Mixed valency in the high-temperature phases of transition metal molybdates, $A\,MoO_4$ (A = Fe, Co, Ni)†

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Abstract. Transition metal molybdates of the formula $AMoO_4$ where A = Fe, Co or Ni exhibit a first-order phase transition between 670 K–970 K. An investigation of the low-temperature (LT) and high-temperature (HT) phases by x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, magnetic susceptibility and other physical methods shows that the phase transition is associated with a valence change of the type $A^{2+} + Mo^{6+} \rightleftharpoons A^{3+} + Mo^{5+}$ in the cases of iron and cobalt molybdates.

1. Introduction

Divalent metal molybdates $AMoO_4$, where A = Fe, Co or Ni, crystallize under ambient conditions in a defect rocksalt structure (LT phase) with the transition metal atoms in octahedral coordination (Smith and Ibers 1965). These molybdates undergo first-order phase transitions at high temperatures (670–970 K) with a large change ($\approx$ 6%) in volume (Sleight and Chamberland 1968). The high temperature (HT) phase can be quenched in the case of the iron compound. The structure of the HT phase has not been determined but powder diffraction data reveal that the HT phase is isostructural with $MnMoO_4$ (Abrahams and Reddy 1965; Sleight *et al* 1968) wherein Mn is in octahedral and Mo in tetrahedral coordination. The main structural change associated with the phase transition appears to be a change in Mo coordination from six to four. Since the transition occurs only in $FeMoO_4$, $CoMoO_4$ and $NiMoO_4$ and not in the other divalent metal molybdates (Sleight and Chamberland 1968), it has been suspected that the transition may involve valence change of the type, $A^{2+} + Mo^{6+} \rightleftharpoons A^{3+} + Mo^{5+}$. We have prepared $AMoO_4$ molybdates of Fe, Co and Ni and characterized both the HT and LT phases by x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, Mössbauer spectroscopy, magnetic susceptibility and electrical resistivity measurements besides x-ray crystallography. The results reveal that the transition is likely to be associated with a valence change of the cations at least in the cases of iron and cobalt molybdates and that the HT phases are mixed valent as described, by $A^{2+}_{1-x}A^{3+}_{x}Mo^{6+}_{1-x}Mo^{5+}_{x}O_4$.

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2. Experimental

FeMoO$_4$ was prepared by heating the required quantities of Fe, Fe$_2$O$_3$ and MoO$_3$ in a sealed tube at 1270 K for 48 hours. Depending on the cooling rate, either the HT or the LT phase was obtained (Sleight *et al* 1968). The pure LT phase was obtained by slow cooling, first to room temperature and then to liquid nitrogen temperature. The HT phase was obtained by quenching the sealed tube from 870 K to room temperature.

LT phases of CoMoO$_4$ and NiMoO$_4$ were prepared by heating stoichiometric quantities of nickel oxide or cobalt oxalate respectively with MoO$_3$ at 1270 K for 48 hours in air, followed by slow cooling to room temperature (Sieber *et al* 1983). HT phases of CoMoO$_4$ and NiMoO$_4$ could not be obtained by quenching from high temperatures. HT CoMoO$_4$ could, however, be prepared (Chojnacki *et al* 1974) by precipitating CoMoO$_4 \cdot x$H$_2$O through the addition of cobalt(II) nitrate to a solution of ammonium paramolybdate at a pH of 5·5 and heating the precipitate at 670 K for 18 hours in air. HT NiMoO$_4$ could not be prepared by this precipitation method.

Formation of compounds and their phase purity were ascertained by x-ray powder diffraction (Philips PW 1050/70 diffractometer). The unit cell parameters agree with the reported values of the HT and LT phases of the AMoO$_4$ compounds (Sleight *et al* 1968).

The HT-LT transition of AMoO$_4$ was studied by differential scanning calorimetry (Perkin-Elmer, Model 2) using indium as standard. X-ray photoelectron spectra (XPS) were reported using an ESCA-III mark 2 spectrometer with Al $K\alpha$ radiation. X-ray absorption spectra were recorded using a bent crystal spectrograph; analysis of the spectra was carried out by using a Carl-Zeiss MD-100 microdensitometer. Magnetic susceptibility measurements were made in the 15-1000 K range using a Faraday balance. Electrical resistivity of pressed pellets of FeMoO$_4$ was measured using the four-probe technique. Room temperature (300 K) Mössbauer spectra were recorded using 25 mc/^{57}Co (Rh) source; the spectra were least-squares fitted assuming Lorentian line shape.

