EPR of VO$^{2+}$ Doped Cd$_2$ZrF$_8\cdot$6H$_2$O Single Crystals

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X-band EPR measurements have been carried out on VO$^{2+}$ doped single crystals of Cd$_2$ZrF$_8\cdot$6H$_2$O. The angular variation of the $^{19}$F superhyperfine structure did show that the VO$^{2+}$ ion occupies an interstitial site with C$_4v$ symmetry.

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Introduction

The magnetic complex associated with VO$^{2+}$ ions in M$^1$M$^3$(SO$_4$)$_2\cdot$6H$_2$O Tutton salts is the vanadyl pentahydrate [VO(H$_2$O)$_5$] complex. In these crystals V$^4+$ substitutes M$^3+$ ions, an one water molecule of the M$^3$(H$_2$O)$_5$ octahedron is replaced by O$^2-$. Since VO$^{2+}$ possesses strong directional properties it is interesting to give a complete description of the M$^3$(H$_2$O)$_5$ complex in the crystal. Conclusive evidence regarding the orientation of the complex in Tutton salts was provided only by an ENDOR study of VO$^{2+}$ in (NH$_4$)$_2$Mg(SO$_4$)$_2\cdot$6H$_2$O [1]. The proton superhyperfine structure (SHFS) along certain orientations did show that the V$^4+$ ion, substituting the Mg$^{2+}$ ion, is lifted out of the equatorial plane containing the four water molecules. In (NH$_4$)$_3$AlF$_6$, VO$^{2+}$ formed VOF$^{3-}$ according to the observed Fluorine ($^{19}$F, $I=1/2$) SHFS [2].

Recently we undertook a series of studies in lattices where both interstitial and substitutional occupation sites were possible for transition metal impurities. In ethylenediammonium hexafluorozirconate, vanadyl ions were shown to occupy two types of interstitial sites with the help of the $^{14}$N and $^{19}$F SHFS [3], whereas VO$^{2+}$ in 1,5-pentanediammonium hexafluorozirconate was found to occupy an interstitial site with the EPR spectra exhibiting a transition from isotropy to anisotropy between 353 K and 77 K [4]. In the case of Mn$^{2+}$ doped Cd$_2$ZrF$_8\cdot$6H$_2$O, Mn$^{2+}$ occupied the Zr$^{4+}$ site [5]. This was unusual in view of the existence of an isomorphous Mn$_2$ZrF$_8\cdot$6H$_2$O [6]. Here we report an EPR study of VO$^{2+}$ doped Cd$_2$ZrF$_8\cdot$6H$_2$O.

Experimental

5 mm$^3$ sized single crystals were grown from an acidic solution containing CdF$_2$ and ZrF$_4$ in stoichiometric ratio in 40% Hydrofluoric acid. The VO$^{2+}$ impurity content in the solution was <0.1% and in the crystals <100 ppm. Cd$_2$ZrF$_8\cdot$6H$_2$O monoclinic [7] with space group B2/b and unit cell dimensions $a=11.464$ Å, $b=13.732$ Å, $c=8.223$ Å and $\gamma=119.82^\circ$ with $Z=4$.

In the CdF$_3$O$_5$ polyhedron the arrangement of atoms is pentagonal bipyramidal. The equatorial plane is formed by CdF$_4$O$_5$ with two oxygens occupying the apical positions. The Cd-F distances vary between 2.295 Å and 2.483 Å. Eight fluorines form a distorted cube around the Zirconium ion. These can be divided into two sets of four fluorines with Zr-F distances in each set varying between 2.074 Å and 2.132 Å. Figure 1 (a) and (b) show the geometry around the Cd$^{2+}$ and Zr$^{4+}$ ions.

EPR spectra were recorded at room temperature on Varian E-12 and JEOL – RE-3X spectrometers operating in the X-band (9.42–9.46 GHz), employing 100 kHz magnetic field modulation.

