CHAPTER 8

ELECTRON SPIN RESONANCE OF VO$_2^+$ DOPED

ZnSeO$_4$.6H$_2$O SINGLE CRYSTALS

ABSTRACT

The electron spin resonance spectrum of the vanadyl ion doped in single crystals of zinc selenate hexahydrate is studied at 296K and in the X-band frequency range. The VO$_2^+$ enters the Zn$^{2+}$ site. A correlation between V=O bond and Zn-O bond is observed. The spin-Hamiltonian parameters at 296K have been calculated.

INTRODUCTION

In recent years, several ESR studies of VO$_2^+$ ion in different crystal lattices have been reported. ESR of randomly oriented vanadyl ions in solutions and single crystals has been studied by several investigators. It is found that the vanadyl ions are preferentially oriented in crystals like GeO$_2$, Alums, and Tutton salts. In GeO$_2$,

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The contents of this chapter have been published in phys. stat. sol. (b) 115, k113 (1983).
the cation is surrounded by a regular octahedron of oxygens. The alums and Tutton salts possess almost regular octahedra of water molecules. The water octahedra surround the trivalent cation in the alums and the divalent cation in Tutton salts. On doping the above mentioned crystals with $\text{VO}_2^+$, the cations surrounded by water or oxygen octahedra are replaced by $\text{V}^{4+}$ of $\text{VO}_2^+$. The $\text{V}^{4+}$ can thus have the necessary octahedral coordination as described by Ballhausen and Gray for the case of $\text{VO} (\text{H}_2\text{O})_5^{2+}$. The $\text{V}=\text{O}$ bond will then be preferentially along the axes of the octahedron.

This Chapter describes the ESR of $\text{VO}_2^+$ in $\text{ZnSeO}_4\cdot6\text{H}_2\text{O}$ single crystals at 296K. It is felt that it would be interesting to study the ESR of $\text{VO}_2^+$ in $\text{ZnSeO}_4\cdot6\text{H}_2\text{O}$ to obtain the information about the structure of the vanadyl complex in the lattice. The ESR of $\text{Cu}^{2+}$, $\text{Co}^{2+}$, $\text{Ni}^{2+}$ and $\text{Mn}^{2+}$ in $\text{ZnSeO}_4\cdot6\text{H}_2\text{O}$ has been reported earlier.\textsuperscript{10-12}

CRYSTAL STRUCTURE

The crystal structure of $\text{ZnSeO}_4\cdot6\text{H}_2\text{O}$ has not been determined but it is isomorphous to $\alpha$-$\text{NiSO}_4\cdot6\text{H}_2\text{O}$. The crystal structure of $\alpha$-$\text{NiSO}_4\cdot6\text{H}_2\text{O}$ and its deuterate has been determined.\textsuperscript{13-15} The unit cell is tetragonal with space group $\text{P}4_{1}2_{1}2$ containing four molecules. The
unit cell dimensions for \( \alpha \)-NiSO\(_4\).6H\(_2\)O are

\[ a_0 = b_0 = 0.6790 \text{ nm and } c_0 = 1.8305 \text{ nm}. \]

Figure 8.1 shows a projection of one half of a unit cell on the (001) plane along the c axis. The two layers at \( z = 0 \) and \( z = c_0/4 \) are depicted here with the relative positions of Ni, S and O atoms. The numbers within circles represent the coordinates in units of \( c_0 \) along the c axis as determined by Beevers and Lipson.\(^{13}\) The numbers in parentheses indicate the five nonequivalent oxygen atoms as denoted by O' Connor and Dale.\(^{15}\)

The nickel and sulfur atoms are in the special positions

\[ 4(a) \quad x,x,0; \bar{x},\bar{x},\frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{4}; \]

\[ \frac{1}{2} + x, \frac{1}{2} - x, \frac{3}{4} \]

and all others are in the general positions

\[ 8(b) \quad x,y,z; \bar{x},\bar{y},\frac{1}{2} + z; \frac{1}{2} - y, \frac{1}{2} + x, \frac{1}{4} + z \]

\[ \frac{1}{2} + y, \frac{1}{2} - x, \frac{3}{4} + z; y,x,\bar{z}; \bar{y},\bar{x},\frac{1}{2} - z; \]

\[ \frac{1}{2} - x, \frac{1}{2} + y,\frac{1}{4} - z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{4} - z \]

