ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES OF SOME TRANSITION METAL IONS IN GLASSES AND AMMONIUM MAGNESIUM TRICHLORIDE HEXAHYDRATE SINGLE CRYSTAL

ABSTRACT

THESIS
SUBMITTED FOR THE DEGREE OF
Doctor of Philosophy
IN
Physics

BY
NIMAI CHAN BISWAS

DEPARTMENT OF PHYSICS
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
1994
ABSTRACT

ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES OF SOME TRANSITION METAL IONS IN GLASSES AND AMMONIUM MAGNESIUM TRICHLORIDE HEXAHYDRATE SINGLE CRYSTAL

Various transition metal and rare earth ions doped in solids (glass, solution or crystal) show paramagnetism due to unpaired electron in their incomplete d or f shells. In Electron Paramagnetic Resonance (EPR) a steady magnetic field splits the ground state energy level of a paramagnetic ion while an oscillating magnetic field at microwave frequency induces magnetic dipole transitions. The technique of EPR has been employed successfully to extract structural information about atomic or ionic arrangements at different sites in solids through paramagnetic ion probes. Optical absorption bands in glasses and crystals associated with transition metal or rare earth ion complexes arise from electronic transitions between energy levels of the ion in the ligand field. The absorption of radiation in the ultraviolet-visible region in solids involves - i) interionic transitions in which an electron leaves an orbital situated on one ion to occupy an orbital of a nearby ion, ii) intraionic transitions which take place between non-degenerate levels of the same ion in glass, solution or crystal with unfilled inner d or f shells and iii) transitions in colour centres due to presence of electron and positive holes. Nature of the bonds formed by
a doped transition metal ion with surrounding ligands and structure of the glassy network and single crystal may be studied with the help of EPR and optical absorption techniques.

Fast ion conducting glassy materials have stimulated much interest in recent years due to their potential utilization in solid state batteries and related electrochemical devices. The sodium ion conducting solid exhibits ionic conductivity values as high as $4.0 \times 10^{-2} \text{cm}^{-1}$ at 573K and is used as electrolyte in Na/S cells and other battery applications. As the investigation made on alkali fluoroborate glasses are limited and no EPR and optical absorption have been made on these systems, it was proposed to study these glasses through EPR and optical absorption techniques by doping Cu$^{2+}$, VO$^{2+}$ and Mn$^{2+}$ ions into them. My Ph.D. thesis contains EPR and optical absorption investigations of Cu$^{2+}$ and VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ glasses, Mn$^{2+}$ in RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ (R = Li,Na or K) glasses and optical absorption of VO$^{2+}$ in ammonium magnesium trichloride hexahydrate- NH$_4$MgCl$_3$.6H$_2$O (AMTH) single crystal.

In Chapter I, the phenomena of EPR and optical absorption are described in brief. The importance and applications of EPR are also discussed. The properties and application of inorganic and fast ion conducting glasses are presented in short.
A brief introduction to the Hamiltonian of a free paramagnetic ion, crystal field effects and the formulation of spin Hamiltonian are given in Chapter II. The interpretation of spin Hamiltonian parameters, selection rules and relaxation processes are described. Origin of optical absorption spectra of 3d ions along with d-d transition is discussed in brief.

Chapter III describes the preparation of glass samples, working of the EPR spectrometer and ultraviolet-visible spectrophotometer and procedures of recording EPR and optical absorption spectra.

Chapter IV deals with the results of EPR and optical absorption spectra of Cu$^{2+}$ in $x$Na$_2$F$_2$.$(100-x)$B$_2$O$_3$ \(5 \leq x \leq 35\) and $x$(Na$_2$F$_2$.Na$_2$O)$/\(100-2x\)$B$_2$O$_3$ \(2.5 \leq x \leq 17.5\) glasses at 290 and 77K. The theory related to EPR and optical absorption of Cu$^{2+}$ has been described and spin Hamiltonian parameters \((g||, g\perp, A||, A\perp)\), molecular orbital coefficients \((\alpha^2, \beta^2)\) and normalized covalency parameters \((\pi, \sigma)\) have been evaluated from the observed spectra. The optical absorption spectra exhibit a single band due to $^2B_{1g} \rightarrow ^2B_{2g}$ transition. EPR results show that the Cu$^{2+}$ in these glasses forms a complex with octahedral symmetry having strong tetragonal distortion \((D_{4h})\) and appears to adopt to a surrounding shared by oxygens and fluorines. The changes in the values of \(g||, A||\) and \(\beta^2_1\) confirm the existence of boron oxide anomaly. Values of \(\beta^2_1\) \((0.97 \text{ to } 0.82)\) show that the in-plane \(\pi\)-bonding of
Cu$^{2+}$ and ligands is significantly ionic in nature. The ionicity decreases with increasing concentration of Na$_2$F$_2$ or Na$_2$O. There exists a moderate covalency for the in-plane $\sigma$-bonding.

Chapter V presents EPR and optical absorption studies of VO$^{2+}$ in xNa$_2$F$_2$.(100-\(x\))B$_2$O$_3$ (5<\(x<35\)) and xNa$_2$F$_2$.(30-\(x\))Na$_2$O.70B$_2$O$_3$ (0<\(x<25\)) glasses at 290 and 77K. EPR and optical absorption spectra of VO$^{2+}$ in these glasses have been analysed assuming C$_{4v}$ site symmetry. Spin Hamiltonian parameters, dipolar hyperfine coupling parameter (P), Fermi contact interaction parameter (K), molecular orbital coefficients ($\xi$, $\beta$) and $\Delta g_{||}$ and $\Delta g_{\perp}$ have been evaluated.

The optical absorption spectra show three bands corresponding to $b_2 \rightarrow \epsilon^*$, $b_2 \rightarrow b_1^*$ and $b_2 \rightarrow a_1^*$ transitions. Variation of g$_{||}$, g$_{\perp}$ and the degrees of covalency between 15 and 20 mol% Na$_2$F$_2$ indicate the presence of boron oxide anomaly in xNa$_2$F$_2$.(100-\(x\))B$_2$O$_3$ (5<\(x<35\)) glasses. Decreasing P shows a decreased interaction of the 3d$_{xy}$ electron with $^{51}$V nucleus. 4s orbital of the vanadium atom contributes greatly to the $\sigma$-bonding orbital with increasing Na$_2$F$_2$ concentration which is in conformity with formation of stronger $\sigma$ bond with increasing energy of $b_2 \rightarrow a_1^*$ transition. Smaller values of K suggest a decrease in tetragonality. At the higher concentrations of Na$_2$F$_2$, covalencies of $\pi$- and $\sigma$-bondings are found to decrease.
The $xNa_2F_2.(30-x)Na_20.70B_2O_3 \ (0\leq x \leq 25)$ system excludes boron oxide anomaly region and provides a replacement of $O^{2-}$ by $2F^-$ at a fixed concentration of $Na^+$ and 70 mol% $B_2O_3$. A decrease in the values of $g_{||}$, $g_\perp$ and increasing dipolar hyperfine coupling parameter indicate the participation of fluorine ions in affecting the environment of $VO^{2+}$ through $BO_3F^-/BO_2F_2$ tetrahedra. Presence of an additional $F^-$ for each $O^{2-}$ would cause structural changes by forming more $BO_3F$ tetrahedra which along with $BO_2F_2$ would gradually decrease the connectivity of the structure. Covalencies of $\pi$- and $\sigma$-bondings of $VO^{2+}$ are found to decrease with increasing fluorine ion concentrations. This also implies that the participation of fluorine ions may be either non-bridging or forming a bond with $V^4$ in the equatorial plane.

Chapter VI describes EPR and optical absorption investigations of $Mn^{2+}$ in $RF.B_2O_3$ and $RF.Na_2O.B_2O_3$ ($R = Li, Na$ or $K$) glasses at 290 and 77K. The EPR spectra show an intense $g \approx 2.02$ resonance with a hyperfine structure parameter $A = (82-85) \times 10^{-4}$ cm$^{-1}$. Higher values of $A$ indicate higher ionicity of bonds with $Mn^{2+}$ in octahedral coordination at $g \approx 2.02$. Resonances weak in intensity are also observed at $g \approx 3.3$ and $g \approx 4.3$, the intensity however varies with the composition of host glasses. Remarkable changes have been observed in the intensity and resolution of EPR spectra of $Mn^{2+}$ in
25Na$_2$F$_2$.75B$_2$O$_3$ glass with varying Mn$^{2+}$ concentration. The intensity changes show that Mn$^{2+}$ prefers to occupy octahedral site with $g \cong 2.02$ resonance. The existence of boron oxide anomaly is indicated in $x$Na$_2$F$_2$.$(100-x)$B$_2$O$_3$ glasses in the composition region $5 \leq x \leq 30$ through splitting at $g \cong 4.3$ resonance. Liquid nitrogen temperature EPR spectra show no changes in $g \cong 2.02$ and $g \cong 4.3$ resonance. The optical absorption spectra of Mn$^{2+}$ in RF.B$_2$O$_3$ show one band and in RF.Na$_2$O.B$_2$O$_3$ glasses, two bands at 290K and confirm octahedral coordination of Mn$^{2+}$.

Chapter VII reports the results of optical absorption spectrum of VO$^{2+}$ doped in NH$_4$MgCl$_3$.6H$_2$O single crystal at 290K considering vanadyl ion in $C_{4v}$ symmetry. NH$_4$MgCl$_3$.6H$_2$O has a monoclinic structure in which Mg$^{2+}$ is surrounded by water octahedron. The observed absorption spectrum of VO$^{2+}$ shows two bands at 13157cm$^{-1}$ and 15674cm$^{-1}$ which have been assigned to $^2$B$_{2g} \rightarrow ^2$E$_g$ and $^2$B$_{2g} \rightarrow ^2$B$_{1g}$ transitions respectively. Values of $P$, $K$, $\epsilon_\pi^2$ and $\beta_1^2$ are evaluated using optical absorption and EPR results. Values of $\epsilon_\pi^2$ and $\beta_1^2$ indicate that both out-of-plane $\pi$- and in-plane $\sigma$-bonding are covalent in nature so that the unpaired electron is delocalized. The results indicate a replacement of Mg(H$_2$O)$_6^{2+}$ by VO(H$_2$O)$_5^{2+}$ in NH$_4$MgCl$_3$.6H$_2$O lattice.
The present study indicates the presence of boron oxide anomaly in Na$_2$F.B$_2$O$_3$ glasses. The environment of Cu$^{2+}$ appears to adopt to a surrounding shared by oxygens and fluorines in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ systems. The surrounding of VO$^{2+}$ is affected by fluorine ions through BO$_3$F$^-$/BO$_2$F$_2$ tetrahedra in NaF.Na$_2$O.B$_2$O$_3$. In alkali fluoro-borate (Li, Na or K) glasses, Mn$^{2+}$ sites are characterized by different degrees of distortion from cubic symmetry and Mg(H$_2$O)$_6^{2+}$ is replaced by VO(H$_2$O)$_5^{2+}$ in NH$_4$MgCl$_3$.6H$_2$O lattice.
ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES OF SOME TRANSITION METAL IONS IN GLASSES AND AMMONIUM MAGNESIUM TRICHLORIDE HEXAHYDRATE SINGLE CRYSTAL

THESIS
SUBMITTED FOR THE DEGREE OF
Doctor of Philosophy
IN
Physics

BY
NIMAI CHAN BISWAS

DEPARTMENT OF PHYSICS
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
1994
DEDICATED
TO
MY PARENTS
CERTIFICATE

Certified that the work presented in the thesis entitled "Electron Paramagnetic Resonance and Optical Absorption studies of some transition metal ions in glasses and ammonium magnesium trichloride hexahydrate single crystal" is the original work of Mr. Nimai Chan Biswas carried out under my supervision and it has not been submitted elsewhere for a degree.

Prof. R. Dayal
ACKNOWLEDGEMENTS

It is a matter of great pleasure to express my deep sense of gratitude and indebtedness to my supervisor Prof. R. Dayal, for his keen interest, constant guidance, invaluable suggestions and encouragement during the course of the work.

I am thankful to Chairman, Department of Physics, A.M.U., Aligarh for providing the working facilities in the Department and taking interest in the progress of this work.

I am indebted to Dr. Prem Chand, EPR Laboratory, I.I.T. Kanpur for meaningful suggestions in recording EPR spectra and permission to use other facilities. Thanks are due to Mr. D.K. Kannajjia, EPR Laboratory, I.I.T. Kanpur for his help and cooperation.

I thank Prof. R.J. Singh, Department of Physics, A.M.U., Prof. K.M. Lal and Dr. O.P. Agarwal, Department of Applied Physics, Z.H. College of Engineering and Technology, A.M.U. for their help and necessary suggestions.

I am thankful to Coordinator, DSA, Department of Physics, A.M.U. for financial assistance during the course of the work. The financial support from the Govt. of Bangladesh and India under Cultural Exchange Programme is gratefully acknowledged.
It is a pleasure to thank all my friends, specially M/S. Nazma Akhter Banu, Dr. Md. Abul Hossain, Abdus Sattar, B.P. Maurya, Md. Abul Quasem and Surendra Baboo for their help and encouragement during the work.

The technical assistance from the staff of the Department of Physics, A.M.U. is appreciated. I thank Mr. Musharraf Ali for typing the manuscript carefully.

Finally, I thank my wife Arpana and sons Saugata and Saumya for their patience and encouragement during my stay at Aligarh.

Nimai Chan Biswas
# CONTENTS

<table>
<thead>
<tr>
<th>List of Figures</th>
<th>viii</th>
</tr>
</thead>
<tbody>
<tr>
<td>List of Tables</td>
<td>xiv</td>
</tr>
<tr>
<td>Preface</td>
<td>xvi</td>
</tr>
</tbody>
</table>

## CHAPTER I

### INTRODUCTION

<table>
<thead>
<tr>
<th>Abstract</th>
<th>01</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1 Introduction</td>
<td>02</td>
</tr>
<tr>
<td>1.2 Inorganic Glasses</td>
<td>05</td>
</tr>
<tr>
<td>1.3 Borate Glasses</td>
<td>12</td>
</tr>
<tr>
<td>1.4 Fast Ion Conducting Glasses</td>
<td>15</td>
</tr>
<tr>
<td>1.5 Principle of EPR</td>
<td>16</td>
</tr>
<tr>
<td>1.6 Fine Structure</td>
<td>22</td>
</tr>
<tr>
<td>1.7 Hyperfine Structure</td>
<td>22</td>
</tr>
<tr>
<td>1.8 Detection of Resonance</td>
<td>23</td>
</tr>
<tr>
<td>1.9 Applications of EPR</td>
<td>25</td>
</tr>
<tr>
<td>References</td>
<td>27</td>
</tr>
</tbody>
</table>

## CHAPTER II

### GENERAL THEORY OF ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION

<table>
<thead>
<tr>
<th>Abstract</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Hamiltonian of a Free Paramagnetic Ion</td>
<td>31</td>
</tr>
<tr>
<td>2.2 Paramagnetic Ion in a Crystal Field</td>
<td>34</td>
</tr>
</tbody>
</table>
CHAPTER III

EXPERIMENTAL DETAILS

Abstract 62
3.1 Preparation of Samples 63
3.1.1 Glasses 63
3.1.2 Crystals 63
3.2 EPR Spectrometer 64
3.3 Recording of EPR Spectra 69
3.4 Optical Absorption Spectra 70
General References 74

CHAPTER IV

ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES OF Cu$^{2+}$ IN NaF.B$_2$O$_3$ AND NaF.Na$_2$O.B$_2$O$_3$ GLASSES

Abstract 75
4.1 Introduction 76
4.2 Experimental 76
4.3 Theory 78
## LIST OF FIGURES

<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Relationship between the glassy, liquid and solid states.</td>
<td>07</td>
</tr>
<tr>
<td>1.2</td>
<td>Schematic diagram of (a) structure of ordinary glass (B₂O₃, SiO₂ etc.,) and (b) modification of glass structure by a glass modifier (Li₂O, Na₂O etc.,).</td>
<td>10</td>
</tr>
<tr>
<td>1.3</td>
<td>Boron-oxygen structural groupings in various borate glasses.</td>
<td>13</td>
</tr>
<tr>
<td>1.4</td>
<td>Splitting of energy levels and the allowed transitions of a free ion with J = 5/2 in a static magnetic field.</td>
<td>18</td>
</tr>
<tr>
<td>1.5</td>
<td>Energy level splitting in a crystal field and a magnetic field for an ion (J = 5/2) doped in a crystal. Allowed transitions are indicated.</td>
<td>21</td>
</tr>
<tr>
<td>1.6</td>
<td>Energy level splittings of the ground state of Mn²⁺ (⁶S₅/2).</td>
<td>24</td>
</tr>
<tr>
<td>2.1</td>
<td>Schematic diagram to demonstrate Direct, Raman and Orbach processes.</td>
<td>51</td>
</tr>
<tr>
<td>2.2</td>
<td>Diagram showing point groups. (a) A regular octahedron and (b) a regular tetrahedron.</td>
<td>54</td>
</tr>
</tbody>
</table>
CHAPTER VI

ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES OF Mn\(^{2+}\) IN RF.B\(_2\)O\(_3\) AND RF.Na\(_2\)O.B\(_2\)O\(_3\)
(R = Li, Na or K) GLASSES

Abstract

6.1 Introduction 147
6.2 Experimental 147
6.3 Results and Discussion 148
6.3.1 EPR Measurements 148
6.3.1.1 Resonance at \(g \approx 2.02\) 152
6.3.1.2 Resonance at \(g \approx 3.3\) 155
6.3.1.3 Resonance at \(g \approx 4.3\) 155
6.3.1.4 Concentration Dependence 156
6.3.1.5 Boron Oxide Anomaly 156
6.3.1.6 Variation of Alkali Content 159
6.3.1.7 Temperature Variation 160
6.3.2 Optical Absorption 162
References 169

CHAPTER VII

OPTICAL ABSORPTION STUDY OF VO\(^{2+}\) IN AMMONIUM MAGNESIUM TRICHLORIDE HEXAHYDRATE SINGLE CRYSTAL

Abstract 173

7.1 Introduction 174
7.2 Experimental 174
7.3 Crystal Structure 175
7.4 Theory 179
7.5 Results and Discussion 181
References 187
2.3 Energy level diagram showing the splitting of the set of d orbitals by octahedral and tetrahedral environments.

3.1 Block diagram of an EPR spectrometer.

3.2 Block diagram of a UV-visible spectrophotometer.

3.3 Diagram showing the optical system of Ciba- Corning UV-visible spectrophotometer (Model 2800).

4.1 Splitting of the free ion ground state of Cu$^{2+}$. Transitions are indicated (after Alger [16]).

4.2 The octahedral complex with tetragonal elongation Cu$^{2+}$ in oxide glasses (after Griscom [13]).

4.3 EPR spectra of Cu$^{2+}$ in NaF.B$_2$O$_3$ glasses at 290K. (a) Glass NC2, (b) glass NC3, (c) glass NC5 and (d) glass NC7. D represents the DPPH line (0.3337T).

4.4 EPR spectra of Cu$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K. (a) Glass NNC2, (b) glass NNC3, (c) glass NNC4 and (d) glass NNC6. D represents the DPPH line (0.3337T).

4.5 EPR spectra of Cu$^{2+}$ in 25Na$_2$F$_2$.75B$_2$O$_3$ glass. (a) At 290K and (b) 77K.
4.6a Variation of $g_1$ (solid line) and $|A_1|$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.B$_2$O$_3$ glasses.

4.6b Variation of $g_1$ (solid line) and $|A_1|$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.

4.7 Optical absorption spectra of Cu$^{2+}$ in NaF.B$_2$O$_3$ glasses at 290K.

4.8 Optical absorption spectra of Cu$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K.

4.9a Variation of $\beta_1^2$ (solid line) and $\bar{\pi}$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.B$_2$O$_3$ glasses.

4.9b Variation of $\beta_1^2$ (solid line) and $\bar{\pi}$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.

5.1 Molecular orbital scheme for the VO(H$_2$O)$_5^{2+}$ ion.

5.2 The vanadyl complex in oxide glasses (after Griscom [13]).

5.3 Hyperfine splittings with S = 1/2 and I = 7/2.

5.4 Energy level splittings for d$^1$ configuration in octahedral and tetragonal fields.
5.5 EPR spectra of VO$^{2+}$ in NaF.B$_2$O$_3$ glasses at 290K. (a) Glass NV1 and (b) glass NV4. The spectrum top (a) is for glass NV1 with twice increase in gain.

5.6 EPR spectra of VO$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K. (a) Glass NNV3 and (b) glass NNV5. The spectrum top (a) is for glass NNV3 with twice increase in gain.

5.7 Variation of (a) $g_{\parallel}, g_{\perp}$; (b) $A_{\parallel}$ and $A_{\perp}$ with change in Na$_2$F$_2$ concentration in NaF.B$_2$O$_3$ glasses.

5.8 Variation of (a) $g_{\parallel}, g_{\perp}$; (a) $A_{\parallel}$ and $A_{\perp}$ with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.

5.9 Optical absorption spectra of VO$^{2+}$ in NaF.B$_2$O$_3$ glasses at 290K. (a) Glass NV1, (b) glass NV2 and (c) glass NV3.

5.10 Variation of covalency of vanadium (IV) with change in Na$_2$F$_2$ concentration in NaF.B$_2$O$_3$ glasses.

5.11 Optical absorption spectra of VO$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K. (a) Glass NNV1, (b) glass NNV5 and (c) glass NNV6.

5.12 Variation of covalency of vanadium (IV) with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.
6.1 Representative EPR spectra of Mn\(^{2+}\) (0.1 mol\%) in RF.B\(_2\)O\(_3\) and RF.Na\(_2\)O.B\(_2\)O\(_3\) (Li, Na or K) glasses at 290K. (a) Glass M2, (b) glass M4 and (c) glass M6.

6.2 EPR spectra of Mn\(^{2+}\) in 25Na\(_2\)F\(_2\).75B\(_2\)O\(_3\) glass at 290K. (a) 0.1 mol\% and (b) 3.0 mol\% of manganese.

6.3 The concentration dependence of peak-to-peak linewidth (\(\Delta H_{pp}\)) of the hyperfine component with \(m = -1/2\) of the \(g \approx 2.02\) spectrum for 25Na\(_2\)F\(_2\).75B\(_2\)O\(_3\) glass.

6.4 Representative EPR spectra of Mn\(^{2+}\) (0.5 mol\%) in 25Na\(_2\)F\(_2\).75B\(_2\)O\(_3\) glass. (a) At 77K and (b) 290K.

6.5 Schematic energy level diagram of Mn\(^{2+}\) in octahedral symmetry.

6.6 Optical absorption spectra of Mn\(^{2+}\) in RF.B\(_2\)O\(_3\) (R = Li, Na or K) glasses at 290K.

6.7 Optical absorption spectra of Mn\(^{2+}\) in (a) 20Na\(_2\)F\(_2\).10Na\(_2\)O.70B\(_2\)O\(_3\) and (b) 20KF.-10Na\(_2\)O.70B\(_2\)O\(_3\) glasses at 290K.

7.1 Monoclinic unit cell of NH\(_4\)MgCl\(_3\).6H\(_2\)O (after X. Solans et al.[4]).

*Hydrogens of NH\(_4\) have not been shown.
7.2 Structure of the complex VO(H₂O)²⁺ (after Ballhausen and Gray [5]).

7.3 Optical absorption spectrum of VO²⁺ doped in NH₄MgCl₃·6H₂O single crystal at 290K.
<table>
<thead>
<tr>
<th>No.</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Simple Glass-forming Substances</td>
<td>08</td>
</tr>
<tr>
<td>1.2</td>
<td>Boron-Oxygen Structural Groupings in Different Compounds</td>
<td>14</td>
</tr>
<tr>
<td>2.1</td>
<td>Crystal Field Splitting of the Free Ion Terms in Octahedral and Tetrahedral Fields</td>
<td>36</td>
</tr>
<tr>
<td>2.2</td>
<td>Crystal Field Splitting of the Ground States of Transition Metal Ions</td>
<td>39</td>
</tr>
<tr>
<td>4.1</td>
<td>The Composition Data For the Cu$^{2+}$ Doped-glasses in i) xNa$_2$F$_2$.(100-x)B$_2$O$_3$ (5£x£35) and ii) x(Na$_2$F$_2$·Na$_2$O)(100-2x)B$_2$O$_3$ (2.5£x£17.5)</td>
<td>77</td>
</tr>
<tr>
<td>4.2</td>
<td>EPR and Optical Parameters, Molecular Orbital Coefficient and Normalized Covalency Parameter of Cu$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ and Some Other Glass Systems</td>
<td>100</td>
</tr>
<tr>
<td>5.1</td>
<td>The Composition Data For the VO$^{2+}$ Doped-glasses in i) xNa$_2$F$_2$.(100-x)B$_2$O$_3$ (5£x£35) and ii) xNa$_2$F$_2$·(30-x)Na$_2$O.70B$_2$O$_3$ (0£x£25)</td>
<td>109</td>
</tr>
<tr>
<td>5.2a</td>
<td>Spin Hamiltonian Parameters, P and K of VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K.</td>
<td>123</td>
</tr>
</tbody>
</table>
5.2b $A_{||}$, $A_{\perp}$, PK and $\Delta \epsilon_{||}/\Delta \epsilon_{\perp}$ of VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ Glasses at 290K

5.3 Optical Parameters of VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ Glasses

6.1 Spin Hamiltonian Parameters For Mn$^{2+}$ in RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ (R = Li,Na or K) Glasses at 290K

6.2 Experimental Peak Positions and Assignments of Absorption Bands For Mn$^{2+}$ in RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ (R = Li,Na or K) Glasses at 290K

7.1 Final Atomic Coordinates ($x10^4$) of NH$_4$MgCl$_3$.6H$_2$O

7.2 Interatomic Distances (Å) and Angles (°) in the Unit Cell of NH$_4$MgCl$_3$.6H$_2$O

7.3 Optical Absorption Band Positions and Assignments For VO$^{2+}$ in AMTH Single Crystal

7.4 Spin Hamiltonian Parameters of VO$^{2+}$ in AMTH Single Crystal

7.5 Molecular Orbital Parameters of VO$^{2+}$ Doped in Different Systems
PREFACE

In Electron Paramagnetic Resonance (EPR), a steady magnetic field splits the ground state energy level of a paramagnetic ion while an oscillating magnetic field at microwave frequency induces magnetic dipole transitions. Optical absorption bands in solids associated with transition metal or rare earth ion complexes arise from electronic transitions between energy levels of the ion in the ligand field. Electronic transitions due to 3d ions are spin-forbidden. Molecular vibrations of a transition metal ion complex allow coupling to occur between electronic and vibrational energy levels in both the ground and excited states and normally forbidden d-d transitions become allowed through electric dipole transition with low intensity.

