EPR studies on molybdenum phosphates $\text{Mo}_2\text{P}_4\text{O}_{15}$, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ in the temperature range 300–4·2 K

B B DAS^{*†}, G CONSTENTIN, M M BOREL, A GRANDIN,
A LECLAIRE and B RAVEAU

Laboratoire de Cristallographie et Sciences des Materiaux, CRISMAT-ISMRA, Boulevard du Marechal Juin, 14050 Caen, Cedex, France

[†]Present address: School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad 500 134, India

MS received 27 January 1994; revised 8 August 1994

Abstract. EPR studies of molybdenum phosphates, $\text{Mo}_2\text{P}_4\text{O}_{15}$, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ in the range 300–4·2 K was carried out. Delocalization of $4d^1$ electron on a Mo^{5+} site in the MoO_6 octahedra occurs due to tunneling process. This gives rise to unresolved EPR lineshapes in all the cases except in $\text{Mo}_2\text{P}_4\text{O}_{15}$. The slight indication of hyperfine structure in $\text{Mo}_2\text{P}_4\text{O}_{15}$ is due to less feasibility of delocalization of the $4d^1$ electron, as MoO_6 octahedron is connected through a PO_4 group to only three octahedra as compared with higher numbers in the case of others. The negative g-shift is observed in all the cases due to positive sign of the spin-orbit coupling constant. The decreasing trend in g_{iso} -values in $\text{Mo}_2\text{P}_4\text{O}_{15}$ and $\text{NaMo}_3\text{P}_3\text{O}_{16}$ with decreasing temperature is observed, whereas in $\text{BaMo}_2\text{P}_4\text{O}_{16}$ the g_{iso} -value increases with decreasing temperature.

Keywords. EPR; electron delocalization; molybdenum phosphates; exchange interaction.

1. Introduction

Until recently it has been observed that the molybdenum phosphates have great ability to stabilize Mo^{5+} state (Kierkegaard and Westerlund 1964; Leclaire *et al* 1983; Costentin *et al* 1992). Further, the mixed valent states of molybdenum viz. Mo^{5+} and Mo^{6+} in phosphate matrix are not very common in literature (Costentin *et al* 1991). The Mo^{5+} state with $4d^1$ electronic configuration is an interesting paramagnetic probe to study these phosphate structures by electron paramagnetic resonance (EPR) spectroscopy. In this paper, we report a comparative study on molybdenum phosphates such as $\text{Mo}_2\text{P}_4\text{O}_{15}$ (Costentin *et al* 1992), $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (Costentin *et al* 1991) and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (Costentin *et al* 1990) by EPR spectroscopy in the temperature range 300–4·2 K.

2. Experimental

For the preparation of $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (Costentin *et al* 1990), first BaCO_3 , $\text{H}(\text{NH}_4)_2\text{PO}_4$ and MoO_3 were mixed in appropriate proportions to obtain the composition $\text{Ba}_2\text{Mo}_{1.667}\text{P}_4\text{O}_{16}$ and heated in air at 600 K to eliminate CO_2 , H_2O and NH_3 . Then required amount of molybdenum was added to the product and heated at 1173 K for 48 h in an evacuated silica ampoule. For $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (Costentin *et al* 1991), first an appropriate mixture of Na_2CO_3 , $\text{H}(\text{NH}_4)_2\text{PO}_4$ and MoO_3 was heated at 673 K in air.

^{*}To whom all correspondence should be addressed.

Then the resulting product was mixed with appropriate amount of molybdenum and the finely ground mixture was heated in evacuated silica ampoule at 873 K for 48 h. While for $\text{Mo}_2\text{P}_4\text{O}_{15}$, first an appropriate mixture of $\text{H}(\text{NH}_4)_2\text{PO}_4$ and MoO_3 was heated at 873 K. Then the resulting product was mixed with an appropriate amount of molybdenum, sealed in an evacuated silica ampoule and heated at 1073 K for 96 h.

