ESR Spectrum of the 9-Molybdomanganate(IV) Ion in Dilute Single Crystal

P. G. RASMUSSEN, K. M. BEEM, AND E. J. HORNYAK

Department of Chemistry, The University of Michigan, Ann Arbor, Michigan 48104

(Received 14 November 1968)

The ESR spectrum of a single crystal of $(NH_4)_6[Ni(IV)O_6Mo_9O_{26}] \cdot 8H_2O$ containing 1% $(NH_4)_6$-$[Mn(IV)O_6Mo_9O_{26}] \cdot 8H_2O$ has been investigated. This is the first ESR report on quadrivalent manganese in a chemically well-characterized environment. The site symmetry is D_3, and anisotropic g values, hyperfine splittings, and zero-field splitting values were obtained by fitting the spectrum with an axial spin Hamiltonian.

INTRODUCTION

Although Mn^{4+} is isoelectronic with Cr^{3+}, the ESR investigations of this oxidation state have been few in number.[1] In the previous investigations[2–6] the manganese was *doped* into the host lattices ($SrTiO_3$, Al_2O_3, TiO_2) which were formed at high temperatures. We have investigated the Mn^{4+} ESR spectrum in a chemically well-characterized compound and can confirm a spectrum due to $S=\frac{3}{2}$ manganese and not the more common $S=\frac{5}{2}$ (Mn^{2+}) species.

EXPERIMENTAL

The compounds were prepared by the method of Baker and Weakley.[7,8] Single crystals of 1 mole% manganese in the nickel host were grown from water solution. Alignment of the crystals was obtained with the use of an optical goniometer and precession x-ray methods. The spectrometer was essentially the Varian V-4502 unit operated at X band, except that the magnet was converted from an old 40-Mc NMR instrument. Because the magnet does not rotate, a single-crystal transfer and rotation device was designed for use with this magnet and the Varian general-purpose rectangular cavity. The construction and accuracy of this device

is discussed elsewhere.[9] Magnetic field was determined using proton NMR, and klystron frequency was measured with a calibrated government-surplus radar spectrum analyzer TS-148/UP.[10] Spectra were taken at room temperature since one run at 77°K did not show significant line narrowing but did result in the fracturing of a single crystal.

RESULTS

One of the few stable compounds containing Mn^{4+} is the hetero-9-molybdate $(NH_4)_6[MnMo_9O_{32}] \cdot 8H_2O$. This compound, and its nickel isomorph, have been known for many years[7] although the properties have only recently been elucidated by Baker and Weakly.[8] The nickel compound containing Ni^{4+}, is diamagnetic as should be the case for a low spin d^6 ion. We have examined the single-crystal ESR spectrum of the manganese compound, diluted to 1% in the diamagnetic nickel host compound, as a function of orientation. Waugh *et al.* performed a partial structure determination of the manganate and found that it belonged to the space group D_3^7-R_32, with one molecule per unit cell.[11] This required the Mn position to be on the three-fold or c axis, surrounded by six oxygens and to have a space-group demanded site symmetry of 32 (D_3). This site symmetry demands that the tensor properties of the site be at least axial. In particular, second-order tensors will have the same principal axes, with two

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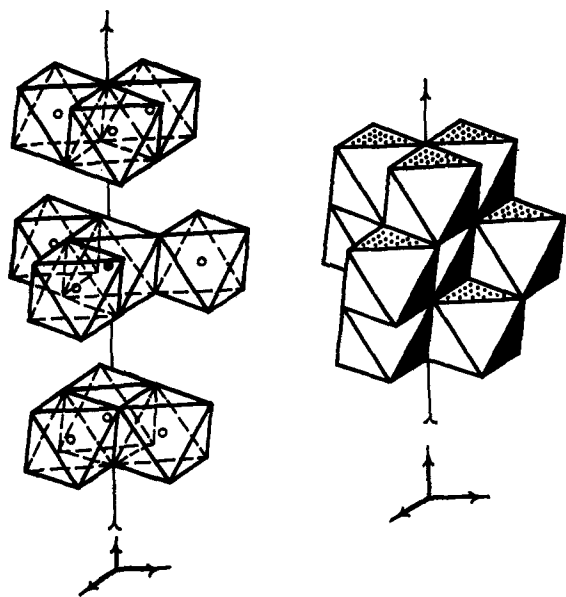
FIG. 1. The structure of the $[MnO_6Mo_9O_{28}]^{6-}$ anion. Left: a view exploded along the threefold axis, open circles are molybdenum, filled circle manganese. Right: perspective view of assembled polyhedra.