EPR studies of transition metal ions yield a great deal of information about the interaction of the unpaired electrons with local environment which leads to understanding of the nature of the bonding of the metal ion with its ligands if combined with the optical absorption. The EPR spectra give the values of spin Hamiltonian parameters which can be related to the chemical bonding and electronic structure at the site of the unpaired electron using molecular orbital theory or any other approach. Our interest has been centred around three transition metal ions namely Cu^{2+}, VO^{2+} and Mn^{2+} for EPR and optical absorption.
investigations. Copper (II) has 3d\(^1\) hole configuration and its EPR spectra in many cases give hyperfine splitting due to \(^{63}\text{Cu}\) and \(^{65}\text{Cu}\). VO\(^{2+}\) ion is useful as its principal g-values are most readily related to the immediate environment. The interesting feature of S-state Mn\(^{2+}\) is that in principle it has no interaction with crystal field to first order and thus it does not disturb the local symmetry. The EPR spectrum due to \(^{55}\text{Mn}\) hyperfine structure shows unambiguous assignments of resonance lines and the magnitude of hyperfine coupling constant provides a measure of covalency between Mn\(^{2+}\) and its ligands.

The investigations made so far on alkali fluoroborate glasses which have drawn the attention of research workers recently, are limited and no EPR and optical absorption have been made on these systems, therefore it was thought appropriate to carry out investigations the glasses through EPR and optical absorption by doping Cu\(^{2+}\), VO\(^{2+}\) and Mn\(^{2+}\) ions into them. This thesis presents the EPR and optical absorption investigations of Cu\(^{2+}\) and VO\(^{2+}\) in NaF.B\(_2\)O\(_3\) and NaF.Na\(_2\)O.B\(_2\)O\(_3\) glasses, Mn\(^{2+}\) in RF.B\(_2\)O\(_3\) and RF.Na\(_2\)O.B\(_2\)O\(_3\) (R = Li, Na or K) glasses and optical absorption of VO\(^{2+}\) in Ammonium Magnesium Trichloride Hexahydrate (AMTH) – NH\(_4\)MgCl\(_3\).6H\(_2\)O single crystal.

In Chapter I, the phenomena of EPR and optical absorption are described in brief. The importance and applications of EPR, properties and uses of inorganic and
fast ion conducting glasses are discussed.

A brief introduction to the Hamiltonian of a free paramagnetic ion, crystal field effects and the formulation of spin Hamiltonian are given in Chapter II. The interpretation of spin Hamiltonian parameters, selection rules and relaxation processes are mentioned. Origin of optical absorption spectra of 3d ions along with d-d transition is discussed in brief.

Chapter III describes the preparation of glass samples, working of the EPR spectrometer and ultraviolet-visible spectrophotometer along with procedures of recording EPR and optical absorption spectra.

Chapter IV presents the results of EPR and optical absorption of Cu$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ glasses at 290 and 77K. The optical absorption spectra exhibit a single band due to $^{2}B_{1g} \rightarrow ^{2}B_{2g}$ transition. The spin Hamiltonian parameters ($g_{||}, g_{\perp}, A_{||}, A_{\perp}$), molecular orbital coefficients ($\alpha^2, \beta^2_1$) and normalized covalency parameters ($|\pi|, |\sigma|$) have been evaluated from the observed EPR and optical absorption spectra. EPR results show that the Cu$^{2+}$ in these glasses forms a complex with octahedral symmetry having strong tetragonal distortion ($D_{4h}$) and appears to adopt to a surrounding shared by oxygens and fluorines. Presence of boron oxide anomaly is indicated in these glasses. The in-plane $\pi$-bonding ($\beta^2_1$) of Cu$^{2+}$ with ligands
is significantly ionic in nature and the ionicity decreases with increasing Na$_2$F$_2$ or Na$_2$O concentration while there exists a moderate covalency for the in-plane $\sigma$-bonding.

Chapter V deals with EPR and optical absorption studies of VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ glasses at 290 and 77K. EPR and optical absorption spectra of VO$^{2+}$ have been analysed assuming $C_{4v}$ site symmetry and spin Hamiltonian, dipolar hyperfine coupling (P), Fermi contact interaction (K) parameters, molecular orbital coefficients ($\varepsilon_1^\pi$, $\beta_1^\pi$) and $\Delta g_{||}/\Delta g_{\perp}$ have been evaluated. Variation of $g_{||}$, $g_{\perp}$ and the degrees of covalency of vanadium between 15 and 20 mol% Na$_2$F$_2$ indicate boron oxide anomaly in NaF.B$_2$O$_3$ glasses. 4s orbital of the vanadium atom contributes greatly to the $\sigma$-bonding orbital with increasing Na$_2$F$_2$ concentration which is in conformity with formation of stronger $\sigma$ bond with increasing energy of $b_2 \rightarrow a_1^*$ transition. At the higher concentrations of Na$_2$F$_2$, covalencies of $\pi$- and $\sigma$-bondings are found to decrease.

In NaF.Na$_2$O.B$_2$O$_3$ system, boron oxide anomaly region is excluded at 70 mol% B$_2$O$_3$ and a replacement of O$^{2-}$ by 2F$^-$ keeps the concentration of Na$^+$ fixed. Increase in the Na$_2$F$_2$ concentration leads to decrease in the values of $g_{||}$ and $g_{\perp}$ and increase in P indicating the participation of fluorine ions in affecting the environment of VO$^{2+}$ through BO$_3$F$^-$/BO$_2$F$_2$ tetrahedra. Covalencies of $\pi$- and $\sigma$-bondings of VO$^{2+}$ are found to decrease with increasing fluorine ion
concentrations and the participation of fluorine ions may be either non-bridging or forming a bond with $V^{4+}$ in the equatorial plane.

Chapter VI describes EPR and optical absorption investigations of $\text{Mn}^{2+}$ in $\text{RF.B}_2\text{O}_3$ and $\text{RF.Na}_2\text{O.B}_2\text{O}_3$ ($R = \text{Li,Na or K}$) glasses at 290 and 77K. The EPR spectra show an intense $g \approx 2.02$ resonance with a hyperfine structure parameter $A = (82-85) \times 10^{-4} \text{ cm}^{-1}$. Higher values of $A$ indicate higher ionicity of bonds with $\text{Mn}^{2+}$ in octahedral coordination at $g \approx 2.02$. Resonances weak in intensity are also observed at $g \approx 3.3$ and $g \approx 4.3$, the intensity however varies with composition of host glasses. Remarkable changes have been observed in the intensity and resolution of EPR spectra in $25\text{Na}_2\text{F}_2.75\text{B}_2\text{O}_3$ glass with varying $\text{Mn}^{2+}$ concentration. Boron oxide anomaly is indicated near 15-20 mol% $\text{Na}_2\text{F}_2$ through splitting at $g \approx 4.3$ resonance. Liquid Nitrogen Temperature (LNT) EPR spectra show no changes in $g \approx 2.02$ and $g \approx 4.3$ resonances. The optical absorption spectra of $\text{Mn}^{2+}$ in $\text{RF.B}_2\text{O}_3$ show one band and in $\text{RF.Na}_2\text{O.B}_2\text{O}_3$ glasses, two bands at 290K and confirm octahedral coordination of $\text{Mn}^{2+}$.

Chapter VII reports the results of optical absorption of $\text{VO}^{2+}$ doped in $\text{NH}_4\text{MgCl}_3.6\text{H}_2\text{O}$ single crystal at 290K considering vanadyl ion in $C_{4v}$ symmetry. The observed absorption spectrum of $\text{VO}^{2+}$ shows two bands at $^2B_{2g} \rightarrow ^2E_g$ and $^2B_{2g} \rightarrow ^2B_{1g}$ transitions and values of $P, K, \epsilon^{2}, \beta^{2}$ are
evaluated using EPR results. The results indicate a replacement of \( \text{Mg(H}_2\text{O)}_6^{2+} \) octahedra in \( \text{NH}_4\text{MgCl}_3.6\text{H}_2\text{O} \) lattice by \( \text{VO(H}_2\text{O)}_5^{2+} \).

The present study indicates the presence of boron oxide anomaly (through \( \text{Cu}^{2+} \), \( \text{VO}^{2+} \) and \( \text{Mn}^{2+} \) probes) in \( \text{NaF.B}_2\text{O}_3 \) glasses. The environment of \( \text{Cu}^{2+} \) appears to be shared by oxygens and fluorines in \( \text{NaF.B}_2\text{O}_3 \) and \( \text{NaF.Na}_2\text{O.B}_2\text{O}_3 \) glasses. The surrounding of \( \text{VO}^{2+} \) is affected by fluorine ions through \( \text{BO}_3\text{F}^-/\text{BO}_2\text{F}_2^- \) tetrahedra in \( \text{NaF.Na}_2\text{O.B}_2\text{O}_3 \). In alkali fluoroborate glasses (Li, Na or K), \( \text{Mn}^{2+} \) sites are characterized by different degrees of distortion from cubic symmetry. \( \text{Mg(H}_2\text{O)}_6^{2+} \) is replaced by \( \text{VO(H}_2\text{O)}_5^{2+} \) in \( \text{NH}_4\text{MgCl}_3.6\text{H}_2\text{O} \) lattice.
CHAPTER I

INTRODUCTION

Abstract

The phenomena of electron paramagnetic resonance and optical absorption are described briefly in this Chapter. The importance and applications of EPR are also discussed. The properties and application of inorganic and fast ion conducting glasses are presented in short.
1.1 Introduction

Electron paramagnetic resonance is a powerful spectroscopic technique for structural investigation of atomic or ionic arrangements at different sites in solids through paramagnetic ion probes. Electronic paramagnetism arises from electronic configurations with unpaired electrons. In EPR the absorption of microwave energy from an oscillating magnetic field induces magnetic dipole transitions between the ground state energy levels of a paramagnetic system placed in a steady magnetic field usually perpendicular to the oscillating magnetic field. The microwave energy absorbed at resonance, reorients some of the magnetic dipoles aligned in the steady magnetic field. The total integrated intensity of a paramagnetic resonance spectrum depends upon the interacting electronic magnetic moment and it can be over at least $10^6$ times that of a Nuclear Magnetic Resonance (NMR) spectrum [1].

The EPR provides the most direct and accurate description of the ground state of the paramagnetic ion, the effects of nearest-neighbours on its energy levels and enables one to determine the crystal field parameters required for the interpretation of their optical spectra in solids. The principal information contained in the EPR spectra is the values of spin Hamiltonian parameters which account for various interactions such as Zeeman interaction,
hyperfine interaction, etc. The spin Hamiltonian parameters are also related to the chemical bonding and electronic structure at the site of the unpaired electron through molecular orbital theory.

The EPR spectra of a paramagnetic system may be recorded at different orientations, temperature, frequencies, and microwave powers to obtain various informations. The paramagnetic centres in the EPR study of solids are generally encountered as substitutional or interstitial impurities such as transition metal or rare earth ions and radiation-induced EPR centres. Transition metal ions have been extensively used for EPR investigation in glassy materials after the first meaningful application of EPR method to glasses by Sands [2].

The paramagnetic species in solids are the atoms, molecules, ions or radicals having non-zero angular momentum so that there is net magnetic moment to interact with the applied steady magnetic field. The ions of various transition groups (such as iron, palladium, platinum, actinide etc.,) and rare earths doped in crystal or glass show paramagnetism as they have unpaired electrons in incomplete d or f shells. In addition free radical type complexes possessing unpaired electrons are also paramagnetic. Unpaired electrons are also found in
molecules NO and NO$_2$, in free atoms like atomic hydrogen or nitrogen, metals, semiconductors, enzymes, catalysts, substances with radiation damage etc.

The optical absorption in doped crystalline solids or glassy materials in the Ultraviolet (UV) and visible region of electromagnetic radiation is important for their structural investigations. The absorption bands in crystal or glasses associated with transition metal ion complexes or rare earth ions arise from electronic transitions between the energy levels of the ion in the structure dependent ligand field. A wide variety of colouring phenomena in different glass systems due to presence of impurities and other centres can be understood from the viewpoint of ligand field theory.

The absorption of radiation in the UV-visible region in solids involves several classes of electronic transitions. The interionic transitions in which an electron leaves an orbital mainly located on one ion to occupy an orbital of a nearby ion are allowed with very intense absorption bands and are known as charge transfer transitions. The absorption bands show maxima in the UV region with an exponential edge towards visible region. Semiconducting glasses are concerned with this type of transitions.

Intraionic transitions occur between non-degenerate
levels of the same ion in glass or crystal with unfilled inner electron shells. 3d transition metal ions incorporated in glasses or crystals with less than 1.0 mol% concentration show intraionic transition depending upon the immediate environment of the ions. General character of absorption spectra for a transition metal ion in a particular coordination can be evaluated from the number and the spacing of the energy levels for the corresponding d configuration. Information about the chemical bonds and the geometry of the nearest neighbour environment of the ion may be derived from absorption spectra.

Transitions also occur in some glasses with colour centres due to presence of electrons and positive holes. If the ionizing radiation produces pairs of electrons and positive holes which get trapped individually at various sites in the glass structure the colour centres are formed. The colour centres absorb a UV or visible light and in return provide information to the understanding of the glass structure. More structural information about solids can be obtained by correlating the parameters evaluated from EPR and optical absorption spectra.

1.2 Inorganic Glasses

A glass is generally formed by cooling a liquid below its freezing point or by compressing a liquid. Absence of
long-range periodic order of the constituent atoms characterize the glass through x-ray or electron diffraction.

Glass formation can be understood by a volume-temperature diagram shown in Fig. 1.1 [3]. As the melt cools, its volume decreases steadily along OP. If the cooling rate is slow, crystallization occurs at the freezing temperature $T_f$. The density increases markedly P to Q and the solid becomes more compact with temperature fall along QR. If the rate of cooling is sufficiently high the volume of the liquid decreases along PS upto a certain temperature $T_g$ and glass is formed. Further decrease in temperature results in a change in slope that continues parallel to QR. $T_g$ is known as glass transition temperature. The material becomes glass only below $T_g$ region and the volume of the glass formed decreases slowly below it.

A small number of elements from the periodic table such as phosphorus, oxygen, sulphur, selenium etc. are involved in the formation of a glass. The inorganic compounds such as $B_2O_3$, $SiO_2$, $GeO_2$, $P_2O_5$ etc. are extensively used in glass formation and are also known as 'glass former'. These are major components and form a glass with other oxide or oxides. Most commercially important glasses are based on these oxides. Few glass forming substances with their melting points are given in Table 1.1. Schematic diagram of
Fig. 1.1 Relationship between the glassy, liquid, and solid states.
Table 1.1

Simple Glass-forming Substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Melting Point (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>490</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1996</td>
</tr>
<tr>
<td>GeO₂</td>
<td>1389</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>723</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>695-853</td>
</tr>
<tr>
<td>As₂O₃</td>
<td>551-582</td>
</tr>
<tr>
<td>ZnCl₂</td>
<td>591</td>
</tr>
<tr>
<td>BeF₂</td>
<td>823</td>
</tr>
<tr>
<td>As₂S₃</td>
<td>583</td>
</tr>
<tr>
<td>Toluene</td>
<td>178</td>
</tr>
<tr>
<td>Ethanol</td>
<td>156</td>
</tr>
<tr>
<td>Glycerol</td>
<td>186</td>
</tr>
</tbody>
</table>
structure of a glass \((B_2O_3, SiO_2 \text{ etc.})\), glass former with a glass modifier \((Na_2O, Li_2O \text{ etc.})\) are shown in Fig.1.2(a) and (b). Glasses can be made over a wide range of compositions in many borate, silicate and phosphate systems. The compounds such as \(Al_2O_3, TeO_3, V_2O_5 \text{ etc.}\) alone do not form a glass. When these are melt with a basic oxide or mixture of oxides in suitable proportions, alluminate, tellurite and vanadate glasses can be formed. Glasses based on the chalcogenide elements \(S, Se \text{ and } Te\) known as chalcogenide glasses have been studied intensively on account of their memory switching properties. The tellurite glasses have high values of refractive index and dielectric constant while the vanadate glasses are semiconductors [3].

The viscosity of a glass melt and its variation with temperature are accounted in shaping processes of glasses. The range of viscosity is of interest and to be controlled in all glass fabrication processes, otherwise dimensional variations and other defects may be encountered.

Glasses expand on heating like most of the solids. The thermal expansion depends on the composition of the glasses. The value of thermal expansion coefficient varies on the temperature range over which it is measured. In some alkali borate glasses \((R_2O.B_2O_3, R = Li, Na, \text{ or } K)\), the thermal expansion shows a quite different behaviour unlike that of \(R_2O.SiO_2\) glasses and this unusual behaviour is termed as boron oxide anomaly [4].
Fig. 1.2 Schematic diagram of (a) structure of ordinary glass (B$_2$O$_3$, SiO$_2$ etc.,) and (b) modification of glass structure by a glass modifier (Li$_2$O, Na$_2$O etc.).
The quality of commercial glass manufacture is controlled by the density which provides relevant information to the problem of the constitution of glass [3]. Density of glasses also depends on their composition. The partial molar volume factor plays an important role in studying thermodynamic properties (such as enthalpy, free energy etc.).

The radiation involved in the study of optical properties of glass covers the range from x-rays to the very long wavelength in the infrared. Oxide glasses are very transparent in the near UV, visible and near infrared region if free from transition metal oxides and certain other colouring agents. Sulphide and some other chalcogenide glasses are less transparent in the visible region but transmit in the infrared.

The variation of refractive index of a glass with wavelength in the UV-visible-infrared region provides information for the applications of glasses in optical systems. The refractive index also depends on the glass composition. Most oxide glasses have refractive indices between 1.45 to 2.00. The chalcogenide glasses have higher values in refractive index and are used in infrared transmitting windows [3]. In alkali silicate and alkali fluoride-beryllium fluoride systems the refractive index varies almost linearly with composition. Optical fibres are invariably made from two
materials of different refractive indices. Glass fibres are very important for optical communications.

1.3 Borate Glasses

The structure of boron oxide glass has been characterized by x-ray, Raman, infrared, NMR and neutron diffraction studies and shows that it consists of an infinite network of boroxol groups \( \text{B}_3\text{O}_3 \) \([5-9]\). The boron and oxygen atoms inside the group are interconnected in the form of a planar ring (Fig. 1.3) and the B-O-B angle is 120°. These boroxol hexagons are interconnected by an oxygen bridge -O- and have the external B-O-B angle of 130° (approximately). According to Krogh-Moe theory, the borate glasses may contain some number of polyborate groupings along the \( \text{B}_3\text{O}_3 \) triangles and \( \text{B}_4\text{O}_4 \) tetrahedra which occur in related crystalline materials \([7,10]\). The structural groupings such as boroxol, pentaborate, triborate and diborate may exist up to 35 mol% alkali or silver oxide in the composition of alkali and silver borate glass systems. A list of boron-oxygen structural groupings in various compounds is presented in Table 1.2 \([4, 11-13]\). The structures of some typical borate groups are shown in Fig.1.3 \([14]\).

In binary borate glasses, abrupt property changes found at composition near 15 mol% modifier oxide have been attributed to boron oxide anomaly \([4]\). In complex borate
Fig. 1.3 Boron-oxygen structural groupings in various borate glasses.
Table 1.2

Boron-Oxygen Structural Groupings in Different Compounds

<table>
<thead>
<tr>
<th>No.</th>
<th>Group</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Boroxol</td>
<td>Vitreous $B_2O_3$</td>
</tr>
<tr>
<td>2</td>
<td>Diborate</td>
<td>$Li_2O.2B_2O_3$</td>
</tr>
<tr>
<td>3</td>
<td>Triborate</td>
<td>$Cs_2O.3B_2O_3$</td>
</tr>
<tr>
<td>4</td>
<td>Pentaborate</td>
<td>$\alpha-K_2O.5B_2O_3$, $\beta-K_2O.5B_2O_3$</td>
</tr>
<tr>
<td>5</td>
<td>Tetraborate</td>
<td>$Na_2O.4B_2O_3$</td>
</tr>
<tr>
<td>6i</td>
<td>Metaborate (ring type)</td>
<td>$Na_2O.B_2O_3$, $K_2O.B_2O_3$</td>
</tr>
<tr>
<td>ii</td>
<td>Metaborate (chain type)</td>
<td>$Li_2O.B_2O_3$, $CaO.B_2O_3$</td>
</tr>
<tr>
<td>7</td>
<td>Pyroborate</td>
<td>$2MgO.B_2O_3$, $2CaO.B_2O_3$</td>
</tr>
<tr>
<td>8</td>
<td>Orthoborate</td>
<td>$3MgO.B_2O_3$, $3CaO.B_2O_3$</td>
</tr>
</tbody>
</table>
glasses, it has been observed through the existence of maxima, minima or inflections in the property versus composition curves. Biscoe and Warren [15] observed a distinct minimum in the thermal expansion coefficient versus composition curve at 16 mol% soda content of soda boric oxide glasses indicating boron oxide anomaly. Boron oxide anomaly has also been observed in sodium fluoroborate glasses [16,17] through measurements of thermal expansion coefficient, viscosity, refractive index, density and so on.

The borate glasses are considered among the best materials for manufacturing of solid state batteries. B$_2$O$_3$ is a good glass former and a good insulator.

1.4 Fast Ion Conducting Glasses

In recent years, solid electrolytes in glassy state have become the focus of interest as they have definite advantages over their crystalline counterparts due to isotropic properties, ease of thin film formation, flexibility of size and shape, suitability for miniaturization, simplicity of design etc. [14]. The glassy solid electrolyte materials can be prepared over a wide range of composition and used in solid state batteries and related electrochemical devices. It is well known that fast ionic conduction in solid is possible due to monovalent cations such as Na$^+$, Li$^+$ etc., or anions such as F$^-$. The fast ion conducting glassy materials are formed by a glass former, a
glass modifier (Li$_2$O, Ag$_2$O etc.,) and a doping salt. The Na$^+$ ion conducting solid exhibits ionic conductivity values as high as $4.0 \times 10^{-2} \text{ (cm$^{-1}$)}$ at 573 K and is used as electrolyte in Na/S cells and for other battery applications. Power enhancement of the order of 100 KW may be achieved in Na$^+$ ion conduction based batteries. Lithium ion conducting glasses play an important role as solid electrolytes in batteries used for timers, coulometers, solid state display devices, sensors etc. [18]. Fluorine ions (ionic radius = 0.133 nm) have a significant role in oxide glasses as they can modulate the electrical and structural properties owing to their size similar to that of the oxygen ions (ionic radius = 0.132 nm). Oxide glasses containing fluorine ions find applications in the manufacture of laser windows, ultra low-loss optical fibres and domes and high power laser host materials [19].

1.5 Principle of EPR

A free paramagnetic ion having a total angular momentum $J$, has a magnetic moment $\mu$ given by

$$\mu = - g_\lambda J,$$

where $g$ is Landé splitting factor expressed by

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

and $\lambda$ is Bohr magneton given by
Here, \( S \) and \( L \) are the electron spin and orbital angular momentum vectors giving \( J = L + S \), \( e \) and \( m \) are electronic charge and mass, \( h \) is Planck's constant and \( c \) is the velocity of light. The negative sign in the right hand side of Eq.(1.1) appears due to negative charge on the electron. If this paramagnetic ion is placed in a steady magnetic field \( H \), the energy levels produced by the interaction of \( \mu \) are given by the relation

\[
E_M = g \beta_0 H M
\]  
(1.4)

where \( M \) is the projection of \( J \) along \( H \), having \((2J+1)\) integral values, \( M = J, J-1, \ldots, -J+1, -J \). The spacing of energy levels is directly proportional to the field \( H \) (Fig.1.4).

Magnetic dipole transitions occur by absorbing microwave energy from an oscillating magnetic field usually kept normal to the steady magnetic field \( H \). The photons resonantly absorbed for dipole transitions are those whose energy is equal to the spacing between adjacent energy levels i.e.,

\[
h \nu = g \beta_0 H
\]  
(1.5)

where \( \nu \) is frequency of radiation. For \( J = 5/2 \) (\( M = \pm 5/2, \pm 3/2, \pm 1/2 \)), five possible transitions permitted by the selection rule \( \Delta M = \pm 1 \) are \( +5/2 \leftrightarrow +3/2, +3/2 \leftrightarrow +1/2 \). 
Fig. 1-4 Splitting of energy levels and the allowed transitions of a free ion with $J=5/2$ in a static magnetic field.
+1/2 ↔ -1/2, -1/2 ↔ -3/2, and -3/2 ↔ -5/2. As the energy levels are equally spaced, these transitions are superimposed. Eq. (1.5) gives the condition of electron paramagnetic resonance [20]. For \( H = 330 \) mT and \( g = 2 \), the resonance frequency is found 10 GHz i.e., the condition of EPR is satisfied for most paramagnets. The energy levels in the ground state multiplet are populated according to Boltzmann distribution, the lower ones are more populated than the upper ones. The dipole transition increases the population in the upper levels disturbing the normal population difference in thermal equilibrium. The relaxation processes maintain the population difference between ground state energy levels and resonance absorption continues.

A paramagnetic ion in a solid is surrounded by the charged particles or neutral molecules which produce a crystal field (ligand field) at the ion site. The ligand field is electrostatic in nature and splits each state of the paramagnetic ion in a number of components similar to Stark effect. The orbital motion of the electrons is said to be quenched removing some of the orbital degeneracy and leaving a ground state with a reduced orbital momentum.

The crystal field affects indirectly the magnetic moment of the ion through the influence of spin-orbit interaction which couples the spin to the axis of the crystal. Some of the orbital magnetic moment is left admixed with the spin. However, the electronic ground state in a crystal field may be characterized by a single quantum
number $S'$ known as effective spin and its multiplicity is then equal to $2S'+1$. Actually the ground state consists of a mixture of spin and orbital wavefunctions of the free ion [21]. The splitting of the ground state in the external magnetic field (Fig. 1.4) is modified by the crystal field as shown in Fig. 1.5 for $J = 5/2$. The degeneracy of the ground state is not completely removed by the crystal field. The remaining degeneracy is removed by the external magnetic field. The EPR is exhibited between the ground state energy levels of the ion split by the magnetic field and the condition for the absorption of microwave radiation given by Eq. (1.5) has a modified splitting factor known as g-factor [22]. In case of orbital singlet ground state, the actual and effective spins are same and the g value remains nearly equal to that of the free electron. The g-factor in solids depends upon the orbital contribution to the magnetic moment and symmetry of the crystal field. In general g-factor has nine components which can be reduced to three by a transformation to a principal axis system. If $g_x$, $g_y$ and $g_z$ denote the principal values, then

$$g = \left( l^2 g_x^2 + m^2 g_y^2 + n^2 g_z^2 \right)^{1/2}$$  \hspace{1cm} (1.6)

where $l$, $m$ and $n$ are direction cosines of $g$ with respect to $x$, $y$ and $z$ axes respectively. For octahedral symmetry $g$ is isotropic.
Fig 1.5 Energy level splitting in a crystal field and a magnetic field for an ion \((J = 5/2)\) doped in a crystal. Allowed transitions are indicated.
1.6 Fine Structure

For a free ion with \( J = \frac{5}{2} \), the transitions between energy levels \( M = \pm \frac{5}{2}, \pm \frac{3}{2}, \pm \frac{1}{2} \) take place following the selection rule \( \Delta M = \pm 1 \) and occur superimposed (Fig. 1.4) at a given magnetic field. If the ion is incorporated in a crystal, ground state energy levels in the magnetic field cease to be equally spaced at a given magnetic field due to crystal field splitting. Therefore for a particular frequency of microwave radiation, the transitions occur at different magnetic field strengths. The superimposed lines thus get resolved (Fig. 1.5). This splitting is known as fine structure splitting [23] and reflects the crystal field strength at the paramagnetic ion site.