Variable temperature X-band EPR spectra of the powdered samples at 300 K, 77 K and 4.2 K were recorded using a Bruker spectrometer system (ER 200D) fitted with a double cavity TE_{110} . The low temperature spectra at 4.2 K were recorded using SMC-TBT (France) cryostat. At all the temperatures 100 kHz magnetic field modulation was used. The measured g -values were calibrated with respect to the Bruker strong pitch ($g = 2.0028$).

3. Results and discussion

In figures 1–3 we present the EPR spectra recorded at 300 K, 77 K and 4.2 K of the $\text{Mo}_2\text{P}_4\text{O}_{15}$, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ systems, respectively. From the figures we observe that in the case of these molybdenum phosphates the EPR lineshapes are unresolved except in the $\text{Mo}_2\text{P}_4\text{O}_{15}$ where there is slight indication of hyperfine structures. We explain these lineshapes considering the structure of these phosphates. The crystal structure of $\text{Mo}_2\text{P}_4\text{O}_{15}$ is discussed elsewhere (Costentin *et al* 1992). It consists of MoO_6 octahedra sharing five of their corners with P_4O_{13} tetrphosphate groups and the sixth oxygen is free. Further, its structure can be described by the

Figure 1. EPR spectra of $\text{Mo}_2\text{P}_4\text{O}_{15}$ recorded at (a) 300 K, (b) 77 K and (c) 4.2 K.

Figure 2. EPR spectra of $\text{NaMo}_3\text{P}_3\text{O}_{16}$ recorded at (a) 300 K, (b) 77 K and (c) 4.2 K.

stacking of the $[\text{Mo}_2\text{P}_4\text{O}_{15}]_\infty$ layers parallel to (012). This shows that in the matrix the MoO_6 octahedra containing the Mo^{5+} sites are essentially separated by a PO_4 group. Thus through a PO_4 group the two Mo^{5+} sites in two adjacent MoO_6 octahedra are separated by a distance of about 5 Å (Costentin *et al* 1992). Thus the overlap of $4d$ wavefunctions of two Mo^{5+} sites occurs to a substantial extent for the delocalization of the $4d^1$ electron by quantum mechanical tunneling process. However, the presence of a P_2O_7 group restrict the number of MoO_6 octahedra separated by a PO_4 group around a MoO_6 octahedron to 3 (Costentin *et al* 1992). Thus due to this network of the $[\text{Mo}_2\text{P}_4\text{O}_{15}]_\infty$ layers, the delocalization of the $4d^1$ electron is hindered to an extent for the indication of the hyperfine structure due to the electronic spin and Mo nuclear spin ($I = 5/2$) interaction, as observed in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$ (figure 1).

The structure of the molybdenophosphate, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ which contains Mo^{5+} and Mo^{6+} is described elsewhere (Costentin *et al* 1991) from its single-crystal X-ray diffraction studies. In this case, the MoO_6 octahedra containing the Mo^{5+} sites are connected through corner-shared PO_4 groups forming $[\text{MoPO}_8]_\infty$ chains along $\vec{a}$. In addition, MoO_5 bipyramids containing the Mo^{6+} sites are connected through corner-shared PO_4 tetrahedra forming $[\text{MoPO}_7]_\infty$ chains along $\vec{a}$. Thus the host-matrix is described by the association of these chains connected through PO_4 groups, forming five-sided tunnels where the Na^+ ions are located. From the above structure, we explain that the $4d^1$ electron on a Mo^{5+} site in the octahedra are delocalized along the $[\text{MoPO}_8]_\infty$ chains by tunneling process as described above in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$.

Figure 3. EPR spectra of $\text{BaMo}_2\text{P}_4\text{O}_{16}$ recorded at (a) 300 K, (b) 77 K and (c) 4.2 K.

