EPR of VO^{2+} in $ZnTiF_6 \cdot 6H_2O$

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Electron Paramagnetic Resonance (EPR) studies have been carried out on the vanadyl (VO^2) ion doped in single crystals of $ZnTiF_6 \cdot 6H_2O$. The spectra indicate the presence of one set of eight lines characteristic of only one occupation site. The V–O bond orientation is along one of the three $Zn-H_2O$ bond directions in the trigonally distorted $[Zn(H_2O)_6]$ octahedra. This behaviour is unlike that reported for vanadyl ion substituting for the $M(H_2O)_6$ sites in the Tutton salts, alums and $AlCl_3 \cdot 6H_2O$. The Spin-Hamiltonian and bonding parameters for the $[VO(H_2O)_5]$ complex have been evaluated. The hyperfine linewidths are 0.8 mT at 300 K and 77 K. No proton superhyperfine structure was observed at both these temperatures.

Introduction

Over the past three decades Electron Paramagnetic Resonance (EPR) has been found to be a useful tool for investigating the structural phase transitions in crystalline lattices. Among the variety of paramagnetic impurities that are available for investigating these transitions, the vanadyl $(VO)^{2+}$ ion has proved extremely useful due to the simple eight line hyperfine spectrum [1]. The complexity of it's spectrum in any lattice is due to the presence of either a multiple site occupancy within the same unit cell or more than one preferred orientation within one site. In the $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ Tutton salt [2], the V–O bond has three possible orientations along the three $Zn-H_2O$ bond directions. However, the occupancy is highest for the longest bond and lowest for the shortest.

In the case of Alums [3–5] the occupancy is the same along all the three bond directions due to the identical $Al-H_2O$ bond distances within the trigonally distorted $[Al(H_2O)_6]^{3+}$ octahedron. The same observation was reported for $AlCl_3 \cdot 6H_2O$ [6]. In these lattices the spectra consisted of three sets of eight lines of equal intensity. Recently several studies [7–10] have been reported on Tutton salts doped with VO^{2+} with a view to study the proton superhyperfine structure observed on some of the vanadyl hyperfine lines at some of the orientations. An ENDOR study of VO^{2+} doped $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ has been reported [11], resulting in a clear understanding of the behaviour of the ion.

The phase transitions of $M^{II}M^{IV}F_6 \cdot 6H_2O$ (M^{II} = Zn, Mg, Cd, Co, Ni, Fe M^{IV} = Si, Ti, Zr) have been well investigated using Mn^{2+} as probe [12]. The static-dynamic Jahn-Teller effect of Cu^{2+} incorporated at high symmetry $M^{II}(H_2O)_6$ sites in these crystals has also been reported [13, 14]. So far no study with VO^{2+} impurity has been reported in these lattices. This study we investigate i) the effect of phase transition on the Vanadyl spectrum, ii) the number of preferred orientations within the $M^{II}(H_2O)_6$ octahedron compared to the observations in Tutton salts and alums, and iii) any proton superhyperfine structure.

1. Experimental

Crystals were grown at room temperature from aqueous solution containing zinc metal and TiO_2 dissolved in 48% HF. VO^{2+} impurity was introduced as $VOSO_4$ ($<0.1\%$). EPR spectra were recorded on a Varian E-9 spectrometer equipped with the Varian low temperature accessory. The microwave frequency was between 9.0 and 9.5 GHz, with magnetic field modulation at 100 kHz.

Early crystallographic data indicate that the fluotitanates belong to the $R\bar{3}$ space group with $Z = 1$, being isomorphous to the fluosilicates [15]. Recent crystallographic studies on $ZnTiF_6 \cdot 6H_2O$ and $MnTiF_6 \cdot 6H_2O$ confirm the above space group. They also report the phase transitions to be of first order involving reorientations of the $Zn(H_2O)_6$ as well as TiF_6 octahedra [16].

