EPR SPECTROSCOPY OF TRANSITION METAL IONS
IN OXIDE HOSTS

* * * *

A thesis submitted for the degree
of
DOCTOR OF PHILOSOPHY
at the
Australian National University
by

A.F.M. Yusuf Haider

* * * *

August 1979
STATEMENT

The studies detailed in this dissertation were carried out during my stay as a full-time Research Scholar in the Department of Solid State Physics, Research School of Physical Sciences, at the Australian National University, Canberra.

The research described in this volume is my own except where otherwise stated.

This thesis has never in any form been submitted to another institution for the award of a higher degree.

A.F.M. Yusuf Haider

Canberra
August 1979
ACKNOWLEDGEMENTS

I express my sincere gratitude to my supervisor, Dr A. Edgar, for his assistance, encouragement, useful discussions and overall guidance during the progress of this work.

I would like to thank Dr N.B. Manson for his helpful discussions and Dr D.C. Price for running the Mössbauer spectra of some of the crystals. It has also been a great help to discuss with my fellow students, particularly Mr I.H. Brunskill.

I am grateful to Professor W.A. Runciman for his encouragement and the interest he has shown in the progress of the present research work.

My thanks are also due to Mr G. Sampietro for growing the MgTiO₃ crystals and to the members of the technical staff of the Department of Solid State Physics for their help during my stay at the Australian National University.

I would like to particularly thank Mrs S. Love for her typing of the thesis.

I am grateful to my wife for helping me with the proof reading.

My thanks are due to the Australian Development Assistance Bureau and the Australian National University for providing me with financial assistance during my stay at the ANU.
ABSTRACT

A theoretical and experimental investigation of the electron paramagnetic resonance spectra of $3d^n$ transition metal ions in single crystals of $\text{MgTiO}_3$ and $\text{SrO}$ is reported.

In $\text{MgTiO}_3$, trigonally symmetric EPR spectra are observed for $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Mn}^{2+}$ and $\text{Mn}^{4+}$ ions at single sites, and $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$ ions at two lattice sites. The parameters in the relevant spin-Hamiltonians have been determined in each case by least squares fittings. It is proposed that the divalent transition metal ions and $\text{Mn}^{4+}$ ions substitute for $\text{Mg}^{2+}$ ions, whereas $\text{Fe}^{3+}$ and $\text{Cr}^{3+}$ ions substitute for both $\text{Mg}^{2+}$ and $\text{Ti}^{4+}$ ions.

The angular variation of the two $\text{Fe}^{3+}$ spectra and their dependences on oxidation-reduction treatments and on dopant concentration suggest that one $\text{Fe}^{3+}$ site is a simple substitution for a $\text{Ti}^{4+}$ ion, whilst the other site involves a substitution for a $\text{Mg}^{2+}$ ion, with the nearest neighbour $\text{Ti}^{4+}$ ion being replaced by a $\text{Mg}^{2+}$ ion. The site structures for the two $\text{Cr}^{3+}$ ion spectra are deduced to be simple substitutions for both $\text{Mg}^{2+}$ and $\text{Ti}^{4+}$ ions by a comparison of the experimental and calculated values of the zero field splittings of the $^4A_2$ ground states. The calculated values are based on crystal field estimates using data from previous work on ruby and the superposition model of crystal fields.

The EPR spectra from divalent $\text{Ni}^{2+}$ and $\text{Fe}^{2+}$ ions in $\text{SrO}$ exhibit trigonal symmetry, in contrast to the octahedral sites observed for $\text{Mn}^{2+}$ and $\text{V}^{2+}$ ions. For trivalent ions, octahedral and orthorhombic ($C_{2v}$) sites were found for $\text{Cr}^{3+}$ and $\text{Fe}^{3+}$ ions respectively. The spectral characteristics of the trigonal sites of $\text{Ni}^{2+}$ and $\text{Fe}^{2+}$ ions, and the $C_{2v}$ site for $\text{Fe}^{3+}$ ions, are consistent with $<111>$-type and $<110>$-type off-centre
displacements for the divalent and trivalent impurity ions respectively. The orthorhombic site observed for Fe$^{3+}$ ions can be converted to a new C$_{1h}$ site by oxidation treatments. This new site is considered to be a modification of the C$_{2v}$ site induced by a neighbouring point defect.