$SrTiO_3(Mn)$[2]	$\langle g \rangle$			$\langle A \rangle$		
	1.994			209		
$TiO_2(Mn)$[3]	g_x	g_y	g_z	A_x	A_y	A_z
	2.008	1.994	1.993	217	211	218
This work	$g_{\parallel}$	$g_{\perp}$		$A_{\parallel}$	$A_{\perp}$	
	1.9917	1.9968		218	203	

principal values. The unique axis, which we shall call the z, is the c axis. (See Fig. 1.)

As expected, the spectrum was found to be invariant with respect to rotation of the crystal about the c axis. At all perpendicular orientations, only one six-line multiplet was observed. As θ, the angle between the field direction and the c axis, was varied from 0 to $\pi/2$, the multiplet moved continuously down field. The great difference in the extreme values, about 3390 and 1710 G, indicated a large zero-field splitting. The experimental error for the individual lines was ± 0.5 G, while the error in hyperfine separations was 0.2 G or less. For values of θ other than 0 or $\pi/2$, additional hyperfine structure was found to be present with appreciable intensity. The breakdown of the selection rule, $M_I = 0$, is a result of the large zero-field splitting.

The interpretation of the data was based on the spin hamiltonion, $H_s = H_e + A_{ij}I_iS_j$, with $H_e = \beta g_{ij}B_iS_j + \Lambda_{ij}S_iS_j$ and $S = 3/2$, $I = 5/2$. The axial site symmetry allows the simplification

$$H_s = \beta[g_{\parallel}B_zS_z + g_{\perp}(B_xS_x + B_yS_y)]$$
$$+ D[S_z^2 - 1/3S(S+1)] + A_{\parallel}I_zS_z$$
$$+ A_{\perp}(I_xS_x + I_yS_y).$$

The hyperfine interaction was treated as a perturbation upon H_e. Explicit solutions of H_e are found for $\theta = 0$, $\pi/2$, $\cos^{-1}1/\sqrt{3}$.

The spectrum for $\theta = 0$ clearly corresponds to the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ transition with $\Delta \langle H_e \rangle = g_{\parallel}\beta B$. For $\theta = \pi/2$, four electronic transitions have nonzero intensities. From

the position of the multiplet and the absence of other transitions, it was concluded that the transition corresponds to

$$\Delta \langle H_e \rangle = G_{\perp} + (G_{\perp}^2 + |D|G_{\perp} + D^2)^{1/2}$$
$$- (G_{\perp} - |D|G_{\perp} + D^2)^{1/2},$$

where

$$G_{\perp} = g_{\perp}\beta B.$$

The parameters $g_{\parallel}$, $g_{\perp}$, D, $A_{\parallel}$, $A_{\perp}$ were calculated using successive approximations. Third-order hyperfine terms were large enough to be included. The imprecision involved in the calculation of the parameters from independent data was, except for D, found to be similar to or less than the experimental error. The results are

$$g_{\parallel} = 1.9917 \pm 0.0003,$$

$$A_{\parallel} = 78.2 \pm 0.2 \text{ G},$$

$$A_{\perp} = 72.6 \pm 0.3 \text{ G},$$

$$g_{\perp} = 1.9968 \pm 0.0004,$$

$$D = \text{approximately } 7400 \text{ G}.$$

With D in this range, the equations change slowly with a relatively large change in D. This is seen by letting D approach infinity and evaluating the other parameters.

$$g_{\parallel} = 1.9917,$$

$$A_{\parallel} = 78.8,$$

$$A_{\perp} = 74.2,$$

$$g_{\perp} = 1.979 \pm 0.002.$$

Only for $g_{\perp}$ is the imprecision greater than experimental error.

The linewidth of the individual hyperfine components is approximately 7 G in the $\theta = 0°$ orientation at room temperature. These relatively narrow lines are indicative of a pure, well-ordered, rigid lattice in which the surroundings of the paramagnetic atom are largely atoms with zero nuclear spin.

Comparison of our g values and hyperfine parameters with values previously obtained for Mn^{4+} as a dopant ion (see Table I) shows close agreement. In a future publication we will offer an interpretation of the parameters and the forbidden transitions at nonspecial angles.