3. Results and discussion

All the three molybdates undergo a first-order phase transition showing an exothermic peak in DSC or DTA. The transition temperatures are in the order, Fe (650 K) < Co (780 K) < Ni(990 K). It is interesting that the transition temperature correlates with the stability of the trivalent oxidation states of the A metal atoms; Ni(III) is the least stable and the transition temperature of NiMoO$_4$ is the highest. This is also consistent with the inability to quench the HT phase of NiMoO$_4$. The transitions were irreversible in DSC/DTA in all the three cases. The heats of transition estimated from the area under the peak are 5·8, 3·6 and 2·5 kJ mol^{-1} for the iron, cobalt and nickel compounds respectively.

X-ray photoelectron spectra (XPS) of the LT phases of all the three molybdates show the presence of Mo^{6+} and A^{2+} cations as illustrated in figure 1 with a Mo($3d_{5/2}$) binding energy of 232·6 eV characteristic of Mo^{6+} (Sarma and Rao 1980; Rao *et al* 1978). XPS of the HT phases of FeMoO$_4$ and CoMoO$_4$ show evidence for the presence of mixed valent Mo and Fe/Co as illustrated in figure 1. Thus, in the Mo($3d$) region there is a shoulder on the lower binding energy side of the Mo($3d_{5/2}$) peak at 231·8 eV due to Mo^{5+}. A rough estimate of the Mo^{6+} to Mo^{5+} ratio obtained by the deconvolution of
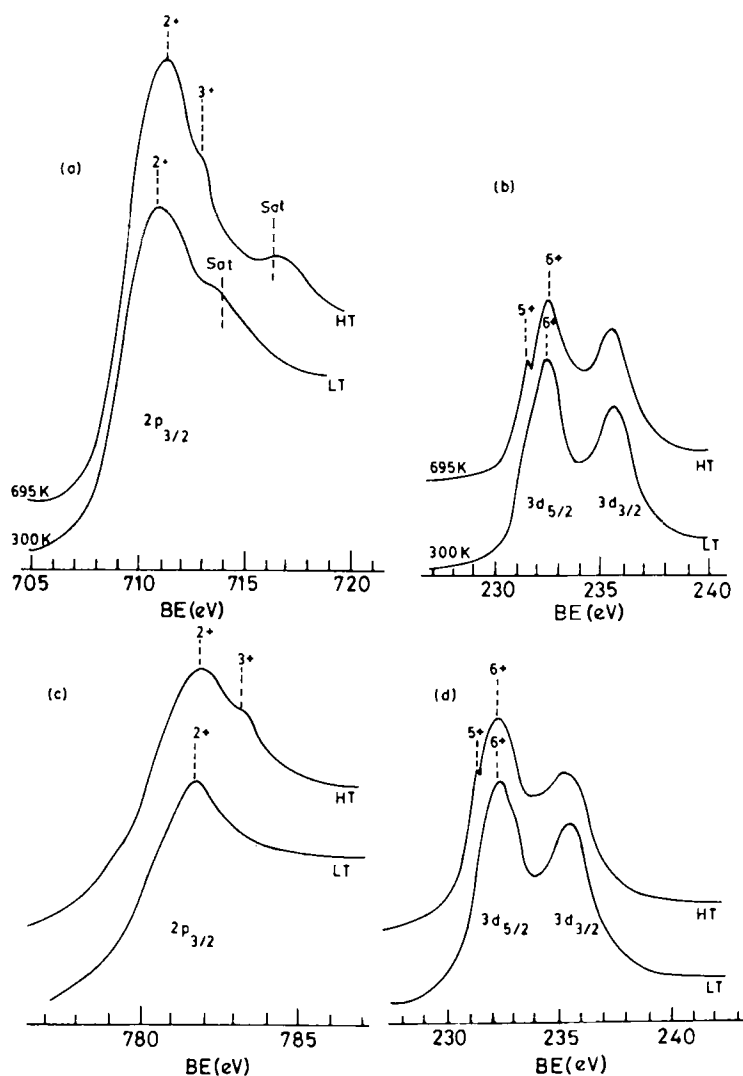
Figure 1. xps of AMoO$_4$ molybdates. (a) Fe($2p$) spectra of LT and HT FeMoO$_4$; (b) Mo($3d$) spectra of LT and HT FeMoO$_4$. The corresponding Co and Mo spectra of CoMoO$_4$ are shown in (c) and (d).

the peaks in the case of HT FeMoO$_4$ is 60:40. The spectra in the Fe($2p$) and Co($2p$) regions also show changes indicating the coexistence of $2+$ and $3+$ ions.