Calculations of static lattice distortions using the polarisable point ion and simple shell models of ionic crystals are in good agreement with the proposed off-centre behaviour of Ni$^{2+}$, Fe$^{2+}$ and Fe$^{3+}$ ions and the on-centre behaviour of Mn$^{2+}$ and Cr$^{3+}$ ions in SrO. The differential effect with regard to the on-centre/off-centre behaviour of Mn$^{2+}$ ions versus Fe$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ ions, and Cr$^{3+}$ versus Fe$^{3+}$ ions is mainly due to the contribution of crystal field stabilization energies.
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>CHAPTER 1:</th>
<th>INTRODUCTION</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Spectroscopic Studies of Transition Metal Ions in MgTiO$_3$</td>
<td>1</td>
</tr>
<tr>
<td>1.2</td>
<td>Transition Metal Ions in Alkaline Earth Oxides</td>
<td>2</td>
</tr>
<tr>
<td>1.2.1</td>
<td>Trivalent 3d$^n$ ions in alkaline earth oxides</td>
<td>2</td>
</tr>
<tr>
<td>1.2.2</td>
<td>Divalent 3d$^n$ ions in alkaline earth oxides</td>
<td>3</td>
</tr>
<tr>
<td>1.2.3</td>
<td>Evidence for off-centre displacement in alkaline earth oxides</td>
<td>4</td>
</tr>
<tr>
<td>1.3</td>
<td>Off-Centre Effects in Other Hosts</td>
<td>7</td>
</tr>
<tr>
<td>1.4</td>
<td>The Structure of this Work</td>
<td>8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>CHAPTER 2:</th>
<th>EXPERIMENTAL TECHNIQUES</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>EPR Measurements</td>
<td>11</td>
</tr>
<tr>
<td>2.2</td>
<td>35 GHz EPR Spectrometer</td>
<td>11</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Specifications</td>
<td>11</td>
</tr>
<tr>
<td>2.2.2</td>
<td>Microwave bridge design</td>
<td>11</td>
</tr>
<tr>
<td>2.2.3</td>
<td>Cavity design</td>
<td>12</td>
</tr>
<tr>
<td>2.3</td>
<td>Field Strength Measurements</td>
<td>14</td>
</tr>
<tr>
<td>2.4</td>
<td>9 GHz Spectrometer</td>
<td>14</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Bridge design and specifications</td>
<td>14</td>
</tr>
<tr>
<td>2.4.2</td>
<td>X-band cavity</td>
<td>16</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Superconducting magnet</td>
<td>16</td>
</tr>
<tr>
<td>2.5</td>
<td>Low Temperature Operation</td>
<td>17</td>
</tr>
<tr>
<td>2.5.1</td>
<td>Q-band flow-tube method</td>
<td>17</td>
</tr>
<tr>
<td>2.5.2</td>
<td>Varian E-265 liquid helium cryostat</td>
<td>17</td>
</tr>
<tr>
<td>2.5.3</td>
<td>Exchange space system</td>
<td>18</td>
</tr>
<tr>
<td>2.5.4</td>
<td>Automatic temperature controller</td>
<td>18</td>
</tr>
<tr>
<td>2.6</td>
<td>EPR Spectrum Analyses</td>
<td>18</td>
</tr>
<tr>
<td>2.6.1</td>
<td>Least-squares fitting methods</td>
<td>18</td>
</tr>
<tr>
<td>2.6.2</td>
<td>Prediction of line positions</td>
<td>21</td>
</tr>
<tr>
<td>2.7</td>
<td>Crystal Growth and Treatments</td>
<td>22</td>
</tr>
<tr>
<td>2.7.1</td>
<td>MgTiO$_3$ crystals</td>
<td>22</td>
</tr>
<tr>
<td>2.7.2</td>
<td>SrO crystals</td>
<td>23</td>
</tr>
<tr>
<td>2.7.3</td>
<td>Heat treatments</td>
<td>24</td>
</tr>
</tbody>
</table>
### CHAPTER III: THEORETICAL REVIEW: THE ELECTRONIC ENERGY LEVELS OF TRANSITION METAL IONS IN CRYSTALLINE HOSTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Introduction</td>
<td>25</td>
</tr>
<tr>
<td>3.2 The Free Ion Hamiltonian</td>
<td>26</td>
</tr>
<tr>
<td>3.3 Classification of States and Coupling Schemes</td>
<td>28</td>
</tr>
<tr>
<td>3.4 Evaluation of Matrix Elements of $H_{\text{Coul}}$</td>
<td>30</td>
</tr>
<tr>
<td>3.5 Evaluation of Spin-Orbit Interaction Matrix Elements by Tensor Operator Methods</td>
<td>31</td>
</tr>
<tr>
<td>3.6 The Crystal Field Interaction</td>
<td>33</td>
</tr>
<tr>
<td>3.7 The Weak Field Scheme</td>
<td>34</td>
</tr>
<tr>
<td>3.8 Evaluation of Matrix Elements of $V_{\text{CF}}$ by Tensor Operator Methods in the Weak Field Scheme</td>
<td>37</td>
</tr>
<tr>
<td>3.9 Complete Solution of the Total Hamiltonian in a Weak Field Scheme</td>
<td>38</td>
</tr>
<tr>
<td>3.10 The Strong Field Scheme</td>
<td>39</td>
</tr>
<tr>
<td>3.11 The Intermediate Field Scheme</td>
<td>40</td>
</tr>
<tr>
<td>3.12 The Superposition Model of Crystal Fields</td>
<td>41</td>
</tr>
<tr>
<td>3.13 The Spin-Hamiltonian Formalism</td>
<td>43</td>
</tr>
</tbody>
</table>

