CHAPTER - V

EPR AND OPTICAL ABSORPTION STUDY OF VO$^{2+}$ DOPED IN CESIUM SULPHATE SINGLE CRYSTAL

5.1 Introduction

The sulphates of ammonium, rubidium and cesium are isomorphous with K$_2$SO$_4$. The crystal structure of this isomorphous series has been determined very accurately by many researchers. The EPR studies of Mn$^{2+}$ in K$_2$SO$_4$ [1] and (NH$_4$)$_2$SO$_4$ were first reported by Chowdari and Venkateswarlu [2]. Further investigation on these systems were carried out by Freeman et al [3] and Abulsoyirov et al [4], Jagannadhan and Venkateswarlu [5]. Abulsoyirov et al [6] also studied Mn$^{2+}$ doped Cs$_2$SO$_4$ by EPR. The present chapter deals with EPR and optical absorption investigations study of VO$^{2+}$ doped Cs$_2$SO$_4$ which hitherto has remained unexplored by both absorption processes.

5.2 Crystal Structure

The crystal structure of cesium sulphate has been determined by Ogg [7]. Recently Schlemper and Hamilton...
have redetermined its structure by neutron diffraction [8]. The orthorhombic unit cell of Cs₂SO₄ (Space group Pnma) has dimensions at 25°C a = 0.6218 b = 1.0884 and c = 0.8198 nm. The general positions of atoms in the space group Pnma are

(re) ± (u, 1/4, v; u+.1/4, 1/2 - v)

(8d) ± (x,y,z; x+1/2,1/2-y, 1/2-z; x, 1/2-y, z; 1/2-x, y,z+1/2)

with parameters for Cs₂SO₄ given in Table 5-I.

Table 5.I. The positions of the various atoms in a unit cell of Cs₂SO₄ at 25°C [9].

<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(i)</td>
<td>(4c)</td>
<td>+0.250</td>
<td>+0.417</td>
<td>-0.311</td>
</tr>
<tr>
<td>Cs(II)</td>
<td>(4c)</td>
<td>+0.250</td>
<td>+0.308</td>
<td>+0</td>
</tr>
<tr>
<td>S</td>
<td>(4c)</td>
<td>+0.250</td>
<td>+0.417</td>
<td>+0.250</td>
</tr>
<tr>
<td>O(1)</td>
<td>(4c)</td>
<td>+0.250</td>
<td>+0.417</td>
<td>+0.680</td>
</tr>
<tr>
<td>O(1)</td>
<td>(4c)</td>
<td>+0.250</td>
<td>-0.455</td>
<td>+0.311</td>
</tr>
<tr>
<td>O(3)</td>
<td>(8d)</td>
<td>+0.53</td>
<td>+0.353</td>
<td>+0.311</td>
</tr>
</tbody>
</table>
The cesium ion in two planes b/2 apart do not have equivalent positions. Of the eight Cs⁺ ions in the unit cell, the four Cs⁺(I) - type are bonded [7] to eleven oxygen atoms each and the remaining four CS⁺(II) - type to nine oxygen atoms each. The distance of closest approach is same for both kinds and is Cs-0 = 0.310 nm.

5.3 Experimental

Single crystals of Cs₂SO₄ doped with VO²⁺ were grown from an aqueous solution of Cs₂SO₄ added with small amount of (0.5% by weight) VO₂SO₄ at room temperature by slow evaporation method. EPR spectra were recorded on a JEOL-JES-RE2X-band EPR Spectrometer at RT. The optical absorption spectrum was recorded on CIBA corning spectrometer 2800 (England) at RT. (Fig. 5.1).

5.4 Theory

Vanadium in its tetravalent state invariably exists as the molecular VO²⁺ ion (vanadyl ion). This molecular ion has been the subject of extensive EPR [9] and optical absorption studies [10] in a variety of host lattices. In an octahedral symmetry the single unpaired 'd' electron occupies two
energy levels viz. $^2E_g$ and $^2T_{2g}$ latter being the ground state. If some how, the symmetry is lower than octahedral, then, these levels split further into $(^2B_{2g}, ^2E_g)$ and $(^2B_{1g}, ^2A_{1g})$ levels respectively [11]. The EPR spectra have been analysed using a spin Hamiltonian for an orbitally nondegenerate electron ($s = \frac{1}{2}$, $I = 7/2$ for VO$^{2+}$ ion) [12]

$$= S \cdot \tilde{g} \cdot H + S \cdot \tilde{A} \cdot \tilde{I}.$$ (6.1)

Where the symbols have their usual meaning, the $g$ and $A$ tensors are assumed to possess coincident axes. The expressions given by Bleany [13] are used for the solution of the spin Hamiltonian.