1.7 Hyperfine Structure

Hyperfine structure arises from the interaction of unpaired electron spin and the nuclear spin of a nucleus. A nucleus with non-zero spin \( I \) will have magnetic moment \( \mu \) expressed as \( g_N \beta_N I \) where \( g_N = \frac{\mu}{\beta_N I} \) (\( \beta_N \) is nuclear magneton). If the nuclear spin \( I \) of the paramagnetic ion interacts with its electronic angular momentum, it gives a further splitting of each energy level of the fine structure into \((2I+1)\) equally spaced levels in the magnetic field. This is known as hyperfine splitting. Transitions are allowed by the selection rules \( \Delta M = \pm 1 \), and \( \Delta m = 0 \). In
general the hyperfine splitting is smaller than the fine structure splitting. Hyperfine structure enables one to identify some of the important elements present in a paramagnet by the nature of their isotopes with non-zero nuclear spin.

The $\text{Mn}^{2+}$ ion (atomic number $Z = 25$) has a half filled shell with electronic and nuclear spin each equal to $5/2$. Under crystal field, its ground state energy levels in a magnetic field are $M = +5/2, +3/2, +1/2$. Each of these levels split into six levels ($2I + 1 = 6$) due to hyperfine coupling with nuclear spin. This splitting is shown in Fig. 1.6 [24].

1.8 Detection of Resonance

Electron paramagnetic resonance occurs in a sample if it absorbs energy from oscillating magnetic field $H(t)$ of microwave radiation of a definite frequency at a rate proportional to the magnetization of the spin system. When the paramagnetic sample gets tuned to the resonance condition $h\nu = g\beta_0 H$, the unpaired spins absorb microwave energy producing magnetization of the sample. The resonance is generally obtained by slowly varying the steady magnetic field and keeping the microwave frequency constant (for experimental convenience) and observing the effect of magnetization of the sample. The magnetization of the spin
Fig. 1.6 Energy level splittings of the ground state of Mn\(^{2+}(6S_{5/2})\).
system may be represented by a complex susceptibility as

\[ \chi = \chi' - i \chi'' \]  \hspace{1cm} (1.7)

where the real part \( \chi' \) is in-phase with oscillating magnetic field \( H_\perp(t) \) which does not affect the power absorption at resonance. This absorption is modulated at frequency \( \sim 10^5 \) Hz and amplified. Absorption signal is demodulated and detected in the form of a derivative of absorption peak which gives clear lineshapes of EPR signal on an EPR spectrometer.

1.9 Applications of EPR

The EPR spectrum of a doped diamagnetic single crystal with proper level of paramagnetic impurity identifies the impurity occupied lattice sites, their symmetry and valence state. Informations can be obtained about the nuclei in the immediate neighbourhood of the paramagnetic probe ion. The investigations of colour centres in insulators, radiation-damage centres in crystals, conduction electrons in metals, electron or hole traps in photoconductors, unpaired electrons in semiconductors, organic free radicals in various biological systems, catalysts etc. can be made using the EPR technique. Chemical bonds in molecules, crystals and glasses may be characterized by EPR studies. Effective masses of atoms in semiconductors may be deduced. Diffusion
constants, correlation times and type of hydration can be determined through EPR spectra of solutions. Concentration of paramagnetic species and information regarding the phase transitions in solids can be obtained. EPR may also be used to obtain details information on ferromagnetic, antiferromagnetic and ferrimagnetic materials. The extremely complicated EPR spectrum can be studied by introducing the approximate coupling constants in a computer and then comparing the simulated spectrum with the experimental one.

In recent years, fast ion conducting glasses such as alkali fluoroborate glasses have attracted much attention as they have potential applications in solid state batteries and related electrochemical devices. Therefore it has been found interesting to study the alkali fluoroborate glasses by paramagnetic probes. The EPR and optical absorption spectra of 3d transition metal ions together provide sufficient information to understand the structure of glasses with varying composition. The research work presented in this thesis includes EPR and optical absorption investigations of Cu$^{2+}$ and VO$^{2+}$ doped in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ glasses (Chapter IV and V), Mn$^{2+}$ doped in RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ ($R$ = Li, Na, or K) glasses (Chapter VI), and optical absorption spectrum of VO$^{2+}$ doped in ammonium magnesium trichloride hexahydrate (NH$_4$MgCl$_3$·6H$_2$O) single crystal (Chapter VII).
REFERENCE


GENERAL REFERENCES


CHAPTER II

GENERAL THEORY OF ELECTRON PARAMAGNETIC RESONANCE
AND OPTICAL ABSORPTION

Abstract

In this Chapter, a brief introduction to the Hamiltonian of a free paramagnetic ion, crystal field effects and the formulation of spin Hamiltonian are given. The interpretation of spin Hamiltonian parameters, selection rules and relaxation processes are described. Origin of optical absorption spectra of 3d ions along with d-d transition is discussed in brief.
The energy levels of paramagnetic ion in a crystalline environment are modified by its surroundings and transitions induced due to EPR depend in a complicated manner on various interactions. Quantum mechanical formulation of the Hamiltonian of the paramagnetic ion in a proper environment is helpful in interpreting the paramagnetic behaviour.

2.1 Hamiltonian of a Free Paramagnetic Ion

The free ion Hamiltonian consists of various electrostatic and magnetic interactions arising from charge and magnetic moments of electrons outside the closed electronic shells, nuclear charge, nuclear magnetic and quadrupole moment. A brief account of these interactions is given below in decreasing order of energy.

The Coulomb interaction concerned with the interaction of the electrons with nuclear charge Ze and the mutual repulsion of the electrons is given by

\[ H_C = \sum_{k=1}^{N} \left( \frac{P_k^2}{2m} - \frac{Ze^2}{r_k} \right) + \sum_{k>j=1}^{N} \frac{e^2}{r_{kj}}, \]  

(2.1)

where \( e \) and \( m \) are electronic charge and mass, \( P_k \) is linear momentum and \( r_k \) is the radius vector joining the kth electron to the nucleus. The summation is taken for all possible Coulombic interactions and \( k \) and \( j \) refer to the electron in the ion.
The spin-orbit interaction arises from the magnetic dipole-dipole coupling between the electron spins and their orbits and is of the form

$$H_{LS} = \sum_{j,k} \lambda_{jk} \mathbf{l}_j \cdot \mathbf{s}_k. \quad (2.2)$$

where $\lambda_{jk}$ are constants, $\mathbf{l}_j$ is the orbital angular momentum of jth electron and $\mathbf{s}_k$ is the electron spin of kth electron.

The spin-spin interaction gives the energy of mutual interaction [1] between magnetic dipoles with spin $\mathbf{s}_j$ and $\mathbf{s}_k$ and is expressed as

$$H_{SS} = \sum_{jk} 4\beta_o^2 \frac{\mathbf{s}_j \cdot \mathbf{s}_k}{r_{jk}^3} - \frac{3(r_{jk} \cdot \mathbf{s}_j)(r_{jk} \cdot \mathbf{s}_k)}{r_{jk}^5}. \quad (2.3)$$

The hyperfine interaction consists of two terms:

i) the dipole-dipole interaction of nuclear magnetic moment $\mu_N$ with orbital and spin magnetic moment of the electron,

ii) the Fermi contact term from the anomalous interaction between $s$ electrons and the nuclear spin in the form [2]

$$H_{FC} = 2\gamma \beta_o \mu_N \frac{8\pi}{3} \delta(r_k) (\mathbf{s}_k \cdot \mathbf{l}), \quad (2.4)$$

where $\gamma$ is the nuclear gyromagnetic ratio.
The hyperfine interaction term is thus written as sum of the above contributions [2,3]

\[
H_N = 2\gamma_o \beta_N \sum_k \left\{ \frac{(1_k - s_k).I}{r_k^3} + \frac{3(r_k.s_k)(r_k.I)}{r_k^5} \right\} + \frac{8\pi}{3} \delta(r_k)(s_k.I). \tag{2.5}
\]

Nuclear quadrupole interaction represents the energy of electrostatic interaction of electrons with quadrupole moment \(Q\) of the nucleus expressed as [4]

\[
H_Q = \frac{e^2Q}{2I(2I-1)} \sum_k \left[ \frac{I(I+1)}{r_k^3} + \frac{3(r_k.I)^2}{r_k^5} \right]. \tag{2.6}
\]

The interaction of electronic magnetic moment with external magnetic field gives the term [5]

\[
H_H = \beta_o (L + 2S).H. \tag{2.7}
\]

The direct effect of \(H\) on the nuclear magnetic moment also contributes a small term to the Hamiltonian

\[
H_{HN} = -\gamma_N I.H. \tag{2.8}
\]

The magnitudes of various terms of the Hamiltonian
mentioned above are of the following order:

\[ H_C \sim 10^5 \text{ cm}^{-1} \]
\[ H_{LS} \sim 10^4 \text{ cm}^{-1} \text{ Crystal field iron group} \]
\[ \sim 10^2 - 10^3 \text{ cm}^{-1} \text{ Far Infrared} \]
\[ \sim 10 - 10^2 \text{ cm}^{-1} \text{ Crystal field rare earths} \]
\[ H_{SS} \sim 0 - 1 \text{ cm}^{-1} \]
\[ H_N \sim 10^{-1} - 10^{-3} \text{ cm}^{-1} \]
\[ H_Q \sim 10^{-3} \text{ cm}^{-1} \]
\[ H_H \sim 0 - 1 \text{ cm}^{-1} \]
\[ H_{HN} \sim 10^{-3} \text{ cm}^{-1} \].

The total Hamiltonian of free ion in the presence of external magnetic field is a sum of all the terms:

\[ H_{\text{ion}} = H_C + H_{LS} + H_{SS} + H_N + H_Q + H_H + H_{HN}. \] (2.9)

### 2.2 Paramagnetic Ion in a Crystal Field

The inter-electronic forces of the free ions give rise to a number of energy levels, known as terms for each \( 3d^n \) configuration, \( n \) being the number of electrons in the \( 3d \) shell. Free ion terms are represented by \( S, P, D, F, G, H \) and \( I \) corresponding to \( L \) equal to 0, 1, 2, 3, 4, 5 and 6. The ground state of a free ion is denoted by \( ^{2S+1}L_J \).
by using Hund's rule which states that the ground state would have the greatest \( L \) value in conformity with maximum spin \( S \) allowed by Pauli's exclusion principle and the total angular momentum \( J \) being \(|L-S|\) for less than half filled shells and \(|L+S|\) for more than half filled shells. For example, the ground state for a \( 3d^1 \) configuration (such as \( T_{1}^{3+}, V^{4+} \), etc.) is \( ^2D_{3/2} \).

EPR is concerned with ground state of the paramagnetic ion situated in a crystal field. Valuable information can be obtained if the paramagnetic ion is located at a distance sufficient to reduce magnetic interaction with other similar ions to negligible value. This situation is practically achieved when small concentrations (less than 0.1%) of magnetic ions are incorporated as impurities in diamagnetic crystals. The energy levels of transition metal ions are split by the action of ligand field (crystal field). Splittings of various free ion states in octahedral and tetrahedral fields predicted by group theory are presented in Table 2.1. The energy levels are represented by \( A_1, A_2, E, T_1 \) and \( T_2 \) where \( A_1 \) and \( A_2 \) are non-generate, \( E \) is two-fold degenerate and \( T_1 \) and \( T_2 \) are three-fold degenerate. The subscript \( g \) may be used in all terms for \( d \) orbitals in octahedral symmetry due to their inherent inversion property.

The effect of crystalline field on the paramagnetic ion may be expressed as a perturbation term \( H_{cr} \) in the
Table 2.1

Crystal Field Splitting of The Free Ion
Terms in Octahedral and Tetrahedral Fields

<table>
<thead>
<tr>
<th>Free Ion Term</th>
<th>$O_h$ Field</th>
<th>$T_d$ Field</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>$^A_1g$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>P</td>
<td>$^T_1g$</td>
<td>$T_1$</td>
</tr>
<tr>
<td>D</td>
<td>$^E_g + ^T_2g$</td>
<td>$E + T_2$</td>
</tr>
<tr>
<td>F</td>
<td>$^A_2g + ^T_{1g} + ^T_{2g}$</td>
<td>$A_2 + T_1 + T_2$</td>
</tr>
<tr>
<td>G</td>
<td>$^A_{1g} + ^E_g + ^T_{1g} + ^T_{2g}$</td>
<td>$A_1 + E + T_1 + T_2$</td>
</tr>
<tr>
<td>H</td>
<td>$^E_g + 2^T_{1g} + ^T_{2g}$</td>
<td>$E + 2T_1 + T_2$</td>
</tr>
</tbody>
</table>
Hamiltonian and thus the Hamiltonian becomes

\[ H = H_{\text{ion}} + H_{\text{cr}} \]  

(2.10)

The relative magnitude of crystal field interaction determines the nature of magnetism in solids. Following three cases may arise:

i) Low field case - applicable for lanthanide ions \((4f^n)\)

\[ H_{\text{cr}} < H_{\text{LS}} \]

ii) Medium field case - iron group ions \((3d^n)\)

\[ H_{\text{LS}} < H_{\text{cr}} < \sum_{k>j=1} e^2 r_{kj} \]

iii) High field case - transition group ions \((4d^n),(5d^n)\) and covalent complexes of 3d ions

\[ H_{\text{cr}} > \sum_{k>j=1} e^2 r_{kj} \]

For high spin complexes of iron group (crystal field energy < electron-electron repulsion energy) the effect of the crystal field is considered on the Russel-Saunders (R-S) states of the free ions. The crystal field splits the R-S states and remove some of the degeneracy as in Stark effect. Effect of \( H_{\text{LS}} \) is considered next on these resulting states.

The crystal field potential \( V_{\text{cr}} \) corresponding to \( H_{\text{cr}} \) at the site of paramagnetic ion satisfies the Laplace's equations \( \nabla^2 V_{\text{cr}} = 0 \) and can be expressed as

\[ V_{\text{cr}} = \sum_n \sum_{n=m}^n \sum_k A_n^m r_k^n v_n^m (\theta_k, \phi_k) \]

\[ = \sum_n \sum_m V_{\text{cr}}^m \]  

(2.11)
where $Y_n^m = (-1)^m Y_n^m$ are spherical harmonics with coefficients satisfying the relation $A_n^m = (-1)^n A_n^{-m}$. The sum over $k$ takes into account all electrons. The surrounding ligands are supposed not to overlap with paramagnetic ion orbitals. A Hamiltonian symmetric under all symmetry operations requires that $V_{cr}$ should also transform as a totally symmetric representation. This condition reduces the number of terms in the expansion of $V_{cr}$ and all harmonics of odd order are dropped. The nature of the paramagnetic ion further limits the expansion of $V_{cr}$ for $d$ and $f$ electrons to $n = 4$ and $n = 6$ respectively. The octahedral crystal field potential with a four-fold axis of symmetry for $d$ electrons has the form [6].

$$V = Y_4^0 + \sqrt{5/14} \left( Y_4^4 + Y_4^{-4} \right)$$

omitting the multiplication factor.

The crystal field splitting under any symmetry can be determined by group theory which predicts only the pattern of splitting. Table 2.2 describes the crystal field splitting of the ground states of 3d ions under octahedral symmetry. For example, Cr$^{3+}$ has a ground state $^4F$ which splits into $^4A_{2g} + ^4T_{1g} + ^4T_{2g}$ in a crystal field of $O_h$ symmetry. The orbital degeneracy is further lifted out by lowering the symmetry.
Table 2.2

Crystal Field Splitting of the Ground States of Transition Metal Ions

<table>
<thead>
<tr>
<th>No. of d Electrons</th>
<th>Transition Metal Ions</th>
<th>Ground Term of Free Ion</th>
<th>Total Spin S</th>
<th>Splitting Under $O_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d$^1$</td>
<td>V$^{4+}$, Ti$^{3+}$</td>
<td>$^2D$</td>
<td>1/2</td>
<td>$^2E_g + ^2T_{2g}$</td>
</tr>
<tr>
<td>3d$^2$</td>
<td>Cr$^{4+}$, Ti$^{2+}$</td>
<td>$^3F$</td>
<td>1</td>
<td>$^3T_{1g} + ^3T_{2g} + ^3A_{2g}$</td>
</tr>
<tr>
<td>3d$^3$</td>
<td>Mn$^{4+}$, Cr$^{3+}$, V$^{2+}$</td>
<td>$^4F$</td>
<td>3/2</td>
<td>$^4A_{2g} + ^4T_{1g} + ^4T_{2g}$</td>
</tr>
<tr>
<td>3d$^4$</td>
<td>Mn$^{3+}$, Cr$^{2+}$</td>
<td>$^5D$</td>
<td>2</td>
<td>$^5E_g + ^5T_{2g}$</td>
</tr>
<tr>
<td>3d$^5$</td>
<td>Fe$^{3+}$, Mn$^{2+}$, Cr$^+$</td>
<td>$^6S$</td>
<td>5/2</td>
<td>$^6A_{1g}$</td>
</tr>
<tr>
<td>3d$^6$</td>
<td>Co$^{3+}$, Fe$^{2+}$, Mn$^+$</td>
<td>$^5D$</td>
<td>2</td>
<td>$^5E_g + ^5T_{2g}$</td>
</tr>
<tr>
<td>3d$^7$</td>
<td>Ni$^{3+}$, Co$^{2+}$, Fe$^+$</td>
<td>$^4F$</td>
<td>3/2</td>
<td>$^4A_{2g} + ^4T_{1g} + ^4T_{2g}$</td>
</tr>
<tr>
<td>3d$^8$</td>
<td>Cu$^{3+}$, Ni$^{2+}$, Co$^+$</td>
<td>$^3F$</td>
<td>1</td>
<td>$^3A_{2g} + ^3T_{1g} + ^3T_{2g}$</td>
</tr>
<tr>
<td>3d$^9$</td>
<td>Cu$^{2+}$, Ni$^+$</td>
<td>$^2D$</td>
<td>1/2</td>
<td>$^2E_g + ^2T_{2g}$</td>
</tr>
</tbody>
</table>
2.3 The Spin Hamiltonian

As the actual Hamiltonian represented by Eq.(2.10) has many interaction terms and involves complicated calculations, it is very difficult to determine the energy levels and interpret the actual EPR spectrum. Therefore a simpler method has been adopted to describe the Hamiltonian in terms of a small number of parameters expressing the experimental results in a concised form. This is known as the method of spin Hamiltonian and has been introduced by Pryce and Abragam [7,8] using perturbation calculations.

The spin Hamiltonian expresses all the interactions in terms of effective spin. The total Hamiltonian for actual ground state orbital singlet with spin S can be expressed in two parts as

\[ \mathcal{H} = \mathcal{H}_o + \mathcal{H}' \]  \( (2.13) \)

where \( \mathcal{H}_o \) is the unperturbed Hamiltonian and includes Coulomb and crystal field interaction terms. The perturbing Hamiltonian \( \mathcal{H}' \) includes all small perturbing terms such as spin-orbit interaction, spin-spin interaction etc. \( \mathcal{H}' \) can be written in the form

\[ \mathcal{H}' = \Sigma R \alpha T \alpha \]  \( (2.14) \)

\[ \alpha = x, y, z \]
where $R_\alpha$ operates only on spatial variables and $T_\alpha$ only on spin variables. Applying perturbation theory it is found that [6]

$$\mathcal{H}' = \sum_\alpha \langle o| R_\alpha | o \rangle \, T_\alpha - \sum_{\alpha, \alpha'} \sum_{n \neq o} \frac{\langle o| R_\alpha | n \rangle \langle n| R_{\alpha'} | o \rangle}{E_n - E_o} \, T_\alpha T_{\alpha'},$$

(2.15)

where $E_o$ is the unperturbed energy eigenvalue and $E_n$ is the energy eigenvalue of the $n$th state ($n = 1, 2, 3, \ldots$).

For iron group, the dominating terms of $\mathcal{H}'$ are spin-orbit interaction and electronic Zeeman interaction and $\mathcal{H}'$ may be written as

$$\mathcal{H}' = \lambda L \cdot S + \beta_o (L + g_e S) \cdot H$$

(2.16)

or

$$\sum_\alpha R_\alpha T_\alpha = \lambda \sum_\alpha L_\alpha S_\alpha + \beta_o \sum_\alpha S_\alpha H_\alpha$$

(2.17)

By applying first order perturbation calculations we obtain

$$\sum_\alpha \langle o| R_\alpha | o \rangle \, T_\alpha = \beta_o g_e \sum_\alpha \langle o| S_\alpha | o \rangle \, H_\alpha$$

$$= \beta_o g_e \, H \cdot S$$

(2.18)

as the terms containing $\langle o| L_\alpha | o \rangle$ vanish because singlet orbital state has no orbital angular momentum.

Second order contributions from equation (2.16) are as follows:

$$- \sum_{\alpha, \alpha'} \sum_{n \neq o} \frac{\langle o| R_\alpha | n \rangle \langle n| R_{\alpha'} | o \rangle}{E_n - E_o} \, T_\alpha T_{\alpha'},$$
\[ \begin{align*}
- \Sigma_{\alpha\alpha'} \sum_{n \neq o} \frac{2 \langle o | L_\alpha | n \rangle \langle n | L_\alpha' | o \rangle}{E_n - E_o} & \cdot S_\alpha S_{\alpha'} \\
- \Sigma_{\alpha\alpha'} & \sum_{n \neq o} \frac{\beta_o^2 \langle o | L_\alpha | n \rangle \langle n | L_\alpha' | o \rangle}{E_n - E_o} \cdot H_\alpha H_{\alpha'} \\
- \Sigma_{\alpha\alpha'} & \sum_{n \neq o} \frac{2 \lambda \beta_o \langle o | L_\alpha | n \rangle \langle n | L_\alpha' | o \rangle}{E_n - E_o} \cdot H_\alpha S_{\alpha'} 
\end{align*} \tag{2.19} \]

The quantity
\[ \sum_{n \neq o} \frac{\langle o | L_\alpha | n \rangle \langle n | L_\alpha' | o \rangle}{E_n - E_o} \]
is a tensor and defined as
\[ \Lambda_{\alpha\alpha'} \equiv \sum_{n \neq o} \frac{\langle o | L_\alpha | n \rangle \langle n | L_\alpha' | o \rangle}{E_n - E_o} \equiv \Lambda_{\alpha'} \alpha. \tag{2.20} \]

Therefore equation (2.19) takes the form
\[ \begin{align*}
- \Sigma_{\alpha\alpha'} \sum_{n \neq o} \frac{\langle o | R_\alpha | n \rangle \langle n | R_\alpha' | o \rangle}{E_n - E_o} & \cdot T_\alpha T_{\alpha'} \\
- 2 \Sigma_{\alpha\alpha'} & \Lambda_{\alpha\alpha'} S_\alpha S_{\alpha'} - \beta_o^2 \sum_{\alpha\alpha'} H_\alpha H_{\alpha'} - \beta_o \sum_{\alpha\alpha'} 2 \lambda \Lambda_{\alpha\alpha'} H_\alpha S_{\alpha'} 
\end{align*} \tag{2.21} \]

Adding the perturbation contributions up to second order the \( H' \) may be expressed as \( H_{\text{spin}} \),

\[ H_{\text{spin}} = \sum_{\alpha\alpha'} \beta_o \beta_o H_\alpha S_{\alpha'} - \beta_o^2 \sum_{\alpha\alpha'} 2 \lambda \Lambda_{\alpha\alpha'} H_\alpha S_{\alpha'} \\
- \lambda^2 \sum_{\alpha\alpha'} \Lambda_{\alpha\alpha'} S_\alpha S_{\alpha'} - \beta_o^2 \sum_{\alpha\alpha'} \Lambda_{\alpha\alpha'} H_\alpha H_{\alpha'} \]
\[
\begin{align*}
= \beta_o \sum_{\alpha \alpha'} \left( g_{\alpha} \delta_{\alpha \alpha'} - 2\lambda \Lambda_{\alpha \alpha'} \right) \mathbf{S} \cdot \mathbf{S} - \lambda^2 \sum_{\alpha \alpha'} \Lambda_{\alpha \alpha'} \mathbf{S} \cdot \mathbf{S} + \mathbf{H} \cdot \mathbf{H}, \\
- \beta_o \sum_{\alpha \alpha'} \Lambda_{\alpha \alpha'} \mathbf{H} \cdot \mathbf{H} = \beta_o \sum_{\alpha \alpha'} g_{\alpha} \delta_{\alpha \alpha'} - 2\lambda \Lambda_{\alpha \alpha'}.
\end{align*}
\]

(2.22)

where \( g_{\alpha} = g_{e} \delta_{\alpha} - 2\lambda \Lambda_{\alpha} \),

(2.23)

and \( D_{\alpha \alpha'} = -\lambda^2 \Lambda_{\alpha \alpha'} \).

(2.24)

The last term of equation (2.22) may be dropped as it is not observable in EPR due to an equal shift of all energy levels.

If the perturbing Hamiltonian includes spin-spin, hyperfine, quadrupole and nuclear Zeeman interactions also, the perturbation calculations give additional contribution to \( \mathbf{H}_{\text{spin}} \). The spin Hamiltonian now becomes

\[
\mathbf{H}_{\text{spin}} = \beta_o \sum_{\alpha \alpha'} g_{\alpha} \delta_{\alpha \alpha'} \mathbf{S} \cdot \mathbf{S} + \sum_{\alpha \alpha'} D_{\alpha \alpha'} \mathbf{S} \cdot \mathbf{S} + \sum_{\alpha \alpha'} A_{\alpha} \mathbf{S} \cdot \mathbf{I} \mathbf{I} + \sum_{\alpha \alpha'} Q_{\alpha} \mathbf{I} \cdot \mathbf{I} - \gamma \beta_\mathbf{N} \mathbf{H} \cdot \mathbf{I},
\]

(2.25)

where \( g_{\alpha \alpha'}, D_{\alpha \alpha'}, A_{\alpha \alpha'} \) and \( Q_{\alpha \alpha} \) are second rank tensors.