### CHAPTER IV: GROUND STATE SPECTRA AND SUBSTITUTIONAL CHARACTERISTICS OF 3d$^n$ TRANSITION METAL IONS IN MAGNESIUM TITANATE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Introduction</td>
<td>52</td>
</tr>
<tr>
<td>4.2 Crystal Structure</td>
<td>53</td>
</tr>
<tr>
<td>4.3 Crystal Growth and Characterisation</td>
<td>56</td>
</tr>
<tr>
<td>4.4 Experimental Measurements</td>
<td>59</td>
</tr>
<tr>
<td>4.4.1 EPR spectra of Cr$^{3+}$ ions in MgTiO$_3$</td>
<td>59</td>
</tr>
<tr>
<td>4.4.2 EPR spectra of Mn$^{2+}$ and Mn$^{4+}$ ions in MgTiO$_3$</td>
<td>62</td>
</tr>
<tr>
<td>4.4.3 EPR spectra of Fe$^{3+}$ ions in MgTiO$_3$</td>
<td>67</td>
</tr>
<tr>
<td>4.4.4 Mössbauer spectra of MgTiO$_3$:Fe</td>
<td>69</td>
</tr>
<tr>
<td>4.4.5 EPR spectrum of MgTiO$_3$:Ni$^{2+}$</td>
<td>75</td>
</tr>
<tr>
<td>4.4.6 EPR spectrum of MgTiO$_3$:Co$^{2+}$</td>
<td>75</td>
</tr>
<tr>
<td>4.4.7 EPR spectrum of MgTiO$_3$:Cu</td>
<td>77</td>
</tr>
<tr>
<td>4.5 Oxidation and Reduction Effects for MgTiO$_3$ Containing Cr$^{3+}$, Fe$^{3+}$ and Mn$^{4+}$ Ions</td>
<td>77</td>
</tr>
<tr>
<td>4.6 Site Location of Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ Ions in MgTiO$_3$</td>
<td>80</td>
</tr>
<tr>
<td>4.7 Site Determination for Fe$^{3+}$ Ions in MgTiO$_3$</td>
<td>80</td>
</tr>
</tbody>
</table>

### CHAPTER V: CALCULATIONS OF THE GROUND STATE SPLITTING AND SITE STRUCTURES FOR Cr$^{3+}$ IONS IN MgTiO$_3$

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>88</td>
</tr>
<tr>
<td>Section</td>
<td>Page</td>
</tr>
<tr>
<td>------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.2 Crystal Field Calculations for Ruby</td>
<td>89</td>
</tr>
<tr>
<td>5.3 Crystal Field Model for MgTiO$_3$</td>
<td>95</td>
</tr>
<tr>
<td>5.3.1 Point charge contribution from distant ions</td>
<td>96</td>
</tr>
<tr>
<td>5.3.2 Superposition model contributions from the ligands</td>
<td>97</td>
</tr>
<tr>
<td>5.3.3 Evaluation of superposition model parameters</td>
<td>98</td>
</tr>
<tr>
<td>5.3.4 Crystal field Hamiltonian</td>
<td>100</td>
</tr>
<tr>
<td>5.3.5 Crystal fields for MgTiO$_3$:Cr$^{3+}$</td>
<td>101</td>
</tr>
<tr>
<td>5.4 Results of the Calculations</td>
<td>104</td>
</tr>
<tr>
<td>5.5 Site Structures for MgTiO$_3$:Cr$^{3+}$</td>
<td>107</td>
</tr>
</tbody>
</table>

