$
MoS_3	2.414 Å		2.741 Å		3.145 Å	
	5.93	0.0037	0.93	-0.0010	1.63	0.0037
WS_3	2.379 Å		2.757 Å			
	8.11	0.0171	1.30	-0.0030		

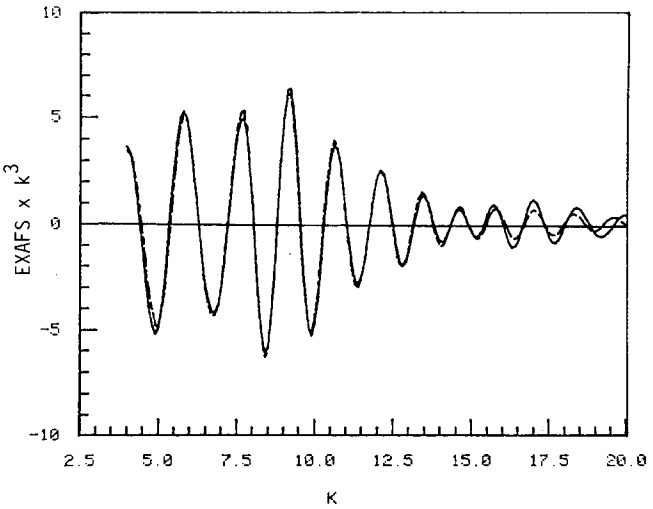

Figure 5

Fourier-filtered EXAFS of MoS_3 (solid line) and fit (dashed line)

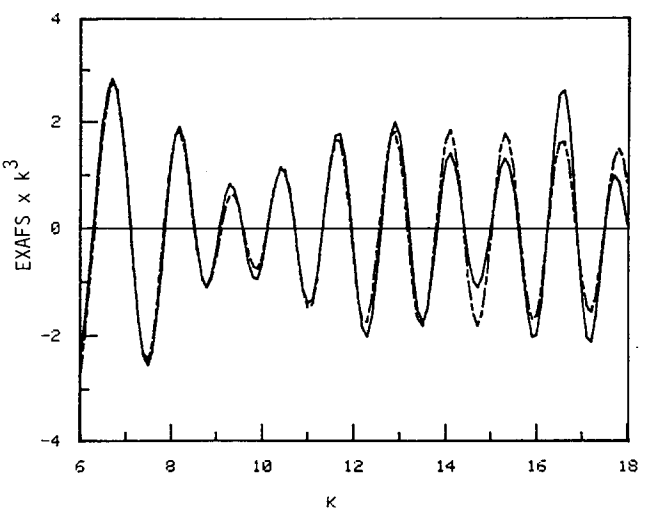

Figure 6

Fourier-filtered EXAFS of WS_3 (solid line) and fit (dashed line)

THE CHARGE STATE

X-ray photoelectron spectroscopy reveals the presence of two types of sulfur species in a-MoS_3, $(S\text{-}S)^{=}$ and $S^{=}$ with a 1:2 ratio of their intensities (Figure 7). Based on this result, a formal charge state of $M^{V}(S_2^{=})_{1/2}S^{=}$ was assigned for these compounds[5]. The spin pairing of M^{V} cations is suggested as the origin of the dimerization of metal atoms in these compounds. Further, the polysulfide species in a-MoS_3 are present in quite a unique ratio. Presumably, one polysulfide is present in every other bridging sulfur triangle (Figure 3).

