

Amorphous MoS_3 and A_xMoS_3 ($\text{A} = \text{Li}$ or Na ; $0 < x < 4$)†

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MS received 12 June 1981

Abstract. Amorphous A_xMoS_3 ($\text{A} = \text{Li}$ or Na ; $0 < x < 4$) prepared by the reaction of MoS_3 with *n*-butyllithium or sodium naphthalide in organic solvents have been characterized by x-ray photoelectron spectroscopy, infrared spectroscopy as well as electrical and magnetic measurements. The results indicate that sulphur exists as polysulphide species in MoS_3 and mainly as monosulphide in A_xMoS_3 when $x \sim 4$; there is no discernible change in the Mo(3d) binding energies of MoS_3 and A_xMoS_3 . Both MoS_3 and A_xMoS_3 are diamagnetic and non-metallic at room temperature. The data suggest that MoS_3 probably exists as $\text{Mo}^{2+}(\text{S}_3^{2-})$ with Mo-Mo bonds, incorporation of alkali metal atoms resulting in the reduction of proportion of polysulphide ions.

Keywords. Amorphous MoS_3 ; Li_xMoS_3 ; Na_xMoS_3 ; x-ray photoelectron spectra.

1. Introduction

Among the transition metal trisulphides MS_3 ($\text{M} = \text{Ti}, \text{Zr}, \text{Hf}, \text{Nb}, \text{Ta}, \text{Mo}$ and W), MoS_3 and WS_3 can be prepared only in the amorphous state by low-temperature chemical or thermal decomposition of ammonium tetrathiomellates (Wilder-vanck and Jellinek 1964; Diemann 1977). Until recently, the identity of these sulphides as true chemical compounds was somewhat in doubt. It has now been established that these are definite compounds (not a mixture of disulphide and amorphous sulphur) possessing a chain-like structure similar to that of crystalline trichalcogenides of other transition metals (Liang *et al* 1980a,b). It has recently been found that MoS_3 can incorporate reversibly upto four atoms of alkali metal per formula unit, A_xMoS_3 ($\text{A} = \text{alkali metal}$; $0 < x < 4$) making it a good candidate for cathode material in solid state batteries (Jacobson *et al* 1979). A_xMoS_3 may be regarded as thioanalogues of the alkali metal oxygen bronzes of molybdenum. We have investigated the structure and electronic properties of MoS_3 and A_xMoS_3 ($\text{A} = \text{Li}$ or Na) by various physical methods in an attempt to understand the nature of these solids.

† Contribution No. 125 from the Solid State and Structural Chemistry Unit.

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2. Experimental

MoS₃ was prepared by thermal decomposition of (NH₄)₂MoS₄ at 500 K in a stream of dry nitrogen (Jacobson *et al* 1979). The composition was found to be MoS_{2.98} from the chemical analysis of sulphur [S (found) = 49.73% ; S (calc.) = 50.06%]. Samples of Li_xMoS₃ (x = 0.9, 2.2 and 3.7) and Na_xMoS₃ (x = 0.8 and 3.5) were prepared, as reported in the literature (Jacobson *et al* 1979), by reaction with *n*-butyllithium in *n*-hexane and sodium naphthalide in tetrahydrofuran respectively. To prepare Li_xMoS₃, a known amount of MoS₃ was treated with a 1 M solution of *n*-butyllithium in *n*-hexane in a flowing nitrogen atmosphere. After the reaction, the solid was filtered and the concentration of *n*-butyllithium in the filtrate was determined by the addition of standard potassium hydrogen phthalate and back titration with standard potassium hydroxide. From the difference in concentration, the amount of lithium inserted into MoS₃ was calculated. Similarly samples of Na_xMoS₃ were prepared by reaction of MoS₃ with sodium naphthalide in dry tetrahydrofuran followed by determination of the concentration of sodium naphthalide in the filtrate as in the case of reaction with *n*-butyllithium. Details are given in table 1.

X-ray powder diffraction patterns, recorded with CuK_α radiation, showed a broad diffuse scattering with a maximum around 14° 2θ. The diffuse band became sharper with increasing alkali metal content in A_xMoS₃. The absence of any other discrete diffraction lines in the patterns indicates that the samples are x-ray amorphous similar to MoS₃.

