

## On the coordination of molybdenum in AgI-Ag<sub>2</sub>O-MoO<sub>3</sub> glasses using XANES and EXAFS

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**Abstract.** XANES and EXAFS analysis of the Mo K-edge spectra in a series of AgI-Ag<sub>2</sub>O-MoO<sub>3</sub> glasses has been performed in order to determine the coordination of molybdenum in the glass. Mo has been found to exist in a tetrahedrally coordinated shell of four oxygens. Limitation of the EXAFS technique in discerning small distance differences in the first shell has also been discussed.

**Keywords.** EXAFS; XANES; coordination number; molybdate glass.

### 1. Introduction

Molybdenum trioxide, MoO<sub>3</sub>, and silver molybdate, Ag<sub>2</sub>MoO<sub>4</sub>, along with silver iodide, AgI, have been used recently in the preparation of fast ion conducting glasses (Minami *et al* 1977; Hemlata *et al* 1983b). In the structural description of these glasses it is often implied that the oxymolybdate groups are present as MoO<sub>4</sub><sup>2-</sup> tetrahedra or as corner shared Mo<sub>2</sub>O<sub>7</sub><sup>2-</sup> ditetrahedra. However, it is known that in MoO<sub>3</sub> and alkali polymolybdates molybdenum is present as MoO<sub>6</sub> octahedra (Anderson and Magneli 1950). Structures built with octahedra are more open and provide advantages particularly conducive to fast ion conduction. Since the spherical volumes swept by ionic (MoO<sub>4</sub>) tetrahedra and (MoO<sub>6</sub>) octahedra are identical, when MoO<sub>6</sub> octahedra are present a part of the oxygen ion volume may be looked upon as packed into the MoO<sub>6</sub> octahedra, thereby giving rise to a larger structural free volume. From a chemical point of view, maintaining an excess of oxygen-ion concentration in the system by incorporating a higher proportion of Ag<sub>2</sub>O (than MoO<sub>3</sub>) in the glass may be expected to favour such a situation. However, in earlier IR spectroscopic studies we obtained evidence only for the presence of tetrahedral MoO<sub>4</sub><sup>2-</sup> ions, with the possibility that their symmetries could be lower than T<sub>d</sub> (Hemlata *et al* 1983b). Therefore we felt it desirable to investigate the structure of oxygen polyhedra around the molybdenum ion in order to develop a structural model for this fast ion conducting glass system. Since it is known that a judicious combination of spectroscopic information from x-ray absorption near edge structure (XANES) and the structural information from extended x-ray absorption fine structure (EXAFS) analysis can give rise to reliable and fairly detailed local structure (Rao *et al* 1983), we have in this study performed the XANES and EXAFS analysis of the Mo-K-edge spectra of these glasses.

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## 2. Experimental

Glasses in the system AgI-Ag<sub>2</sub>O-MoO<sub>3</sub> were prepared by heating the required amounts of AgI, Ag<sub>2</sub>O and MoO<sub>3</sub> (reagent grade) upto 800 K over a period of 3 hrs and quenching the resulting melts between polished glass plates. Glass formation was confirmed by observing the glass transition temperature in a differential scanning calorimetric run (Hemlata *et al* 1983b). The transparent glass discs so obtained were powdered to less than 400 mesh and mixed with DUCO cement. The slurry was cast into films by spreading it between microscope slides which were then slid apart to expose two identical films, and these were allowed to set in air. The concentration of the glass powder in slurry and the film thickness were manipulated so that the concentration of Mo across the thickness of the resulting film was equivalent to 1–2 absorption lengths at the K-absorption edge of Mo (19·999·5 eV).

