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# ESR of $Mo^{5+}$ in $YVO_4$: A Substitutional Off-Center Ion*

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The electron spin resonance of $MoO_4^{3-}$ in $YVO_4$ was studied at 4.2K. The $Mo^{5+}$ has a $d_{xy}$ ground state and is shown to move off the $V^{5+}$ substitutional site of $D_{2d}$ symmetry to one of four crystallographically equivalent off-center sites of $C_2$ symmetry, located in the ⟨110⟩ direction. The $Mo^{5+}$ spectrum is compared to $Cr^{5+}$ in $YVO_4$ and $YPO_4$ and $V^{4+}$ in $ZrSiO_4$ and other zircon-like crystals which show dynamic effects that we interpret as tunneling or thermally activated hopping between off-center sites.

## Introduction

We have recently reported studies of electron spin resonance (ESR) and polarized optical absorption spectra of $V^{4+}$ in single crystals of the isostructural series of zircon-type compounds: $ZrSiO_4$, $HfSiO_4$, $ThSiO_4$, and $ThGeO_4$ (*1*). The zircon structure is made up of a chain of alternating edge-sharing $SiO_4$ tetrahedra and $ZrO_8$ dodecahedra parallel to the *c* crystal axis. Both the tetrahedral and dodecahedral sites of zircon have $D_{2d}$ symmetry and a simple crystal field analysis predicts a $d_{xy}$ ground state for the $d^1$ electron of $V^{4+}$ in either of these sites (*2*). The ESR data for $V^{4+}$ in all four zircon analogs indicate a $d_{xy}$ ground state. However, the principal values of *g* and *A* in $ZrSiO_4$ and $HfSiO_4$ are anomalous and significantly different from those in $ThSiO_4$ and $ThGeO_4$. The optical spectra indicate that $V^{4+}$ enters the tetrahedral rather than the dodecahedral site. The spectra are all similar except for the occurrence of strong $D_{2d}$-forbidden transitions in $ZrSiO_4$ and $HfSiO_4$. We showed that the optical and ESR data in these two crystals could not be accounted for by conventional crystal field theory, and that the symmetry and parameter restrictions imposed by the dynamic Jahn–Teller effect (DJTE) theory

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precluded analysis of the data in terms of DJTE (*3–5*). We tentatively attributed the observed anomalies to dynamic local distortions of the $VO_4$ tetrahedron of unknown origin.

Similar anomalies were found in the ESR of $Cr^{5+}$ in $YPO_4$ and $YVO_4$ (*6*), another case of a $d^1$ ion in the tetrahedral site of a zircon-type crystal. In $YPO_4$ and $YVO_4$ the $PO_4$ and $VO_4$ tetrahedra are distorted to $D_{2d}$ symmetry by a stretching motion along the $c$ crystallographic direction (as is $SiO_4$ in $ZrSiO_4$) and a crystal field model predicts a $d_{xy}$ ground state for the $d^1$ electron on $CrO_4^{3-}$ in these hosts. The ESR results indicated a $d_{z^2}$ ground state. The inversion was attributed to covalency and to interaction with the two neighboring yttrium ions above and below the $Cr^{5+}$ ion along the crystal $c$ axis which shows up as a superhyperfine structure in the ESR. We concluded that our inability to fit the observed $g$ values to crystal field equations assuming $D_{2d}$ (or lower) symmetry is due to a spontaneous local dynamic distortion of the $CrO_4$ tetrahedron. The observed field- and orientation-dependent linewidth of the superhyperfine lines was suggested as evidence of this motion.

The object of this study was to clarify the observed vibrational anomalies of transition metal ions in zircon-type crystals and to establish the origin of such dynamic distortions. We present a single-crystal ESR study of $Mo^{5+}$ substituted for $V^{5+}$ in $YVO_4$. We find that the ESR results are anomalous but there is no evidence for dynamic motion at 4.2K. Instead the $MoO_4$ tetrahedron has several crystallographically equivalent spectra of lower symmetry than would be expected from the symmetry of the $VO_4$ site. Our interpretation is that the $Mo^{5+}$ has moved off the normal lattice site in the ⟨110⟩ direction to one of four nearby crystallographically equivalent lower symmetry sites. We suggest that the dynamic effects observed in other zircon analogs is due to motion of the paramagnetic ions between these off-center sites.