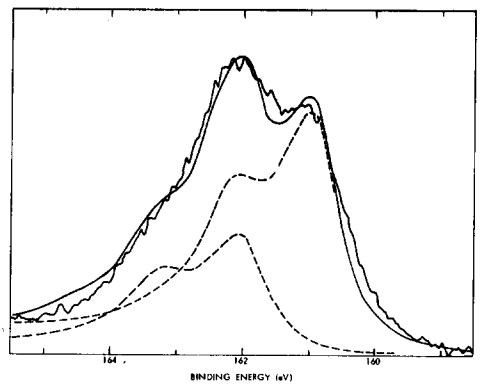

Figure 7

XPS S2p spectrum of amorphous MoS_3. Fitted curves correspond to contribution of two types of sulfur, separated by 1.1 eV in binding energy with a 1:2 ratio of intensities

Magnetization measurements were carried out on a variety of high purity samples of a-MoS_3 in an applied field of 6.35 kG between 10 and 300 K using the Faraday technique. Susceptibilities were extracted from these magnetization data by correcting for the contributions due to ferromagnetic impurities as deduced from magnetization vs. field isotherms obtained at several temperatures for each sample. A brief description of these results is given here; a more complete account and a comparison with previously reported susceptibility data[15,16] on MoS_3 will appear elsewhere.

Typical susceptibility data are shown in Figure 8. The data were fitted by the following relation,

$$\chi = \chi_0 + \frac{C}{T-\theta}$$

The temperature independent term χ_0 (-61×10^{-6} cm^3/mole), the Curie constant C (7.0×10^{-3} cm^3-K/mole), and the Weiss temperature θ ($\sim$-3 K) were determined by a least square fit of the above equation to the data; this fit is shown as a solid line in Figure 8 and in a plot of $(\chi-\chi_0)^{-1}$ versus temperature in Figure 9. From both figures, the quality of the fit to the data is seen to be excellent.

The value of the Curie constant indicates that this sample contained a level of paramagnetic species which is negligible (<2 mole %) compared to the Mo content, and therefore is consistent with our structural and formal charge models for MoS_3 which together require that the Mo^{V} cations be spin paired to form dimers. The magnitude of χ_0 for MoS_3 is far smaller than the sum of the molar susceptibilities of crystalline[17] or poorly crystalline[16] MoS_2 ($\sim$-80 $\times 10^{-6}$ cm^3/mole) and sulfur (-15×10^{-6} cm^3/mole[18]). This finding provides independent evidence that MoS_3 is a distinct compound and is not a solid solution of MoS_2 and sulfur.

Finally, Raman and IR vibrational spectroscopies were also performed to study the local bonding of a-MoS_3. The results are shown in Figure 10. These spectra bear no common feature to that of crystalline[19] or amorphous[20] MoS_2. The presence of a broad band at about 520 cm^{-1} in both Raman and IR spectra may be due to polysulfide species. Similar S-S stretching frequencies of 510 cm^{-1} (IR) and 515 cm^{-1} (Raman) have been observed on a tetramethyl ammonium salt containing polysulfide bonds.[21] These results again confirm that a-MoS_3 is a genuine compound.

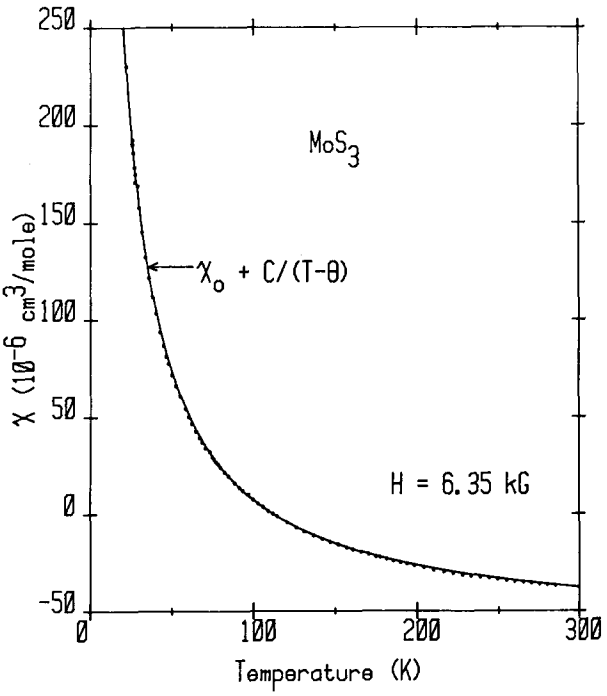

Figure 8

Molar magnetic susceptibility versus temperature for MoS_3. The solid curve is a fit of the displayed equation to the data; the fitting parameters χ_o, θ and C are given in the text.

