Electron Spin Resonance Studies of Vanadate, Niobate, Phosphate, and Arsenate in γ-Irradiated Calcium Molybdate and Calcium Tungstate

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THE hole-centre formed on γ-irradiation of $CaWO_4$ at 77° K has e.s.r. properties (Table) in accord with expectation for WO_4^-, although there is some evidence that the electron deficiency is shared with an adjacent anion.[1] It has been suggested that the analogous species MoO_4^- is formed in $CaMoO_4$.[2] We find that traces of VO_4^{3-}, NbO_4^{3-}, PO_4^{3-}, and AsO_4^{3-} result in almost complete replacement of the tungsten or molybdenum centres by centres associated with the impurities.

E.s.r. results for the tetroxy-anion radicals. (The A-tensor is in gauss.)

Species	Matrix	Temp. (°K)	g_{11}	g_{22}	g_{33}	a_{11}	a_{22}	a_{33}
VO_4^{2-}	$CaMoO_4$	77	2·0240		2·0228	20·0		19·3
NbO_4^{2-}	$CaMoO_4$	195	2·0256		2·0211	29·8		30·3
		77	2·0061	2·0146	2·0480	25·5	28·5	31·5
PO_4^{2-}	$CaWO_4$	77	2·0139		2·0112	27·7		27·3
AsO_4^{2-}	$CaWO_4$	195	2·0208		2·0177	19·5		18·0
		77	2·0070	2·0122	2·0470	23·0	19·0	18·7
[a]WO_4^-	$CaWO_4$	77	2·0013	2·0064	2·0352	10	9	10
[a]MoO_4^-	$CaMoO_4$	77	2·007	2·011	2·023	—	—	9·3

[a] These may be better written as $(WO_4\text{–}WO_4)^{3-}$ and $(MoO_4\text{–}MoO_4)^{3-}$

The Scheelite host crystals are tetragonal with four molecules per unit cell. In some cases the magnetic centres produced by γ-irradiation reflect this symmetry, being in four magnetically distinct sites related by fourfold axes parallel to the crystallographic c-axis. When this occurs the g- and A-tensors each have three distinct principal values (Table). However, in other instances (Table) only a single magnetic site can be detected, the g- and A-tensors being then axially symmetric. The latter situation can be obtained from the former by warming the Nb and As centres in $CaMoO_4$ and $CaWO_4$, respectively, the change being reversible. The effect, which could be achieved either by a mobile distortion or by some form of rotation, may be associated with the occasional appearance of satellite lines at 77° K which we believe to be superhyperfine structure arising from weak interaction with neighbouring WO_4^{2-} or MoO_4^{2-} ions. The e.s.r. parameters of these species are listed in the Table. The results for WO_4^- are in excellent agreement with those given previously,[1] and for PO_4^{2-} are similar to those assigned to this radical in a calcite lattice.[3]

We suggest that VO_4^{2-}, NbO_4^{2-}, PO_4^{2-}, and AsO_4^{2-} are formed by transfer of an electron from the parent ion to either WO_4^- or MoO_4^- initially produced by the radiolysis. The g-tensor is consistent with that expected for a hole-centre, having $g_{av} >$ free-spin. In all cases the A-tensor indicates that the orbital of the unpaired electron is entirely on oxygen, the coupling to the central atom being largely a consequence of spin-polarisation of the σ-electrons.[4] Therefore, the highest occupied level of the parent diamagnetic ion is, as expected,[5] associated with oxygen.

If these identifications are correct they provide an interesting link between tetroxy-anions of the non-transition and transition elements.

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