The XANES and EXAFS spectra were recorded with the C-2 spectrometer at CHESS (Cornell High Energy Synchrotron Source) with CESR (Cornell Electron Storage Ring) running at 5·3 GeV and an injection current of 12–15 mA. Three glasses with compositions of 60 AgI·20 Ag<sub>2</sub>O·20 MoO<sub>3</sub>, 40 AgI·30 Ag<sub>2</sub>O·30 MoO<sub>3</sub> and 55 AgI·25 Ag<sub>2</sub>O·20 MoO<sub>3</sub> were investigated. Na<sub>2</sub>MoO<sub>4</sub> and MoO<sub>3</sub> were initially chosen as model compounds to compare the near edge features and to obtain phase parameters. MoO<sub>4</sub><sup>2-</sup> ions in Na<sub>2</sub>MoO<sub>4</sub> are known to be tetrahedral (Lindquist 1950; Clark and Doyle 1960) with Mo-O distance of 1·83 Å. The octahedron of oxygens in MoO<sub>3</sub> is distorted and there are five Mo-O distances (Anderson and Magneli 1950) which make it less suitable as a model compound.

Spectra were recorded repeatedly (5–6 times) with a large  $I_0$  count of 50,000–100,000 and spectral features were confirmed to be free from artefacts resulting from any spurious effects arising from either radiation source or experimental sample. Pre-edge and post-edge back-ground removal, edge normalization, extraction of the EXAFS signal  $\chi(k)$ , Fourier transformation of  $\chi(k)$ , and inverse Fourier transformation of the first peak in the radial structure function (in order to isolate  $\chi(k)$  from the first shell) were performed using procedures described elsewhere (Lytle *et al* 1975; Lee *et al* 1981; Wong 1981). On obtaining the normalised XANES spectra the pre-edge region (–220 to –50 eV) was linearly fitted and extrapolated above the edge. The post-edge back-ground in the EXAFS region was generated analytically using a series of cubic splines of equal length (DeBoor 1968). The ends of each segment were so connected as to make their derivatives continuous across the ends and five such segments were found adequate.

The energy scale was converted to the  $k$  scale using the relation  $k = (1/\hbar) [2m(E - E_b)]^{1/2} = 0·263 (E - E_b)^{1/2}$ , where  $E_b$  is the Mo-K-edge energy. The normalised EXAFS,  $\chi(k)$  at energies above 30 eV was obtained using the relation  $\chi(k) = [\mu(k) - \mu_0(k)]/S \cdot M(k)$ , where  $\mu(k)$  is the measured absorption,  $\mu_0(k)$  is the smooth post-edge background,  $S$  is the step jump at the absorption edge and  $M(k)$  the McMaster (1969) correction energy function.

## 3. Results and discussion

The near edge spectra at the Mo-K-edge (XANES) of MoO<sub>3</sub> (a) Na<sub>2</sub>MoO<sub>4</sub> (b) and the three glasses, (c) (60 AgI·20 Ag<sub>2</sub>O·20 MoO<sub>3</sub>), (d) (40 AgI·30 Ag<sub>2</sub>O·30 MoO<sub>3</sub>) and

(e) (55 AgI · 25 Ag<sub>2</sub>O · 20 MoO<sub>3</sub>), are shown in figure 1. The differentiated spectra are given as insets. Results of the Mo-K-edge EXAFS analysis of Na<sub>2</sub>MoO<sub>4</sub> and the three glasses c, d and e are given in figures 2, 3, 4 and 5 respectively. In Na<sub>2</sub>MoO<sub>4</sub> only discrete tetrahedral MoO<sub>4</sub><sup>2-</sup> ions are known to be present, while in MoO<sub>3</sub> molybdenum is known to be present in distorted octahedra. (Lindquist 1950; Clark and Doyle 1960). In view of the similarity of the near edge spectra of the glasses to that of Na<sub>2</sub>MoO<sub>4</sub> rather than to that of MoO<sub>3</sub>, Na<sub>2</sub>MoO<sub>4</sub> was chosen as the model compound. Since Mo<sup>6+</sup> is coordinated by four oxygen ions at identical distances, the EXAFS from Na<sub>2</sub>MoO<sub>4</sub> was self-fitted to obtain both amplitude and phase parameters. The phases were fitted into a four parameter (Lee *et al* 1977) equation:

$$\phi = P_0 + P_1 k + P_2 k^2 + P_3/k^3 \quad (1)$$

and the best fit values were  $P_0 = 5.8216$ ;  $P_1 = 1.4941$ ;  $P_2 = 0.0403$  and  $P_3 = 77.25$ . Using the phase and amplitude parameters from the EXAFS of the Mo-K edge in Na<sub>2</sub>MoO<sub>4</sub>, the Mo-EXAFS of the three glasses were examined. The procedure for analysis of the EXAFS data has been given in detail elsewhere (Teo and Lee 1979; Rao *et al* 1983). Briefly an assumed value of the number of neighbours ( $N_j$ ) and their distances ( $R_j$ ) were given as input parameters along with guesstimate values of  $\sigma_j$ , the spread in the first neighbour distances (a parameter analogous to the Debye-Waller term in x-ray diffraction analysis). The EXAFS of the first shell ( $j = 1$ ) was obtained by the inverse Fourier transform of the first peak in the radial structure function (between 0.5 Å to 1.85 Å for all glasses). Fitting to the theoretical EXAFS was performed using the

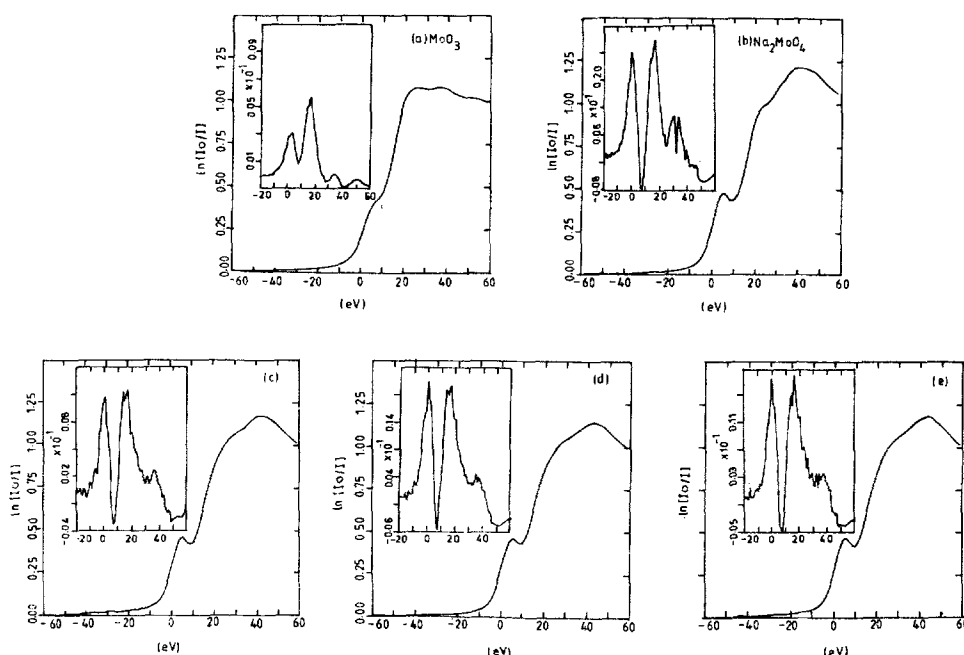
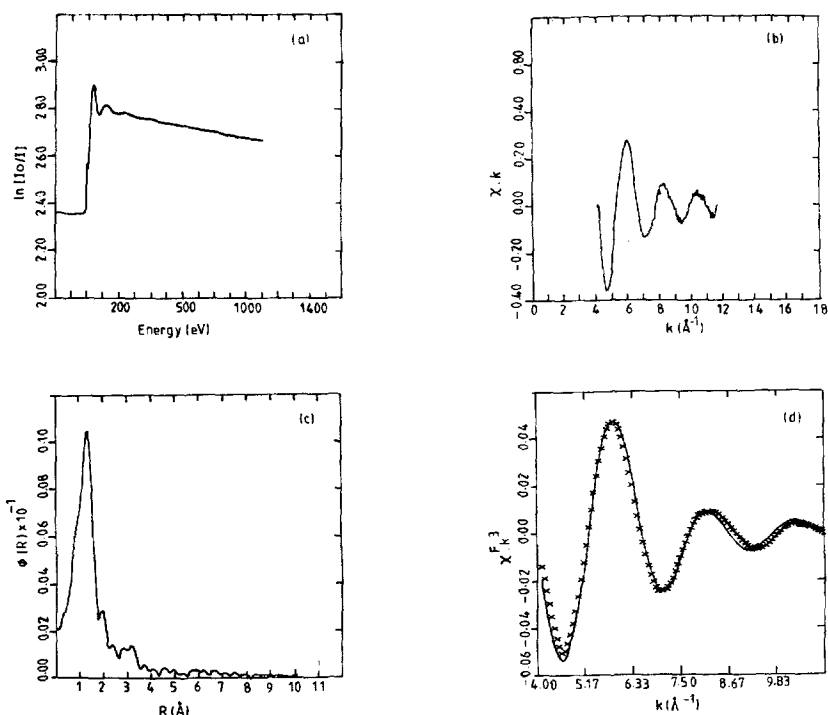