X-ray photoelectron spectra (XPS) of the samples were recorded with a ESCA-3 Mark II sepectrometer (VG Scientific Co. Ltd., UK) using AlK_α radiation. Infrared spectra were recorded with a Perkin-Elmer Model 580 spectrometer. Electrical resistivities of the pelletized samples were measured by a two-probe technique. Magnetic susceptibilities were measured by Faraday method between 150–300 K.

Table 1. Preparation of A_xMoS₃ (A = Li or Na ; 0 < x < 4).

Amount of MoS ₃ , g (m moles)	Concentration of <i>n</i> -butyllithium or sodium naphthalide (m moles)		Alkali metal inserted per mole of MoS ₃ (moles)	Composition
	Before the reaction	After the reaction		
2.88 (15)	13.50	0.0	0.9	Li _{0.9} MoS ₃
2.88 (15)	33.00	0.0	2.2	Li _{2.2} MoS ₃
2.40 (12.5)	50.00	3.75	3.7	Li _{3.7} MoS ₃
3.84 (20)	16.00	0.0	0.8	Na _{0.8} MoS ₃
3.36 (17.5)	61.25	0.0	3.5	Na _{3.5} MoS ₃

3. Results and discussion

We have studied the valence band and core level XPS of MoS_3 , $\text{Li}_{0.9}\text{MoS}_3$, $\text{Li}_{2.2}\text{MoS}_3$ and $\text{Li}_{3.7}\text{MoS}_3$ to find out the nature of molybdenum and sulphur in these compounds. The spectra are given in figures 1 and 2 and the binding energies in table 2. For purpose of comparison, the spectra of MoS_2 are also included in the figures.

The $\text{S}(3s)$ peak of MoS_3 occurs as a doublet at 12.7 and 16.6 eV binding energies in contrast to a single (3s) peak at 14 eV in the case of MoS_2 (figure 1). To account for the doublet structure, it was proposed in our earlier study from this laboratory (Manthiram *et al* 1980) that two different kinds of sulphur are present in MoS_3 : $\text{Mo}^{4+}(\text{S}_2^{2-})(\text{S}^{2-})$. Similar $\text{S}(3s)$ doublet structure in MoS_3 with a relative intensity of 2 : 1 has been found by Liang *et al* (1980a). They proposed that MoS_3 consists of $\frac{1}{2}\text{S}_2^{2-}$ and 2S^{2-} which requires that molybdenum is present in 5+ formal oxidation state: $\text{Mo}^{5+}\frac{1}{2}(\text{S}_2^{2-})(\text{S}^{2-})_2$. According to this formulation, formation of A_xMoS_3 with x upto four would imply a reduction of Mo^{5+} to Mo^{2+} :

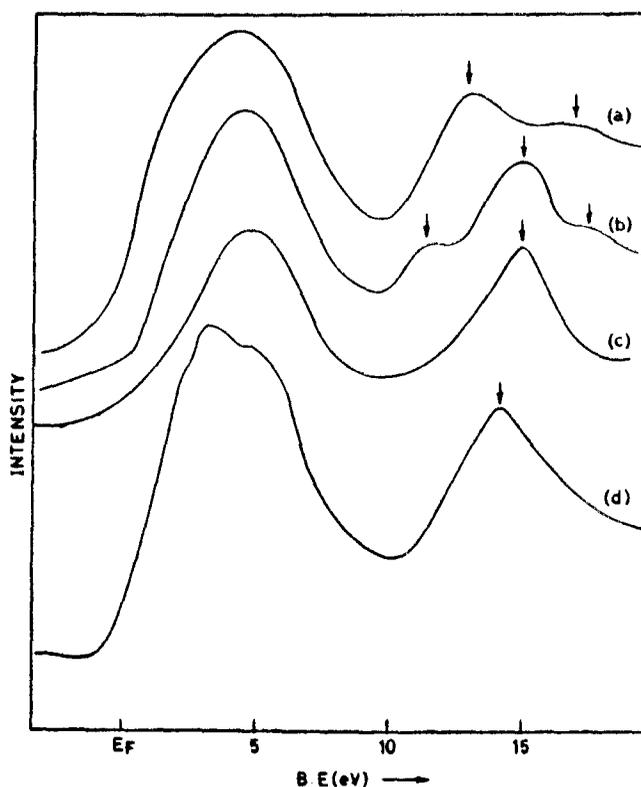


Figure 1. XPS valence bands of (a) MoS_3 , (b) $\text{Li}_{0.9}\text{MoS}_3$, (c) $\text{Li}_{2.2}\text{MoS}_3$, and (d) MoS_2 .