Results

EPR spectra were recorded in two mutually perpendicular planes. In a general direction in the ab* plane (b* chosen perpendicular to a-axis), the spectrum was complicated due to number of weak lines, presumably due to the interaction of the $^{51}$V unpaired electron ($S=1/2$, $I=7/2$), with more than one equivalent as well as inequivalent fluorines. This would split the Vanadium hyperfine lines into smaller compo-

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Angular variation showed that the eight hf lines had their maximum separation on either side of the $z$-axis making an angle of $(16 \pm 2)^{\circ}$. However, these hyperfine lines were broad, $\Delta H_{pp} = 25-35$ G (Figure 2(a)). A slight rotation from these directions resulted in the splitting of the 8 hyperfine lines into a large number of weak lines which could not be followed in the angular variation. This feature was seen throughout the $ab^*$ plane. The large linewidth could be attributed to unresolved $^{19}$F SHFS.

In the $bc$ plane the spectrum consisted of eight closely spaced vanadium hyperfine lines, each of which was split into ten components. A rotational study in this plane showed no measurable angular variation of the hf lines, a feature typical of axial symmetry at the VO$_2^+$ sites. The only change seen throughout this plane was in the positions of the superhyperfine components. There was considerable overlap among these lines for the low field $^{51}$V hf lines. Figure 2(b) shows a typical well resolved spectrum in the $b^*c$ plane.

The spin-Hamiltonian used to describe the spectrum is given by

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

The magnetic field positions of the Vanadium hf lines along the $z$-axis are calculated by the following general formula for rhombic symmetry:

$$
H_z(m_f) = H_z^0 - A_z m_f - [(A_z^2 + A_y^2)/4 H_z^0] [I(I+1) - m_f^2].
$$

For the case of axial symmetry we have

$$
A_z = A; \quad A_x = A_y = B; \quad g_z = g_\parallel; \quad g_x = g_y = g_\perp.
$$

The expression describing the line positions along a perpendicular direction is obtained by a cyclic permutation of the subscripts of the above equation. The evaluated parameters are given in Table 1 along with other reported values.

From the angular variation of the spectra in the VO$F_4$ plane, $A_{\text{max}}(^{19}F_{eq})$ and $A_{\text{min}}(^{19}F_{eq})$ are calcu-
Fig. 2. EPR spectrum a) in the $a^*b$ plane for $H$ oriented at $+18^\circ$ with respect to $a$-axis and b) in the $b^*c$ plane.

Table 1. Spin-Hamiltonian parameters of VO$^{2+}$ ions in some lattices.

<table>
<thead>
<tr>
<th>System</th>
<th>$\theta_\parallel$</th>
<th>$\theta_\perp$</th>
<th>$A^*$</th>
<th>$B^*$</th>
<th>$A_{\text{max}}^*$ (19F)</th>
<th>$A_{\text{min}}^*$ (19F)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$_2$ZrF$_8$·6H$_2$O</td>
<td>1.935</td>
<td>1.981</td>
<td>185</td>
<td></td>
<td>76.4</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td>[H$_3$N(CH$_2$)$_2$NH$_3$]·ZrF$_6$</td>
<td>1.956</td>
<td>1.997</td>
<td>179</td>
<td>68</td>
<td>9.5</td>
<td>5.0</td>
<td>[3]</td>
</tr>
<tr>
<td>(NH$_4$)$_3$AlF$_6$</td>
<td>1.937</td>
<td>1.977</td>
<td>178</td>
<td>64</td>
<td>34.7</td>
<td>13.4</td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_3$Zn(SO$_4$)$_2$·6H$_2$O</td>
<td>1.933</td>
<td>1.981</td>
<td>183</td>
<td>71.4</td>
<td>–</td>
<td>–</td>
<td>[12]</td>
</tr>
<tr>
<td>(NH$_4$)$_3$InCl$_4$·H$_2$O</td>
<td>1.945</td>
<td>1.985</td>
<td>173</td>
<td>63.8</td>
<td>–</td>
<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>(NH$_4$)$_3$SbCl$_5$</td>
<td>1.948</td>
<td>1.979</td>
<td>169</td>
<td>62.8</td>
<td>–</td>
<td>–</td>
<td>[11]</td>
</tr>
<tr>
<td>(NH$_4$)$_2$Zn$_2$(SO$_4$)$_3$</td>
<td>1.934</td>
<td>1.979</td>
<td>183</td>
<td>72.5</td>
<td>–</td>
<td>–</td>
<td>[8]</td>
</tr>
<tr>
<td>NH$_4$Al(SO$_4$)$_2$·12H$_2$O</td>
<td>1.933</td>
<td>1.981</td>
<td>183</td>
<td>71.4</td>
<td>–</td>
<td>–</td>
<td>[8]</td>
</tr>
</tbody>
</table>