Figure 1. Mo-K-edge XANES in MoO<sub>3</sub> (a) Na<sub>2</sub>MoO<sub>4</sub> (b) and three AgI-Ag<sub>2</sub>O-MoO<sub>3</sub> glasses (c, d and e). The differentiated spectra are given as an inset in each case.



**Figure 2.** Various stages of EXAFS analysis of the model compound  $\text{Na}_2\text{MoO}_4$ . (a) raw Mo-K-edge spectrum, (b) normalized EXAFS trace, (c) radial structure function obtained from Fourier transform of (b), (d) inverse Fourier transform (solid line) and simulated EXAFS (crosses) of the first peak from (c) (see text for other details).

expression:

$$\chi(k) = \frac{-1}{k} \sum A_j \sin[2R_j k + \phi_j(k)] \quad (2)$$

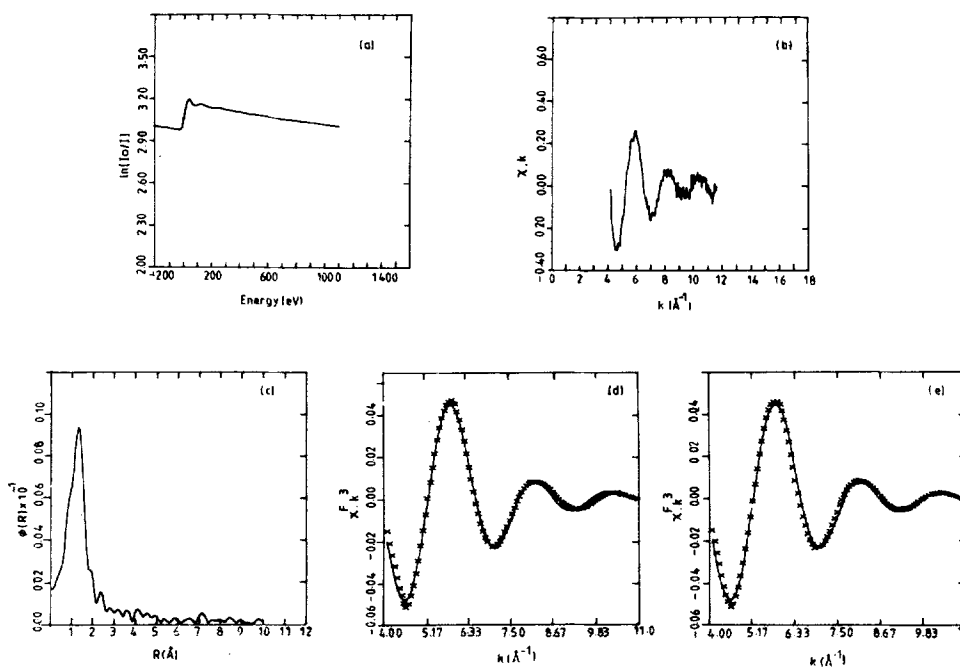
with  $j = 1$ . Where  $A_j$  is given by:

$$A_j = (N_j/R_j^2) f_j(\pi, k) \exp(-2R_j/\lambda) \exp(-2\sigma_j^2 k^2). \quad (3)$$