DISCUSSION

Based on the results of RDF, EXAFS, XPS, magnetic susceptibility measurements and vibrational spectroscopy, we conclude that the amorphous trisulfides of Mo and W are genuine compounds with their own unique structure. We propose a chain-like structure with metal atoms along the chain bridged with three S atoms. The metal atoms in the chain are paired, giving rise to alternate short (2.8 Å) and long (3.2 Å) metal-metal distances. The formation of polysulfide bonds among the S atoms was also observed. These compounds therefore appear to have a unique formal charge state of $M^{V}(S_2^{=})_{1/2}S_2^{=}$. The pairing of M^{V} cations to form dimeric clusters is consistent with the observed magnetic properties of a-MoS_3.

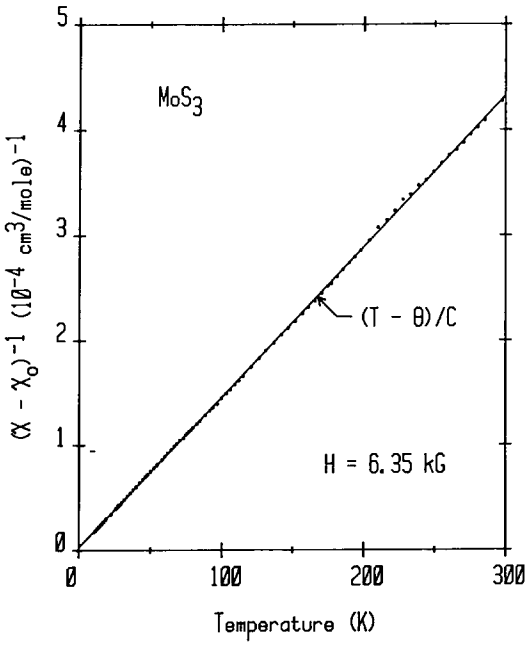

Figure 9

Inverse of the molar magnetic susceptibility of MoS_3, corrected for the temperature independent contribution χ_0, plotted versus temperature. The solid line is the fit to the data (cf. Fig. 8 caption).

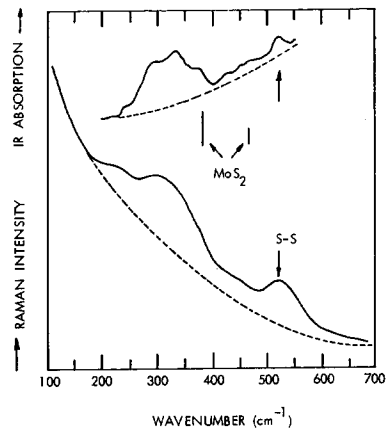

Figure 10

Vibrational spectra of MoS_3, top, IR absorption; bottom, Raman intensity. Dotted lines are estimated backgrounds.

As stated in the Introduction, the work presented here is part of a continuing effort aimed at understanding the interesting electrochemical and catalytic properties of these compounds, such as the reversible reaction of Li with a-MoS_3. we will comment briefly on this reaction.

The chain-like structure of a-MoS_3 is evidently favorable to topochemical reaction with Li. However, by comparing the reversibility of Li reaction in the trichalcogenides and dichalcogenides of both crystalline[22] and amorphous[7,23] forms, the open structure associated with the low-dimensionality of the chains cannot be the primary factor in determining the reversibility of the reaction. In Table 3, some known dichalcogenides and trichalcogenides are grouped roughly into three classes in accordance with the reversibility of their reaction with Li. There appears to be no clear trend associated with the structure. At present, we conjecture that the reversibility might be associated with the electronic nature of these materials. In particular, we feel that the metal-metal bonding and the polysulfide bonds could be important in the reversible reaction with Li. It may be possible to verify this conjecture from structural and other studies on lithiated MoS_3 compounds.