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

Discussed and given in Table 1 along with corresponding values for VO$^{2+}$ in [H$_3$N(CH$_2$)$_2$NH$_3$]ZrF$_6$ and (NH$_4$)$_3$AlF$_6$.

Discussion

In earlier studies the vanadyl ion was found to occupy sites where a) the V-O bond replaces an M-O bond as in Tutton salts and langebenites [8], hexaurea AlX$_3$ (X = ClO$_4$, Cl, Br, I) [9, 10], and b) the V-O bond in oriented perpendicular to the plane containing the MX$_4$ ion (X = Cl, Br) as in (NH$_4$)$_2$SbCl$_5$ [11]. From the structure of Cd$_2$ZrF$_8$·6H$_2$O, four fluorines and one oxygen surround the Cd$^{2+}$ ion forming the equatorial plane (Figure 1 (a)). The Cd atom is lifted above this plane by 0.3 Å. The F-Cd-F bond angles deviate considerably from orthogonality, viz., 62.3°, 80.5° and 64.1°. These features prevent the four fluorines from being equivalent for any orientation of the external magnetic field. Hence the V-O bond orienting itself along a Cd-O bond does not explain the above observation.

We consider two possible orientations of the V-O bond with reference to the distorted cube of eight fluorines around the Zr$^{4+}$ ion: The V-O bond 1) replaces any of the Zr-F bonds, 2) is in a position intermediate to any two Zr-F bonds, resulting in three
distinct mutually perpendicular orientations. In the first case, if the shortest pair of Zr-F bonds are replaced, then the probability of replacing the remaining three pairs of Zr-F bonds would decrease with increasing bond lengths, as observed in (NH₄)₂Zn(SO₄)₂·6H₂O [12]. One would then expect four sets of eight hf lines with varying intensities. The second possibility would result in three sets of eight lines along a general direction. But when the magnetic field is along one of the three V-O bond orientations, the spectrum would consist of one set of eight lines with maximum separation and a second set with minimum separation and twice the intensity. This is due to one V-O bond oriented parallel and two V-O bonds oriented perpendicular to the magnetic field. The observed spectra did not correspond to either of the above two possibilities.

The ten SHFS lines could be considered as two sets of five lines due to two independent sets of four fluorines. The V⁴⁺ ion occupies an interstitial position in the plane formed by either set of four fluorines within the distorted ZrF₈ cube (Figure 1(b)). The V-O bond is oriented perpendicular to the plane and makes an angle of +18° with the a-axis. When the magnetic field is along the V-O bond of one of the VOF₄ complexes, the SHFS on each of the ⁵¹V hf lines is smeared and appears only as a broadening. This is due to the two fluorine planes being relatively twisted to each other by about 40°. Figure 3 shows the orientation of the V-O bonds as well as the twisting of the fluorine planes. It is not unusual for the V-O bond to bring about small twists or tilts of the VOF₄ complexes [13].

From the comparison of the parameters for ¹⁹F in VO²⁺ doped Cd₂ZrF₈·6H₂O and (NH₄)₃AlF₆ one can say that the arrangement of the four fluorines around V⁴⁺ ion is nearly the same in both the systems. Thus there is a fairly tight in-plane σ-bond. The superhyperfine splitting would have been larger in the former lattice if the V⁴⁺ ion had replaced the Zr⁴⁺ ion, because the Zr-F bond distances are rather short (2.074–2.132 Å).

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