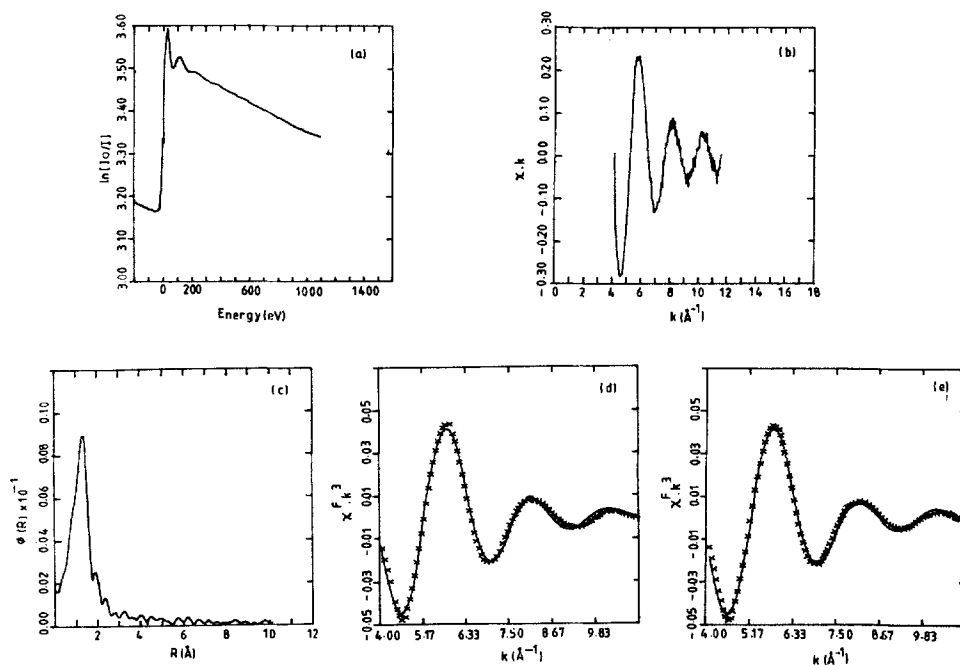
The results of the theoretical fit for the three glasses are shown in figures 3(d) and 5(d). Self-consistent  $N_j$ ,  $R_j$  and  $\sigma_j$  values thus obtained are given in table 1 along with the standard deviation (percentile fitting to the experimental EXAFS). The Mo-O distances obtained from EXAFS analysis appear to be in excellent agreement with the values reported in literature (Clark and Doyle 1960) and are also consistent in the three glasses. The number of neighbours appears to be close to four within about 10–15%. Therefore the analysis supports that the molybdate ions are present as  $\text{MoO}_4^{2-}$  tetrahedra in these glasses.

### 3.1 Near edge spectra

The tetrahedrality of oxygen coordination is also supported by the near edge spectra shown in figure 1. The XANES of  $\text{Na}_2\text{MoO}_4$  and the three glasses are very similar. On the contrary the XANES of  $\text{MoO}_3$  is quite distinct.



**Figure 3.** EXAFS analysis of 60 AgI · 20 Ag<sub>2</sub>O · 20 MoO<sub>3</sub> glass, (a), (b) and (c) have the same significance as in figure 2. (d) and (e) are inverse Fourier transform and theoretical fit using one and two oxygen shells respectively.



**Figure 4.** EXAFS analysis of 40 AgI · 30 Ag<sub>2</sub>O · 30 MoO<sub>3</sub> glass (a), (b), (c), (d) and (e) have the same significance as in figure 3.