## Experimental

$YVO_4$ crystals doped with the $Mo^{5+}$ were grown from $Pb_2V_2O_7$ flux as previously described (*7*). The molybdenum concentration is less than 0.1 mole%. The color of the crystals was olive green. The ESR spectra showed that $Cr^{5+}$ impurities were also present in about the same concentration as the $Mo^{5+}$. The electron spin resonance spectra were taken with an X-band coherent superheterodyne spectrometer operating in the absorption derivative mode using field modulation. The klystron frequency was ~9 GHz. No ESR was observed at room temperature or liquid nitrogen temperature, but at 4.2K sharp resonances were detected. The crystals were oriented by X-ray diffraction techniques and the ESR spectra were recorded as the magnetic field was rotated in 10° intervals about the $c$ and $a$ tetragonal axes.

## Crystal Structure

$YVO_4$ has the tetragonal zircon structure ($I4_1/amd$) with four molecules per unit cell. The $VO_4$ tetrahedra are strongly distorted to $D_{2d}$ symmetry by a stretching motion along the $c$ axis such that the two angles bisected by the $c$ axis [O(1)–V–O(2)] are smaller and the remaining four angles [O(1)–V–O(3)] are larger than the tetrahedral angle (109.4°) (*8*). The yttrium site is surrounded by eight oxygens at the vertices of a tetragonal dodecahedron with site symmetry $D_{2d}$. The four $VO_4$ tetrahedra in the unit cell are magnetically equivalent as are the $YO_8$ dodecahedra.

## Results and Preliminary Analysis

Molybdenum has two isotopes with nuclear spin $I = 5/2$—$^{95}Mo$ (15.8% abundant) and $^{97}$Mo (9.6% abundant)—in addition to the even $I = 0$ isotopes. The two $I = 5/2$ isotopes have almost identical gyromagnetic ratios. Thus the ESR signature of a paramagnetic molybdenum ion is an intense central line accompanied by six weak equally spaced hyperfine lines having ~1/25 the intensity of the central line.

The observed spectrum of Mo in $YVO_4$ consists of two intense, narrow (≃2 G) central lines with accompanying sets of hyperfine lines. No superhyperfine lines are observed. The two sets of lines coalesce when $H$ is along ⟨100⟩ or ⟨001⟩. When $H$ is rotated about the $c$ crystal axis the two sets of lines have the same variation, but the spectra are shifted by 180°. Thus we conclude that the Mo occupies at least two crystallographically equivalent sites that are magnetically nonequivalent. The spectrum can be fit to the spin Hamiltonian

$$\mathcal{H} = g_xS_xH_x + g_yS_yH_y + g_zS_zH_z + A_xI_xS_x + A_yI_yS_y + A_zI_zS_z. \quad (1)$$

Figure 1 shows the angular variation of the $g$ values of the central line for rotation of the magnetic field about the $a$ and $c$ axes. The solid lines are a three-parameter fit to

$$g^2 = g_x^2l^2 + g_y^2m^2 + g_z^2n^2, \quad (2)$$

where $l$, $m$, $n$ are direction cosines of $H$ with respect to the principal axes of the $g$ tensor. $g_z$ lies along ⟨001⟩ and $g_x$ and $g_y$ are in the $ab$ plane at an angle of 45° ± 1° from the $a$ axis. The hyperfine splittings were fit to a similar expression (*2*) for $gA$. It was difficult to accurately measure the hyperfine splittings due to overlap with the $Cr^{5+}$ spectrum. But within the rather considerable experimental error the principal axes of $A$ are parallel to those of $g$. The results of the fits are shown in Table I.