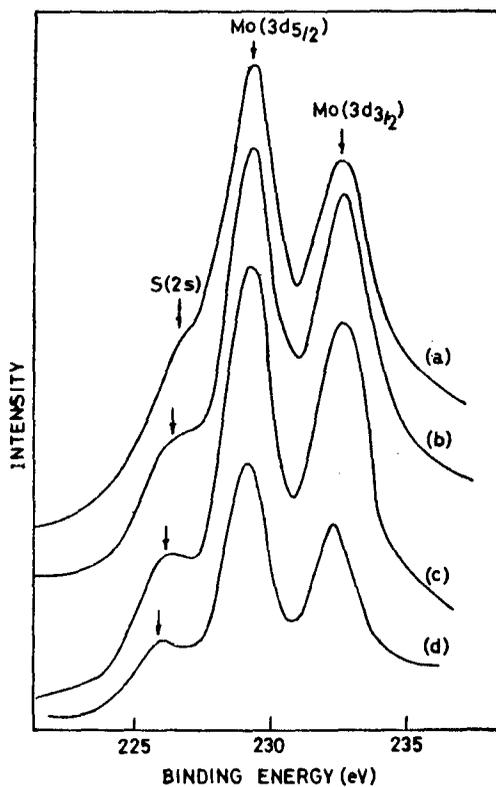


Figure 2. S(3s) and Mo(3d_{5/2}, 3d_{3/2}) core level spectra of (a) MoS₃, (b) Li_{0.9}MoS₃, (c) Li_{1.7}MoS₃ and (d) MoS₂.

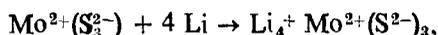
Table 2. XPS binding energy, electrical resistivity and magnetic susceptibility data of MoS₃ and A_xMoS₃ (A = Li or Na; 0 < x < 4).

Compound	S(3s) binding energy (eV)	S(2s) binding energy (eV)	Mo(3d _{5/2}) binding energy (eV)	Electrical resistivity ρ at 300 K (Ohm-cm)	Magnetic susceptibility $\chi_m \times 10^6$ at 300 K (cgs emu)
MoS ₃	12.7, 16.6	226.7	229.1	3.8×10^4	-48
Li _{0.9} MoS ₃	11.2, 14.8, 17.3	226.4	229.1	4.6×10^4	-67
Li _{1.2} MoS ₃	broad	226.4	229.1	3.6×10^4	-86
Li _{1.7} MoS ₃	14.8	226.3	229.1	4.0×10^4	-92
Na _{0.8} MoS ₃	3.4×10^4	-70
Na _{3.5} MoS ₃	..	226.3	229.1	3.7×10^4	-104

We should see this change of oxidation state of molybdenum in the XPS as well as in other electronic properties of $A_x\text{MoS}_3$. We, however, find hardly any change in the valence band $\text{Mo}(4d)$ states, while the $\text{S}(3s)$ shows marked changes (figure 1) in $\text{Li}_{1.9}\text{MoS}_3$ and $\text{Li}_{2.2}\text{MoS}_3$, the $\text{S}(3s)$ shows complex features and at the limiting composition $\text{Li}_{3.7}\text{MoS}_3$, the $\text{S}(3s)$ becomes a single band similar to that in MoS_2 . In addition, the $\text{Mo}(3d)$ binding energies remain almost constant [229.1 eV for $\text{Mo}(3d_{5/2})$] in MoS_3 and Li_xMoS_3 . We also see a slight decrease in the $\text{S}(2s)$ binding energy as we go from MoS_3 to $\text{Li}_{3.7}\text{MoS}_3$ (table 2). The results seem to indicate that incorporation of alkali metal into MoS_3 affects only sulphur and not molybdenum.

If we assume that MoS_3 consists of a trisulphide ion, S_3^{2-} , and Mo-Mo chain, $\text{Mo}^{2+}(\text{S}_3^{2-})$, the experimental results can be explained as follows:

(i) incorporation upto a maximum of four alkali metal atoms without change in the oxidation state of molybdenum,



(ii) presence of two different kinds of sulphur in MoS_3 in the ratio 2 : 1, and

(iii) the complex nature of $\text{S}(3s)$ at intermediate values of x in $A_x\text{MoS}_3$. In these cases, the polysulphide ion bonds would have been partially broken resulting in S_3^{2-} , and S_2^{2-} species.