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2. Theory

In the theory of the $[VO(H_2O)_5]^{2+}$ complex given by Ballhausen and Gray [15], V^{4+} is under the influence of a strong axial field, and the spin-Hamiltonian is

$$\mathscr{H} = g_{\parallel}\,\beta H_z S_z + g_{\perp}\,\beta(H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y)\,. \tag{1}$$

With the magnetic field in a general direction the resonance field is given by

$$\begin{aligned} \boldsymbol{H} = H_0 &- (K m_I/g\,\beta) \\ &- [B^2(A^2+K^2)/4H_0 g^2 \beta^2 K^2][I(I+1) - m_I^2] \\ &- [(A^2-B^2) g_{\parallel}^2 g_{\perp}^2/2H_0 g^2 \beta^2 K^2]\sin^2\theta\cos^2\theta\, m_I^2\,, \end{aligned} \tag{2}$$

where

$$g^2 = g_{\parallel}^2\cos^2\theta + g_{\perp}^2\sin^2\theta, \qquad H_0 = h\nu/g\,\beta$$

and

$$K^2 g^2 = A^2 g_{\parallel}^2 \cos^2\theta + B^2 g_{\perp}^2 \sin^2\theta$$

(θ is the angle made by the z-axis, viz., the V–O bond direction, with the magnetic field in the plane containing the c-axis.)

3. Results and Discussion

Angular variation studies at room temperature were carried out in a plane i) perpendicular to the c-axis and ii) containing the c-axis. The presence of a small amount of Mn^{2+} impurity (< 50 ppm) was seen in the form of a weak characteristic spectrum, extremal along the c-axis and minimal perpendicular to it. The latter was invariant in the plane perpendicular to the c-axis. These features were used to identify the orientation of the V–O bond and correlate this with the observed VO^{2+} spectrum (Figure 1).

Only one set of eight hyperfine (hf) lines ($\Delta H_{pp} < 1$ mT) was observed in all directions, indicating the presence of one V–O bond orientation. With the c-axis in the H plane, an angular dependence study showed the presence of one maximum (Fig. 1 a) and one minimum along the directions 2 and 1 in Fig. 2, respectively, for the vanadyl hyperfine lines. The maximum hf line separation was smaller and the minimum separation was greater than those reported in [2–5] for Tutton salts and alums. The extra hyperfine lines seen in Fig. 1 a, which were invariant when rotation was about the c-axis, were due to Mn^{2+} impurity in trigonal symmetry [12]. These are verified from a crystal containing Mn^{2+} impurity.

The maximum spread of the hf lines occurred with $H \perp c$, as shown in Figure 1 a. The presence of the manganese hf lines in the central portion of the spectrum masked the perpendicular vanadyl hf lines, and to obtain the minimum spread, a powder spectrum had to be taken. Figure 1 b shows the set of eight hf lines at minimum separation from the powder spectrum. This suggested that the V–O bond orientation was neither in the plane containing the c-axis nor in the plane perpendicular to the c-axis.

For the spectrum with H along the c-axis the experimental g and A values could be fitted the equation

$$g^2 A^2 = g_{\parallel}^2 A^2 \cos^2\theta + g_{\perp}^2 B^2 \sin^2\theta\,, \quad \text{where} \quad \theta = 54^\circ\,. \tag{3}$$

(For the parameters cf. Table 1.) Hence it is clear that the V–O bond orientation is along one of the $Zn-H_2O$ bond directions, as seen from the crystal structure [15, 16], where the $M^{II}-H_2O$ bonds are known to make an angle of 54° 44′ with the c-axis (see Figure 2).

In an $M^{II}(H_2O)_6$ octahedron where all the three bond distances are identical it is surprising that the V–O bond prefers only one of these. This is in contrast to the observation of V–O substituting for $M^{III}(H_2O)_6$ in Alums [3–5], $M^{III}O_6$ in hexa-urea aluminium perchlorate [17], $M^{III}(H_2O)_6$ in $AlCl_3 \cdot 6H_2O$ [6] and MgO_6 in tris (octamethylpyrophosphoramide) magnesium perchlorate [18], where the V–O bond was found to be oriented along all the three bond directions with equal preference. In all the above systems a single set of eight lines was observed along the c-axis, indicating the equivalence of the three species

Table 1. Spin-Hamiltonian parameters for VO^{2+} in various lattices.