## Discussion

The observed ESR spectrum is consistent with $Mo^{5+}$ ($4d^1$) rather than $Mo^{3+}$ ($4d^3$)

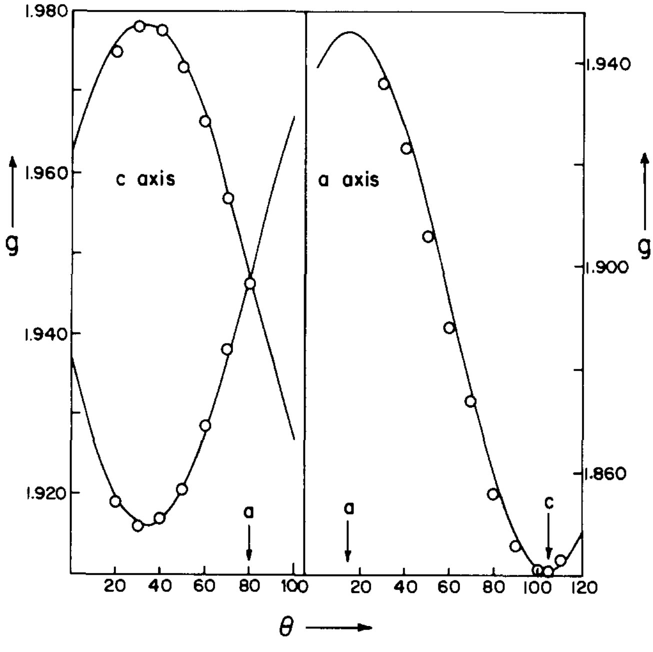

FIG. 1. Angular dependence of the $g$ factor of the ESR signal of $Mo^{5+}$ in $YVO_4$ as the magnetic field is rotated about the $c$ and $a$ crystal axes.

TABLE I

Principal $g$ and $A$ Values of $MoO_4^{3-}$ in $YVO_4$

| | |
|---|---|
| $g_x$ | 1.9783 ± 0.0005 |
| $g_y$ | 1.9160 ± 0.0005 |
| $g_z$ | 1.8410 ± 0.005 |
| $\|A_x\|$ ($10^{-4}$ cm$^{-1}$) | 18.7 ± 0.8 |
| $\|A_y\|$ ($10^{-4}$ cm$^{-1}$) | 16.7 ± 0.8 |
| $\|A_z\|$ ($10^{-4}$ cm$^{-1}$) | 24.2 ± 0.3 |
| Angle $A_z$ to $g_z$ | 0 ± 5° |

(*9*), so we assume that Mo substitutionally replaces $V^{5+}$ in $YVO_4$ rather than $Y^{3+}$. This is to be expected since $YMoO_4$ has been prepared (*10*) and has the sheelite structure which is closely related to zircon.

The energy levels of the $d^1$ electron on $Mo^{5+}$ in $MoO_4^{3-}$ are primarily determined by the crystal field of the oxygen tetrahedron which reduces the initial fivefold degeneracy of $d$ orbitals to a ground-state doublet $E$ state and a triplet $T_2$ excited state raised above $E$ by an energy of $\sim 10^4$ cm$^{-1}$ for $T_d$ symmetry.

Distortion of the tetrahedron to $D_{2d}$ symmetry splits both the doublet and triplet states as shown in Fig. 2. The ordering of the energy levels varies with the nature of the $D_{2d}$ distortion (*1*). In $YVO_4$ the substitutional $MoO_4^{3-}$ tetrahedron is expected to be strongly stretched along the $c$ crystal axis, predicting $d_{xy}$ as the ground state. ESR can easily distinguish between a $d_{z^2}$ ($A_1$) or $d_{xy}$ ($B_2$) ground state since crystal field analysis (*2*) predicts $g_z < g_x, g_y$ and $|A_z| > |A_x|, |A_y|$ for a $d_{xy}$ ground state, with the converse holding for $d_{z^2}$. For $D_{2d}$ symmetry, the $g$ and $A$ tensors must be axial. The ESR parameters of $Mo^{5+}$ in $YVO_4$ (Table I) indicate a $d_{xy}$ ground state. However, there is no axial symmetry of the electric axis. In addition we see two symmetry-related spectra, whereas all four $VO_4$ tetrahedra in the unit cell of $YVO_4$ are magnetically equivalent. We interpret this to mean that the $Mo^{5+}$ has moved off the $V^{5+}$ site to a nearby site of lower symmetry. Some relaxation of the oxygen cage is also to be expected.