Infrared absorption spectra and electrical and magnetic properties of $A_x\text{MoS}_3$ are consistent with the above model. MoS_3 shows characteristic S-S stretching vibration of the polysulphide ion at 515 and 540 cm^{-1} as shown in figure 3 (Rittner *et al* 1979). The disappearance of these bands in $\text{Li}_{3.7}\text{MoS}_3$ indicates that polysulphide species is absent. In addition, a new band at 420 cm^{-1} appears in Li_xMoS_3 ; the band may be assigned to Li-S stretching vibration. Similar changes in the infrared spectra of Li_xTiS_3 have been reported by Chianelli and Dines (1975).

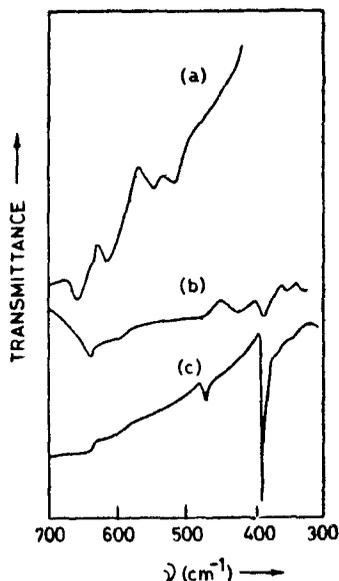


Figure 3. Infrared spectra of (a) MoS_3 , (b) $\text{Li}_{3.7}\text{MoS}_3$ and (c) MoS_3 (crystalline)

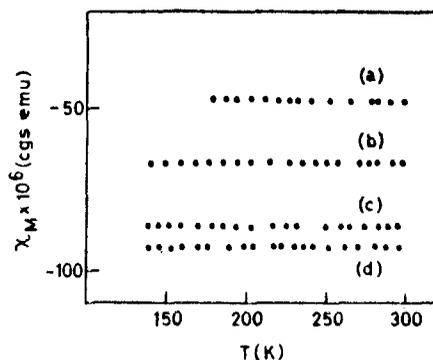
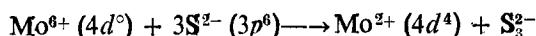


Figure 4. χ_M - T plots for (a) MoS_3 , (b) $\text{Li}_{0.9}\text{MoS}_3$, (c) $\text{Li}_{2.2}\text{MoS}_3$ and (d) $\text{Li}_{2.7}\text{MoS}_3$.

Room temperature electrical resistivity, ρ , and magnetic susceptibility, χ_M , of MoS_3 and A_xMoS_3 are given in table 2. It is seen that there is no significant difference between the resistivities of Mo_3S and A_xMoS_3 . The magnetic susceptibility data (figure 4) show that the diamagnetic character of MoS_3 is retained in A_xMoS_3 albeit with increase in the magnitude of diamagnetic χ_M . The results support our formulation of MoS_3 as $\text{Mo}^{2+}(\text{S}_3^{2-})$, the diamagnetism being due to Mo-Mo bonds as proposed by Liang *et al* (1980a). Insertion of alkali metal does not seem to disrupt the Mo-Mo bonds in MoS_3 .

The presence of molybdenum in a formal oxidation state of 2+ in MoS_3 can be understood in terms of Jellinek's (1968) model for transition metal sulphides. Transition metal ions having large positive oxidation state such as Mo^{6+} and W^{6+} would be unstable in the solid state in the presence of S^{2-} ions because the valence $\text{S}(3p)$ states overlap with the empty $\text{Mo}(4d)$ or $\text{W}(5d)$ states, resulting in electron transfer from $\text{S}(3p)$ to the $\text{M}(d)$ until the metal d -states are lifted just above those of $\text{S}(3p)$. In chemical terms, this would correspond to the reduction of the metal ion to lower oxidation states and oxidation of sulphide to polysulphide :



A formal oxidation state around 2+ for molybdenum as well as Mo-Mo bonds occur in molybdenum sulphides, e.g. Chevrel phases, $\text{A}_x\text{Mo}_6\text{S}_8$ (Yvon 1978).

Acknowledgements

The authors thank Professor C N R Rao for suggesting the problem and taking keen interest in the progress of the work. The authors also thank Dr M S Hegde for XPS measurements and the UGC for financial support.

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