LT FeMoO$_4$ and LT CoMoO$_4$ show characteristic satellites at 3·5–4·0 eV and 6·2 eV respectively in the Fe/Co ($2p$) spectra similar to FeO and CoO (Rao *et al* 1978). In HT FeMoO$_4$ the satellite is at 5·5 eV confirming the presence of Fe^{3+} (Vasudevan *et al* 1979); a similar change is observed in the Co($2p$) spectrum of HT CoMoO$_4$.

Further evidence for the mixed valence character of the HT phases of FeMoO$_4$ and CoMoO$_4$ is provided by x-ray absorption spectroscopy. Chemical shifts of the K-absorption edges of transition metals are known to reflect changes in the oxidation

states of transition metals (Sarode *et al* 1979). The shifts in the case of the molybdates are listed in table 1. The chemical shifts in the K-edges of both the Mo and A metal ions in LT phases are consistent with Mo^{6+} and A^{2+} states (Sarode *et al* 1979; Manthiram *et al* 1980). The Mo K-edge shows a smaller chemical shift in the HT phases; correspondingly, the Fe and Co edges show larger chemical shifts as compared to the LT phases consistent with the presence of 3 + ions as well.

The Mössbauer spectrum of LT $FeMoO_4$ at room temperature (figure 2a) exhibits a two-finger pattern similar to that reported with an isomer shift of 0·92 mm sec^{-1} and quadrupole splitting of 1·77 mm sec^{-1} (Sleight *et al* 1968). The spectrum is consistent with the presence of high-spin Fe^{2+} in LT $FeMoO_4$. The Mössbauer spectrum of HT $FeMoO_4$ shows a four-finger pattern indicating the presence of two sets of iron atoms (figure 2b). The spectrum of HT $FeMoO_4$ has been attributed to two different kinds of iron sites both containing high-spin Fe^{2+} (Sleight *et al* 1968). Considering lines 1 and 3

Table 1. Chemical shifts of the K-absorption edge of the $AMoO_4$ molybdates.

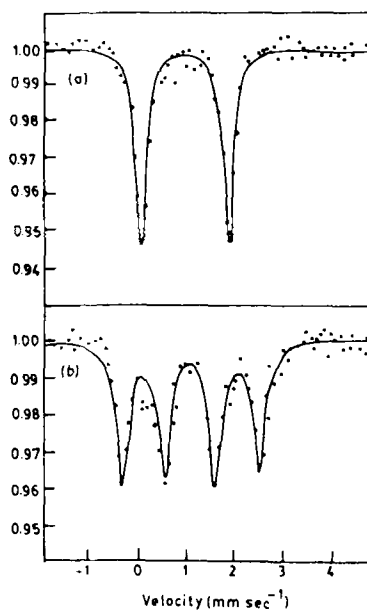| Compound	Chemical shift in eV ($\pm$ 0·5)	
	A ion	Mo ion
LT $FeMoO_4$	6·4	13·9
HT $FeMoO_4$	10·4	13·1
LT $CoMoO_4$	7·8	13·3
HT $CoMoO_4$	9·4	12·9
LT $NiMoO_4$	6·9	13·9

Figure 2. Mössbauer spectra of (a) LT $FeMoO_4$ and (b) HT $FeMoO_4$ at room temperature.

as belonging to one type of iron and lines 2 and 4 as belonging to another set of iron atoms, we derive isomer shifts of 1·45 and 0·57 mm sec^{-1} with quadrupole splittings of 1·97 and 1·91 mm sec^{-1} respectively. These results can be taken to support the existence of Fe^{2+} and Fe^{3+} ions in the HT phase in agreement with XPS and absorption edge measurements. The large quadrupole splittings may be due to a highly distorted environment around the iron atoms.