We can deduce the direction of motion from the symmetry of ESR spectrum. Motion in an arbitrary direction would produce four magnetically inequivalent sites. But only two spectra are seen. So the motion must be in a high-symmetry direction. Motion along the ⟨100⟩, ⟨010⟩, or ⟨001⟩ directions can be eliminated since then the complex would retain at least one of the two mirror planes (*ac* and *bc*) that characterize $D_{2d}$ symmetry. Then if $g_x$ makes a 45° angle with the $a$ axes, the mirror symmetry requires $g_x = g_y$, which is not observed. Motion along ⟨110⟩ is the only direction consistent with the observed spectrum. There are four symmetry-related sites for a ⟨110⟩ displacement but only two are magnetically inequivalent.

For ⟨110⟩ motion the $MoO_4$ complex retains $C_2$ symmetry with the twofold symmetry axis along the direction of motion. In order to make a crystal field analysis of the data we use crystal field equations we have previously given (*11*, *12*) for $MnO_4^{2-}$ in $K_2SO_4$. This analysis was for a $d_{xy}$ ground state in $C_s$ symmetry. However, it can be adopted to $C_2$ symmetry without change since in both $C_s$ and $C_2$ the states of $d_{xy}$, $d_{x^2-y^2}$, and $d_{z^2}$ fall in the same irreducible representation ($A'$ and $A$, respectively), while $d_{yz}$ and $d_{xz}$ fall in another ($A''$ and $B$). Thus for either symmetry we can take the

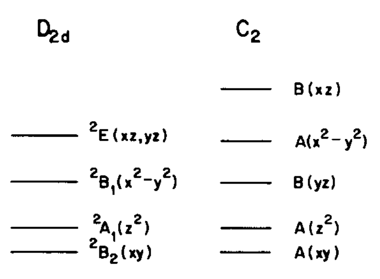

FIG. 2. Ordering and qualitative splittings of the energy levels of a $d$ electron in a distorted tetrahedral crystal field of $D_{2d}$ and $C_2$ symmetry. The vertical scale is arbitrary.

doublet states to be

$$\psi_{xy} = ed_{xy} + fd_{yz}, \qquad (3)$$

$$\psi_{z^2} = ad_{z^2} + bd_{x^2-y^2} + cd_{xz}, \qquad (4)$$

where $a,e \sim 1$ and $b,c,f \ll 1$. We can then use the crystal field equations to relate the experimental principal values of the $g$ and $A$ tensors to the nine parameters:

$$\xi/(E_{yz} - E_{xy}),\ \xi/(E_{z^2} - E_{xy}),$$

$$\xi/(E_{xz} - E_{xy}),\ \xi/(E_{x^2-y^2} - E_{xy}), \qquad b,c,f,$$

$P$ and $K$, where $\xi$ is the spin orbit coupling constant, $K$ is the isotropic Fermi contact term, and $P = g_0 g_N \beta_e \beta_N < r^{-3} >_{\mathrm{av}}$. We choose $c = 0$, which amounts to rotating the wavefunction axes about the twofold axis. Our hyperfine data, although not very accurate, are consistent with $A_z$ being parallel to $g_z$. This implies $f = 0$. We have only six pieces of data so our fit can only yield the product $b\xi/(E_{z^2} - E_{xy})$. The results are given in Table II. The errors given in the table are obtained from the fitting program by individually varying the input parameters from Table I by their estimated errors. The large error in the product $b\xi/(E_{z^2} - E_{xy})$ arises because the fit is extremely sensitive to the difference $A_x - A_y$ which we cannot measure accurately. The fit indicates a very large splitting of the triplet states with an ordering (Fig. 2).

$$E_{xz} > E_{x^2-y^2} > \mathrm{E}_{yz}.$$

These splittings are determined from our measured $g$ values and thus are not subject to the uncertainty arising from the hyperfine measurements. If we assume $\xi \sim 270$ cm$^{-1}$ as previously observed (*13*) for $Mo^{5+}$, we find $E_{xz} \simeq 24{,}500$, $E_{x^2-y^2} \simeq 13{,}500$, and $E_{yz} \simeq 6000$ cm$^{-1}$. The energy spacing for $d_{x^2-y^2}$ is reasonable and consistent with $Mo^{5+}$ in tetrahedral symmetry in other hosts (*13*). However, the very large splitting of $d_{xz}$ and $d_{yz}$, which are degenerate in $D_{2d}$ symmetry, is surprising and should be checked by optical absorption measurements.