Lattice	$g_{\parallel}$	$g_{\perp}$	g_0	A	B	Ref.
$ZnTiF_6 \cdot 6H_2O$	1.946[a]	1.988[b]	1.974	185.2[a]	77.6[b]	This work
$Zn(NH_4)_2(SO_4)_2 \cdot 6H_2O$	1.932	1.981	1.965	182.2	71.6	[3]
$RbAl(SO_4)_2 \cdot 12H_2O$	1.932	1.975	1.961	182.2	66.6	[4]
$AlCl_3 \cdot 6H_2O$	1.929	1.974	1.959	187.0	72.0	[7]
$(Urea)_6Al(ClO)_4$	1.932	1.987	1.969	175.0	64.0	[17]

A and B are in units of 10^{-4} cm^{-1}.

[a] Errors: $g_{\parallel}$ (± 0.002), A ($+2$)

[b] Errors: $g_{\perp}$ (± 0.005), B ($+2$).

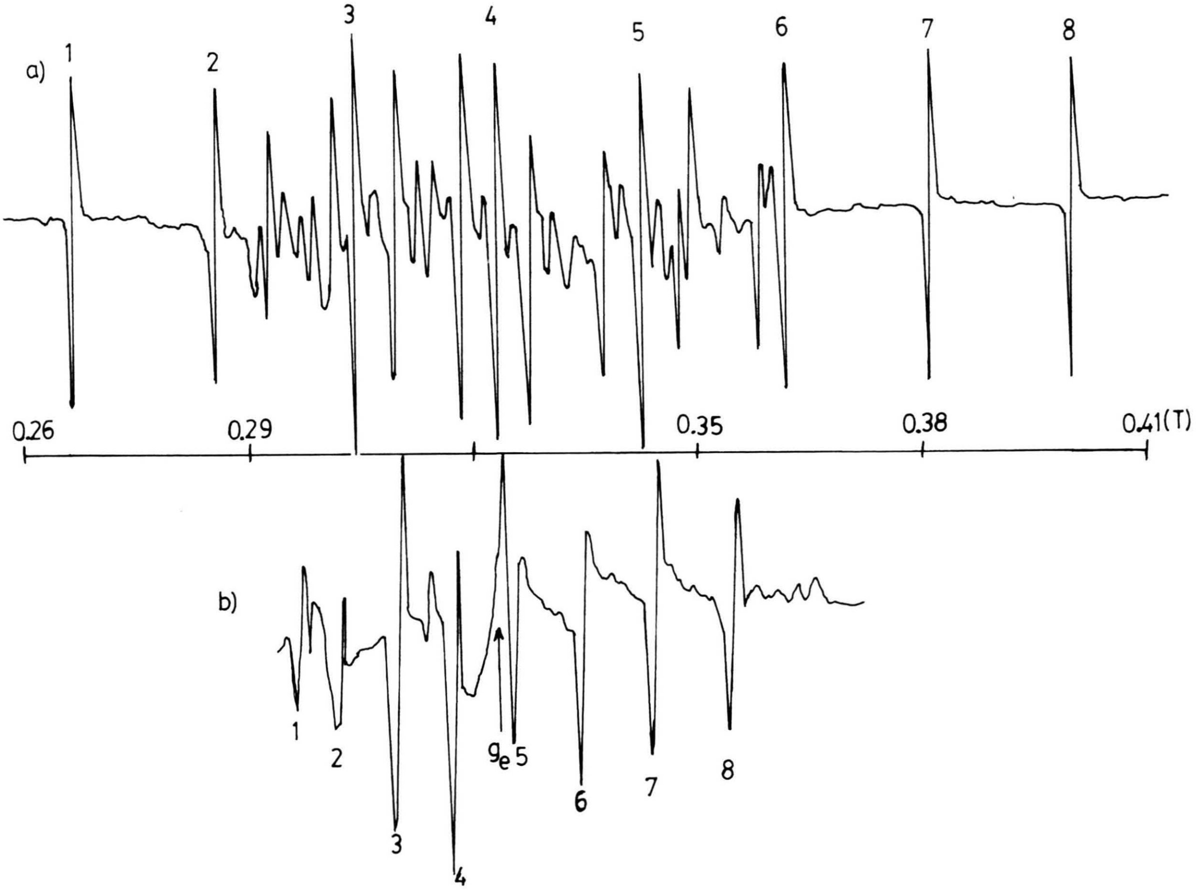

Fig. 1. a) EPR spectrum of VO^{2+} ion with the maximum spread of the hf lines with $H_\perp$ to c-axis. b) EPR powder spectrum showing the vanadyl hf lines with minimum separation.