Finally, it should be pointed out that amorphous MoS_2 was also found to react reversibly with Li, although Li does not react topochemically at room temperature with crystalline MoS_2. In fact, the capacity of Li uptake in MoS_2 was found to decrease continuously with increased crystallinity. Therefore, the role of defect states in the chemistry of Li reaction in these amorphous compounds needs to be addressed.

Table 3

Reversibility of Li Reaction

Poor	Average	Good
c-MoS_2	c-NbS_2	c-TiS_2
		a-MoS_2
c-TiS_3	c-NbS_3	c-$NbSe_3$
		a-MoS_3

ACKNOWLEDGMENTS

The authors would like to thank Professors A. Bienenstock, K. Hodgson and S. C. Moss for helpful discussions. Special thanks are due to Dr. F. Betts for assistances with the x-ray diffraction experiments. We are also indebted to SSRL for the EXAFS measurements.

REFERENCES

1. R. J. H. Voorhoeve and H. M. B. Wolters, Z. Anorg. Chem. 376, 165 (1970).
2. P. Ratnasamy, L. Rodrique and A. J. Leonard, J. Phys. Chem. 77, 3242 (1973).
3. G. C. Stevens adn T. Edmonds, J. Catal. 37, 544 (1975).
4. E. Diemann, Z. Anorg. Allg. Chem. 432, 127 (1977).
5. K. S. Liang, J. P. deNeufville, A. J. Jacobson, R. R. Chianelli and F. Betts, J. Non-cryst. Sol. 35 and 36, 1249 (1980).
6. O. Weisser and S. Landa, "Sulfide Catalysts, Their Properties and Application" Pergamon Press, New York (1973).
7. A. J. Jacobson, R. R. Chianelli, S. M. Rich and M. S. Whittingham, Mat. Res. Bull. 14, 1437 (1979).

8. For a Review, see E. Diemann and A. Muller, Coord. Chem. Rev. 10, 79 (1973)
9. S. P. Cramer, K. S. Liang, A. J. Jacobson and R. R. Chianelli, to be published.
10. B. E. Warren, "X-Ray Diffraction", Addison-Wesley Publishing Co., Reading, Massachusetts, 1969.
11. F. Hulliger, "Structural Chemistry of Layered-Type Phases", Ed. F. Levy, D. Reidel Publishing Co., Dordrecht, Holland, 1976.
12. G. S. Cargill III, J. Appl. Cryst. 4, 277 (1971).
13. See, for example, S. H. Hunter, A. I. Bienenstock, and T. M. Hayes, in "Structure of Non-Crystalline Materials", edited by P. H. Gaskell, Taylor and Francis, London, 1977.
14. S. P. Cramer, K. O. Hodgson, E. I. Stiefel and W. E. Newton, J. Am. Chem. Soc. 100, 2748 (1978).
15. S. Meyer, Ann. Physik 69, 236 (1899).
16. P. Belougne and J. V. Zenchetta, Revue de Chimie Minerale 16, 565 (1979).
17. R. M. M. Fonville, W. Geertsma and C. Haas, Phys. Stat. Sol. (b) 85, 621 (1978).
18. CRC Handbook of Chemistry and Physics, 60th Edition, R. C. Weast, Editor, (CRC Press, Boca Raton, Florida, 1979), p. E-127.
19. T. J. Wieting and J. L. Verble, Phys. Rev. B3, 4286 (1971).
20. J. S. Lannin, in Proc. 7th Int. Conf. Amorphous and Liquid Semiconductors, Ed. W. E. Spear, University of Edinburgh, 1977.
21. W. Rittner, A. Müller, A. Neumann, W. Bäther and R. C. Sharmo, Angew. Chem. Int. Ed. Engl. 18, 530 (1979).
22. R. R. Chianelli and M. B. Dines, Inorg. Chem. 14, 2417 (1975).
23. A. J. Jacobson, R. R. Chianelli and M. S. Whittingham, J. Electrochem. Soc. 126, 2277 (1979).