Thus due to this delocalization of the $4d^1$ electron we observe the unresolved EPR lineshapes at 300 K, 77 K and 4.2 K in the $\text{NaMo}_3\text{P}_3\text{O}_{16}$ system (figure 2). However, it is important to note that in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$ the delocalization of the $4d^1$ electron in the $[\text{Mo}_2\text{P}_4\text{O}_{15}]_\infty$ layer is through the MoO_6 octahedra connected through PO_4 groups in a zig-zag way, whereas in the case of $\text{NaMo}_3\text{P}_3\text{O}_{16}$, the delocalization of $4d^1$ electron is through MoO_6 octahedra connected by PO_4 groups forming $[\text{MoO}_8]_\infty$ chains. Thus, there is difference in the delocalization pathways for the $4d^1$ electron on Mo^{5+} sites in the $\text{Mo}_2\text{P}_4\text{O}_{15}$ and $\text{NaMo}_3\text{P}_3\text{O}_{16}$ systems and this difference is reflected through the observed EPR lineshapes for $\text{Mo}_2\text{P}_4\text{O}_{15}$ (figure 1) and $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (figure 2). In the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$ there is indication of hyperfine interaction, whereas in $\text{NaMo}_3\text{P}_3\text{O}_{16}$ unresolved EPR lineshapes are observed.

We now explain the observed unresolved EPR lineshapes of $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (figure 3) in the light of its structure as described elsewhere (Costentin *et al* 1990) from its single-crystal X-ray diffraction studies. In this case, each P_2O_7 group shares two corners with the same MoO_6 octahedra containing the Mo^{5+} sites forming $[\text{MoP}_2\text{O}_{11}]$ units and the host-matrix can be described from these structural units which share their corners leading to $[\text{MoP}_2\text{O}_{10}]_\infty$ chains along $\vec{b}$. From this structure, we visualize that there are essentially chains of MoO_6 octahedra connected through corner-shared PO_4 groups running along $\vec{b}$ in $[\text{MoP}_2\text{O}_{10}]_\infty$ chain (Costentin *et al* 1990). Thus delocalization of the $4d^1$ electron of Mo^{5+} sites in MoO_6 octahedra occurs along the $[\text{MoP}_2\text{O}_{10}]_\infty$ chains by tunnelling process as described above in

$\text{Mo}_2\text{P}_4\text{O}_{15}$ and $\text{NaMo}_3\text{P}_3\text{O}_{16}$ systems. As a result, we observed the completely unresolved EPR lineshapes for $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (figure 3) as in $\text{NaMo}_3\text{P}_3\text{O}_{16}$ discussed above.