This can be written in abbreviated form as

\[
\mathbf{H}_{\text{spin}} = \beta_o \mathbf{H} \cdot \mathbf{g} \mathbf{S} \cdot \mathbf{S} + \mathbf{D} \cdot \mathbf{S} \cdot \mathbf{S} + \mathbf{A} \cdot \mathbf{I} \cdot \mathbf{I} + \mathbf{Q} \cdot \mathbf{I} \cdot \mathbf{I} - \gamma \beta_\mathbf{N} \mathbf{H} \cdot \mathbf{I},
\]

(2.26)

The tensors \( \mathbf{D}, \mathbf{g}, \mathbf{A} \) and \( \mathbf{Q} \) are also known as spin Hamiltonian parameters.
A system of orthogonal axes may be chosen to represent the principal axis system depending on crystal field symmetry. Each tensor in equation (2.26) may be diagonalized in this system. In orthorhombic symmetry all the tensors have a common principal axis system and the form of spin Hamiltonian is

\[
\mathbf{H}_{\text{spin}} = \beta_0 \left[ g_x H_x S_x + g_y H_y S_y + g_z H_z S_z \right] 
+ D \left[ S_z^2 - \frac{1}{3} S(S+1) \right] + E \left[ S_x^2 - S_y^2 \right] 
+ A_x S_x I_x + A_y S_y I_y + A_z S_z I_z 
+ Q' \left[ I_z^2 - \frac{1}{3} I(I+1) \right] + Q'' \left[ I_x^2 - I_y^2 \right] \tag{2.27}
\]

where D and E are axial and rhombic field splitting parameters,

\[
D = D_z - \frac{1}{2} \left[ D_x + D_y \right], \quad E = \frac{1}{2} \left[ D_x - D_y \right],
\]

Q' and Q'' are the axial and rhombic part of the nuclear quadrupole interaction,

\[
Q' = Q_z - \frac{1}{2} \left[ Q_x + Q_y \right], \quad \text{and} \quad Q'' = \frac{1}{2} \left[ Q_x - Q_y \right].
\]

2.4 Spin Hamiltonian Parameters

The spin Hamiltonian parameters determined from
observed EPR spectrum can provide information about a paramagnetic system. Their significance is described below.

a) $g$-Tensor: For a free electron, the spectroscopic splitting factor '$g$' has the value 2.0023 and is known as free spin value $g_e$. The $g$-factor value differs from $g_e$ in solids. In the principal axis system it can be expressed as

$$g_{\alpha\alpha'} = g_e  \delta_{\alpha\alpha'} - 2\lambda \Lambda_{\alpha\alpha'}$$

where $\Lambda_{\alpha\alpha'}$ is the matrix element connecting $\alpha$ and $\alpha'$ states and $\lambda$ is the spin-orbit coupling constant. When there is no perturbation due to spin-orbit coupling, the $g$-tensor becomes isotropic. It is in fact an experimentally determined quantity obtained by equating the number of magnetic dipole transitions in the ground state to $2S'$ and is given by

$$<L + 2S> = gS'$$

which accounts for any orbital momentum in terms of effective spin. In octahedral crystal field $g$ is isotropic with $g_x = g_y = g_z$ while in case of tetragonal, trigonal or hexagonal crystal field $g_z = g_\parallel$ and $g_x = g_y = g_\perp$ where $z$ is the axis of symmetry. The principal values of $g$ are unequal for orthorhombic symmetry.
b) **Fine Structure Coefficients** $D$ and $E$: The fine structure splitting is caused by the spin-spin and spin-orbit interactions when the paramagnetic ions have ground state multiplet in asymmetrical crystal field. The tensor $D$ is a measure of this splitting in an axial crystal field. In the spin Hamiltonian the term $S \cdot D \cdot S$ can be written for the orthorhombic symmetry as

$$ S \cdot D \cdot S = D[S_z^2 - \frac{1}{3} S(S+1)] + E[S_x^2 - S_y^2] $$

$$ + \frac{1}{3} [(D_{xx} + D_{yy} + D_{zz}) S(S+1)] $$

where

$$ D = D_{zz} - \frac{1}{2} (D_{xx} + D_{yy}) $$

and

$$ E = \frac{1}{2} (D_{xx} - D_{yy}) $$

where $E$ represents the rhombic component of the crystal field. In usual definition of elements of $D$, $\Sigma D_{\alpha \alpha} = 0$, thus $D_{xx} + D_{yy} + D_{zz} = 0$ and third term of Eq.(2.30) becomes zero. Eq.(2.31) and (2.32) can be written as

$$ D = D_{zz} - \frac{1}{2} (D_x + D_y), $$

and

$$ E = \frac{1}{2} (D_x - D_y). $$

c) **Hyperfine Structure Coefficient**, $A$: The contribution to the hyperfine structure comes from the interaction between the electronic and nuclear spins and interaction due to
anomalous s electrons. The tensor $A$ gives the separation between hyperfine levels and its principal values are $A_x$, $A_y$, and $A_z$. In case of axial symmetry $A_z = A_{||}$, and $A_x = A_y = A_{\perp}$ while for orthorhombic symmetry $A_x \neq A_y \neq A_z$.

d) Quadrupole Tensors $Q$ and $Q'$: The quadrupole interaction arises due to coupling between nuclear spin and the electric field gradient in an atom or ion. It also contributes to the hyperfine structure. $Q$ and $Q'$ express the axial and rhombic components of the nuclear quadrupole interaction to a first order. Their magnitudes are very small and may be determined from forbidden hyperfine transitions $\Delta m = \pm 1, \pm 2$.

2.5 Selection Rules

The resonance transitions can be accounted by applying time-dependent perturbation theory between eigenstates of the spin Hamiltonian operator. In electron paramagnetic resonance, the ground state of a paramagnetic ion is split under a constant magnetic field $H_0$ and magnetic dipole transitions are induced between Zeeman levels when oscillating magnetic field component $H_1(t)$ of the microwave radiation is perpendicular to $H_0$. The total magnetic field may be expressed as [9]

$$H = H_1 (\hat{x} \cos \omega t + \hat{y} \sin \omega t) + H_0 \hat{z}$$  \hspace{1cm} (2.33)
where $\omega/2\pi$ is the frequency of microwave radiation.

The spin Hamiltonian terms containing $H_o$ such as $\beta_o H_o \cdot g \cdot S$ and $\gamma \beta_N H_o \cdot I$ may then be considered as the perturbation terms by substituting $H_1$ in place of $H_o$ and the perturbing spin Hamiltonian is

$$H_1' = \beta_o H_1 \cdot g \cdot S - \gamma \beta_N H_1 \cdot I$$

(2.34)

The oscillating perturbation induces transition between states $|i\rangle$ and $|j\rangle$ and the transition probability per unit time is proportional to $|\langle j|H_1'|i\rangle|^2$. Now the intensity of transition can be written as

$$I_{ij} \equiv |\langle j|H_1'|i\rangle|^2$$

$$= \beta_o^2 |\langle j|H_1 \cdot g \cdot S|i\rangle|^2 + \gamma^2 \beta_N^2 |\langle j|H_1 \cdot I|i\rangle|^2$$

$$- 2 \gamma \beta_o \beta_N \text{Re}[\langle j|H_1 \cdot g \cdot S|i\rangle \langle j|H_1 \cdot I|i\rangle^*]$$

(2.35)

If the first term of equation (2.35) is non-zero, this will dominate in case of almost all paramagnets and produce EPR transitions. Low frequency NMR transitions are caused by the second term while the third one is negligibly small. If the direction of spin quantization is along the steady magnetic field and NMR transitions are ignored, the allowed EPR transitions are induced by the selection rules

$$\Delta M = \pm 1, \quad M = S, S-1, S-2, \ldots, -S.$$
\[ \Delta m = 0, \ m = I, I-1, I-2, \ldots -I. \]

Transitions not allowed by above selection rules are known as forbidden transitions and may also occur with much smaller intensity. As the eigenstates with spin quantization along \( \mathbf{H} \cdot \mathbf{g} \) are not pure \( |M,m\rangle \) states, off-diagonal terms due to \( D \) will generally mix in \( |M+1,m\rangle \) and \( |M-2,m\rangle \) with an amplitude of the order of \( D/g \beta_0 H \). Other functions also get mixed in but with even smaller amplitudes of \( D^2/g^2 \beta_0^2 H^2 \) as higher order. Thus fine forbidden transitions take place corresponding to \( \Delta M = \pm 2, \pm 3 \) with much smaller intensities depending on \( (D/g \beta_0 H)^2 \).

If the hyperfine term \( S \cdot A \cdot I \) is present with \( \beta_0 H \cdot g \cdot S \) in the spin Hamiltonian, the intensity of some transitions is even lower by \( A^2/(g \beta_0 H)^2 \) due to admixtures of the eigenstates \( |M+1,m\rangle, |M+1, m+1\rangle \), and \( |M+1, m-1\rangle \). Such transitions occur due to \( \Delta m = \pm 1 \) and are known as 'hyperfine forbidden' transitions. These transitions may be observed when quadrupole interaction also contributes to the spin Hamiltonian.

2.6 Relaxation Processes

The EPR transitions in an external magnetic field occur from the lower levels to higher ones by absorbing microwave radiation. The electrons transferred to upper
levels return to lower levels by relaxation processes and the absorption of microwave radiation continues. The relaxation processes proceed by two mechanisms — i) interactions of the spins with the lattice, and ii) interactions among the spins themselves.

A. Spin-Lattice Relaxation

The spin system initially in thermal equilibrium gets heated by absorbing radiation of frequency \( \nu_0 \) at resonance. The heated spins return to thermal equilibrium by an exponential process with time constant \( T_1 \) which serves as a measure of energy transfer from the spins to the lattice. This process is called spin-lattice relaxation process. The crystal field surrounding the paramagnetic ion gets phonon modulated [9] and the relaxation proceeds by the processes discussed below.

1) Direct Process

This process proceeds by emission of a phonon whose energy is equal to the difference in the energy of two levels of the ground state between which the spin transition has already occurred. Figure 2.1 [10] shows the spin transition from state 2 to 1, the energy being converted into a single phonon at resonance frequency \( \nu_0 \). The direct process occurs at low temperatures.
Fig. 2.1 - Schematic diagram to demonstrate Direct, Raman and Orbach processes.
ii) **Raman Process**: It is a two phonon process occurring relatively at higher temperatures in which one phonon at frequency $\nu_1$ is absorbed and the second one at $\nu_2$ is emitted, the frequency difference ($\nu_2 - \nu_1$) being equal to resonance frequency $\nu_o$. This frequency difference ($\nu_2 - \nu_1 = \nu_o$) is the only condition for the Raman process which may involve phonons from any part of the frequency spectrum whereas in the direct process only phonons of a particular frequency $\nu_o$ are involved.

iii) **Orbach Process**: This process involves two successive transitions which occur through an intermediate state. The spin transferred from 1 to high level 2 by absorbing $h\nu_o$, then further transferred to an excited level by absorbing another phonon $h\nu_{32}$. The excited level 3 does not belong to the ground state. A phonon $h\nu_{31}$ is emitted due to spontaneous transition from the higher level 3 to the initial level 1 such that $h\nu_{31} = h\nu_o + h\nu_{32}$. Low lying excited states for this type of process are found in rare earth impurities doped in crystals.

B. **Spin-Spin Relaxation**: The magnetic dipoles situated close enough experience dipolar fields of their neighbours. The spins exchange energy among themselves by their mutual orientations change and reestablish [11] the thermal equilibrium exponentially with time constant $T_2$ known as
spin-spin relaxation time. The spin-spin relaxation process leads to exchange of energy at a faster rate than the spin-lattice relaxation process and therefore $T_2$ is smaller than $T_1$.

2.7 Optical Absorption of 3d Ions

In a solid the doped transition metal ion is supposed to be present in an electric field whose symmetry depends on the number and arrangement of the surrounding ligands and whose strength depends on the electrical nature of the ligands. The optical absorption bands are associated with electronic transitions between the energy levels of the transition metal ion split by the electric field.

In octahedral arrangement, the metal ion is situated at the centre and the nearest-neighbour ligands at the corners of the octahedron (Figure 2.2a). If a 3d ion is present at octahedral site, the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals are closer to ligands and will be raised in energy relative to free ion value by Coulomb repulsion while the remaining three $d_{xy}$, $d_{yz}$ and $d_{zx}$ orbitals situated away from ligands will be lowered in energy. Upper states are designated as $e_g$ and lower ones as $t_{2g}$. The energy required to promote a $d$ electron from $t_{2g}$ orbital to $e_g$ orbital is equal to energy of splitting which depends upon the interaction between the metal electron and those of ligands. The energy splitting $\Delta_0$ and the intensities
Fig. 2.2 Diagram showing point groups. (a) A regular octahedron and (b) a regular tetrahedron.
of spectral bands associated with above transitions may be utilized to study the nature and geometry of nearest-neighbour of the ion in crystalline and glassy solids.

For 3d ion in a tetrahedral environment, the ligands are at the opposite corners of a cube (Figure 2.2b). The orbital $e$ is lowered in energy and $t_2$ has higher energy. The energy required to promote an electron from $e$ to $t_2$ orbital would be $\Delta_t$ (Figure 2.3). From electrostatic argument [12] it has been shown that the d orbital splitting in tetrahedral field is less than that in an octahedral field and the two are related by

$$\Delta_t = \frac{4}{9} \Delta_o$$

(2.36)

which is applicable for the same or similar type of ligands, even if the ion contains more unpaired electrons. If the symmetry is lowered such as from cubic to tetragonal or orthorhombic, the degeneracy of the levels $e$ and $t_2$ is lifted and they split into more levels with lesser degeneracy. In case of ions with a $3d^1$ hole, the pattern of splitting is inverted to the corresponding $3d^1$ electron system.

2.8 d-d Absorption Spectrum

The intensities of absorption bands arising from transition metal ions vary with their concentration and
Fig. 2.3 Energy level diagram showing the splitting of the set of d orbitals by octahedral and tetrahedral environments.
from glass to glass. The electric dipole plays an important role for the absorption of light by complex ions. If $\phi_o$ and $\phi_e$ are the wavefunctions of the ground and excited states between which electrons are excited by absorbing radiation energy from a part of visible spectrum, then the condition for the transition to occur is [13]

$$\omega_{oe} \propto |\phi_o|p|\phi_e|^2 \text{ or } |\phi_o|\tau|\phi_e|^2 \neq 0$$

where $p$ is electric dipole moment ($p = er$) and $\omega_{oe}$ is transition probability. The intensity of the absorption band is proportional to the square of the transition probability $\omega_{oe}$. The transition probability has non-zero value only if the direct product of the functions is totally symmetric under the point group symmetry involved.

The selection rule for the spin allowed transition is $\Delta S = 0$, where $\Delta S$ is the change in multiplicity between two energy states. Electronic transitions are said to be spin-forbidden for which $\Delta S \neq 0$. The Laporte selection rule tells that transitions are allowed only between states with opposite parity. For transition metal ion, d orbitals are all $g$ in character i.e., have same parity and therefore their ion complexes would show no absorption spectra according to Laporte rule. However, molecular vibrations present in a complex allow coupling to occur between electronic and vibrational energy levels in both the ground and excited states. Resulting energy levels are
called vibronic energy levels which may be g as well as u type. The ground state and excited state combined with vibronic level will have both g and u symmetry. Normally forbidden d-d transition will become allowed through electric dipole transition with a low intensity among these levels.

The coupling between spin and orbit angular momentum in an atomic complex makes the spin selection rule less rigid and allows weak spin-forbidden bands. The intensity of these bands increases as the spin-orbit coupling constants increase particularly for the more half filled 3d shell ions. These spin-forbidden transitions steal the intensity of the nearby allowed transitions when a vibrational level due to spin-orbit mixing combines with both forbidden and allowed electronic levels. There are several other conditions under which normally forbidden d-d transitions become allowed with low intensity [14].

Tanabe and Sugano [15] have calculated the energy values of different states of free 3dn ions (3d2 to 3d8) in the form of matrices. The diagrams based on Racah parameters B and C which specify the interelectronic Coulomb interaction [16] are known as Tanabe-Sugano (T-S) diagrams and are used for interpretation of optical absorption spectra. The crystal field parameter Dq, B and C can be determined using T-S diagrams.
REFERENCES


GENERAL REFERENCES


CHAPTER III

EXPERIMENTAL DETAILS

Abstract

This Chapter describes the preparation of glass samples, working of the EPR spectrometer and ultraviolet-visible spectrophotometer and procedures of recording EPR and optical absorption spectra.
3.1 Preparation of Samples

3.1.1 Glasses

The starting materials for the preparation of glasses were reagent grade chemicals with purity better than 99.5%. The composition of different systems of glasses have been given in the following Chapters wherever required. Transition metal ions such as \( \text{Cu}^{2+}, \text{V}^{4+}, \text{Mn}^{2+} \) etc. were incorporated into the samples as probes by adding required amount of oxide or carbonate of these metals to various compositions. Chemicals were mixed thoroughly in the appropriate proportions by mortar and pastle. The mixture was placed in alumina crucible in a muffle furnace and melt in a temperature range 1123 to 1273 K for a duration of 20-25 minutes. The melts were stirred from time to time to promote homogenity and were then quenched in air by pouring them into brass moulds. Glasses formed without dopants are clear. Some glasses are found hygroscopic. Glasses were also prepared in the form of circular discs of diameter \( \sim 10 \) to 15 mm and thickness \( \sim 1.00 \) to 1.50 mm for optical absorption study.

3.1.2 Crystals

The crystals were grown at room temperature by slow evaporation of saturated aqueous solution of the desired compounds mixed in stoichiometric proportion.
3.2 EPR Spectrometer

The EPR spectra of transition metal ions doped in glasses have been recorded using Varian E-line Century Series E-109 X-band (~9.0 to 9.5 GHz) spectrometer. A block diagram of an EPR spectrometer is shown in Fig.3.1. The various units and their functions are described briefly below:

i) Electromagnet

The electromagnet produces a homogeneous magnetic field \( H_0 \) which can be varied from zero to at least 500 mT.

ii) Magnet Power Supply

The power supply for the electromagnet provides a stable and controlled current for energizing the coils of the electromagnet to produce the required magnetic field.

iii) Scanning Unit

To obtain the EPR spectrum at a given microwave frequency, the magnetic field in the air gap is varied by changing power through coils continuously. This is provided by scanning unit which supplies a control voltage to the input of the current regulated magnet power supply. The control voltage varies linearly with time providing a linear sweep of the magnetic field.
Fig. 3.1 Block diagram of an EPR spectrometer.
iv) 100 KHz Sweep Generator

Modulation is achieved by placing small Helmholtz coils on each side of the resonant cavity walls along the axis of the static magnetic field $H_0$. The 100 KHz sweep generator provides a small modulation of the static field at the sample within the resonant cavity and supply a phase reference voltage to the signal phase detector.

v) Audio Sweep Generator

It produces an additional magnetic field modulation to the resonant cavity as well as a sweep for the oscilloscope X-axis.

vi) Klystron Oscillator

In most EPR spectrometers, the source of microwave radiation is Klystron or Gunn diode oscillator. The microwave radiations produced by klystron oscillator are allowed to enter the hybrid tee through rectangular waveguide in $TE_{10}$ mode. The power flow is controlled by a variable attenuator connected between the klystron and the hybrid tee. An Automatic Frequency Control (AFC) system is usually included for optimum stability of the microwave oscillator. The klystron output frequency is modulated with respect to the resonant frequency of the sample cavity. This frequency modulation is done by employing the AFC phase detector and the klystron reflector.
vii) Hybrid Tee

This device does not allow microwave power to pass directly from arm 1 to opposite arm 4 (Fig. 3.1). The power from arm 1 is equally divided between arms 2 and 3. No power will enter arm 4 if all of it is absorbed in the arms 2 and 3. Thus the crystal detector placed in arm 4 will not receive any energy and arrangement will be balanced. A change in the terminating impedance of arm 3 or 2 will unbalance the hybrid tee and power will reach in arm 4. The crystal detector in arm 4 then responds to unbalanced energy which usually appears when resonance occurs in the sample placed in the resonant cavity attached to arm 2.

viii) Resonant Cavity

The resonant cavity system is fabricated from high conductivity metal with dimensions comparable to the wavelength of microwaves. At resonance, the cavity is capable of sustaining microwave oscillations which form standing wave pattern or mode. The cavity is constructed in TE_{102} mode such that microwave magnetic field \( H_1 \) acts at right angles to the static magnetic field \( H_0 \) at the sample which is placed at the maximum of microwave magnetic field. The resonant cavity acts like a tuned circuit of high quality factor \( Q \) where
\[ Q = \frac{2\pi}{\text{energy dissipated per cycle}} \]

At resonance in the sample, the impedance of the cavity changes producing unbalanced energy which is reflected to the crystal detector attached to the hybrid tee. Thus detection of resonance becomes possible.

ix) Crystal Detector

The commonly used silicon crystal detector acts as a microwave rectifier and demodulates the microwave energy. The demodulated 100 KHz signal voltage containing EPR information is amplified by 100 KHz amplifier following the crystal detector. A crystal detector produces an inherent noise which decreases with increase in frequency of the detector signal \( \frac{1}{f} \). This noise is minimized with 100 KHz magnetic field modulation.

x) Signal Phase Detector

The reduction in noise is further achieved by phase sensitive detection following amplification. The amplified signal is carried out to the input of the signal phase detector. The phase detector combined with an integrator and a graphic recorder provides the recording of the EPR spectrum.
xi) Oscilloscope

An oscilloscope is included in the spectrometer for initial set-up, adjustment of sample and visual observation of the resonance signal. It is also used for check-out and adjustment of system units.

3.3 Recording of EPR Spectra

The glasses were crushed coarsely into powder and poured into quartz tubes of diameters upto 5 mm. The sample tube is then placed inside the Varian E-231 multipurpose resonant cavity between the poles of the electromagnet and positioned in the region irradiated by microwave energy from the klystron such that the magnetic field component of electromagnetic wave is perpendicular to the steady magnetic field. The magnetic field is varied slowly at the sample in the cavity to reach a value required for resonance.

By adjusting the tuning of the klystron both mechanically and electronically and the AFC system, the mode of operation can be shifted to match the frequency of the resonance sample cavity. This is indicated by an absorption dip in the klystron power mode precisely at the resonance frequency of the cavity. The depth of absorption mode indicates the amount of power being absorbed by the sample. The klystron frequency is adjusted with that of the sample cavity by AFC system. As a result of resonance, some of the
power reaching the cavity is absorbed by the sample and the hybrid tee gets unbalanced. The unbalanced power is received by the crystal detector which responds to the 100 KHz signal voltage containing EPR information. Once EPR signal is obtained, the amount of radio frequency power delivered to the sample is adjusted empirically and the first harmonic presentation of EPR signal against magnetic field can be observed on the oscilloscope. When oscilloscope displays a suitable spectrum visually, it is recorded on the chart paper by a graphic recorder. The weights of glass samples (≈ 0.15 gm) and all instrument settings were kept same and gains are only varied as required.

As a reference for the measurement of the magnetic fields at various resonance lines, the resonance line of Di-Phenyl Picryl Hydrazyl (DPPH) with \( g = 2.0036 \) is used. Spectra at liquid nitrogen temperature are recorded by immersing glasses in liquid nitrogen dewar with a cold finger fitted to the resonant cavity.

### 3.4 Optical Absorption Spectra

The optical absorption spectra of the glass samples and single crystals were recorded with Ciba-Corning UV-visible 2800 and Shimadzu UV-visible 160 spectrophotometers in the wavelength region 200-1100 nm. Fig.3.2 and 3.3 show a block-diagram and the optical system of a UV-visible spectrophotometer respectively. The source of
Fig. 3.2 Block diagram of a UV-visible spectrophotometer.
Fig. 3.3 Diagram showing the optical system of Ciba-Corning UV-visible spectrophotometer (Model 2800).
light most commonly used in the visible-near infrared region (330-1100 nm) is a tungsten iodine lamp and the UV (200-350 nm) source is deuterium discharge lamp. Radiation from the source lamps (WI and D₂) is reflected by the mirror M₁ and is incident on the slit S₁ after passing through a high order light cut-off filter. The light is then monochromated by a concave diffraction grating (G) and emerges from the slit S₂. The image of the exit slit is split into two beams by the beam splitter (BS). The light beams pass through the sample and reference cells alternately and are incident on the silicon photocell detector D. Detector converts the light signal into the proportionate amount of electrical energy. The alternating component of the photocell output is amplified and subjected to A-D conversion. Measurement data thus converted is then subjected to necessary spectrum processing by a microcomputer. The optical absorption can be displayed on Cathode Ray Tube (CRT) screen. When a properly resolved spectrum is observed, the printer is used to print out parameters, measurement results along with spectrum on prescribed chart. The wavelength scale is accurate to better than 0.4 nm throughout its range 200-1100 nm.
GENERAL REFERENCES


CHAPTER IV

ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES
OF Cu$^{2+}$ IN NaF$_x$B$_2$O$_3$ AND NaF$_x$Na$_2$B$_2$O$_3$ GLASSES*

Abstract

EPR and optical absorption of Cu$^{2+}$ in $x$Na$_2$F$_2$. (100-x)B$_2$O$_3$ (5$\leqslant$x$\leqslant$35) and $x$(Na$_2$F$_2$.Na$_2$O)(100-2x)B$_2$O$_3$ (2.5$\leqslant$x$\leqslant$17.5) glasses have been studied in the X-band at 290 and 77K. The theory related to EPR and optical absorption of Cu$^{2+}$ has been described and spin Hamiltonian parameters (g$_{||}$, g$_\perp$, A$_{||}$, A$_\perp$), molecular orbital coefficients ($\alpha^2$, $\beta^2$) and normalized covalency parameters ($\overline{\alpha}$, $\overline{\beta}$) have been evaluated from the observed spectra. The optical absorption spectra exhibit a single band due to $^2$B$_{1g}$ $\rightarrow$ $^2$B$_{2g}$ transition. EPR results show that the Cu$^{2+}$ in these glasses forms a complex with octahedral symmetry having strong tetragonal distortion (D$_{4h}$) and appears to adopt to a surrounding shared by oxygens and fluorines. The changes in the values of g$_{||}$, A$_{||}$ and $\beta^2$ confirm the existence of boron oxide anomaly. Values of $\beta^2_1$ (0.97 to 0.82) show that the in-plane $\pi$-bonding of Cu$^{2+}$ and ligands is significantly ionic in nature. The ionicity decreases with increasing concentration of Na$_2$F$_2$ or Na$_2$O. There exists a moderate covalency for the in-plane $\sigma$-bonding.

* Paper based on this work has been communicated to 'Physics and Chemistry of Glasses'.

4.1 Introduction

Alkali haloborate glasses find potential applications as solid electrolytes of variable composition for fast ion conduction [1-8] with most of the research work centred on lithium chloroborate system. Among other haloborate glasses, sodium fluoroborate has been studied by several research workers [4-10]. Measurement of glass forming behaviour, density, refractive index, viscosity, thermal expansion, glass transformation temperature and electrical conductivity have been recently reported [9,10] on NaF.B_2O_3 and NaF.Na_2O.B_2O_3 glasses.

Detailed reviews written by various authors [11-14] provide information about EPR and optical absorption of transition group ions in glasses. The EPR of Cu^{2+} has been first reported by Sands [15] in the soda-lime silicate system. Present Chapter deals with EPR and optical absorption investigations of Cu^{2+} doped NaF.B_2O_3 and NaF.Na_2O.B_2O_3 glasses.