5.5 Results and discussions

It is well known that EPR and optical data can be correlated to obtain useful information about bonding in vanadyl complexes. EPR study of VO$^{2+}$ ions doped in Cs$_2$SO$_4$ have been reported earlier [9]. We have grown single crystals of Cs$_2$SO$_4$ with VO$^{2+}$ ion and found that our EPR results are the same as those of Jain et al. It has been suggested by Jain et al [14] that all the vanadyl complexes in X$_2$SO$_4$ where X= Rb, K etc.; are essentially having axial
symmetry and almost the same spin Hamiltonian parameter (SHP). Therefore we have used the values of SHP obtained for powder spectrum at RT and optical absorption values for the following relations [11].

\[ \Delta g_{\|} = - \frac{8\lambda\beta^2}{\Delta_{\|}}; \quad A_{\|} = P \left[ - \frac{4}{7} + K \right] - \frac{8\lambda\beta^2}{\Delta_{\|}} - \frac{6\lambda\gamma^2}{7\Delta_{\perp}} \]

\[ \Delta g_{\perp} = - \frac{8\lambda\gamma^2}{\Delta_{\perp}}; \quad A_{\perp} = P \left[ - \frac{2}{7} - K \right] - \frac{11}{7} - \frac{\lambda\gamma^2}{\Delta_{\perp}} \]

(6.2)

Where \( \Delta g_{\|,\perp} = \Delta g_{\|,\perp} - 2.0023 \) and \( \beta^2 \) and \( \gamma^2 \) are the bonding coefficients of the excited orbitals and \( \Delta_{\|} \) and \( \Delta_{\perp} \) are the energy splitting in the host. The SHP determined are:

\( g_{\|} = 1.930, \quad g_{\perp} = 0.978, \quad A_{\|} = 178 \) and \( A_{\perp} = 70 \) (in \( 10^4 \) cm\(^{-1}\)) ±0.05 error)

The optical absorption spectrum of VO\(^{2+} \) doped Cs\(_2\)SO\(_4\) single crystal is shown in figure 6.1. The nature of bands [3] doped is similar to those in ZnNH\(_4\)PO\(_4\), 6H\(_2\)O and all such vanadyl complexes. The two d-d transition bands are centered around 13300 and 15900 cm\(^{-1}\) the third expected
d-d transition band may be hidden under the strong charge transfer band and is not observed in the present system. By correlating the EPR and optical data and taking spin orbit coupling coefficient $\lambda = 170$ cm$^{-1}$, we find $P = 119.70 \times 10^{-4}$ cm$^{-1}$; $K = 0.835$; $\beta^2 = 0.830$ and $\nu^2 = 0.846$. The values of $\beta^2$ and $\nu^2$ indicate that both in-plane 'σ' and out of plane 'π' bonding are covalent in nature. The values of the MO coefficients obtained for VO$^{2+}$ complexes in some phosphate and sulphate hosts [3,4,5] are shown in Table 5.II and our values are very close to those obtained for various axial vanadyl complexes. Hence we conclude that VO$^{2+}$ in Cs$_2$SO$_4$ also possess the C$_{4v}$ symmetry as in the other Vanadyl complexes.

Table 5.II MO Parameters of Vo$^{2+}$ in some hosts with C$_{4v}$ symmetry

<table>
<thead>
<tr>
<th>Host</th>
<th>$P(10^{-4}$ Cm$^{-1}$)</th>
<th>$K$</th>
<th>$\beta^2$</th>
<th>$\nu^2$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Cs$<em>2$zn(so$</em>{4\ir}$)$_2$6H$_2$O</td>
<td>-119</td>
<td>0.8</td>
<td>0.82</td>
<td>0.64</td>
<td>10</td>
</tr>
<tr>
<td>2. MgNH$_4$PO$_4$6H$_2$O</td>
<td>-122</td>
<td>0.89</td>
<td>0.87</td>
<td>0.11</td>
<td>15</td>
</tr>
<tr>
<td>3. (NH$_{4\ir}$)$_4$Sb$<em>4$(SO$</em>{4\ir}$)$<em>3$F$</em>{12}$</td>
<td>-136.3</td>
<td>0.79</td>
<td>0.70</td>
<td>0.78</td>
<td>16</td>
</tr>
<tr>
<td>4. Cs$_2$SO$_4$</td>
<td>-119</td>
<td>0.83</td>
<td>0.83</td>
<td>0.84</td>
<td>Present work</td>
</tr>
</tbody>
</table>
REFERENCES


7. A. Ogg; Phil. Mag. 5, 354 (1928).


13. B. Bleaney; Phil. Mag, 42, 441 (1951).


Fig. 5.1 Optical absorption spectrum of $\text{VO}^{2+}$ doped in $\text{Cs}_2\text{SO}_4$ single crystal at RT.