EPR of VO$^{2+}$ in ZnTiF$_6\cdot 6$H$_2$O

Geetha Jayaram and V. G. Krishnan

Physics Department, Osmania University, Hyderabad-500 007, India

Z. Naturforsch. 51a, 245–248 (1996); received November 16, 1995

Electron Paramagnetic Resonance (EPR) studies have been carried out on the vanadyl (VO$^{2+}$) ion doped in single crystals of ZnTiF$_6\cdot 6$H$_2$O. 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$_2$O bond directions in the trigonally distorted [Zn(H$_2$O)$_6$] octahedra. This behaviour is unlike that reported for vanadyl ion substituting for the M(H$_2$O)$_6$ sites in the Tutton salts, alums and AlCl$_3\cdot 6$H$_2$O. The Spin-Hamiltonian and bonding parameters for the [VO(H$_2$O)$_5$] 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 its 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$_4$)$_2$Zn(SO$_4$)$_2\cdot 6$H$_2$O Tutton salt [2], the V–O bond has three possible orientations along the three Zn–H$_2$O 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$_2$O bond distances within the trigonally distorted [Al(H$_2$O)$_6$]$^{3+}$ octahedron. The same observation was reported for AlCl$_3\cdot 6$H$_2$O [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$_4$)$_2$Mg(SO$_4$)$_2\cdot 6$H$_2$O has been reported [11], resulting in a clear understanding of the behaviour of the ion.

Reprint requests to Dr. G. Jayaram.

The phase transitions of M$^{II}$M$^{IV}$F$_6\cdot 6$H$_2$O (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$_2$O)$_6$ 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$_2$O)$_6$ 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 VO(SO$_4$)$_2$ (<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 fluoritotanates belong to the R$^3$ space group with $Z = 1$, being isomorphous to the fluosilicates [15]. Recent crystallographic studies on ZnTiF$_6\cdot 6$H$_2$O and MnTiF$_6\cdot 6$H$_2$O confirm the above space group. They also report the phase transitions to be of first order involving reorientations of the Zn(H$_2$O)$_6$ as well as Ti$_6$ octahedra [16].
2. Theory

In the theory of the \([\text{VO}(\text{H}_2\text{O})_5]^{2+}\) complex given by Ballhausen and Gray [15], \(\text{V}^{4+}\) is under the influence of a strong axial field, and the spin-Hamiltonian is

\[
\mathcal{H} = g_{||} \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y).
\]  

(1)

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

\[
H = H_0 - (K m / g \beta)
\]  

(2)

\[
- \left[ B^2 (A^2 + K^2) / 4 H_0 g^2 \beta K^2 \right] [I (I + 1) - m_i^2]
\]  

\[
- \left[ (A^2 - B^2) g_{||} g_{\perp}^2 / 2 H_0 g^2 \beta K^2 \right] \sin^2 \theta \cos^2 \theta m_i^2
\]

where

\[
g^2 = g_{||}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta, \quad H_0 = h \nu / g \beta
\]

and

\[
K^2 g^2 = A^2 g_{\perp}^2 \cos^2 \theta + B^2 g_{||}^2 \sin^2 \theta
\]

(\(\theta\) is the angle made by the \(z\)-axis, viz., the \(\text{V}-\text{O}\) 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 \(\text{Mn}^{2+}\) 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 \(\text{V}-\text{O}\) bond and correlate this with the observed \(\text{VO}^{2+}\) spectrum (Figure 1).

Only one set of eight hyperfine (hf) lines (\(\Delta H_{pp} < 1\, \text{mT}\)) was observed in all directions, indicating the presence of one \(\text{V}-\text{O}\) bond orientation. With the \(c\)-axis in the \(H\) plane, an angular dependence study showed the presence of one maximum (Fig. 1a) 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. 1a, which were invariant when rotation was about the \(c\)-axis, were due to \(\text{Mn}^{2+}\) impurity in trigonal symmetry [12]. These are verified from a crystal containing \(\text{Mn}^{2+}\) impurity.

The maximum spread of the hf lines occurred with \(H \perp c\), as shown in Figure 1a. 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 1b shows the set of eight hf lines at minimum separation from the powder spectrum. This suggested that the \(\text{V}-\text{O}\) 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

\[
g^2 A^2 = g_{||}^2 A^2 \cos^2 \theta
\]  

\[+ g_{\perp}^2 B^2 \sin^2 \theta, \quad \text{where} \quad \theta = 54 \degree.
\]  

(3)

(For the parameters cf. Table 1.) Hence it is clear that the \(\text{V}-\text{O}\) bond orientation is along one of the \(\text{Zn}-\text{H}_2\text{O}\) bond directions, as seen from the crystal structure [15, 16], where the \(\text{M}^{2+}-\text{H}_2\text{O}\) bonds are known to make an angle of 54° 44' with the \(c\)-axis (see Figure 2).