4.2 Experimental

The starting materials for the preparation of glasses were reagent grade NaF, Na_2CO_3 and H_3BO_3 with purity better than 99.5%. The composition data of glasses studied are given in Table 4.1 based on xNa_2F_2.(100-x)B_2O_3 (5≤x≤35) and x(Na_2F_2.Na_2O).(100-2x)B_2O_3 where 2.5≤x≤17.5. Cupric
Table 4.1

The Composition Data For the Cu^{2+} Doped-glasses in
i) xNa_2F_2.(100-x)B_2O_3 (5<x<35) and
ii) x(Na_2F_2.Na_2O)(100-2x)B_2O_3 (2.5<x<17.5)

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Na_2F_2</th>
<th>Na_2O</th>
<th>B_2O_3</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC1</td>
<td>5</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>NC2</td>
<td>10</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>NC3</td>
<td>15</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>NC4</td>
<td>20</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>NC5</td>
<td>25</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>NC6</td>
<td>30</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>NC7</td>
<td>35</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>NNC1</td>
<td>2.5</td>
<td>2.5</td>
<td>95</td>
</tr>
<tr>
<td>NNC2</td>
<td>5.0</td>
<td>5.0</td>
<td>90</td>
</tr>
<tr>
<td>NNC3</td>
<td>7.5</td>
<td>7.5</td>
<td>85</td>
</tr>
<tr>
<td>NNC4</td>
<td>12.5</td>
<td>12.5</td>
<td>75</td>
</tr>
<tr>
<td>NNC5</td>
<td>15.0</td>
<td>15.0</td>
<td>70</td>
</tr>
<tr>
<td>NNC6</td>
<td>17.5</td>
<td>17.5</td>
<td>65</td>
</tr>
</tbody>
</table>
ions were incorporated in the samples by adding 1.0 mol% of CuO to each composition. The procedures described in Chapter III were followed for the preparation of glass samples, recording of EPR and optical absorption spectra. The optical absorption spectra of Cu$^{2+}$ in these glasses were recorded on Ciba-Corning UV-visible 2800 spectrophotometer at 290K.

4.3 Theory

4.3.1 EPR

The divalent copper ion (atomic number $Z = 29$) has the electronic configuration $[\text{Ar}]3d^9$ ($[\text{Ar}]$ stands for $1s^22s^22p^63s^23p^6$, the argon ground configuration) and represents a single hole. When incorporated into a glassy material it provides useful information regarding the structure of the network environment through its optical and EPR spectra. The $3d^1$ hole has a ground state $^2D_{5/2}$ with spin $S = 1/2$. In a cubic field, fivefold orbital level of Cu$^{2+}$ ion is split into an upper triplet $^2T_{2g}$ and a lower doublet $^2E_g$; the energy difference being $10Dq$ ($Dq$ is crystal field parameter). For lower symmetry the $^2T_{2g}$ and $^2E_g$ further split as shown in Fig. 4.1. The EPR is concerned with the lowest doubly-degenerate state the degeneracy of which can be removed in the magnetic field producing two energy levels. The magnetic properties of the lowest orbital singlet may be modified slightly by admixing
Fig. 4.1 Splitting of the free ion ground state of Cu$^{2+}$. Transitions are indicated (after Alger [16]).
the excited states through spin-orbit interaction which results in anisotropy in g-factor. The nuclear spin of the copper nucleus is $3/2$ for both $^{63}\text{Cu}$ (the natural abundance ratio is 69%) and $^{65}\text{Cu}$ (31%) and each of the two lower most levels gets split into four ($2I + 1 = 4$). EPR would show four hyperfine transitions according to the selection rules $\Delta M = \pm 1$ and $\Delta m = 0$. Fig.4.1 shows the splitting of the ground state of $\text{Cu}^{2+}$ under various interactions [16].

**Molecular Orbital Treatment**

For $\text{Cu}^{2+}$ ion in crystalline environment there may not exist static regular octahedral site because the cubic symmetry is disturbed by electronic hole in the degenerate $d_{x^2-y^2}$ orbital which produces the tetragonal distortion. According to Jahn-Teller theorem, any non-linear system with a degenerate ground state must distort in order to remove the degeneracy. This effect causes predominantly an elongated static octahedral coordination with four short in-plane bond lengths and two longer axis bond lengths. The molecular orbital treatment of EPR spectrum of $\text{Cu}^{2+}$ by Maki and Mc Garvey [17] and slightly modified by Kivelson and Neiman [18] is applicable to this configuration. A typical diagram of $\text{Cu}^{2+}$ complex in oxide glasses is shown in Fig.4.2 [13].

It is assumed that each oxygen as a ligand provides $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals for the formation of molecular
Fig. 4.2 The octahedral complex with tetragonal elongation Cu$^{2+}$ in oxide glasses (after Griscom [13]).
orbitals with 3d orbitals of the Cu$^{2+}$ ion. The four ligands placed on the $+x$ and $+y$ axes are labelled by superscripts starting with one on the $+x$ axis and proceeding counterclockwise. The electrons occupying the bonding orbitals populate primarily on the ligand atoms and those with antibonding orbitals centre largely on the Cu$^{2+}$ ion. The 3d$^1$ cupric hole exists in $B_{1g}$ antibonding orbital in the ground state and in $B_{2g}$ in the first excited state. The necessary antibonding orbitals, those of highest energy are given here in the order of increasing energy for a 3d$^1$ hole configuration.

$$B_{1g} = \alpha d_{x^2-y^2} - \frac{\alpha'}{2} [\sigma_1^{(1)} + \sigma_2^{(2)} + \sigma_3^{(3)} - \sigma_4^{(4)}], \quad (4.1)$$

$$B_{2g} = \beta d_{xy} - \frac{(1-\beta^2)^{1/2}}{2} [p_1^{(1)} + p_2^{(2)} - p_3^{(3)} - p_4^{(4)}], \quad (4.2)$$

$$A_{1g} = \alpha d_{3z^2-r^2} - \frac{\alpha'}{2} [\sigma_1^{(1)} + \sigma_2^{(2)} - \sigma_3^{(3)} + \sigma_4^{(4)}], \quad (4.3)$$

$$E_g = \left\{ \begin{array}{l}
\beta d_{xz} - \frac{(1-\beta^2)^{1/2}}{2} [p_1^{(1)} - p_3^{(3)}] \\
\beta d_{yz} - \frac{(1-\beta^2)^{1/2}}{2} [p_2^{(2)} - p_4^{(4)}]
\end{array} \right\} \quad (4.4)$$

The $\alpha$ and $\beta$ are coefficient of ion wavefunctions and $\alpha'$ is
the coefficient of ligand wavefunctions. \( \sigma_k \) are \( sp^n \) hybridized \( \sigma \) orbitals of the ligands where \( k \) gives the symmetry properties. Normalization of the \( \sigma \) orbitals, \( B_{1g} \) and \( A_{1g} \) yields
\[
\alpha^2 + \alpha'^2 - 2\alpha\alpha' S_{\alpha\alpha} = 1, \quad (4.5)
\]
\[
\alpha_1^2 + \alpha'^2_1 - 2\alpha_1\alpha'_1 S_{\alpha_1\alpha'_1} = 1, \quad (4.6)
\]
where \( S_{\alpha\alpha} \) and \( S_{\alpha_1\alpha'_1} \) are the overlap integrals concerning the 3d atomic orbitals of the central ion and the \( \sigma \)-symmetry orbitals of the ligands, both belonging to the same irreducible representations. The square of the coefficients of the atomic orbitals in a given molecular orbital take the values between two extremes; 1 and 0 for the purely ionic bond and \( \frac{1}{2} (1+S) \) for the purely covalent bond. The overlap integral for the \( \pi \)-bonding is small and may be neglected.

4.3.2 Optical Absorption

The energy level scheme of 3d\(^1\) hole in solids is the same as that of 3d\(^1\) ion but the splitting pattern would be inverted to the corresponding 3d\(^1\) electron system. Fig.4.1 shows the splitting of energy levels for 3d\(^1\) hole in different crystal environments. In lower symmetry, the \( ^2E_g \) is split into \( ^2A_{1g} \) and \( ^2B_{1g} \); the upper \( ^2T_{2g} \) into \( ^2B_{2g} \) and \( ^2E_g \). The ordering of the levels depends upon site symmetry and coordination of the ion. The energy terms in \( D_{4h} \)
symmetry correspond to the orbitals as follows:

\[ |3z^2 - r^2\rangle \quad \longrightarrow \quad ^2A_{1g} \]
\[ |x^2 - y^2\rangle \quad \longrightarrow \quad ^2B_{1g} \]
\[ |xz\rangle, |yz\rangle \quad \longrightarrow \quad ^2E_g \]
\[ |xy\rangle \quad \longrightarrow \quad ^2B_{2g}. \]

For Cu\(^{2+}\) in a regular octahedral complex, one absorption band is expected corresponding to the \(^2E_g \rightarrow ^2T_{2g}\) transitions, whereas at sites of lower symmetry more than one band will be observed. For example in D\(_{4h}\), Cu\(^{2+}\) complex may give a pair of absorption bands corresponding to \(^2B_{1g} \rightarrow ^2B_{2g}\) and \(^2B_{1g} \rightarrow ^2E_g\) transitions.

4.4 Results and Discussion

4.4.1 EPR Measurements

No EPR spectrum is observed in undoped glasses indicating that there are no transition metal ions present in the undoped material. Fig. 4.3 and 4.4 show the spectra recorded at 290K for Cu\(^{2+}\) doped in NaF.B\(_2\)O\(_3\) and NaF.Na\(_2\)O.B\(_2\)O\(_3\) glasses. These spectra are similar to those reported earlier for Cu\(^{2+}\) in many other glass systems [19,20] and show four weak parallel components in the lower field region; the perpendicular components in the higher field
Fig. 4.3 EPR spectra of Cu$^{2+}$ in NaF.B$_2$O$_3$ glasses at 290K. 
(a) Glass NC2, (b) glass NC3, (c) glass NC5 and glass NC7. 
D represents the DPPH line (0.3337T).
Fig. 4.4 EPR spectra of Cu$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K.
(a) Glass NNC2, (b) glass NNC3, (c) glass NNC4 and (d) glass NNC6. D represents the DPPH line (0.3337T).
region however are not well resolved. The spectra may be analysed by using the spin Hamiltonian of the form [18,21]

$$\mathcal{H} = \beta_0 [g|| H_z S_z + g\perp (H_x S_x + H_y S_y)]$$

$$+ A|| I_z S_z + A\perp (I_x S_x + I_y S_y),$$

(4.7)

where \(z\) is the symmetry axis of the cupric complex, \(H_x, H_y\) and \(H_z\) are the components of the static magnetic field; \(g||\) and \(g\perp\) are the parallel and perpendicular components of the anisotropic g tensor and other symbols have their usual meaning. The nuclear quadrupole interaction has been neglected [22]. The solution of the spin Hamiltonian gives resonance conditions related to \(g\) and \(A\) tensors as [23]

$$h \nu = g|| \beta_0 H + mA|| + \left(\frac{15}{4} - m^2\right) \frac{A^2}{2g|| \beta_0 H},$$

(4.8)

and

$$h \nu = g\perp \beta_0 H + mA\perp + \left(\frac{15}{4} - m^2\right) \frac{A^2|| + A^2\perp}{4g\perp \beta_0 H},$$

(4.9)

for the parallel and perpendicular hyperfine peaks respectively. \(m\) is the nuclear magnetic quantum number of the copper nucleus with values \(\pm 3/2, \pm 1/2\) and \(\nu\) is microwave frequency at resonance.
The spin Hamiltonian parameters have been evaluated [15,24] using Equations (4.8) and (4.9) and presented in Table 4.2 along with those of copper in other glasses [19,20] for comparison. All \( A_{\parallel} \) and \( A_{\perp} \) are negative for reasonable solutions. The uncertainty in the values of \( g \) and \( A \) is \( +0.003 \) and \( +2.0 \times 10^{-4} \) cm\(^{-1}\) respectively. At liquid nitrogen temperature (77K) the spectra are similar to those at room temperature. Fig. 4.5 shows the EPR spectra of Cu\(^{2+}\) in 25 Na\(_2\)F\(_2\).75B\(_2\)O\(_3\) glass at 290 and 77K.

The observed \( g_{\parallel} \) and \( g_{\perp} \) values (\( g_{\parallel} = 2.376 \) to 2.330, and \( g_{\perp} \approx 2.06 \) to 2.05, Table 4.2) are characteristic of Cu\(^{2+}\) coordinated by six ligands which form an octahedron elongated along the z-axis [19,25]. As \( g_{\parallel} > g_{\perp} > 2.0023 \), the ground state for the paramagnetic electrons is \( d_x^2-d_y^2 \) orbital (\( ^2B_{1g} \) state); the Cu\(^{2+}\) being located in distorted octahedral site (\( D_{4h} \)). Experimental data show that the cupric ion in solutions, solids and glasses form a complex with octahedral symmetry having strong tetragonal distortion [11, 26-29]. In both systems, the values of \( g_{\parallel} \), \( A_{\perp} \) and \( A_{\parallel} \) show a perceptible change indicating a general trend with increasing Na\(_2\)F\(_2\) concentration, while there is no appreciable change in the value of \( g_{\perp} \). Variation of \( g_{\parallel} \) and \( A_{\parallel} \) with Na\(_2\)F\(_2\) content are shown in Fig. 4.6.

Fig. 4.6a shows that in NaF.B\(_2\)O\(_3\) glasses \( g_{\parallel} \) decreases with increasing percentage of Na\(_2\)F\(_2\) while \( A_{\parallel} \) increases.
Fig. 4.5 EPR spectra of Cu$^{2+}$ in 25Na$_2$Z$_7$B$_2$O$_3$ glass. (a) At 290K and (b) 77K.
Fig. 4.6a Variation of $g_{\parallel}$ (solid line) and $|A_{\|}|$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.B$_2$O$_3$ glasses.
Fig. 4.6b Variation of $g_{||}$ (solid line) and $|A_{||}|$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.
A steep fall is observed in $g_{\|}$ for Na$_2$F$_2$ concentration of 15 mol% to 30 mol% and a relatively slower rise in $A_{\|}$. The steep change in $g_{\|}$ in the range (85-70) mol% of B$_2$O$_3$ (i.e., 15-30 mol% of Na$_2$F$_2$) is indicative of boron oxide anomaly (Chapter I, Section 1.3). Boron free glasses do not show this anomaly. It is interesting to note that in the present system there is no modifier oxide but a modifier fluoride. Shelby and Downie [9] have recently reported the measurements of the glass forming behaviour, refractive index, density, viscosity, thermal expansion, transformation temperature and electrical conductivity with NaF.B$_2$O$_3$ glass composition. The property composition behaviour in this system is found similar to Na$_2$O.B$_2$O$_3$ system. Our EPR results confirm the observation made by Shelby and Downie. Abrupt fall in $g_{\|}$ is associated with sudden change in the environment of Cu$^{2+}$ i.e., in the ligand field at the site of Cu$^{2+}$. This is due to the structural changes in NaF.B$_2$O$_3$ glasses with increasing concentration of Na$_2$F$_2$. Abrupt or stepwise changes in $g_{\|}$ and $A_{\|}$ have been reported by several research workers [19,30,31] in the systems showing boron oxide anomaly. The $g_{\|}$ and $A_{\|}$ variations with composition in NaF.B$_2$O$_3$ system indicate that the role played by modifier fluoride is identical to modifier oxide.

In NaF.Na$_2$O.B$_2$O$_3$ glasses, a gradual fall in the value of $g_{\|}$ and a continuous rise in the value of $A_{\|}$ are observed with increasing concentration of Na$_2$F$_2$ (Fig. 4.6b).
The replacement of Na$_2$O by Na$_2$F$_2$ causes a smooth change in property-composition curves as reported by Shelby and Ortalano [10]. The EPR results confirm the observations of Shelby and Ortalano. In this ternary system the boron oxide anomaly still exists but modified in position and magnitude. Structural changes at the site of Cu$^{2+}$ are gradual and so are the ligand field changes.

4.4.2 Optical Absorption

The optical absorption spectra of Cu$^{2+}$ in our glasses show at 290K a single absorption band with a peak position ranging from 12804 cm$^{-1}$ to 13333 cm$^{-1}$ or varying glass composition. This is attributed to the $^2$B$_{1g}$ $\rightarrow$ $^2$B$_{2g}$ transition of Cu$^{2+}$. The absorption spectra of Cu$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ are shown in Fig. 4.7 and 4.8.

The bonding characteristics of the Cu$^{2+}$ ion are evaluated using the peak positions of the absorption bands of Cu$^{2+}$ and EPR data. If the EPR and optical absorption data are correlated, the bonding coefficients are given by relations [18,19]

$$
\|g\| = g_e \left[ 1 - \frac{4\lambda a^2 \beta^2}{E(2B_{2g})} \right],
$$

and

$$
\perp g = g_e \left[ 1 - \frac{\lambda a^2 \beta^2}{E(2E_g)} \right],
$$

relations [18,19]
Fig. 4.7 Optical absorption spectra of Cu$^{2+}$ in NaF.B$_2$O$_3$ glasses at 290K.
Fig. 4.8 Optical absorption spectra of Cu$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K.
where \( \lambda \) is the spin-orbit coupling coefficient, \( \alpha^2 \) represents the in-plane \( \sigma \)-bonding coefficient, \( \beta_{\perp}^2 \) characterizes in-plane \( \pi \)-bonding, \( \beta_{\parallel}^2 \) is out-of-plane \( \pi \)-bonding coefficient, \( E(2B_{2g}^0) \) and \( E(2E_g^0) \) indicate the energy differences of the \( 2B_{1g}^0 \rightarrow 2B_{2g}^0 \) and \( 2B_{1g}^0 \rightarrow 2E_g^0 \) transitions respectively.

\( \alpha^2 \) is a measure of covalency of the \( \sigma \) bonds with equatorial ligands which gives the probability of finding the electron in ligand-d orbitals. \( \beta_{\perp}^2 \) accounts for the covalency of the \( 2B_{1g}^0 \) and \( 2B_{2g}^0 \) back-bondings between Cu\(^{2+}\) and ligand oxygens (Cu\(^{2+}\)-O in-plane \( \pi \)-bonding). As only one absorption band corresponding to the transition \( 2B_{1g}^0 \rightarrow 2B_{2g}^0 \) has been observed, the peak position corresponding to the excitation energy from \( 2B_{1g}^0 \) to \( 2E_g^0 \) may be estimated by the approximation [27]

\[
E(2B_{1g}^0 \rightarrow 2E_g^0) = \frac{2K^2 \alpha}{g_e - g_{\perp}} \quad (4.12)
\]

where \( K \) is orbital reduction factor (\( K^2 = 0.77 \)) and \( \lambda \) is the spin-orbit coupling constant (\( = -828 \text{ cm}^{-1} \)) [11]. The values of \( \beta_{\parallel}^2 \) may be expected to have values closer to unity in the bonding coefficient calculations [19].

The observed band positions for NaF.B\(_2\)O\(_3\) : Cu\(^{2+}\) and NaF.Na\(_2\)O.B\(_2\)O\(_3\) : Cu\(^{2+}\) glasses and their corresponding calculated bonding coefficients (\( \beta_{\parallel}^2 \)) values for Cu\(^{2+}\) are
shown in Table 4.2. The peak position of optical absorption is shifted slightly towards higher wavelength side with increase of Na$_2$F$_2$ content. Values of bonding parameters $\beta^2_1$ change markedly (Fig. 4.9) with changing compositions of glasses while those of $\alpha^2 (= 0.769)$ remain constant for all compositions as in other systems [32,33]. These values of $\beta^2_1$ are nearly identical with those for borate, phosphate, sulphate and sodium aluminosilicate glasses [19,33,34]. From the values of $\beta^2_1$ it may be concluded that the in-plane $\pi$-bonding is significantly ionic in nature. The ionic nature of in-plane $\pi$-bonding decreases with the increase of Na$_2$F$_2$ content.

The normalized covalency of the Cu$^{2+}$-O in-plane bondings of $\sigma$ and $\pi$ symmetry can be expressed [25] in terms of bonding coefficients $\alpha^2$ and $\beta^2_1$ as follows:

$$\overline{\sigma} = \frac{200(1-S)(1-\alpha^2)}{1-2S} \, (\%),$$

$$\overline{\pi} = 200(1-\beta^2_1) \, (\%)$$

where $S$ is the overlap integral ($S_{\text{oxygen}} = 0.076$). The values of $\overline{\pi}$ are dependent on $\beta^2_1$ and are given in Table 4.2. It may be concluded that the Cu$^{2+}$-O in-plane bonding of $\pi$ symmetry ($\overline{\pi}$) increases with increase of Na$_2$F$_2$ content. Values of $\overline{\sigma} (= 50.34)$ are same for all
Fig. 4.9a Variation of $\beta_1^2$ (solid line) and $\overline{\pi}$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF-B$_2$O$_3$ glasses.
Fig. 4.9b Variation of $B_1^2$ (solid line) and $\sqrt{\pi}$ (dotted line) with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.
Table 4.2

EPR and Optical Parameters, Molecular Orbital Coefficient and Normalized Covalency Parameter of Cu$^{2+}$ in NaF$_2$O$_3$, NaF·Na$_2$O·B$_2$O$_3$ and Some Other Glass Systems

| Glass No. | $g_\perp$ | $g_\parallel$ | $|A_\perp|$ | $|A_\parallel|$ | $E(2B_g)$ | $\beta_1^2$ | $\pi$ | Ref. |
|-----------|-----------|---------------|-------------|--------------|-------------|----------|-----|------|
| NC1       | 2.059     | 2.365         | -           | 142.85       | 13333       | 0.94     | 12  |
| NC2       | 2.058     | 2.364         | -           | 144.57       | 12953       | 0.91     | 18  |
| NC3       | 2.058     | 2.357         | 23.06       | 148.57       | 12903       | 0.89     | 22  |
| NC4       | 2.057     | 2.337         | 23.68       | 152.79       | 12870       | 0.84     | 32  |
| NC5       | 2.056     | 2.333         | 24.63       | 156.15       | 12820       | 0.83     | 34  |
| NC6       | 2.056     | 2.331         | 25.27       | 157.06       | 12804       | 0.82     | 36  |
| NC7       | 2.055     | 2.330         | 25.90       | 157.38       | 12804       | 0.82     | 36  |
| NNC1      | 2.061     | 2.376         | -           | 140.55       | 13333       | 0.97     | 6   |
| NNC2      | 2.060     | 2.366         | -           | 143.63       | 13262       | 0.94     | 12  |
| NNC3      | 2.058     | 2.360         | 21.45       | 145.85       | 13210       | 0.92     | 16  |
| NNC4      | 2.056     | 2.339         | 23.35       | 150.17       | 13037       | 0.86     | 28  |
| NNC5      | 2.054     | 2.337         | 23.97       | 155.52       | 12919       | 0.84     | 32  |
| NNC6      | 2.054     | 2.333         | 24.93       | 157.98       | -           | -        | -   |
| Soda borate glass | 2.060- | 2.381- | 22-26 | 142-156 | 12658- | 0.91- | - | [19] |
|            | 2.050 | 2.330 |        |           | 12500 | 0.82 | - |   |
| Fluorooaluminate glass | 2.055 | 2.320 | 23.98-28.78 | 140.80 | - | - | - | [20] |
glasses and indicate that there is a moderate covalency for the $\sigma$-bonding between the cupric ion and equatorial ligands.

It may be further noted that in NaF$\cdot$B$_2$O$_3$ glasses $\beta_1^2$ decreases almost suddenly (Fig. 4.9a) over a region centred at 15 mol% of Na$_2$F$_2$ confirming boron oxide anomaly by optical absorption spectra. In NaF$\cdot$Na$_2$O$\cdot$B$_2$O$_3$ glasses also $\beta_1^2$ decreases gradually (Fig. 4.9b) which confirms the results of property composition curves reported by Shelby and Ortalano.

The changes of $\beta_1^2$ are related to changes in B-O bonds; there is a decrease in the strength of B-O bonds resulting in the increase in covalency of Cu$^{2+}$-O bonds. Cu$^{2+}$-O bonds may be affected by the direct adjacent B-O bonds as well as by a little more distant ones. Cu-F bonds may also expected to be formed because of the presence of sodium fluoride.

The conductivity measurements have shown that the effect of adding sodium fluoride is indistinguishable from the effects of adding Na$_2$O in the borate glass. Sodium fluoride serves as a net breaker converting 3-into-4 coordinated boron with formation of BO$_3$F containing non-bridging F-atoms [10]. It seems that the coordination of Cu$^{2+}$ complexes does not change and keeps approximately the same symmetry in these glasses. It may be further noted
that the values of $g_{||}$ and $A_{||}$ in Na$_2$O.B$_2$O$_3$ [19] for Cu$^{2+}$ with oxygen environment and those in CaF$_2$.BaF$_2$.AlF$_3$ for Cu$^{2+}$ with a possible fluorine environment [20] are almost same as observed by us in sodium fluoroborate glasses (Table 4.2). This indicates that Cu$^{2+}$ probably adopts to a surrounding shared by oxygens and fluorines.
REFERENCES


CHAPTER V

ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION
STUDIES OF VO$^{2+}$ IN NaF.B$_2$O$_3$ AND NaF.Na$_2$O.B$_2$O$_3$ GLASSES

Abstract

This Chapter presents EPR and optical absorption studies of VO$^{2+}$ in xNa$_2$F$_2$. (100-x)B$_2$O$_3$ (5≤x≤35) and xNa$_2$F$_2$. (30-x)Na$_2$O.70B$_2$O$_3$ (0≤x≤25) glasses at 290 and 77K. EPR and optical absorption spectra of VO$^{2+}$ in these glasses have been analysed assuming C$_{4v}$ site symmetry. Spin Hamiltonian parameters, dipolar hyperfine coupling parameter (P), Fermi contact interaction parameter (K), molecular orbital coefficients (ς$^2$, ρ$^2$) and Δg∥/Δg⊥ have been evaluated. The optical absorption spectra show three bands corresponding to b$_2$ → e$^*_x$, b$_2$ → b$^*_1$ and b$_2$ → a$^*_1$ transitions. Variation of g∥, g⊥ and the degrees of covalency between 15 to 20 mol% Na$_2$F$_2$ indicate the presence of boron oxide anomaly in xNa$_2$F$_2$. (100-x)B$_2$O$_3$ (5≤x≤35) glasses. Decreasing P shows a decreased interaction of the 3d$_{xy}$ electron with $^5$l$^1$V nucleus. 4s orbital of the vanadium atom contributes greatly to the σ-bonding orbital with increasing Na$_2$F$_2$ concentration which is in conformity with formation of stronger σ bond with increasing energy of b$_2$ → a$^*_1$ transition. Smaller values of K suggest a decrease in tetragonality. At the higher concentration

* Paper based on this work has been communicated to 'Physics and Chemistry of Glasses'.
of Na$_2$F$_2$, covalencies of $\pi$- and $\sigma$-bondings are found to decrease.