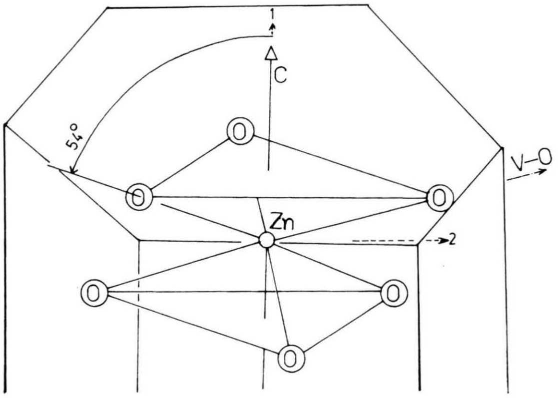

Fig. 2. V–O bond orientation within the $Zn(H_2O)_6$ octahedron inscribed inside a hexagonal crystal. Along directions marked 1 and 2 the hf spectrum shows the minimum and the maximum spread.

along the 3-fold axis. It was possible to fit (3) to the spectrum with $\theta = 54°$.

In the plane containing the c-axis the spectra, recorded at room temperature as well as at 77 K with H oriented perpendicular to the c-axis, showed no splitting of hyperfine lines. In the low temperature low symmetry phase with inequivalent sites, such a splitting of the hyperfine lines should have been observed. Intensity changes would have occurred if the three orientations, which are equally populated due to the equal Zn–O bond distances (2.078 Å [16]) in the room temperature phase, were unequally populated owing to the altered bond distances in the low temperature phase. If the low temperature low symmetry phase had resulted in inequivalent sites, a splitting of the hyperfine lines should have been observed.

At this stage it is not possible to say which of the three $Zn-H_2O$ bonds replaces the $V-O$ bond because each of these makes an identical angle (54°) with the *c*-axis (Figure 2). It is also not clear why any one of the three Zn-O directions should be preferred, as the three are identical in all respects including the hydrogen bonding patterns with the neighbouring fluorines of the TiF_6 octahedra.

Thus the Vanadyl ion with a strong axially distorted Vanadyl pentahydrate $[VO(H_2O)_5]$ complex behaves neither like the similar d^9 Cu^{2+} ion, which reflects the change from high to low symmetry [13, 14] via the Jahn-Teller effect, nor like the *S*-state Mn^{2+} ion, which is sensitive to the smallest change in the surrounding crystalline field through zero-field splitting (both axial and rhombic components).

Even though the linewidths of the hyperfine lines at room temperature and 77 K are less than 1 mT, no superhyperfine structure indicating an interaction between the unpaired electron of ^{51}V and the surrounding ligands was observed [19]. More crystals belonging to this system are being investigated in order to understand the observed differences.

The bonding parameters have been evaluated for the vanadyl pentahydrate complex in $ZnTiF_6 \cdot 6H_2O$ and compared with those for the Tutton salts and Alums. We have used the reported [20] values of optical absorption maxima, viz., $\Delta E_1 = 16.0$ kK and $\Delta E_2 = 13.0$ kK. The parameters given in Table 2 show close agreement.

Table 2. Bonding parameters for VO^{2+} in various complexes.

Complexes	ΔE_1	ΔE_2	K	β_{2}^{2*}	β_{2}^{2*}	e_{π}^{2*}	Ref.
$VO(H_2O)_5^{2+}$	16.0	13.0	0.86	1.00	0.84	0.90	This work
$VO(H_2O)_5^{2+}$	16.0	13.0	0.83	1.00	0.82	0.84	[20]
$VO(Cl)_5^{3-}$	16.4	15.5	0.77	0.98	0.71	0.79	[1]
$VO(C_2O_4)_2^{2-}$	16.6	12.6	0.74	0.98	0.78	0.98	[1]

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