Again from figures 1–3 we observe that at lower fields there is distortion of the base lines of the EPR lineshapes in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$. However, this distortion of the base lines is found to be very less in the case of $\text{Mo}_2\text{P}_4\text{O}_{16}$ (figure 1) where it is observed only at room temperature. But in the case of $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (figure 2) and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (figure 3) the distortion is nearly the same at room temperature but at 77 K or 4·2 K the distortion is more prominent in the case of $\text{BaMo}_2\text{P}_4\text{O}_{16}$ as compared with that of $\text{NaMo}_3\text{P}_3\text{O}_{16}$. This distortion of the base lines at lower fields is explained in terms of electron exchange interaction by considering the structures of the molybdenum phosphates, $\text{Mo}_2\text{P}_4\text{O}_{15}$ (Costentin *et al* 1992), $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (Costentin *et al* 1991) and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (Costentin *et al* 1990) as reported earlier. It is known that in all the above three molybdenum phosphates each MoO_6 octahedron has a free oxygen at the apex. The distance between the two free oxygens of the two adjacent octahedra in the above three cases are shown in table 1. Again, in the case of $\text{NaMo}_3\text{P}_3\text{O}_{16}$ the Na^+ ions in the five-sided tunnels are essentially surrounded by 9 oxygen atoms, whereas in the case of $\text{BaMo}_2\text{P}_4\text{O}_{16}$, the Ba^{2+} ions in the cages are surrounded by 10 oxygen atoms. The effective ionic radii (Shannon and Prewitt 1969) of Na^+ ion with 9 coordinations and Ba^{2+} ion with 10 coordinations are 1·32 Å and 1·52 Å, respectively. Due to the proximity of the two free oxygen atoms in the two adjacent MoO_6 octahedra in the host lattices exchange of electrons occurs between the two free oxygen atoms (Costentin 1992) and this exchange is favoured by the intervening ion present between the oxygen atoms. It appears plausible that such exchange interaction is of fairly low magnitude and affects the EPR lineshapes at lower fields. Thus in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$, the O – O distance of 2·55 Å (table 1) without any intervening ion, the base line distortion due to the exchange interaction is observed only at room temperature (figure 1), whereas at lower temperatures at 77 K or below the magnitude of the exchange interaction becomes too low to distort the EPR base lines. In the cases of $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (figure 2) and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (figure 3) in spite of the fairly large O – O separations (table 1) of 5·81 Å and 4·36 Å, respectively, due to the presence of Na^+ ions in $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and Ba^{2+} ions in $\text{BaMo}_2\text{P}_4\text{O}_{16}$ the exchange interaction is higher in both the cases as compared with that of $\text{Mo}_2\text{P}_4\text{O}_{15}$ at room temperature. As a result, the base line distortions at room temperature in $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ are more than in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$. However, in $\text{NaMo}_3\text{P}_3\text{O}_{16}$, the O – O separation of 5·82 Å with smaller Na^+ ion of ionic radius

Table 1. Distance between the two free oxygen atoms of two adjacent MoO_6 octahedra of the molybdenum phosphates studied.

System	O – O distance between the free oxygen atoms of two adjacent MoO_6 octahedra (Å)
$\text{Mo}_2\text{P}_4\text{O}_{15}$	2·55
$\text{NaMo}_3\text{P}_3\text{O}_{16}$	5·81
$\text{BaMo}_2\text{P}_4\text{O}_{16}$	4·36

Table 2. Calculated g_{iso} - and A_{iso} -values from the EPR spectra recorded at 300 K, 77 K and 4·2 K of the $\text{Mo}_2\text{P}_4\text{O}_{15}$, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ systems.

System	g_{iso} -values			A_{iso} -values ($\times 10^{-4} \text{ cm}^{-1}$)		
	300 K	77 K	4·2 K	300 K	77 K	4·2 K
$\text{Mo}_2\text{P}_4\text{O}_{15}$	1·921	1·917	1·915	51·5	39·3	38·4
$\text{NaMo}_3\text{P}_3\text{O}_{16}$	1·917	1·915	1·914	—	—	—
$\text{BaMo}_2\text{P}_4\text{O}_{16}$	1·920	1·923	1·925	—	—	—

1·32 Å as compared with O – O separation of 4·36 Å with in between Ba^{2+} ion of ionic radius 1·52 Å in $\text{BaMo}_2\text{P}_4\text{O}_{16}$, the exchange interaction is lower in $\text{NaMo}_3\text{P}_3\text{O}_{16}$ than in $\text{BaMo}_2\text{P}_4\text{O}_{16}$ at 77 K and 4·2 K. This is also in agreement with our observed EPR lineshapes of $\text{NaMo}_3\text{P}_3\text{O}_{16}$ (figure 2) and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ (figure 3) where $\text{NaMo}_3\text{P}_3\text{O}_{16}$ has less distortion than in the case of $\text{BaMo}_2\text{P}_4\text{O}_{16}$ at 77 K and 4·2 K. From the extent of the distortion of the base lines in all the above three cases we infer that the exchange interaction in the systems decreases with decreasing temperature. However, in the range of 77–4·2 K, the exchange interaction is of same magnitude in each case of the three molybdenum phosphates studied.