$x$Na$_2$F$_2$.($30-x$)Na$_2$O.70B$_2$O$_3$ (0≤$x$≤25) system excludes boron oxide anomaly region and provides a replacement of O$^{2-}$ by 2F$^{-}$ at a fixed concentration of Na$^+$ and 70 mol% B$_2$O$_3$. A decrease in the values of $g_||$, $g_\bot$ and increasing dipolar hyperfine coupling parameter indicate the participation of fluorine ions in affecting the environment of VO$^{2+}$ through BO$_3$F$^-$/BO$_2$F$_2$ tetrahedra. Presence of an additional F$^-$ for each O$^{2-}$ would cause structural changes by forming more BO$_3$F tetrahedra which along with BO$_2$F$_2$ would gradually decrease the connectivity of the structure. Covalencies of $\pi$- and $\sigma$-bondings of VO$^{2+}$ are found to decrease with increasing fluorine ion concentrations. This also implies that the participation of fluorine ions may be either non-bridging or forming a bond with V$^{4+}$ in the equatorial plane.
5.1 Introduction

Electron paramagnetic resonance of \( V^{4+} \) shows hyperfine structure due to the \( ^{51}V \) nucleus (nuclear spin \( I = 7/2 \)) and is easily observable in most glass systems at room temperature [1-4]. The optical absorption by \( V^{4+} \) along with EPR investigations provides detailed and useful information about the structure of glassy network. The structure, properties and electrical conductivities of \( \text{NaF}.B_2O_3 \) and \( \text{NaF}.\text{Na}_2O.B_2O_3 \) glasses have been intensively studied by various research workers [5-10]. Sreedhar et al. [11] have also reported the EPR of \( VO^{2+} \) in alkali fluoroborate glasses recently but they could not detect the boron oxide anomaly which has been observed by us through EPR as well as optical absorption. In this chapter the results of EPR and optical absorption of \( VO^{2+} \) in \( \text{NaF}.B_2O_3 \) and \( \text{NaF}.\text{Na}_2O.B_2O_3 \) glasses at 290 and 77K are reported.

5.2 Experimental

The materials taken for the preparation of glasses were reagent grade NaF, \( \text{Na}_2\text{CO}_3 \), and \( H_3\text{BO}_3 \). To prepare glasses of various composition, the chemicals were weighed accurately based on \( x \text{Na}_2F_2.(100-x)B_2O_3 \) \((5 \leq x \leq 35)\) and \( x \text{Na}_2F_2.(30-x)\text{Na}_2O.70B_2O_3 \) \((0 \leq x \leq 25)\) and mixed thoroughly by adding 1.0 mol\% of \( V_2O_5 \) in each composition. The composition data for the glasses studied are presented in Table 5.1. For preparation of samples, EPR recording and optical
Table 5.1

The Composition Data for the VO$^{2+}$ Doped-glasses in

i) $xNa_{2}F_{2}.(100-x)B_{2}O_{3}$ (5$\leq x \leq$35); and

ii) $xNa_{2}F_{2}.(30-x)Na_{2}O.70B_{2}O_{3}$ (0$\leq x \leq$25)

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>Na$_2$F$_2$</th>
<th>Na$_2$O</th>
<th>B$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NV1</td>
<td>5</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>NV2</td>
<td>10</td>
<td>-</td>
<td>90</td>
</tr>
<tr>
<td>NV3</td>
<td>15</td>
<td>-</td>
<td>85</td>
</tr>
<tr>
<td>NV4</td>
<td>20</td>
<td>-</td>
<td>80</td>
</tr>
<tr>
<td>NV5</td>
<td>25</td>
<td>-</td>
<td>75</td>
</tr>
<tr>
<td>NV6</td>
<td>30</td>
<td>-</td>
<td>70</td>
</tr>
<tr>
<td>NV7</td>
<td>35</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>NNV1</td>
<td>-</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>NNV2</td>
<td>5</td>
<td>25</td>
<td>70</td>
</tr>
<tr>
<td>NNV3</td>
<td>10</td>
<td>20</td>
<td>70</td>
</tr>
<tr>
<td>NNV4</td>
<td>15</td>
<td>15</td>
<td>70</td>
</tr>
<tr>
<td>NNV5</td>
<td>20</td>
<td>10</td>
<td>70</td>
</tr>
<tr>
<td>NNV6</td>
<td>25</td>
<td>5</td>
<td>70</td>
</tr>
</tbody>
</table>
absorption, the procedures described in Chapter III were followed.

5.3 Theory

5.3.1. EPR

Vanadium (atomic number $Z = 23$) has an electronic structure $[\text{Ar}]3d^34s^2$. Tetravalent vanadium $V^{4+}$ with electronic structure $[\text{Ar}]3d^1$ exists in most stable form as VO$^{2+}$ molecular ion. The $V^{4+}$ ion with $3d^1$ configuration and $O^{2-}$ ion with $2p^4$ configuration form strong covalent bonds [12]. A very strong $\sigma$ bond is formed between the $(2p_z + 2s)$ hybrid of oxygen and $(3d_z^2 + 4s)$ hybrid of vanadium ion; $2p_x$ and $2p_y$ orbitals on oxygen make a strong $\pi$ bond with $3d_{xz}$ and $3d_{yz}$ orbitals on the $V^{4+}$ ion. These $\sigma$ and $\pi$ bonds make VO$^{2+}$ such a stable molecular ion. Remaining $(3d_z^2 - 4s)$ hybrid and the orbitals $3d_{x^2-y^2}$, $4p_x$, $4p_y$ and $4p_z$ are capable of forming five $\sigma$ bonds directed in a tetragonal pyramid with $V^{4+}$ ion located at its base. In many cases, these five $\sigma$ bonds may be formed if other oxygens are available in the vicinity such as through water molecules in solution or hydrated crystals, oxygen environment in other crystalline or glassy materials and so on. The $3d_{xy}$ orbital of $V^{4+}$ ion remains as non-bonding orbital.

Bonding scheme for VO$^{2+}$ in a complex $[\text{VO(H}_2\text{O})_5]^{2+}$ may be visualized by considering a tetragonal crystal field $C_{4v}$.
for central $V^{4+}$ ion and surrounding ligands. Various orbitals and ligands transform under $C_{4v}$ symmetry in the following way:

**Vanadium orbitals:**
- $3d \rightarrow a_1^+ b_1^+ b_2^+ e$
- $4p \rightarrow a_1^+ e$
- $4s \rightarrow a_1$

**Oxygen orbitals:**
- $\sigma \rightarrow a_1$
- $\pi \rightarrow e$

**Water ligands:**
- $\sigma \rightarrow 2a_1^+ b_1^+ e$

The bonding scheme for VO$^{2+}$ is shown in Fig. 5.1. Unpaired $3d^1$ electron resides in the non-bonding vanadium orbital $3d_{xy}$ with symmetry of $b_2$. Fig. 5.2 shows the diagram of tetragonally distorted octahedral complex VO$^{2+}$ in oxide glasses [13].

In a crystalline field of symmetry less than cubic (tetragonal or lower), the lowest level will be an orbital singlet and its spin degeneracy ($3d^1$ electron with $S = 1/2$) will be removed in a magnetic field producing two energy levels with separation dependent on the strength of the magnetic field. In such a case only one fine structure transition can be expected in EPR. As the nuclear spin of vanadium nucleus $^{51}V$ (abundance is 99.8%) is $7/2$, its magnetic interaction with $S = 1/2$ further splits the fine
Fig. 5.1 Molecular orbital scheme for the VO(\(\text{H}_2\text{O}\))\(_5^{2+}\) ION.

(\(b\) - Bonding, \(n\) - Non-Bonding, \(*\) - Anti-Bonding)
Fig. 5.2 The vanadyl complex in oxide glasses (after Griscom [13]).
structure level into eight hyperfine levels \((2I + 1 = 8)\) and EPR would show eight hyperfine transitions according to the selection rules \(\Delta M = \pm 1\); and \(\Delta m = 0\) (Fig.5.3). The \(\text{VO}^{2+}\) ion itself has an axial field, normally EPR spectrum cannot be expected to reveal any cubic site symmetry of a lattice.

**Analysis by Linear Combination of Atomic Orbital-Molecular Orbital (LCAO-MO)**

The observed values of spin Hamiltonian parameters are used to calculate covalency of \(\text{VO}^{2+}\) ions in a simple molecular orbital scheme. The necessary antibonding molecular orbitals on the basis of \(A_1, B_1, B_2\) and \(E\) representations are \([2,3, 14-16]\)

\[A_1 : \Phi_{a_1}^* = \alpha_1^* \left( \frac{1}{\sqrt{2}} \right) \left( 4s + 3d_{z^2} \right) - \alpha_1^* (\sigma_5) \quad (5.1)\]

\[B_1 : \Phi_{b_1}^* = \beta_1^* \left( 3d_{x^2-y^2} \right) - \beta_1^* \left( \frac{1}{2} \right) (\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4) \quad (5.2)\]

\[B_2 : \Phi_{b_2}^* = \beta_2^* \left( 3d_{xy} \right) - \beta_2^* \left( \frac{1}{2} \right) (p_{y1} + p_{x2} - p_{y3} - p_{x4}) \quad (5.3)\]

\[E : \Phi_{e^*} = \epsilon^* \left( 3d_{xz} \right) - \epsilon^* (p_{x5})\]

or

\[\Phi_{e^*} = \epsilon^* \left( 3d_{yz} \right) - \epsilon^* (p_{y5}) \quad (5.4)\]

where \(\alpha, \beta, \epsilon\) are coefficients of the ion wavefunctions, the \(\alpha', \beta', \epsilon'\) are coefficients of the ligand wavefunctions.
Fig. 5.3 - Hyperfine Splittings with $S = \frac{1}{2}$ and $I = \frac{7}{2}$. 
and * indicates antibonding orbital. The ligand orbitals involved in \( \pi \)-bonding are pure 2p orbitals while the orbitals involved in \( \sigma \)-bonding are sp hybrids.

5.3.2 Optical Absorption

The vanadyl ion in its free ionic form has ground state as \( ^2D_{3/2} \). The energy level diagram for 3d\(^1\) configuration in different symmetries is shown in Fig. 5.4. The strength and symmetry of the crystal field and various other interactions control the number of energy levels split and separation between them. If the VO\(^{2+}\) ion is in an octahedral symmetry, the single unpaired d electron occupies the \( t_{2g} \) orbital with ground state designated as \( ^2T_{2g} \). The electron occupying the upper orbital \( e_g \) will be in excited state \( ^2E_g \). Therefore in optical absorption, only one band corresponding to \( ^2T_{2g} \rightarrow ^2E_g \) transition is expected.

In a crystalline field of lower symmetry, the energy levels are split further and more transitions would be observed. When the ion is located at a site of \( C_{4v} \) symmetry, the \( ^2T_{2g} \) is split up into \( ^2B_{2g} \) and \( ^2E_g \) and the \( ^2E_g \) into \( ^2B_{1g} \) and \( ^2A_{1g} \) levels. The relative positions of energy levels are shown in Fig. 5.4. As 3d\(^1\) electron exists in \( b_2 \) orbital, the absorption energies corresponding to the phonon assisted d-d transitions are

\[
E_1 = b_2 \rightarrow e^* ,
E_2 = b_2 \rightarrow b_1^* ,
\]
Fig. 5.4 Energy level *splittings* for $d^1$ configuration in octahedral and tetragonal fields.
and

\[ E_3 = b_2 \rightarrow a_1^* \quad (5.5) \]

in order of increasing energy [15].

5.4 Results and Discussion

5.4.1 EPR Measurements

Fig. 5.5 and 5.6 show the EPR spectra of VO$^{2+}$ doped glasses at 290K. The spectra are very similar to those obtained for vanadyl ions in various alkali borate glasses [2,17,18] showing characteristic hyperfine structure arising from an unpaired electron with $^{51}$V nucleus and may be analysed using axial spin Hamiltonian of the form

\[
H = \beta_0 g_\parallel H_z S_z + \beta_0 g_\perp (H_x S_x + H_y S_y) \\
+ A_\parallel S_z I_z + A_\perp (S_x I_x + S_y I_y),
\]

(5.6)

where the symbols have their usual meaning. Quadrupole and nuclear Zeeman interaction terms have been ignored [19,20]. The solution of the above spin Hamiltonian gives the eight hyperfine components of the electron nuclear spin interaction which are envelopes with divergencies at magnetic field positions

\[
H_\parallel (m) = H_\parallel (o) - mA_\parallel - \frac{(63}{4} - m^2) \frac{A_\parallel^2}{2H_\parallel (o)},
\]

(5.7)
Fig. 5.5 EPR spectra of V$^{2+}$ in NaF$\cdot$B$_2$O$_3$ glasses at 290K. (a) Glass NV1 and (b) glass NV4. The spectrum top (a) is for glass NV1 with twice increase in gain.
Fig. 5.6 EPR spectra of VO$^{2+}$ in NaF-Na$_2$O-B$_2$O$_3$ glasses at 290K. (a) Glass NNV3 and (b) glass NNV5. The spectrum top (a) is for glass NNV3 with twice increase in gain.
and shoulders at positions

$$H_{\perp}(m) = H_{\perp}(0) - mA_{\perp} - \left(\frac{63}{4} - m^2\right) \frac{A_{\parallel}^2 + A_{\perp}^2}{4H_{\perp}(0)}, \quad (5.8)$$

where $m$ is the nuclear magnetic quantum number of vanadium nucleus with values $+\frac{7}{2}$, $+\frac{5}{2}$, $+\frac{3}{2}$, $+\frac{1}{2}$; $H_{\parallel} = \frac{h\nu}{g||\beta_o}$ and $H_{\perp} = \frac{h\nu}{g\perp\beta_o}$ with $\nu$ as the microwave frequency.

The spin Hamiltonian parameters calculated by using Equations (5.7) and (5.8) are given in Table 5.2a. The values of $A$ are arbitrary with respect to sign by the method proposed by Muncaster and Pake [21]. The uncertainty in the values of $g$ and $A$ is $\pm 0.0008$ and $\pm 0.6 \times 10^{-4}$ cm$^{-1}$ respectively. Spectra recorded at LNT are almost similar to those at 290K.

Hyperfine coupling terms, $A_{||}$ and $A_{\perp}$ may be expressed by the relations developed by Kivelson and Lee [16] as

$$A_{||} = -P \left[ \beta \frac{2}{7} \left( K + \frac{4}{7} \right) - \Delta g_{||} - \frac{3}{7} \Delta g_{\perp} \right], \quad (5.9)$$

$$A_{\perp} = -P \left[ \beta \frac{2}{7} \left( K - \frac{2}{7} \right) - \frac{11}{14} \Delta g_{\perp} \right], \quad (5.10)$$

where $K$ represents the contribution to hyperfine coupling due to isotropic Fermi contact interaction,

$$K \propto \phi_{b_2}^* \sum_k \delta(r_k) S_k | \phi_{b_2}^* \rangle. \quad (5.11)$$
Here, \( \Phi_{b_2}^{*} \) is the ground state wavefunction for unpaired electron, \( \delta \) is the delta function operator evaluated in the ground state, and \( S_k \) is the spin operator for the kth electron. The term \( \beta_2^2 \) is a measure of the degree of \( \pi \)-bonding with equatorial ligands and may be taken equal to unity for vanadium \[21\]. \( P = 2 \gamma_0 \beta_N <r^{-3}> \) is the dipolar hyperfine coupling parameter, where \( \gamma \) is the gyromagnetic ratio and \( r \) is the distance joining \( ^{51}V \) nucleus and the unpaired electron. \( \Delta g_{||} = g_{||} - 2.0023 \), and \( \Delta g_{\perp} = g_{\perp} - 2.0023 \).

Molecular orbital theory shows that \( A_{||} \) and \( A_{\perp} \) consist of the contributions of \( A'_{||} \) and \( A'_{\perp} \) of the \( 3d_{xy} \) electron to the hyperfine structure and the \( P \beta_2^2 K \) term arising due to the anomalous contribution of the \( s \) electrons \[21\]. Equations (5.9) and (5.10) can be written in terms of component parts as

\[
A_{||} = -P\left[\frac{4}{7}\beta_2^2 - \Delta g_{||} \right] - \frac{3}{7} \Delta g_{\perp} - P \beta_2^2 K = A'_{||} - P \beta_2^2 K, \quad (5.12)
\]

\[
A_{\perp} = P\left[\frac{2}{7} \beta_2^2 + \frac{11}{14} \Delta g_{\perp} \right] - P \beta_2^2 K = A'_{\perp} - P \beta_2^2 K. \quad (5.13)
\]

The values of \( A'_{||} \) and \( A'_{\perp} \) calculated using Equations (5.12) and (5.13) are given in Table 5.2b. The value of tetragonality measure \( \Delta g_{||}/\Delta g_{\perp} \) of the \( V^{4+} \) site has also been presented in Table 5.2b.

Hecht and Johnston \[2\] studied intensively the EPR and optical absorption spectra of \( V^{4+} \) ions in \( Na_2O.B_2O_3 \) glasses.
Table 5.2a

Spin Hamiltonian Parameters, $P$ and $K$ of VO$^{2+}$ in NaF$\cdot$B$_2$O$_3$ and NaF$\cdot$Na$_2$O$\cdot$B$_2$O$_3$ Glasses at 290K

| Glass No. | $g_{||}$ | $g_{\perp}$ | $|A_{||}|$ | $|A_{\perp}|$ | $P$ | $K$ |
|-----------|---------|---------|---------|---------|-----|-----|
| NV1       | 1.9345  | 1.9722  | 179.49  | 61.55   | 129.01 | 0.7392 |
| NV2       | 1.9351  | 1.9722  | 178.87  | 60.50   | 129.56 | 0.7290 |
| NV3       | 1.9323  | 1.9716  | 175.75  | 58.64   | 127.92 | 0.7199 |
| NV4       | 1.9384  | 1.9769  | 170.75  | 56.56   | 125.23 | 0.7173 |
| NV5       | 1.9414  | 1.9757  | 172.20  | 56.65   | 127.20 | 0.7101 |
| NV6       | 1.9396  | 1.9751  | 170.75  | 57.03   | 124.96 | 0.7206 |
| NV7       | 1.9424  | 1.9710  | 169.70  | 55.60   | 125.96 | 0.7066 |
| NNV1      | 1.9402  | 1.9804  | 169.51  | 56.79   | 123.69 | 0.7276 |
| NNV2      | 1.9390  | 1.9798  | 170.04  | 56.90   | 124.01 | 0.7268 |
| NNV3      | 1.9383  | 1.9780  | 170.63  | 57.38   | 124.12 | 0.7288 |
| NNV4      | 1.9378  | 1.9769  | 171.23  | 56.95   | 125.25 | 0.7203 |
| NNV5      | 1.9373  | 1.9763  | 172.48  | 57.96   | 125.47 | 0.7271 |
| NNV6      | 1.9356  | 1.9757  | 173.24  | 57.97   | 126.08 | 0.7246 |
Table 5.2b

$A_\parallel', A_\perp', \text{PK and } \Delta g_\parallel/\Delta g_\perp$ of VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ Glasses at 290K

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>$A_\parallel'$</th>
<th>$A_\perp'$</th>
<th>PK</th>
<th>$\Delta g_\parallel/\Delta g_\perp$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10$^{-4}$ cm$^{-1}$</td>
<td>10$^{-4}$ cm$^{-1}$</td>
<td>10$^{-4}$ cm$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>NV1</td>
<td>84.12</td>
<td>33.81</td>
<td>95.36</td>
<td>2.252</td>
</tr>
<tr>
<td>NV2</td>
<td>84.41</td>
<td>33.96</td>
<td>94.46</td>
<td>2.232</td>
</tr>
<tr>
<td>NV3</td>
<td>83.66</td>
<td>33.45</td>
<td>92.09</td>
<td>2.264</td>
</tr>
<tr>
<td>NV4</td>
<td>80.91</td>
<td>33.27</td>
<td>89.83</td>
<td>2.515</td>
</tr>
<tr>
<td>NV5</td>
<td>81.86</td>
<td>33.68</td>
<td>90.33</td>
<td>2.289</td>
</tr>
<tr>
<td>NV6</td>
<td>80.69</td>
<td>33.02</td>
<td>90.05</td>
<td>2.305</td>
</tr>
<tr>
<td>NV7</td>
<td>81.21</td>
<td>32.89</td>
<td>88.46</td>
<td>1.913</td>
</tr>
<tr>
<td>NNV1</td>
<td>79.50</td>
<td>33.21</td>
<td>90.00</td>
<td>2.835</td>
</tr>
<tr>
<td>NNV2</td>
<td>79.89</td>
<td>33.23</td>
<td>90.14</td>
<td>2.813</td>
</tr>
<tr>
<td>NNV3</td>
<td>80.15</td>
<td>33.09</td>
<td>90.46</td>
<td>2.633</td>
</tr>
<tr>
<td>NNV4</td>
<td>80.10</td>
<td>33.27</td>
<td>90.22</td>
<td>2.539</td>
</tr>
<tr>
<td>NNV5</td>
<td>81.24</td>
<td>33.27</td>
<td>91.23</td>
<td>2.500</td>
</tr>
<tr>
<td>NNV6</td>
<td>81.87</td>
<td>33.38</td>
<td>91.36</td>
<td>2.507</td>
</tr>
</tbody>
</table>
and identified that four-fold symmetry may describe the crystal field at the V$^{4+}$ ion sites. An octahedral site with tetragonal compression would give values of $g_{||} < g_{\perp} < g_e (2.0023)$ and $A_{||} > A_{\perp}$. The values of spin Hamiltonian parameters obtained (Table 5.2a) for V$^{4+}$ in $x$Na$_2$F$_2$.(100-$x$)B$_2$O$_3$ ($5 \leq x \leq 35$); and $x$Na$_2$F$_2$.(30-$x$)Na$_2$O.70B$_2$O$_3$ ($0 \leq x \leq 25$) glasses satisfy the above conditions and are close to those of vanadyl complexes in other glass systems [2,11,18]. Therefore the V$^{4+}$ ions in our samples may be assumed to exist as VO$^{2+}$ in the octahedral coordination having a tetragonal compression with $C_{4v}$ symmetry.

5.4.1.1 $x$Na$_2$F$_2$.(100-$x$)B$_2$O$_3$ ($5 \leq x \leq 35$) Glasses

Fig.5.7 shows the variations of parameters $g_{||}$, $g_{\perp}$, $A_{||}$, and $A_{\perp}$ with Na$_2$F$_2$ concentration for these glasses. $g_{||}$ and $g_{\perp}$ initially decrease slowly with increasing Na$_2$F$_2$ concentration and rise a bit abruptly in the range 15 to 20 mol%. $g_{||}$ shows a behaviour similar to that in soda-boric oxide glasses [2]. With further increase in concentration of Na$_2$F$_2$ g-values decrease slowly but continuously. Sreedhar et al. [11] have also observed the latter fall in their work up to about 33 mol% Na$_2$F$_2$ and have attributed it to the replacement of oxygens forming the environment of VO$^{2+}$ by fluorine ions. These glasses exhibit boron oxide anomaly [22] which has been observed with Cu$^{2+}$ doping in our earlier work (Chapter IV) and in thermal expansion by
Fig. 5.7 Variation of (a) $g_\perp$, $g_\parallel$; (b) $A_\parallel$ and $A_\perp$ with change in Na$_2$F$_2$ concentration in NaF-B$_2$O$_3$ glasses.
Shelby and Downie [9] who indicated a great deal of similarity between structure and properties of sodium borate and sodium fluoroborate glasses.

As $\text{Na}_2\text{F}_2$ is added tetrahedral $\text{BO}_3\text{F}$ (also $\text{BO}_2\text{F}_2$ at higher concentrations of $\text{Na}_2\text{F}_2$) units may be formed [9] with their corners shared to produce a site for $\text{VO}^{2+}$ with a $\text{C}_{4v}$ point-group symmetry [2]. On the basis of molecular orbital theory, it has been approximated that even if $\text{VO}^{2+}$ is coordinated by fluorines, the energy level order of molecular orbitals and the electronic configuration must be very similar to those in the case of $\text{Na}_2\text{O}\cdot\text{B}_2\text{O}_3$ glasses containing $\text{VO}^{2+}$. As superhyperfine splitting due to $^{19}\text{F}$ nuclei ($I = 1/2$) may not be observed in the present EPR spectra, ligands associated with $\text{VO}^{2+}$ may or may not be fluorines.

Fig. 5.7 and Table 5.2a show that $A_{||}$ and $A_{\perp}$ decrease with increasing $\text{Na}_2\text{F}_2$ concentration. $A_{||}$ decreases more rapidly as compared to $A_{\perp}$ in a manner similar to that in soda-boric oxide glasses [2]. The values of $P$ and $K$ obtained from the measured value of $A_{||}$ and $A_{\perp}$ with the help of Equations (5.9) and (5.10) (Table 5.2a), also decrease with increasing $\text{Na}_2\text{F}_2$. $P$ however shows a slight minimum in the region of boron oxide anomaly. Decreasing $P$ indicates a decreased interaction of the $3d_{xy}$ electron with $^{51}\text{V}$ nucleus. This may be attributed to increased screening of $3d_{xy}$ orbital from its nucleus through overlap of the
electron orbits of the surrounding ligands [23]. The values of $K$ are smaller than those obtained for other glasses [3,4,24,25] and point out that as $Na_2F_2$ increases, $4s$ orbital of the vanadium atom contributes greatly to the $\sigma$-bonding orbital ($\Phi_{a_1}^*$) between vanadium and ligand atoms [4]. Smaller values of $K$ also suggest a decrease in tetragonality [26].

5.4.1.2 $xNa_2F_2\cdot(30-x)Na_2O.70B_2O_3$ ($0\leq x \leq 25$) Glasses

Addition of $Na_2O$ to the composition of borate glasses causes one boron-oxygen triangle to get converted into a boron-oxygen tetrahedron for each $Na^+$ added. Local charge neutrality is maintained by $Na^+$ localised in the vicinity of each tetrahedron. The resulting three dimensional structure is fully linked. The concentration of boron-oxygen triangles and tetrahedra are roughly equal up to about 30-40 mol% of $Na_2O$. Further addition of $Na_2O$ decreases the number of tetrahedra forming non-bridging oxygens. Boron oxide anomaly is said to be associated with competing effects of increase in structural linkages due to formation of non-bridging oxygens [10]. Addition of an alkali fluoride to borate glasses alters its structure in the same way as does an alkali oxide. The replacement of sodium oxide by sodium fluoride causes a smooth, continuous change in the properties of borate glasses. The formation of $BO_3F$ tetrahedra with non-bridging fluorine occurs as $NaF$ replaces
Na₂O in the alkali borate glasses. At higher concentration of Na₂F₂, B₂O₃ tetrahedra may also be formed. These tetrahedra reduce the connectivity of the structure while maintaining the ratio of tetrahedral to triangular units.

To observe the relative effects of oxygens of Na₂O and fluorines of Na₂F₂ in borate glasses, we have chosen a fixed composition of alkali borate glass with 30 mol% Na₂O and 70 mol% B₂O₃ which excludes the region of boron oxide anomaly and provides appropriate experimental condition to study replacement of O²⁻ by 2F⁻. It may be assumed that the number of boron-oxygen tetrahedra will not change and non-bridging oxygen will not be formed for this glass composition. The concentration of Na₂F₂ is increased from 5 mol% to 25 mol% keeping the concentration of Na⁺ same but replacing each O²⁻ by 2F⁻. The replacement of O²⁻ by 2F⁻ at 70 mol% B₂O₃ leads to the following observations by EPR.

i) g∥ and g⊥ decrease very slowly while A∥ and A⊥ increase slightly as fluorine ion concentration increases (Fig.5.8).

ii) Dipolar hyperfine coupling parameter P increases as 2F⁻ replace O²⁻ but contribution to hyperfine coupling due to isotropic Fermi contact interaction K remains almost constant.