Magnetic susceptibility of the molybdates was measured in the 15-1000 K range to characterize the phase transition. $FeMoO_4$ was sealed in an evacuated silica tube to prevent oxidation. Susceptibilities of the other two molybdates were determined in vacuum (10^{-4} torr). The χ_m^{-1}-$T(K)$ plots (figure 3) give μ_{eff} (and θ values in parentheses) of 4·98 (28), 4·76 (10) and 3·40 (24) for the LT phases of Fe, Co and Ni molybdates, respectively, consistent with their formulation as $A^{2+}Mo^{6+}O_4$ with divalent Fe and Co in the high-spin states. $FeMoO_4$ and $CoMoO_4$ show a sharp decrease in the susceptibility beyond the transition and the μ_{eff} values of the HT phases ($\sim 1·4$ BM) are smaller than those expected for either A^{3+} (HS) $Mo^{5+}O_4$ or A_{1-x}^{2+} (HS) A_x^{3+} (HS) $Mo_{1-x}^{6+}Mo_x^{5+}O_4$. One possibility is that the Fe^{3+} and Co^{3+} are in the low-spin state. However, it is more likely that this is due to the itinerant nature of d-electrons
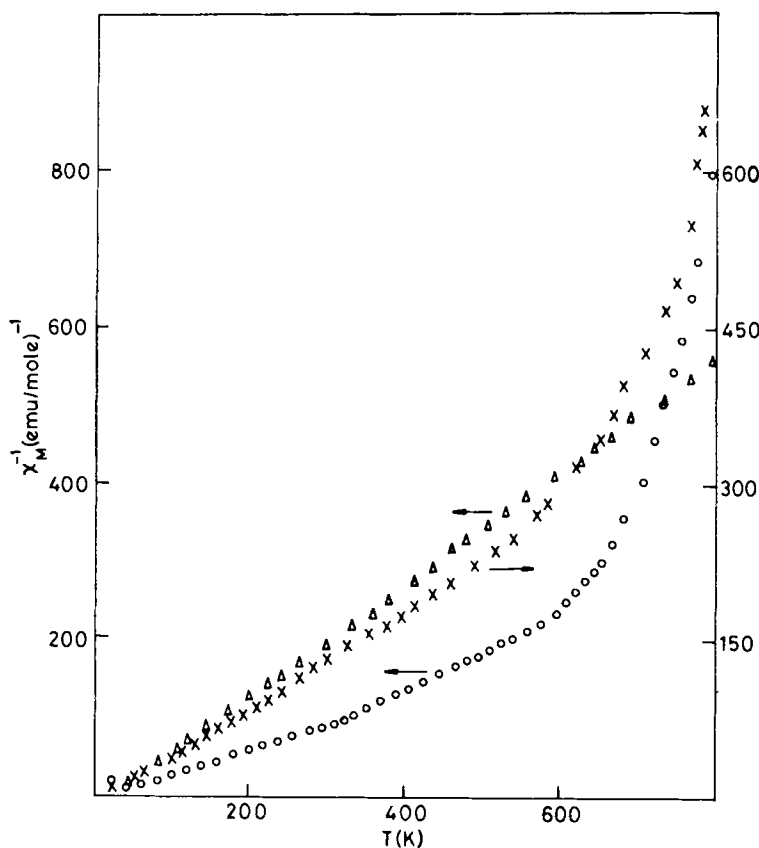

Figure 3. χ_m^{-1}-$T(K)$ plots of $FeMoO_4$ (circles), $CoMoO_4$ (crosses) and $NiMoO_4$ (triangles).

in the HT phases. Accordingly, we do find that HT $FeMoO_4$ shows a considerably lower electrical resistivity ($\approx$ 50 ohm-cm) than LT $FeMoO_4$ ($\approx 3 \times 10^3$ ohm-cm); the lower resistivity of HT $FeMoO_4$ would arise from the itinerancy of the d-electrons caused by the mixed valency.

4. Conclusions

Transition metal molybdates of the formula $AMoO_4$ where A = Fe, Co or Ni exhibit a first order phase transition between 670 K and 970 K. An investigation of the low temperature and high temperature phases by various physical methods including x-ray photoelectron spectroscopy and magnetic susceptibility measurement has revealed that the phase transition is associated with a valence change of the type, $A^{2+} + Mo^{6+} \rightleftharpoons A^{3+} + Mo^{5+}$, at least in the cases of Fe and Co molybdates.

Acknowledgements

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