In table 2, we report our calculated g_{iso} -values of $\text{Mo}_2\text{P}_4\text{O}_{15}$, $\text{NaMo}_3\text{P}_3\text{O}_{16}$ and $\text{BaMo}_2\text{P}_4\text{O}_{16}$ systems and A_{iso} -values of $\text{Mo}_2\text{P}_4\text{O}_{15}$ system from the EPR spectra recorded at 300 K, 77 K and 4·2 K, respectively. The table shows that in all the cases, the observed g_{iso} -values are less than the free electron g -value of 2·0023. The negative g -shift is due to the positive sign of the spin-orbit coupling constant for the $4d^1$ electron on a Mo^{5+} site in the matrices. The table also shows that the observed g_{iso} -values in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$ and $\text{NaMo}_3\text{P}_3\text{O}_{16}$ decrease with temperature from 300 K to 4·2 K. This behaviour is explained as follows: as the temperature decreases the Mo–O bond length of the MoO_6 octahedra also decreases. Thus the size of the MoO_6 octahedra having the paramagnetic Mo^{5+} sites decreases. As an overall effect, in the change in the value of the spin-orbit coupling constant for the molybdenum $4d^1$ electron at the Mo^{5+} site, the molybdenum $4d$ orbital contribution to bonding in the MoO_6 unit and in the crystal field splitting energy, the decrease in the g_{iso} -value with temperature as compared with the value at 300 K is observed, whereas in the case of $\text{BaMo}_2\text{P}_4\text{O}_{16}$, the overall change in the above parameters results in the increase in g_{iso} -value with decreasing temperature.

As discussed earlier, we observed the slight indication of hyperfine structure only in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$ (figure 1). Table 1 shows that the isotropic hyperfine splitting constants at 77 K or 4·2 K are less than that at 300 K. This we rationalize as under: we discussed earlier that as temperature decreases the size of the MoO_6 octahedra decreases due to the shortening of the Mo–O bonds. The O atom is more electronegative than the Mo atom. Thus the average radial distance of the $4d^1$ electron from the Mo nucleus increases. As a result, due to reduced hyperfine interaction we observed lower A_{iso} -values at 77 K and 4·2 K as compared with the value at 300 K. However, this shortening of the Mo–O bond does not occur to a significant extent between 77 K to 4·2 K, as a result we observed the nearly same A_{iso} -values at 77 K and 4·2 K (table 2).

4. Conclusions

From our above studies, we draw the following major conclusions. The unresolved EPR lineshapes are due to the delocalization of the molybdenum $4d^1$ electron of the Mo^{5+} site in the matrix by tunneling process. The slight indication of the hyperfine structure in the case of $\text{Mo}_2\text{P}_4\text{O}_{15}$ is due to the less feasibility of delocalization of the $4d^1$ electron as a MoO_6 octahedron having the Mo^{5+} site connected through a PO_4 group to three other MoO_6 octahedra. The observed g_{iso} -values decrease with temperature in $\text{Mo}_2\text{P}_4\text{O}_{15}$ and $\text{NaMo}_3\text{P}_3\text{O}_{16}$ whereas the g_{iso} -value increases with decreasing temperature in $\text{BaMo}_2\text{P}_4\text{O}_{16}$.

References

- Costentin G 1992 Ph.D. Thesis, Universite de Caen, Caen, France
Costentin G, Borel M M, Grandin A, Leclaire A and Raveau B 1990 *J. Solid State Chem.* **89** 83
Costentin G, Borel M M, Grandin A, Leclaire A and Raveau B 1991 *J. Solid State Chem.* **95** 168
Costentin G, Leclaire A, Borel M M, Grandin A and Raveau B 1992 *Z. Kristallogr.* **201** 53
Kierkegaard P and Westerlund M 1964 *Aca. Chem. Scand.* **18** 2217
Leclaire A, Monier J C and Raveau B 1983 *J. Solid State Chem.* **71** 147
Shannon R D and Prewitt C T 1969 *Acta Crystallogr.* **B25** 925