In this structure the nickel atoms are octahedrally surrounded by six water molecules. All the bond angles of
FIG. 8.1 PROJECTION OF ONE-HALF OF A UNIT CELL OF α-NiSO₄·6H₂O ON THE (001) PLANE. TWO LAYERS OF Ni(H₂O)⁶⁺ AND SO₄⁻ GROUPS ARE DEPICTED HERE WITH THEIR RELATIVE POSITION ALONG THE c-AXIS.
O-Ni-O within a Ni(D$_2$O)$_6^{2+}$ group are close to $90^\circ$, forming nearly a perfect octahedron. The major difference among the six water molecules about Ni$^{2+}$ is that O(1) and O(2) have two hydrogen bonds, while O(3) has three. The O(3) acts as a proton acceptor and its negative charge should be diminished by the additional hydrogen bonding. The oxygen atoms of type 1 and 2 are more strongly bonded to Ni$^{2+}$ than that of type 3. The Ni(H$_2$O)$_6^{2+}$ and SO$_4^{2-}$ groups form a layer lying in the (001) plane at positions of 0, $1/4$, $1/2$ and $3/4$ in units of $c_0$. The four ions in the unit cell are equivalent except for the orientations of their tetragonal axes. Each of the ion's tetragonal axes is tilted by an angle $\alpha$ from the crystal c axis in a plane defined by the c axis and the ab bisector. There are two such planes, and each contains the axes of two ions with the tilt of $\alpha$ being opposite for these ions.

Experimental details and crystal growth are given in Chapter 2.

RESULTS AND DISCUSSION

The ESR signal consisted of a number of overlapping angular dependent eight line hyperfine patterns, each produced by ions located at a specific site. These eight
line patterns result from the hyperfine coupling of a single unpaired electron with a $^{51}$V (99.8% abundant, spin = 7/2) nucleus. At least two chemically different sites having differing intensities (14:1) were observed for certain orientations of the crystal. However, we will deal only with the intense vanadyl center. For an arbitrary orientation of the crystal, the crystal symmetry allows four symmetry related but magnetically inequivalent orientations for the intense vanadyl center. When the magnetic field is in the ac or ab plane the four orientations become equivalent in pairs. This multiplicity is reduced in special orientations; for example, when the magnetic field lies along c or a axes (Figure 8.2, 8.3) all spectra coalesce into a single one. Detailed analysis has been carried out only for the intense vanadyl center. Figure 8.4 shows the spectrum of site I with B||z axis of one of the four inequivalent vanadyl complexes. Figure 8.5 shows the angular variation of hyperfine lines of site I in the zx plane.

The spectrum of VO$^{2+}$ at site I is described by a spin-Hamiltonian for an orbitally non-degenerate electron;

$$H = \beta \mathbf{S}.\mathbf{g}.\mathbf{B} + \mathbf{S}.\mathbf{A}.\mathbf{I}$$

where $S = 1/2$ and $I = 7/2$. Additional terms including the quadrupole and nuclear Zeeman interactions are ignored,
FIG. 8.2 ESR SPECTRUM OF VO$^{2+}$ DOPED ZnS:O$_4$.6H$_2$O SINGLE CRYSTALS AT 296K WITH B PARALLEL TO THE c-AXIS.
FIG. 9.3 ESR SPECTRUM OF VO$^{2+}$ DOPED ZnSeO₄·6H₂O SINGLE CRYSTALS AT 296K, WITH B PARALLEL TO THE £-AXIS.
FIG. 8.4 ESR SPECTRUM OF VO$^{2+}$ DOPED ZnSe$_{0.6}$-Q$_{0.4}$ SINGLE CRYSTALS AT 296K; WITH B PARALLEL TO THE Z-AXIS.
FIG. 8.5 A PLOT OF THE POSITIONS OF THE HYPERFINE LINES OF VO$^{2+}$ DOPED ZnSeO$_4$·6H$_2$O SINGLE CRYSTALS AT 296 K IN THE XX PLANE.
as these terms are sufficiently small to be neglected. The field position of the mth hyperfine line correct to second-order of perturbation for the orthorhombic case is given by Eq. (2.17). However, $\mathbf{g}$ and the hyperfine tensors are found to be axially symmetric thus permitting the use of perturbation results for the axial symmetry first given by Bleaney.\textsuperscript{16}