In an \(\text{M}^{2+}(\text{H}_2\text{O})_6\) octahedron where all the three bond distances are identical it is surprising that the \(\text{V}-\text{O}\) bond prefers only one of these. This is in contrast to the observation of \(\text{V}-\text{O}\) substituting for \(\text{M}^{2+}(\text{H}_2\text{O})_6\) in Alums [3–5], \(\text{M}^{2+}\) in hexa-urea aluminium perchlorate [17], \(\text{M}^{2+}(\text{H}_2\text{O})_6\) in \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\) [6] and \(\text{MgO}_6\) in tris (octamethylpyrophosphoramide) magnesium perchlorate [18], where the \(\text{V}-\text{O}\) 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 \(\text{VO}^{2+}\) in various lattices.

| Lattice     | \(g_{||}\) | \(g_{\perp}\) | \(g_0\) | \(A\) | \(B\)  | Ref. |
|-------------|------------|-------------|---------|------|-------|------|
| \(\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}\) | 1.946 ¹  | 1.988 ¹   | 1.974   | 185.2² | 77.6 ² | This work |
| \(\text{Zn(NH}_3)_4\text{(SO}_4)_2 \cdot 6\text{H}_2\text{O}\) | 1.932   | 1.981     | 1.965   | 182.2 | 71.6  | [3]  |
| \(\text{RhCl}_4\text{(SO}_4)_2 \cdot 12\text{H}_2\text{O}\) | 1.932   | 1.975     | 1.961   | 182.2 | 66.6  | [4]  |
| \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\) | 1.929   | 1.974     | 1.959   | 187.0 | 72.0  | [7]  |
| \(\text{Urea})_4\text{AlCl}_4\) | 1.932   | 1.987     | 1.969   | 175.0 | 64.0  | [17] |

\(A\) and \(B\) are in units of \(10^{-4}\, \text{cm}^{-1}\).

¹ Errors: \(g_{||} (±0.002), \quad A (±2)\)

² Errors: \(g_{\perp} (±0.005), \quad B (±2)\).
showing the vanadyl hf lines with minimum separation.

It was possible to fit (3) to the spectrum with $\theta = 54^\circ$.

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.

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$_2$O)$_6$ octahedron inscribed inside a hexagonal crystal. Along directions marked 1 and 2 the hf spectrum shows the minimum and the maximum spread.
At this stage it is not possible to say which of the three Zn–H₂O 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 TiF₆ octahedra.

Thus the Vanadyl ion with a strong axially distorted Vanadyl pentahydrate [VO(H₂O)₅]²⁺ complex behaves neither like the similar d⁹ Cu²⁺ ion, which reflects the change from high to low symmetry [13, 14] via the Jahn-Teller effect, nor like the S-state Mn²⁺ 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 ⁵¹V 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 ZnTiF₆ • 6H₂O and compared with those for the Tutton salts and Alums. We have used the reported [20] values of optical absorption maxima, viz., ΔE₁ = 16.0 kK and ΔE₂ = 13.0 kK. The parameters given in Table 2 show close agreement.

### Acknowledgement

The authors wish to thank Prof. S. V. Suryanarayana, Head Department of Physics, Osmania University, Hyderabad, for his constant encouragement. We also thank Dr. T. K. Gundu Rao, R.S.I.C., I.I.T., Bombay, for help with the EPR spectrometer.

### Table 2. Bonding parameters for VO²⁺ in various complexes.

<table>
<thead>
<tr>
<th>Complexes</th>
<th>ΔE₁</th>
<th>ΔE₂</th>
<th>K</th>
<th>β₂</th>
<th>β₃</th>
<th>e₅²</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(H₂O)²⁺</td>
<td>16.0</td>
<td>13.0</td>
<td>0.86</td>
<td>1.00</td>
<td>0.84</td>
<td>0.90</td>
<td>This work</td>
</tr>
<tr>
<td>VO(H₂O)²⁺</td>
<td>16.0</td>
<td>13.0</td>
<td>0.83</td>
<td>1.00</td>
<td>0.82</td>
<td>0.84</td>
<td>[20]</td>
</tr>
<tr>
<td>VO(C₂O₄)²⁻</td>
<td>16.4</td>
<td>15.5</td>
<td>0.77</td>
<td>0.98</td>
<td>0.71</td>
<td>0.79</td>
<td>[1]</td>
</tr>
<tr>
<td>VO(C₂O₄)²⁻</td>
<td>16.6</td>
<td>12.6</td>
<td>0.74</td>
<td>0.98</td>
<td>0.78</td>
<td>0.98</td>
<td>[1]</td>
</tr>
</tbody>
</table>