TABLE II

CRYSTAL FIELD PARAMETERS FOR $Mo^{5+}$ IN $YVO_4$

| | |
|---|---|
| $b\xi/(E_{z^2} - E_{xy})$ | 0.012 ± 0.010 |
| $\xi/(E_{xz} - E_{xy})$ | 0.011 ± 0.001 |
| $\xi/(E_{x^2-y^2} - E_{xy})$ | 0.020 ± 0.001 |
| $\xi/(E_{yz} - E_{xy})$ | 0.045 ± 0.001 |
| $P(\times 10^{-4}$ cm$^{-1})$ | −42.0 ± 0.5 |
| $K(\times 10^{-4}$ cm$^{-1})$ | 7.5 ± 0.4 |

It is interesting to compare $Cr^{5+}$ in $YVO_4$(6) with $Mo^{5+}$. The $Cr^{5+}$ has a $d_{z^2}$ ground state, which is presumably stabilized by interaction with the two neighboring Y ions above and below it on the $c$ axis. This interaction clearly shows up as a superhyerfine splitting of the $Cr^{5+}$ ESR spectrum. Only a single temperature-independent, axially symmetric spectrum is seen. But for rotation about the $c$ axis the resolution of the superhyperfine splitting varies with angle, being poorest in the ⟨110⟩ direction. We suggest that this is evidence for tunneling motion between off-center sites with the motion averaging $g_x$ and $g_y$ to give an axial $g$ tensor. Since the ground state and ion size are different for $Cr^{5+}$ and for $Mo^{5+}$, the $Cr^{5+}$ might move to some other off-center sites rather than the ⟨110⟩ sites. But the poor resolution of the superhyperfine lines in the ⟨110⟩ direction strongly suggests that the motion is the same in $Cr^{5+}$ as in $Mo^{5+}$. Superhyperfine structure is not seen for $Mo^{5+}$ because for a $d_{xy}$ ground state the electron charge density does not point in the direction of the $Y^{3+}$ ions.

The question of why $Cr^{5+}$ has a $d_{z^2}$ ground state and $Mo^{5+}$ a $d_{xy}$ is not easily answered. $Cr^{5+}$ is a slightly smaller ion than $Mo^{5+}$. But $Cr^{5+}$ has a $d_{z^2}$ ground state in both $YPO_4$ and $YVO_4$ and $P^{5+}$ is only ~60% the size of $V^{5+}$. So the size of the impurity ion relative to the ion it replaces does not seem to explain the difference.

There are several other systems where

off-center motion of substitutional impurities has been reported. Shechter *et al.* (*14*) have interpreted anomalies in the Mössbauer spectrum of $^{57}$Co-doped $ThO_2$ in terms of motion of the daughter $Fe^{2+}$ in a "wine bottle"-shaped potential centered at the thorium site. In this case the $Fe^{2+}$ is surrounded by a cube of eight $O^{2-}$ ions.

$Li^+$ in KCl (and in many analog systems such as $RbCl:Ag^+$, $CSF:Na^+$, and $KCl:Cu^+$) has been extensively studied (*15*) and shown conclusively (*16*) to move off the octahedrally coordinated $K^+$ site along the ⟨111⟩ crystal directions. The $Li^+$ does not freeze in a particular potential minima but tunnels between the eight ⟨111⟩ sites. Calculations (*16*) indicate that there are secondary potential minima along the ⟨110⟩ and ⟨100⟩ directions.

As far as we know $YVO_4:Mo^{5+}$ is the first example where the potential minima are deep enough so that the ion does not tunnel or thermally hop between sites at 4.2K. In this case freezing may be possible due to the lower symmetry of the V site compared to the $K^+$ site in KCl. Calculations of the equilibrium positions would be of interest not only because of the different coordinations but also because the bonding is highly covalent rather than ionic.

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