The spin-Hamiltonian parameters observed for VO\textsuperscript{2+} in ZnSeO\textsubscript{4}.6H\textsubscript{2}O are given in Table 8.1. In the table, $\theta$ is the angle between the c axis and the z axis and $\phi$ is the angle between the a axis and the projection of z on the ab plane. The spin-Hamiltonian parameters ($\|\downarrow\|$) were also determined from the spectrum of finely crushed ZnSeO\textsubscript{4}.6H\textsubscript{2}O:VO\textsuperscript{2+} single crystals (Figure 8.6) and are included in Table 8.1. The accuracy of the parameters determined from the powder spectrum is limited by the linewidths. The results in Table 8.1 show that $\mathbf{g}$ and $\mathbf{A}$ tensors are nearly axially symmetric. The principal values of these tensors observed here are approximately what one would expect for a VO\textsuperscript{2+} center.

In VO\textsuperscript{2+} containing materials including complexes in solution, the vanadium V\textsuperscript{4+} ion is usually surrounded by a highly distorted octahedron of oxygen ions. One of these is much closer than the other and this defines
Table 8.1. The spin-Hamiltonian parameters for V\textsuperscript{2+} in ZnSeO\textsubscript{4}.6H\textsubscript{2}O at 296K. A values are in units of 10\textsuperscript{-4}cm\textsuperscript{-1}.

<table>
<thead>
<tr>
<th>Spin-Hamiltonian parameters</th>
<th>Site I</th>
<th>Powder</th>
</tr>
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<tbody>
<tr>
<td>(A_\parallel)</td>
<td>182.00±1.0</td>
<td>183.0</td>
</tr>
<tr>
<td>(A_\perp)</td>
<td>72.80±1.0</td>
<td>72.0</td>
</tr>
<tr>
<td>(g_\parallel)</td>
<td>1.917±0.002</td>
<td>1.917</td>
</tr>
<tr>
<td>(g_\perp)</td>
<td>1.974±0.002</td>
<td>1.976</td>
</tr>
<tr>
<td>(\theta)</td>
<td>60°± 1°</td>
<td>-</td>
</tr>
<tr>
<td>(\phi)</td>
<td>74°± 2°</td>
<td>-</td>
</tr>
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</table>
ESR SPECTRUM OF A PO-DER SAMPLE (CRUSHED) OF THE VO₂⁺ DOPED
Zn₈O₄.6H₂O AT 296K.
the axial direction (z axis) for the VO\(^{2+}\) ion, and the remaining oxygens provide the C\(_4\) point symmetry of this group. The Zn\(^{2+}\) site in ZnSe\(_0.4\)\(\cdot\)6H\(_2\)O provides a very suitable surrounding for the VO\(^{2+}\) complex as the zinc is surrounded by six water molecules. When vanadyl ion enters the zinc site, it orients itself along one of the Zn-H\(_2\)O bond direction to form \([\text{VO(H}_2\text{O)}\text{]}^{2+}\) complex. Borcherts and Kikuchi\(^5\) found that among the three a priori expected directions of the V=O bond in vanadyl doped in Zn Tutton salts, the predominant species was found to be the one with the V=O bond taking up the direction of the longest Zn-H\(_2\)O bond. However, a comparison of the value of \(\theta\) and \(\phi\) obtained in this experiment with theoretical values of \(\theta\) and \(\phi\) calculated from the data of Beevers and Lipson\(^13\) and Nizamutdinov et al.\(^12\) for different Zn-H\(_2\)O bonds (Table 8.2) indicates that the z axis is nearly along the shortest Zn-H\(_2\)O bond direction i.e. Zn-H\(_2\)O (1). On the other hand it is found that Cu\(^{2+}\) enters the lattice at Zn\(^{2+}\) sites with z axis nearly along the longest Zn-H\(_2\)O bond direction, i.e. Zn-H\(_2\)O (3).\(^11\)
Table 8.2. The values of $\theta$ and $\phi$, calculated for different Ni-O bond lengths in $\alpha$-NiSO$_4$.6H$_2$O.

<table>
<thead>
<tr>
<th>M-O</th>
<th>Bond length (nm)</th>
<th>$\theta$ (deg.)</th>
<th>$\phi$ (deg.)</th>
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<tr>
<td>Ni-O (1)</td>
<td>0.202</td>
<td>62.1</td>
<td>81.5</td>
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<tr>
<td>Ni-O (2)</td>
<td>0.207</td>
<td>60.23</td>
<td>7.6</td>
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<tr>
<td>Ni-O (3)</td>
<td>0.210</td>
<td>42.1</td>
<td>-45.1</td>
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REFERENCES