Among the spin Hamiltonian parameters, the principal g values are most readily related to the immediate
Fig. 5.8 Variation of (a) $g_\perp$, $g_{\parallel}$; (b) $|A_{\parallel}|$ and $|A_{\perp}|$ with change in $Na_2F_2$ concentration in NaF-Na$_2$O-B$_2$O$_3$ glasses.
environment of a 3d$^1$ ion [13] and therefore values of $g_{||}$ and $g_\perp$ depend upon the environment of VO$^{2+}$ affected via BO$_3$F$^-$/BO$_2$F$_2^-$ tetrahedra. Increasing $P$ shows a stronger interaction of 3d$_{xy}$ orbital electron with $^{51}V$ nucleus which is possible if surrounding ligands have less overlap with 3d$_{xy}$ orbital. As $K$ remains nearly unaffected the contribution of 4s orbital of vanadium atom to $\sigma$-bonding orbital between vanadium atom and ligand atoms does not appear to change with replacement of O$^{2-}$ by 2F$^-$. However, $\Delta g_{||}/\Delta g_\perp$ decreases with increasing fluorine ion concentration showing a decrease in tetragonality of vanadyl site.

In terms of optical basicity concept in NaF.B$_2$O$_3$ glasses, F$^-$ may be regarded as polarized O$^{2-}$ as the two ions are isoelectronic and similar in size [27]. If one assumes that fluorine ion is very similar to oxygen ion for molecular orbital calculation [4], the changes expected even after the substitution of oxygens by fluorines in the vicinity of VO$^{2+}$ may be very small. There may not be even any change in the values of some parameters. Though contribution to hyperfine constant due to Fermi contact interaction remains almost unaffected, other parameters do change slightly with 2F$^-$ replacing O$^{2-}$ confirming a definite participation of fluorine ions directly or indirectly in producing environmental changes in the vicinity of VO$^{2+}$. Presence of an additional F$^-$ for each O$^{2-}$ cannot be ignored
as far as structural changes in the glasses are concerned. Some structural changes in the glasses are eminent as for each \( \text{O}^{2-} \) replaced, \( 2\text{F}^- \) have to be accommodated for keeping \( \text{Na}^+ \) concentration same. This would further decrease the connectivity of the structure. The porbability that \( \text{F}^- \) ions may contribute to electrical conductivity is not ruled out [10].

5.4.2 Optical Absorption Spectra

5.4.2.1 \( x\text{Na}_2\text{F}_2.(100-x)\text{B}_2\text{O}_3 \ (5\leq x\leq35) \) Glasses

Optical absorption spectra alongwith g-factor provide a measure of degree of covalency through the relations dependent on the crystal field splitting energies of the transitions \( b_2 \rightarrow b_1^* \) and \( b_2 \rightarrow e_\pi^* \) and can be expressed as \([1,16,28]\]

\[
g_{||} = g_e \left[ 1 - \frac{4\lambda \beta_1^2 \beta_2^2}{E_2(b_2 \rightarrow b_1^*)} \right], \quad (5.14)
\]

and

\[
g_{\perp} = g_e \left[ 1 - \frac{\lambda \epsilon_\pi^2 \beta_2^2}{E_1(b_2 \rightarrow e_\pi^*)} \right], \quad (5.15)
\]

where \( \lambda \) is the spin-orbit coupling constant (249 cm\(^{-1}\) [21]) for a \( \text{V}^{4+} \) ion, \( E_2(b_2 \rightarrow b_1^*) \) and \( E_1(b_2 \rightarrow e_\pi^*) \) are the energies corresponding to \( b_2 \rightarrow b_1^* \) and \( b_2 \rightarrow e_\pi^* \) transitions respectively. The expressions \( 1 - \epsilon_\pi^2 \) and \( 1 - \beta_1^2 \)
measure the degrees of covalency, the former indicates the influence of out-of-plane $\pi$-bonding between the vanadium ion and the vanadyl oxygen; while the latter gives an indication of influence of in-plane $\sigma$-bonding with equatorial ligands.

The optical absorption spectra of VO$^{2+}$ in these glasses show three absorption bands in frequency ranges $11286-11614$ cm$^{-1}$, $12870-14662$ cm$^{-1}$ and $23201-26736$ cm$^{-1}$ which may be assigned to $b_2 \rightarrow e^*_\pi$, $b_2 \rightarrow b_1^*$ and $b_2 \rightarrow a_1^*$ transitions respectively on the basis of molecular orbital scheme proposed by Ballhausen and Gray [15]. All the observed frequencies of the absorption bands are given in Table 5.3 and are consistent with those obtained for VO$^{2+}$ in KF.B$_2$O$_3$ glasses [4]. Fig. 5.9 shows the representative optical spectra of VO$^{2+}$ in $x$Na$_2$F$_2$.($100-x$)B$_2$O$_3$ ($5 \leq x \leq 35$) glasses. The frequency assigned to $b_2 \rightarrow e^*_\pi$ gets slightly shifted to lower energy region with increasing Na$_2$F$_2$ concentration and indicates the possibility that the ligand coordinated opposite to vanadyl oxygen is also the oxygen atom of B-O-B network [3,4]. Contrary to the observation in KF.B$_2$O$_3$ glasses, the $b_2 \rightarrow a_1^*$ transition is shifted to higher energy region. If it is ligand to metal charge transfer band, it would increase in energy with increasing coordination number of vanadium. On the other hand, the metal to ligand charge transfer band will move to higher energy as coordination number of vanadium decreases [29].
Fig. 5.9 Optical absorption spectra of $\text{VO}^{2+}$ in NaF$_2$B$_2$O$_3$ glasses at 290K. (a) Glass NV1, (b) glass NV2, and (c) glass NV3.
As the coordination number in the vanadyl in the present 
case may be assumed constant, the observed band may be 
attributed to a transition between molecular orbital levels 
b_2 and a_1^*. In a transition like b_2 → a_1^*, both the 
ground and excited state orbitals may not be assumed to be 
localized on the same atomic centre. The two states 
involved are concerned with orbitals of metal ion as well as 
ligands deeply engaged in the molecular bonding. As the 
molecular orbital for a_1^* is mainly concerned with 
σ orbitals, the increasing separation b_2 → a_1^* shows a 
stronger σ bond between vanadium and ligand atoms which is 
consistent with decreasing K.

The values of (1 - \( \varepsilon_2^2 \)) and (1 - \( \beta_1^2 \)) depend upon the 
glass compositions and have been calculated using the peak 
frequencies from the recorded absorption spectra. These 
values are given in Table 5.3 and have been plotted in 
Fig.5.10 against the increasing Na_2F_2 content of the 
glasses. The values of (1 - \( \varepsilon_2^2 \)) decrease very slowly 
initially but increases significantly showing almost a 
sudden rise around 15 to 20 mol%. With further increase in 
Na_2F_2 content, (1 - \( \varepsilon_2^2 \)) is found to decrease a bit sharply. 
The values of (1 - \( \beta_1^2 \)) decreases faster initially showing 
a rise in the region 10-20 mol%. The sudden rise in both 
(1 - \( \varepsilon_2^2 \)) and (1 - \( \beta_1^2 \)) around 15-20 mol% of Na_2F_2 indicates 
boron oxide anomaly which has already been established 
through EPR study. It may be concluded that the covalencies
Table 5.3

Optical Parameters of VO$^{2+}$ in NaF.B$_2$O$_3$ and NaF.Na$_2$O.B$_2$O$_3$ Glasses

<table>
<thead>
<tr>
<th>Glass No.</th>
<th>$b_2 \rightarrow e^*_\pi$ cm$^{-1}$</th>
<th>$b_2 \rightarrow b^*_1$ cm$^{-1}$</th>
<th>$b_2 \rightarrow a^*_1$ cm$^{-1}$</th>
<th>$1 - \epsilon^2_{\pi} \quad 1 - \beta^2_{\pi}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NV1</td>
<td>11441</td>
<td>13071</td>
<td>23201</td>
<td>0.310</td>
</tr>
<tr>
<td>NV2</td>
<td>11614</td>
<td>14662</td>
<td>23474</td>
<td>0.299</td>
</tr>
<tr>
<td>NV3</td>
<td>11534</td>
<td>13175</td>
<td>24691</td>
<td>0.290</td>
</tr>
<tr>
<td>NV4</td>
<td>11325</td>
<td>12870</td>
<td>24875</td>
<td>0.423</td>
</tr>
<tr>
<td>NV5</td>
<td>11286</td>
<td>13175</td>
<td>25641</td>
<td>0.398</td>
</tr>
<tr>
<td>NV6</td>
<td>11286</td>
<td>-</td>
<td>26736</td>
<td>0.385</td>
</tr>
<tr>
<td>NNV1</td>
<td>10246</td>
<td>12755</td>
<td>24509</td>
<td>0.550</td>
</tr>
<tr>
<td>NNV5</td>
<td>10256</td>
<td>12953</td>
<td>23809</td>
<td>0.466</td>
</tr>
<tr>
<td>NNV6</td>
<td>10121</td>
<td>13071</td>
<td>23529</td>
<td>0.460</td>
</tr>
</tbody>
</table>
Fig. 5.10 Variation of covalency of vanadium (IV) with change in Na$_2$F$_2$ concentration in NaF.B$_2$O$_3$ glasses.
of the π- and σ-bondings decrease in the range 5 to 15 mol% Na₂F₂ and increase in the boron oxide anomaly region. (1 - β²₁) remains larger than (1 - ε²) throughout the increase in Na₂F₂ concentration showing that in-plane σ-bonding between vanadium ion and equatorial ligands is more covalent. However both are found to decrease at higher concentration of Na₂F₂ as reported by Sreedhar et al.[11].

5.4.2.2 xNa₂F₂·(30-x)Na₂O·70B₂O₃ (0≤x≤25) Glasses

The optical absorption spectra of VO²⁺ in these glasses (Fig.5.11) show the bands at frequencies 10121 to 10256 cm⁻¹, 12755 to 13071 cm⁻¹ and 23529 to 24509 cm⁻¹ which have been assigned to b₂ → e²⁺, b₂ → b¹ and b₂ → a¹ transitions respectively and are in agreement with the results obtained for VO²⁺ in potassium fluoroborate [4], alkali borate and silicate [30] glasses. The frequencies assigned to b₂ → e²⁺ and b₂ → b¹ shift very little with increasing 2F⁻ content while those of b₂ → a¹ decrease relatively more. The replacement of O²⁻ by 2F⁻ in these glasses has thus noticeable effect on a¹ level if b₂ is supposed not to change with replacement. a¹ is lowered in energy decreasing the energy of the transition b₂ → a¹, i.e., σ-bonding between V⁴⁺ and ligands decreases. This may lead to increase in V⁴⁺ to ligand distances approaching to that of a regular octahedron. Calculated values of optical parameters are given in Table 5.3. (1 - ε²) and
Fig. 5.11 Optical absorption spectra of VO$^{2+}$ in NaF.Na$_2$O.B$_2$O$_3$ glasses at 290K. (a) Glass NNV1, (b) glass NNV5 and (c) glass NNV6.
(1- $\beta_1^2$) both decrease with increasing 2F$^-$ concentration (Fig. 5.12). The decrease in the degree of covalency (1- $\varepsilon_\pi^2$) and (1- $\beta_1^2$), indicates that the concentration of Na$^+$ remaining constant, the replacement of O$^{2-}$ by 2F$^-$ leads to a decrease in $\pi$-bonding between V$^{4+}$ and vanadyl oxygen and $\sigma$-bonding between equatorial ligands with V$^{4+}$. These trends in (1- $\varepsilon_\pi^2$) and (1- $\beta_1^2$) may be associated with rising concentration of F$^-$ ions which may be either non-bridging or forming a bond with V$^{4+}$ in the equatorial plane.
Fig. 5.12 Variation of covalency of vanadium (IV) with change in Na$_2$F$_2$ concentration in NaF.Na$_2$O.B$_2$O$_3$ glasses.
REFERENCES


CHAPTER VI

ELECTRON PARAMAGNETIC RESONANCE AND OPTICAL ABSORPTION STUDIES OF Mn$^{2+}$ IN RF.B$_2$O$_3$ AND RF.Na$_2$O.B$_2$O$_3$
(R = Li, Na or K) GLASSES

Abstract

Mn$^{2+}$ doped RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ (R = Li, Na or K) glasses have been studied by EPR and optical absorption at 290 and 77K. The EPR spectra show an intense $g \approx 2.02$ resonance with a hyperfine structure parameter $A = (82-85) \times 10^{-4}$ cm$^{-1}$. Higher values of $A$ indicate higher ionicity of bonds with Mn$^{2+}$ in octahedral coordination at $g \approx 2.02$. Resonances weak in intensity are also observed at $g \approx 3.3$ and $g \approx 4.3$, the intensity however varies with the composition of host glasses. Remarkable changes have been observed in the intensity and resolution of EPR spectra of Mn$^{2+}$ in 25Na$_2$F$_2$.75B$_2$O$_3$ glass with varying Mn$^{2+}$ concentration. The intensity changes show that Mn$^{2+}$ prefers to occupy octahedral site with $g \approx 2.02$ resonance. The existence of boron oxide anomaly is indicated in $x$Na$_2$F$_2.(100-x)$B$_2$O$_3$ glasses in the composition region $5\leq x \leq 30$ through splitting at $g \approx 4.3$ resonance. Liquid nitrogen temperature EPR spectra show no changes in $g \approx 2.02$ and $g \approx 4.3$ resonances. The optical absorption spectra of Mn$^{2+}$ in RF.B$_2$O$_3$ show one
band and in $\text{RF.Na}_2\text{O.B}_2\text{O}_3$ glasses, two bands at 290K and confirm octahedral coordination of $\text{Mn}^{2+}$. 
6.1. Introduction

Manganese belonging to iron group of transition metals, has electronic configuration \([\text{Ar}]3d^54s^2\). It shows paramagnetism due to unpaired \(3d^5\) electrons. \(\text{Mn}^{2+}\) is S-state ion (other such ions are \(\text{Fe}^{3+}, \text{Eu}^{2+}, \text{Gd}^{3+}\) etc.), with \(S > \frac{1}{2}\) and has no orbital contribution to angular momentum in the ground state. Such ions have been found very much suitable for structural investigations as they do not produce any distortion at the site they occupy in the solids [1]. Further since \(S > 3/2\) for these ions, the splittings obtained make EPR superior to other methods (such as NMR, Mössbauer etc.,) for determining site symmetry. The EPR spectrum due to \(^{55}\text{Mn}\) hyperfine structure shows unambiguous assignments of resonance lines and the magnitude of hyperfine coupling constant provides a measure of covalency between \(\text{Mn}^{2+}\) and its ligands in solids [2,3]. EPR and optical absorption investigations of \(\text{Mn}^{2+}\) have been extensively studied in glasses by several authors [4-17]. This Chapter presents the results of EPR and optical absorption of \(\text{Mn}^{2+}\) in \(\text{RF.B}_2\text{O}_3\) and \(\text{RF.Na}_2\text{O}\cdot\text{B}_2\text{O}_3\) glasses.

6.2 Experimental

Reagent grade NaF, KF, LiF, \(\text{Na}_2\text{CO}_3\) and \(\text{H}_3\text{BO}_3\) are mixed in required proportions for the preparation of \(\text{RF.B}_2\text{O}_3\) and \(\text{RF.Na}_2\text{O}\cdot\text{B}_2\text{O}_3\) glasses. \(\text{MnCO}_3\) is used as a dopant with doping concentrations ranging from 0.1 to 3.0 mol\%. The composition
data of glasses are given in Table 6.1. Li$_2$F$_2$ content in the glasses was limited to 12.5 mol\%, as higher contents lead to serious vaporization loss of the fluorine [18]. For the preparation of glass samples, recording of EPR and optical absorption spectra, the procedure followed has been described in Chapter III.

6.3 Results and Discussion

6.3.1 EPR Measurements

The free ion ground state of Mn$^{2+}$ is orbital singlet $^6S_{5/2}$. As there is no resultant orbital angular momentum, there can be no interaction of Mn$^{2+}$ with a crystalline field to the first order. The ground state transforms as $^6A_1$ in a crystal field of octahedral or cubic symmetry. Fourth order cubic field parameter 'a' splits the sixfold ground state of Mn$^{2+}$ into a twofold degenerate (doublet) and a fourfold degenerate (quartet) component [19]. Small zero field splitting do occur further due to various other mechanisms [20,21] producing three Kramers doublets. A departure from cubic symmetry would change the magnitude of splitting of the three doublets but the degeneracy of the doublets can be removed only by applying an external magnetic field.

In presence of steady magnetic field three Kramers doublets split into six energy levels with magnetic dipole transitions allowed according to selection rule $\Delta M = \pm 1$. 
Each of these fine structure levels (M = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2) further splits into six hyperfine levels (2I + 1 = 6, I = 5/2 for $^{55}$Mn with natural abundance 100%) due to the coupling of the electronic spin with nuclear spin of manganese. The transitions allowed between hyperfine levels are given by $\Delta M = \pm 1$ and $\Delta m = 0$ as shown in Fig. 1.6. The EPR spectrum of Mn$^{2+}$ in a diamagnetic host may be complicated due to presence of Mn$^{2+}$ at several sites or different orientations of equivalent Mn$^{2+}$ complexes or due to forbidden transitions following the selection rules $\Delta M \neq 1$, and $\Delta m \neq 0$.

No EPR signal is detected in undoped glass samples of RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$. The glass samples with about 0.1 mol% Mn$^{2+}$ exhibit the EPR absorption patterns at 290K (Fig. 6.1) similar to those reported for Mn$^{2+}$ in other glasses [4,6,8,10,11,22]. The spectra observed in all the glasses are characterized by three EPR signals, the first centred on $g = 2.02$ showing six hyperfine lines; the second a shoulder on $g = 3.3$ and third around $g = 4.3$ are unresolved and relatively much weaker in intensity. Supershypertine structure from $^{19}$F nuclei (I = 1/2) is not observed in any sample but hyperfine forbidden transitions $\Delta m = \pm 1$ [6] are observed between six hyperfine lines ($\Delta m = 0$) at $g \approx 2.02$ in some glass samples (Fig. 6.1).

The well-resolved six line Mn$^{2+}$ EPR spectra around $g \approx 2.02$ arise from central M = +1/2 $\leftrightarrow$ -1/2 fine
Fig. 6.1 Representative EPR spectra of $\text{Mn}^{2+}$ (0.1 mol%) in RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ (Li, Na or K) glasses at 290K. (a) Glass M2, (b) glass M4 and (c) glass M6.
structure group of \( \text{Mn}^{2+} \) situated in an environment of octahedral symmetry because of allowed hyperfine transitions \( \Delta m = 0 \) with overall structure from outer fine groups. There exists a broad envelope of absorption under this spectrum.

The EPR signal with \( g \approx 4.3 \), weak in intensity and relatively unresolved, falling partially on the steep slope of broad envelope of absorption is characteristic of transition metal ions (\( S = 5/2 \)) incorporated in the glassy network [23] and indicates a distorted crystal field at the site of \( \text{Mn}^{2+} \). It has been interpreted in different ways [24,25] such as in terms of a single broad distribution of D-values for various features of observed spectra [4], presence of various local environments for different \( g \) values [13], concept of two types of sites for \( \text{Mn}^{2+} \) [23,26], well known strong crystal field rhombic formula with condition \( D/E = 3 \) and transition between energy levels of middle Kramers doublet [27]. Recently Cerny et al. [27] have interpreted the magnetically active \( \text{Mn}^{2+} \) centres responsible for \( g \approx 4.3 \) having tetragonal symmetry rather than orthorhombic.

According to the results obtained by Cerny et al.[27], the conditions for observing different isotropic \( g \) values are

\[
g \approx 2.02 \text{ at 9 GHz and } a<0.05 \text{ cm}^{-1} \quad D = E \approx 0 \quad \text{at 35 GHz},
\]
g ≈ 3.3 at 9 GHz, \( a \geq 1.0 \text{ cm}^{-1} \) \( D = E \approx 0 \)

\( g \approx 4.3 \) at 9 GHz, \( a \geq 0 \) (0.5 cm\(^{-1}\)) \( D = \frac{-2a}{3} \) and \( E \approx 0 \).

The condition \( D = -\frac{2a}{3} \) is known as tetragonal condition, \( a \) is fine structure constant. Under this condition, the resonance transition occurs between the energy levels of the lowest Kramers doublet at 9 GHz only and \( g \approx 4.3 \) is independent of \( D/E \) ratio.

The observed spectra of Mn\(^{2+} \) may be analysed using the spin Hamiltonian in the form

\[
H = g\beta_0 H S + S \cdot A \cdot I + \frac{a}{6} \left[ S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S-1) \right] + D[S_z^2 - \frac{1}{3} S(S+1)] + E(S_x^2 - S_y^2),
\]

where symbols have their usual meaning. First three terms are meant for cubic symmetry and represent isotropic Zeeman interaction, isotropic hyperfine interaction and fourth order contribution of cubic crystal field. Fourth term accounts for tetragonal symmetry and the last one takes care of orthorhombic distortion.

6.3.1.1 Resonance at \( g \approx 2.02 \)

The spin Hamiltonian parameters \( g \) and \( A \) are calculated from the hyperfine sextet at \( g \approx 2.02 \) resonance
assuming cubic site symmetry for Mn$^{2+}$. First two terms of the spin Hamiltonian lead to the resonance fields for hyperfine lines given by

$$H_m = H_0 - A m + A^2/2H_0 \left( m^2 - 35/4 \right), \quad (6.2)$$

where $H_m$ is the resonance field position of a hyperfine line, $H_0 = h \nu / g_O \beta_O$, and $m = +5/2, +3/2, +1/2, -1/2, -3/2, -5/2$. $g_O$ is the isotropic $g$ factor and $A$ is isotropic hyperfine structure parameter. The values of $g$ and $A$ for Mn$^{2+}$ in glass samples of RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ are given in Table 6.1. The calculated $A$ values are in the range (82-85)$\times 10^{-4}$ cm$^{-1}$ and are close to those in alkali borate [6] and alkali zinc borosulphate glasses [28]. Higher values of $A$ change slightly with the nature of alkali component and indicate higher ionicity of bonds with Mn$^{2+}$ [2,3,29]. These values also suggest octahedrally coordinated Mn$^{2+}$ at $g \approx 2.02$ [6,10,12].

The $g$-values are isotropic for a given alkali component and are almost equal to free electron value. A very little variation is however observed with nature of alkali components. As there is no observable D-splitting of hyperfine lines $\Delta m = 0$, D may be assumed to be zero. Thus the resonance at $g \approx 2.02$ may be concluded to occur due to non-distorted cubic sites occupied by octahedrally coordinated Mn$^{2+}$. It may be remarked that Mn$^{2+}$ being S-state
Table 6.1

Spin Hamiltonian Parameters for Mn$^{2+}$ in RF.B$_2$O$_3$ and RF.Na$_2$O.B$_2$O$_3$ (R = Li, Na or K) Glasses at 290K

<table>
<thead>
<tr>
<th>Glass System</th>
<th>Composition (mol%)</th>
<th>g</th>
<th>A 10$^{-4}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>25Na$_2$F$_2$.75B$_2$O$_3$</td>
<td>2.028</td>
<td>82.40</td>
</tr>
<tr>
<td>M2</td>
<td>25KF.75B$_2$O$_3$</td>
<td>2.018</td>
<td>84.41</td>
</tr>
<tr>
<td>M3</td>
<td>12.5Li$_2$F$_2$.87.5B$_2$O$_3$</td>
<td>2.023</td>
<td>85.05</td>
</tr>
<tr>
<td>M4</td>
<td>20Na$_2$F$_2$.10Na$_2$O.70B$_2$O$_3$</td>
<td>2.024</td>
<td>82.57</td>
</tr>
<tr>
<td>M5</td>
<td>20KF.10Na$_2$O.70B$_2$O$_3$</td>
<td>2.023</td>
<td>83.24</td>
</tr>
<tr>
<td>M6</td>
<td>10Li$_2$F$_2$.20Na$_2$O.70B$_2$O$_3$</td>
<td>2.024</td>
<td>82.97</td>
</tr>
</tbody>
</table>
ion does not distort the site it occupies, therefore these sites are inherently cubic in nature. Other investigations have led to the conclusion that octahedral coordination at the cubic site is provided by sharing of corners of BO$_4$, BO$_3$F, or BO$_2$F$_2$ tetrahedra in sodium fluoroborate glasses bringing oxygens and probably fluorines also in the position of ligands [30,31]. These glasses acquire relatively more rigid structure when tetrahedra take part in the structure.

6.3.1.2 Resonance at $g \approx 3.3$

The resonance at $g \approx 3.3$ at room temperature in the spectrum of Mn$^{2+}$ in these glass samples lies in the broad absorption region. The broad back ground absorption in the spectra indicates that the Mn$^{2+}$ sites may be characterized by broad distributions of crystal field parameters [23]. Such sites are possible in glassy structure in contrast to crystalline structure which has only definite sites.

6.3.1.3 Resonance at $g \approx 4.3$

The weak resonance with $g \approx 4.3$ has been observed in all the glass samples and resembles with those reported by several other research workers [10,12,14,25,27]. It shows isotropic behaviour and may be attributed to Mn$^{2+}$ in tetragonally distorted octahedral sites with $D = -2a/3$ due to transitions between the energy levels of the first Kramers doublet at $\sim 9$ GHz [27]. Weaker intensity indicates
that either such sites are smaller in number or Mn$^{2+}$ does not prefer to occupy such distorted sites.

6.3.1.4 Concentration Dependence

The resonance spectra in a glass with fixed composition 25Na$_2$F$_2$.75B$_2$O$_3$ show a remarkable Mn$^{2+}$ concentration dependence at $g \approx 2.02$ resonance. For 0.1 mol% Mn$^{2+}$ concentration, the spectrum shows (Fig. 6.2) a characteristic sixline hyperfine structure at $g \approx 2.02$ spread over a region of 50 mT width. With rising concentration of Mn$^{2+}$, resolution of the hyperfine sextet becomes poorer and at 3.0 mol% the sextet structure completely disappears leaving behind single broad line of $\Delta H_{pp}$ 54 mT as a result of dipole-dipole interaction (Fig. 6.2). The peak-to-peak width of hyperfine components also depends on Mn$^{2+}$ concentration. Fig. 6.3 shows the concentration dependence of peak-to-peak linewidth $\Delta H_{pp}$ of the hyperfine component with $m = -1/2$ for glass M1. Concentration dependent intensity of the spectra shows that Mn$^{2+}$ prefers to occupy octahedral sites with $g \approx 2.02$ resonance compared to distorted sites with $g \approx 4.3$ resonance which reflects no change in intensity.