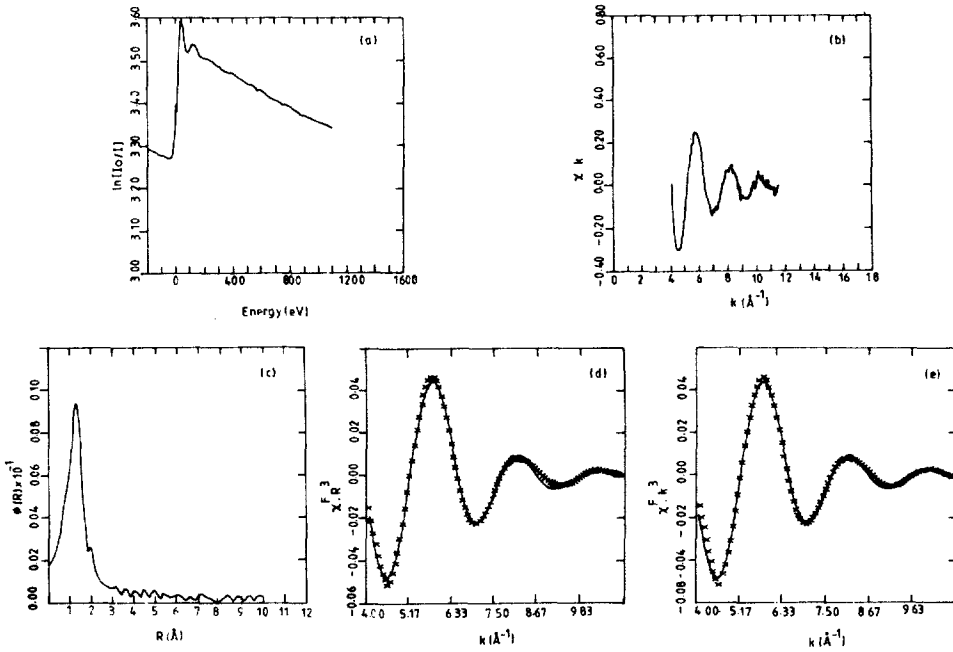


Figure 5. EXAFS analysis of 55 AgI · 25 Ag<sub>2</sub>O · 20 MoO<sub>3</sub> glass. (a), (b), (c), (d) and (e) have the same significance as in figure 3.

Table 1. Coordination number and structural parameters from EXAFS analysis of AgI · Ag<sub>2</sub>O · MoO<sub>3</sub> glasses.

Glass composition AgI:Ag <sub>2</sub> O:MoO <sub>3</sub>	Coordination number <i>N</i>	<i>R</i> (Å)	$\sigma^2$ (Å) <sup>2</sup> × 10 <sup>2</sup>	Standard deviation %
<b>1. One shell</b>				
60:20:20	4.54	1.839	0.216	3.7
40:30:30	4.22	1.837	0.199	3.7
55:25:20	4.57	1.838	0.237	3.7
<b>2. Two shells</b>				
60:20:20	3.20	1.830	0.159	3.9
	1.19	1.923	0.031	
40:30:30	3.13	1.831	0.156	3.9
	1.06	1.923	0.121	
55:25:20	3.27	1.829	0.164	4.1
	1.22	1.924	0.119	

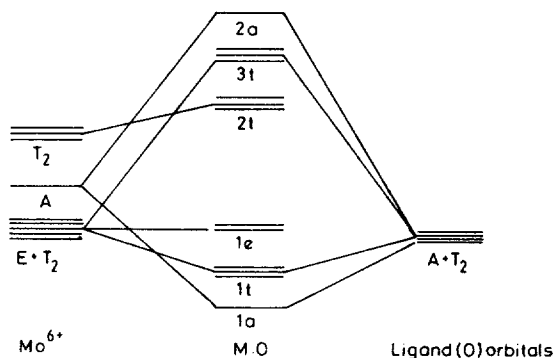


Figure 6. Schematic molecular orbital diagram for  $\text{MoO}_4^{2-}$  ions.

While there is remarkable overall similarity in the differentiated spectra (insets to figure 1) of  $\text{Na}_2\text{MoO}_4$  and the glasses, there are certain clearly recognisable differences; the second peak of the differentiated spectra appears to be split in the case of the glasses. If the molybdate ions were all ideally tetrahedral, the transition should be consistent with the schematic molecular orbital diagram for  $\text{MoO}_4^{2-}$  ion shown in figure 6. The diagram has been drawn using only those orbitals of the ligands which form  $\sigma$  bonds with the central Mo atom. The first two peaks, one low intensity peak and the immediately next intense peak in the spectra of  $\text{Na}_2\text{MoO}_4$  and the glasses arise from transitions of the molybdenum  $1s$  (not shown) electrons to  $1e$  and  $2t$  m.o. levels. The forbiddenness of the transition to  $1e$  level is slightly relaxed in  $T_d$  symmetry (Grunes 1982). Still higher energy transitions ( $> 30$  eV) can originate either from shape-resonances (Rao and Wong 1984) or from any shake-up processes (Rehr *et al* 1978).

Since the 2nd peak in the differentiated spectra of the glasses appears to be split, one could speculate on the possibility that the symmetry of the oxygen coordination shell around Mo is lower than  $T_d$ . Since these glasses are coloured and their electronic conductivity is not negligible (Minami *et al* 1980), there is a possibility that at least a small fraction of the molybdate ions contain molybdenum in the  $\text{Mo}^{5+}$  state. Evidence for the presence of  $\text{Mo}^{5+}$  has been obtained from electron spin resonance studies (unpublished results from this laboratory) and the  $\text{Mo}^{5+}$  ion may be expected to suffer Jahn-Teller distortion. Further, from the point of view of the cluster model (Rao and Rao 1982; Parthasarathy *et al* 1983; Rao 1984) which has been very successfully applied to the present system of glasses (Hemlata *et al* 1983a; Hemlata *et al* 1984), a substantial portion of the  $\text{MoO}_4^{2-}$  ions are expected to be present in the truly disordered tissue region of the glass. These  $\text{MoO}_4^{2-}$  ions (of the tissue region) could be somewhat distorted. Hence, either due to the Jahn-Teller effect in  $\text{Mo}^{5+}$  ions or due to structural reasons, a substantial portion of the tetrahedra are likely to be distorted causing a split in  $2t$  levels. This could be the origin of the splitting observed in the differentiated spectra. Hence more than one Mo-O distance is likely to be present in  $\text{MoO}_4^{2-}$  ions.

In order to investigate the possible distortion of  $\text{MoO}_4^{2-}$  ions which gives rise to different Mo-O distances the EXAFS on these glasses were re-analysed assuming that there are two oxygen each at two different distances ( $j = 2$  in (2) where  $j$  now represents a number of sub-shells). Corresponding EXAFS fits are shown in figures 3(e), 4(e) and 5(e) for the three glasses. Also Mo-O distances and other parameters of fitting are given in

table 1. It is found that the standard deviation has not worsened by the revised fitting and a two-shell fitting appears quite feasible because the coordination number from the fit turns out to be closer to four than in the case of single-shell fitting. The disorder parameter,  $\sigma$  also improves in the sense that it decreases to magnitudes which are in the range of the limit of distance resolution in EXAFS experiments ( $\pm 0.02 \text{ \AA}$ ).

However, such improved fitting raises a fundamental question, namely whether EXAFS procedures generally adopted are capable of discerning such small differences in bond distances in the first-shell of neighbours so as to enable one to comment on the geometry of the first coordination polyhedra. In view of the multiparametric nature of phase-analysis of the model compound and of the fitting procedures employed, it is possible that the EXAFS technique at its present stage of development may also give rise to inherent errors in situations of the present kind.

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