6.3.1.5 Boron Oxide Anomaly

Boron oxide anomaly is evidenced by $g \approx 4.3$ resonance of 0.5 mol% Mn$^{2+}$ in $xNa_2F_2.(100-x)B_2O_3$ glasses over the region 5$\leq x \leq$30. The resonance centred at $g \approx 4.3$ exhibits
Fig. 6.2 EPR spectra of Mn$^{2+}$ in 25Na$_2$F$_2$.75B$_2$O$_3$ glass at 290K.  
(a) 0.1 mol% and (b) 3.0 mol% of manganese.
Fig. 6.3 The concentration dependence of peak-to-peak linewidth (ΔH_{pp}) of the hyperfine component with m = -\frac{1}{2} of the g ≈ 2.02 spectrum for 25Na_2F_2·75B_2O_3 glass.
a weak and relatively unresolved spectrum of 0.5 mol% Mn$^{2+}$ for lower Na$_2$F$_2$ content. With increasing Na$_2$F$_2$ content the spread and resolution of the spectrum increases reflecting a change in the distortion of the site for $g \approx 4.3$ resonance [32]. The resolution is highest from 10 to 15 mol% Na$_2$F$_2$ and decreases with further increase in Na$_2$F$_2$ concentration. This behaviour of the spectrum indicates a possible existence of boron oxide anomaly [Chapter 1, Section 1.3]. The $g \approx 2.02$ resonance of Mn$^{2+}$ sites retains undistorted octahedral nature throughout the variation of Na$_2$F$_2$ and does not appear to take part in anomalous behaviour.

6.3.1.6 Variation of Alkali Content

Keeping the concentration of Mn$^{2+}$ constant (0.1 mol%), the glasses with composition

a) 12.5Li$_2$F$_2$.12.5KF.75B$_2$O$_3$,

b) 12.5Li$_2$F$_2$.12.5Na$_2$F$_2$.75B$_2$O$_3$,

c) 12.5Na$_2$F$_2$.12.5KF.75B$_2$O$_3$,

d) 10Na$_2$F$_2$.10Li$_2$F$_2$.10Na$_2$O.70B$_2$O$_3$,

e) 10Na$_2$F$_2$.10KF.10Na$_2$O.70B$_2$O$_3$,

and

f) 10Li$_2$F$_2$.10KF.10Na$_2$O.70B$_2$O$_3$ do not show any change in the nature of the spectra except
that the intensity of hyperfine sextet at $g \approx 2.02$ resonance becomes much larger than that of $g \approx 4.3$ in case of $\text{Li}_2\text{F}_2$ or KF contents compared to $\text{Na}_2\text{F}_2$ or $\text{Na}_2\text{O}$.

### 6.3.1.7 Temperature Variation

Liquid nitrogen temperature spectra (Fig. 6.4) do not show any shift in the positions $g \approx 2.02$ or $g \approx 4.3$ resonances. However there occurs a redistribution of the intensity of underlying broad absorption which appears to shift partly to $g \approx 2.02$ resonance side and partly towards $g \approx 3.3$ side and indicates that the intermediate sites either reorder into higher symmetry sites with $g \approx 2.02$ or more distorted sites with $g \approx 3.3$.

A study of EPR and optical absorption of $\text{Cu}^{2+}$ and $\text{VO}^{2+}$ in sodium fluoroborate glasses shows that these ions occupy tetragonally distorted octahedral sites [Chapter IV and V] by virtue of their inherent nature and cannot therefore distinguish between different sites in the glass structure. However these ions could detect the boron oxide anomaly very clearly in $\text{Na}_2\text{O}.\text{B}_2\text{O}_3$ [32], $\text{NaF}.\text{B}_2\text{O}_3$ or $\text{NaF}.\text{Na}_2\text{O}.\text{B}_2\text{O}_3$ glasses. $\text{Mn}^{2+}$ appears to have proved its superiority over $\text{Cu}^{2+}$ and $\text{VO}^{2+}$ as it could not only distinguish between different sites but also reflected a possible existence of boron oxide anomaly through splitting of the spectrum at $g \approx 4.3$ resonance.
Fig. 6.4 Representative EPR spectra of Mn$^{2+}$ (0.5 mol%) in 25NaF$_2$·75B$_2$O$_3$ glass. (a) At 77K and (b) 290K.
6.3.2 Optical Absorption

Mn$^{2+}$ with half filled 3d$^5$ shell as a free ion has a number of quartets and doublets such as $^4P$, $^4D$, $^4F$, $^4G$, $^2S$, $^2P$, $^2D$, $^2F$, $^2G$ and the ground state $^6S_{5/2}$. If placed in a six-coordinated cubic ligand field, its 3d$^5$ configuration becomes $t^3_2 g^2$ and the above states transform under point group $O_h$ as

$$^6S_{5/2} \rightarrow ^6A_{1g}$$
$$^4P \rightarrow ^4T_{1g}$$
$$^4D \rightarrow ^4E_g + ^4T_{2g}$$
$$^4F \rightarrow ^4A_{2g} + ^4T_{1g} + ^4T_{2g}$$
$$^4G \rightarrow ^4A_{1g} + ^4E_g + ^4T_{1g} + ^4T_{2g}$$  \quad (6.3)

and so on. The ground state remains unperturbed in the first order. Tanabe and Sugano [33] have calculated the energies of different states of Mn$^{2+}$ along with other 3d$^n$ ions in terms of Racah parameters B and C. Fig. 6.5 shows the splitting of some quartet levels of Mn$^{2+}$ in an octahedral environment. A departure from cubic symmetry causes further splitting of the degenerate levels according to the descent in symmetry.

It is well known that the intensity of Mn$^{2+}$ optical
Fig. 6.5 Schematic energy level diagram of Mn$^{2+}$ in octahedral symmetry.
absorption band is very low as all the transitions responsible for absorption are forbidden in spin and parity [15]. Therefore relatively large quantity of manganese (≈ 3 mol% in our glass samples) has to be incorporated into the glasses for noticeable absorption in the UV-visible region.

Optical absorption spectra of Mn$^{2+}$ in glasses M1 to M5 are shown in Fig. 6.6 and 6.7a and b. In some single crystal and glasses, Mn$^{2+}$ has shown five or six absorption bands [15,28,34,35]. However only one or two bands have been observed in our glass samples with peak positions and assignments presented in Table 6.2. The observed absorption band for glasses M1 to M3 may be assigned to spin-forbidden transition $6\,A_{1g} \rightarrow 4\,A_{1g},4\,E_g(4\,G)$ of Mn$^{2+}$ located in octahedral environment [15]. The positions of the bands are essentially independent of the field strength [15,36] but shift towards higher energy region with nature of the alkali component. Our results in glasses M1 to M3 are in conformity with those of Klonkowski [36] who detected a weak band at 410 nm (24390 cm$^{-1}$) in M(II)O.P$_2$O$_5$ glasses (M(II) = Mg, Ca, Zn or Pb) and Danilchuk et al. [17] who observed intense one at the same frequency (24390 cm$^{-1}$) in phosphate glasses and attributed it to spin-forbidden $6\,A_{1g} \rightarrow 4\,A_{1g},4\,E_g(4\,G)$ of Mn$^{2+}$ ion in octahedral environment. The band at 420 nm (23809 cm$^{-1}$) in Na$_2$O.SiO$_2$ [37],
Fig. 6.6 Optical absorption spectra of Mn$^{2+}$ in RF.B$_2$O$_3$ (R = Li, Na or K) glasses at 290K.
Fig. 6.7 Optical absorption spectra of Mn$^{2+}$ in (a) 20Na$_2$F$_2$.10Na$_2$O.70B$_2$O$_3$ and (b) 20KF.-10Na$_2$O.70B$_2$O$_3$ glasses at 290K.
Table 6.2

Experimental Peak Positions and Assignments of Absorption Bands for Mn\(^{2+}\) in RF.B\(_2\)O\(_3\) and RF.Na\(_2\)O.B\(_2\)O\(_3\) (R = Li, Na or K) Glasses at 290K

<table>
<thead>
<tr>
<th>Glass System</th>
<th>Absorption Peak</th>
<th>Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Wavelength (nm)</td>
<td>Wavenumber (cm(^{-1}))</td>
</tr>
<tr>
<td>M1</td>
<td>410</td>
<td>24390 (\text{cm}^{-1})</td>
</tr>
<tr>
<td>M2</td>
<td>396</td>
<td>25252 (\text{cm}^{-1})</td>
</tr>
<tr>
<td>M3</td>
<td>389</td>
<td>25706 (\text{cm}^{-1})</td>
</tr>
<tr>
<td>M4</td>
<td>431, 484</td>
<td>23202, 20661 (\text{cm}^{-1})</td>
</tr>
<tr>
<td>M5</td>
<td>427, 467</td>
<td>23419, 21413 (\text{cm}^{-1})</td>
</tr>
</tbody>
</table>
400 nm (25000 cm\(^{-1}\)) in ZrF\(_4\) glasses \([38]\), 408 nm (24500 cm\(^{-1}\)) in K\(_2\)SO\(_4\).ZnSO\(_4\) \([39]\) and bands in several other borate and phosphate \([15]\) glasses further confirm the presence of Mn\(^{2+}\) in octahedral symmetry.

Mn\(^{2+}\) in sodium and potassium fluoroborate glasses with Na\(_2\)O content shows two optical absorption peaks: in M4 at 431 nm (23202 cm\(^{-1}\)) and 484 nm (20661 cm\(^{-1}\)) and in M5 at 427 nm (23419 cm\(^{-1}\)) and 467 nm (21413 cm\(^{-1}\)). These bands may be attributed to \(^6A_{1g} \rightarrow ^4T_{2g}(^4G)\) and \(^6A_{1g} \rightarrow ^4T_{1g}(^4G)\) transitions (Table 6.2) \([15]\) which are sensitive to crystalline field surrounding Mn\(^{2+}\) \([17]\). Feuerhelm et al. \([38]\) observed \(^6A_{1g} \rightarrow ^4T_{1g}(^4G)\) transition at 480 nm (20833 cm\(^{-1}\)) in ZrF\(_4\) glasses.

It appears that Mn\(^{2+}\) at octahedrally coordinated cubic sites showing \(g \approx 2.02\) resonance are responsible for the optical absorption bands assigned above. No Mn\(^{2+}\) centres at \(g \neq 3.3\) or 4.3 are sufficient to produce observable absorption peaks.
REFERENCES


CHAPTER VII

OPTICAL ABSORPTION STUDY OF VO\textsuperscript{2+} IN AMMONIUM MAGNESIUM TRICHLORIDE HEXAHYDRATE SINGLE CRYSTAL\textsuperscript{*}

Abstract

This Chapter reports the results of optical absorption of VO\textsuperscript{2+} doped in ammonium magnesium trichloride hexahydrate (AMTH) - NH\textsubscript{4}MgCl\textsubscript{3}.6H\textsubscript{2}O single crystal at 290K considering vanadyl ion in C\textsubscript{4v} symmetry. NH\textsubscript{4}MgCl\textsubscript{3}.6H\textsubscript{2}O has a monoclinic structure in which Mg\textsuperscript{2+} is surrounded by water octahedron. The observed absorption spectrum of VO\textsuperscript{2+} shows two bands at 13157 cm\textsuperscript{-1} and 15674 cm\textsuperscript{-1} which have been assigned to \(2\text{B}\text{\textsubscript{2g}} \rightarrow 2\text{E}\text{\textsubscript{g}}\) and \(2\text{B}\text{\textsubscript{2g}} \rightarrow 2\text{B}\text{\textsubscript{1g}}\) transitions respectively. Values of \(P, K, \xi\text{\textsubscript{\pi}}\) and \(\beta\text{\textsubscript{1}}\) are evaluated using optical absorption and EPR results. Values of \(\xi\text{\textsubscript{\pi}}\) and \(\beta\text{\textsubscript{1}}\) indicate that both out-of-plane \(\pi\)- and in-plane \(\sigma\)-bonding are covalent in nature so that the unpaired electron is delocalized. The results indicate a replacement of Mg(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{2+} by VO(H\textsubscript{2}O)\textsubscript{5}\textsuperscript{2+} in NH\textsubscript{4}MgCl\textsubscript{3}.6H\textsubscript{2}O lattice.

\textsuperscript{*} Paper based on this work has been communicated to 'Solid State Communications'.
7.1. Introduction

Vanadyl ion VO\textsuperscript{2+}, a transition metal oxycation is of much interest as a probe because of important information it provides through its optical and magnetic properties. This extensively studied ion [1,2] normally coordinates both in solid state and solutions having coordination number five or six. Its optical absorption spectrum gives the information about the chemical bonding of metal ion to ligands in solids or solutions while electron paramagnetic resonance furnishes the details of the ligand field at the site of metal ion. In our earlier work we have reported the EPR investigations on VO\textsuperscript{2+} doped in AMTH single crystal [3]. Results of optical absorption of VO\textsuperscript{2+} in AMTH single crystal have been interpreted by correlating them with EPR data and presented in this Chapter.

7.2 Experimental

Single crystals of AMTH doped with VO\textsuperscript{2+} were grown at room temperature by slow evaporation of aqueous solution. Analar grade ammonium chloride and magnesium chloride were dissolved in distilled water by mixing in stoichiometric ratio and the impurity was introduced into the mixture by adding a little quantity of vanadium sulphate (2.0\% by weight). The saturated solution was filtered and kept at room temperature for two weeks. Transparent parallelopiped-
shape single crystals with clear faces were selected for optical absorption measurement.

The optical absorption spectrum of VO$^{2+}$ doped in AMTH was recorded at 290K on a Shimadzu UV-visible spectrophotometer (model UV-160) in 200-1000 nm wavelength region as mentioned in Chapter III.

7.3 Crystal Structure

The AMTH has monoclinic structure with space group C 2/c and unit cell dimensions as $a = 9.320$ Å, $b = 9.582$ Å, $c = 13.327$ Å, and $\beta = 90.12^\circ$ containing four formula units [4]. The Mg$^{2+}$ ions are surrounded by six water molecules in an octahedral arrangement. The average Mg-O bond length and O-Mg-O bond angle are respectively 2.053 Å and 89.7° forming almost a regular octahedron Mg(H$_2$O)$_6^{2+}$. These octahedra are nearly equally oriented with the c-axis.

Each NH$_4^+$ ion is surrounded by six Cl$^-$ ions in nearly regular octahedral arrangement with average Cl-N distance 3.34 Å while each Cl$^-$ ion is hydrogen-bonded to six water molecules and two NH$_4^+$ ions. Fig. 7.1 shows the crystal structure of AMTH [4]. The crystal structure may be viewed as a network of top sharing [NH$_4$Cl$_6$] octahedra and isolated [Mg(H$_2$O)$_6$]$^{2+}$ octahedra occupying holes in [NH$_4$Cl$_6$] network. The atomic coordinates are given in Table 7.1. Interatomic distances and angles are presented in Table 7.2.
Fig. 7.1 Monoclinic unit cell of $\text{NH}_4\text{MgCl}_3\cdot6\text{H}_2\text{O}$ (after X. Solans et al. [4]).

* Hydrogen of $\text{NH}_4$ have not been shown.
Table 7.1

Final Atomic Coordinates ($\times 10^4$) of $\text{NH}_4\text{MgCl}_3\cdot\text{H}_2\text{O}$

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(1)</td>
<td>5000</td>
<td>0</td>
<td>5000</td>
</tr>
<tr>
<td>Cl(2)</td>
<td>2544(1)</td>
<td>7384(2)</td>
<td>7467(1)</td>
</tr>
<tr>
<td>Mg</td>
<td>5000</td>
<td>5000</td>
<td>5000</td>
</tr>
<tr>
<td>N</td>
<td>5000</td>
<td>13(6)</td>
<td>7500</td>
</tr>
<tr>
<td>O(1)</td>
<td>4103(3)</td>
<td>6876(2)</td>
<td>5381(2)</td>
</tr>
<tr>
<td>O(2)</td>
<td>3194(3)</td>
<td>3990(2)</td>
<td>5511(2)</td>
</tr>
<tr>
<td>O(3)</td>
<td>4084(3)</td>
<td>5134(3)</td>
<td>3601(2)</td>
</tr>
</tbody>
</table>
Table 7.2

Interatomic Distances (Å) and Angles (°) in the Unit Cell of NH₄MgCl₃·6H₂O

<table>
<thead>
<tr>
<th></th>
<th>Distance (Å)</th>
<th>Symmetry Code:</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-O(1)</td>
<td>2.047(2)</td>
<td>Cl(2ⁱ)·O(1)</td>
<td>3.177(3)</td>
</tr>
<tr>
<td>Mg-O(2)</td>
<td>2.059(2)</td>
<td>Cl(2ʰⁱ)·O(2)</td>
<td>3.180(3)</td>
</tr>
<tr>
<td>Mg-O(3)</td>
<td>2.053(2)</td>
<td>Cl(2ʰⁱⁱ)·O(3)</td>
<td>3.186(3)</td>
</tr>
<tr>
<td>Cl(1ʰ)·N</td>
<td>3.332(2)</td>
<td>Cl(2ʰʰ⁻¹)·O(3)</td>
<td>3.159(3)</td>
</tr>
<tr>
<td>Cl(2ʰʰ⁻¹)·N</td>
<td>3.404(3)</td>
<td>O(1)-Mg-O(2)</td>
<td>89.8(1)</td>
</tr>
<tr>
<td>Cl(2ʰʰ⁻¹)·N</td>
<td>3.284(3)</td>
<td>O(1)-Mg-O(3)</td>
<td>90.1(1)</td>
</tr>
<tr>
<td>Cl(1ʰʰ⁻¹)·O(1)</td>
<td>3.149(2)</td>
<td>O(2)-Mg-O(3)</td>
<td>89.5(1)</td>
</tr>
<tr>
<td>Cl(1ʰʰ⁻¹)·O(2)</td>
<td>3.202(2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Symmetry Code:

(i) x,y,z           (v) x⁻¹⁄₂, y+¹⁄₂, z
(ii) x,y⁻1,z        (vi) ¹⁄₂-x, y⁻¹⁄₂, 3/2-z
(iii) x⁺¹⁄₂, y⁻¹⁄₂,z (vii) x, 1-y, z⁻¹⁄₂
(iv) x,y+1,z        (viii) ¹⁄₂-x, 3/2-y, 1-z
7.4 Theory

Tetravalent vanadium $V^{4+}$ with electronic structure $[\text{Ar}]3d^1$ exists in most stable form as $\text{VO}^{2+}$ molecular ion. The vanadium is usually coordinated with other groups, particularly with oxygens both in solids and in vanadyl containing solutions. The bonding scheme for $\text{VO}^{2+}$ in a complex $[\text{VO(H}_2\text{O)}_5]^{2+}$ has been discussed in Chapter V. The molecular orbital picture of $\text{VO}^{2+}$ in $[\text{VO(H}_2\text{O)}_5]^{2+}$ based on Linear Combination of Atomic Orbital-Molecular Orbital has shown that the ground state of $\text{VO}^{2+}$ ion is $^2D_{3/2}$. In the complex $[\text{VO(H}_2\text{O)}_5]^{2+}$, the vanadyl ion has $C_{4v}$ symmetry with six-fold coordination. Such a complex has four equatorial ligands with vanadium to oxygen (V-O) distance of 2.30 Å. The strongly bonded $\text{VO}^{2+}$ ion has a shorter V = O bond of length 1.67 Å and the sixth ligand opposite to $\text{VO}^{2+}$ ion has a V-O distance of 2.40 Å. This sixth ligand shows little effect on the optical and magnetic properties of the complex [6]. Structure of the complex $\text{VO(H}_2\text{O)}_5^{2+}$ is shown in Fig.7.2.

In a crystal field of octahedral symmetry, the single unpaired $3d^1$ electron occupies the $t_{2g}$ orbital having a ground state $^2T_{2g}$. In the excited state $^2E_g$ the electron occupies the upper $e_g$ orbital. Therefore in this symmetry only one band corresponding to $^2T_{2g} \rightarrow ^2E_g$ transition is expected. If the symmetry is lowered, the upper and ground electronic energy levels may split and more bands may be
Fig. 7.2 Structure of the complex $\text{VO(H}_2\text{O)}_5^{2+}$ (after Ballhausen and Gray [5]).
observed. In tetragonal field $C_{4v}$, the $^2T_{2g}$ and $^2E_g$ levels split into $(^2B_{2g}, ^2E_g)$ and $(^2B_{1g}, ^2A_{1g})$ levels respectively. The $3d^1$ electron exists in the $b_2$ orbital and transitions expected in absorption are shown in Fig. 5.4 (Chapter V, Section 5.3.2). All the transitions are allowed vibronically and expected to appear as relatively weak bands in all polarizations [5].

### 7.5 Results and Discussion

The optical absorption spectrum of VO$^{2+}$ doped in single crystal of AMTH recorded at 290K is shown in Fig. 7.3. The spectrum shows the characteristic absorption band centred at 760 nm accompanied by a weak band at 638 nm. These two bands have been assigned to transitions $^2B_{2g} \rightarrow ^2E_g$ and $^2B_{2g} \rightarrow ^2B_{1g}$ respectively (Table 7.3). Similar observations have been reported by Agarwal [7] and Lakshman [8]. The nature and positions of the optical absorption bands suggest the presence of vanadyl ion is in $C_{4v}$ symmetry [8]. The EPR spectrum of VO$^{2+}$ in this system at LNT reported earlier support the above observation [3]. The results of our earlier EPR investigations are reported in Table 7.4 for the evaluation of molecular orbital parameters of VO$^{2+}$.

The molecular orbital coefficients can be determined by correlating the EPR and optical absorption data through
Fig. 7.3 Optical absorption spectrum of VO$^{2+}$ doped in NH$_4$MgCl$_3$.6H$_2$O single crystal at 290K.
Table 7.3

Optical Absorption Band Positions and Assignments for VO$^{2+}$ in AMTH Single Crystal

<table>
<thead>
<tr>
<th>Wavelength (nm)</th>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>13157</td>
<td>$^2B_{2g} \rightarrow ^2E_g$</td>
</tr>
<tr>
<td>638</td>
<td>15674</td>
<td>$^2B_{2g} \rightarrow ^2B_{1g}$</td>
</tr>
</tbody>
</table>

Table 7.4

Spin Hamiltonian Parameters of VO$^{2+}$ in AMTH Single Crystal

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>$g$</th>
<th>$A$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>10$^{-4}$ cm$^{-1}$</td>
</tr>
<tr>
<td>RT Spectrum</td>
<td>$g_o = 1.980$</td>
<td>$A_o = 104.58$</td>
</tr>
<tr>
<td></td>
<td>$\pm 0.005$</td>
<td>$\pm 0.50$</td>
</tr>
<tr>
<td>LNT Spectrum</td>
<td>$g_{</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$g_\perp = 1.987$</td>
<td>$A_\perp = 70.89$</td>
</tr>
<tr>
<td>Calculated from</td>
<td>$g_o = 1.970$</td>
<td>$A_o = 108.16$</td>
</tr>
<tr>
<td>SHP(s) of LNT</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrum</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the relations \([9,10,11]\)

\[
\begin{align*}
\varepsilon_{||} &= 2.0023 - \frac{8\lambda \beta_1^2}{E_2}, \\
\varepsilon_{\perp} &= 2.0023 - \frac{2\lambda \xi_\pi^2}{E_1},
\end{align*}
\tag{7.1}
\]

\[
A_{||} = p\left[- \left(\frac{4}{7} + K\right) - \frac{8\lambda \beta_1^2}{E_2} - \frac{6\lambda \xi_\pi^2}{7E_1}\right],
\]  
\tag{7.3}
\]

and

\[
A_{\perp} = p\left[\left(\frac{2}{7} - K\right) - \frac{11\lambda \xi_\pi^2}{E_1}\right].
\]  
\tag{7.4}
\]

Here \(\beta_1^2\) and \(\xi_\pi^2\) are the bonding coefficients of the excited orbitals \(d_{x^2-y^2}\) and \(d_{xz}(d_{yz})\) respectively of the vanadyl ion, and other symbols have their usual meaning [Chapter V]. The value of \(\lambda\) is assumed to be 170 cm\(^{-1}\) [12]. The parameter \(\beta_1^2\) represents the in-plane \(\sigma\)-bonding between the vanadium atom and equatorial ligands while \(\xi_\pi^2\) indicates the out-of-plane \(\pi\)-bonding with vanadyl oxygen. The values of \(\beta_1^2, \xi_\pi^2, P\) and \(K\) obtained by using Equations (7.1) to (7.4) are given in Table 7.5 along with those of VO\(^{2+}\) in other lattices \([7,8,11,13,14]\) for comparison.

The values \(\beta_1^2\) and \(\xi_\pi^2\) indicate that both in-plane \(\sigma\)- and out-of-plane \(\pi\)-bonding are of covalent nature so that the unpaired electron is delocalized \([8,15]\). The Fermi
Table 7.5

Molecular Orbital Parameters of VO$^{2+}$ Doped in Different Systems

<table>
<thead>
<tr>
<th>System</th>
<th>10$^{-4}$ cm$^{-1}$ P</th>
<th>K</th>
<th>$\beta^2_1$</th>
<th>$\varepsilon^2_{\pi}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH$_4$)$_2$Zn(SO$_4$)$_2$.6H$_2$O</td>
<td>-</td>
<td>0.87</td>
<td>0.81</td>
<td>0.88</td>
<td>[8]</td>
</tr>
<tr>
<td>Cs$_2$Zn(SO$_4$)$_2$.6H$_2$O</td>
<td>-119.1</td>
<td>0.88</td>
<td>0.82</td>
<td>0.64</td>
<td>[8]</td>
</tr>
<tr>
<td>Cs$_2$Cd(SO$_4$)$_2$.6H$_2$O</td>
<td>-114.7</td>
<td>0.88</td>
<td>0.91</td>
<td>0.60</td>
<td>[8]</td>
</tr>
<tr>
<td>MgNH$_4$PO$_4$.6H$_2$O</td>
<td>-122.7</td>
<td>0.89</td>
<td>0.87</td>
<td>0.77</td>
<td>[13]</td>
</tr>
<tr>
<td>(NH$_4$)$_6$Sb$_4$(SO$_4$)$<em>3$F$</em>{12}$</td>
<td>-136.3</td>
<td>0.79</td>
<td>0.70</td>
<td>0.78</td>
<td>[7]</td>
</tr>
<tr>
<td>Rb$_2$SO$_4$</td>
<td>-119.8</td>
<td>0.83</td>
<td>0.83</td>
<td>0.84</td>
<td>[14]</td>
</tr>
<tr>
<td>NH$_4$MgCl$_3$.6H$_2$O (AMTH)</td>
<td>-120.1</td>
<td>0.86</td>
<td>0.75</td>
<td>0.59</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Present work
contact parameter $K$ is related to the unpaired electron density at the vanadium nucleus and is in the range of 0.50 to 0.89 for various vanadyl complexes [11]. It is extremely sensitive to the deformation of electronic structure of vanadium ion. In AMTH $K$ is found to have large value (0.86) indicating a large contribution to the hyperfine constant by the unpaired $s$ electron [8]. The values of $\beta_1^2$ and $\xi_\pi^2$ are close to those for vanadyl ion coordinated to the oxygens (Table 7.5) and suggest a replacement of $\text{Mg(H}_2\text{O)}^{2+}_6$ by $\text{VO(H}_2\text{O)}^{2+}_5$ in AMTH. Through EPR, the tumbling motion of $\text{VO}^{2+}$ has already been established in nearly octahedral site formed by water molecules.
REFERENCES