**CHAPTER VI: ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF Divalent $3d^N$ IONS IN STRONTIUM OXIDE**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Introduction</td>
<td>113</td>
</tr>
<tr>
<td>6.2 The EPR Spectrum of Fe$^{2+}$ Ions in Strontium Oxide</td>
<td>113</td>
</tr>
<tr>
<td>6.2.1 Experimental observation</td>
<td>113</td>
</tr>
<tr>
<td>6.2.2 Interpretation of the spectra</td>
<td>114</td>
</tr>
<tr>
<td>6.2.3 Determination of spin-Hamiltonian parameters</td>
<td>120</td>
</tr>
<tr>
<td>6.2.4 Temperature dependence of linewidth</td>
<td>123</td>
</tr>
<tr>
<td>6.3 The EPR Spectra of Ni$^{2+}$ Ions in Strontium Oxide</td>
<td>125</td>
</tr>
<tr>
<td>6.3.1 Experimental observation</td>
<td>125</td>
</tr>
<tr>
<td>6.3.2 Interpretation of the spectrum</td>
<td>125</td>
</tr>
<tr>
<td>6.3.3 Determination of the spin-Hamiltonian parameters</td>
<td>127</td>
</tr>
<tr>
<td>6.3.4 Temperature dependence of the linewidth</td>
<td>129</td>
</tr>
<tr>
<td>6.4 Effective Perpendicular $g_\bot$ Value for Fe$^{2+}$ and Ni$^{2+}$ Ions in SrO</td>
<td>129</td>
</tr>
<tr>
<td>6.5 The EPR Spectra of Mn$^{2+}$ and V$^{2+}$ Ions in Strontium Oxide</td>
<td>132</td>
</tr>
<tr>
<td>6.5.1 The EPR spectra of Mn$^{2+}$ ions in SrO</td>
<td>132</td>
</tr>
<tr>
<td>6.5.2 The EPR spectra of V$^{2+}$ ions in SrO</td>
<td>136</td>
</tr>
<tr>
<td>6.6 Site Structure for Divalent Ions in SrO</td>
<td>138</td>
</tr>
<tr>
<td>6.6.1 Mn$^{2+}$ and V$^{2+}$ ions</td>
<td>138</td>
</tr>
<tr>
<td>6.6.2 Fe$^{2+}$ and Ni$^{2+}$ ions</td>
<td>138</td>
</tr>
</tbody>
</table>

**CHAPTER VII: ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF Fe$^{3+}$ AND Cr$^{3+}$ IONS IN STRONTIUM OXIDE**

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Introduction</td>
<td>142</td>
</tr>
<tr>
<td>7.2 EPR Spectra of Fe$^{3+}$ Ions in SrO</td>
<td>142</td>
</tr>
<tr>
<td>7.2.1 Spectral characteristics and identification of an orthorhombic Fe$^{3+}$ EPR spectrum</td>
<td>142</td>
</tr>
</tbody>
</table>
7.2.2 Energy levels diagrams
7.2.3 Angular variation of the spectrum
7.2.4 EPR spectrum of Fe$^{3+}$ ion in a $C_{1h}$ site in SrO
7.2.5 Ground state energy levels of Fe$^{3+}$ ions in the $C_{1h}$ site
7.2.6 Angular variation of the spectrum
7.3 The EPR Spectrum of Cr$^{3+}$ Ions in SrO
7.4 7.4.1 Heat treatments of Iron-doped SrO crystals
7.4.2 Linebroadening of the $C_{2v}$ and $C_{1h}$ site Fe$^{3+}$ EPR spectra
7.5 Site Structures for Trivalent Ions in SrO
7.5.1 Site structure of Fe$^{3+}$ ions at the site of orthorhombic symmetry
7.5.2 Site structure for Fe$^{3+}$ ions in the $C_{1h}$ site in SrO

CHAPTER VIII: CALCULATION OF OFF-CENTRE DISPLACEMENTS AND LATTICE DISTORTIONS FOR 3d$^n$ IONS IN ALKALINE EARTH OXIDES

8.1 Introduction
8.2 8.2.1 Origin of Off-centre Displacement
8.2.2 Lattice Models
8.3 Application of the PPI Model to Off-Centre Lattice Distortion Calculations
8.4 Interactions Involved in the Lattice Distortion
8.5 Change in the Monopolar Electrostatic Energy
8.6 The Change in the Polarisation Energy
8.6.1 Dipole-Monopole and Dipole-Dipole Interactions
8.6.2 The polarisation energy of the continuum
8.7 The Change in the Repulsive Interaction Energy
8.8 Crystal Field Stabilization Energy of the Impurity Ion
8.9 Estimation of the Interaction Parameters
8.10 Comments on the Parameters
8.11 Modifications to the Calculations for Trivalent Impurity Ions
8.12 Results of the PPI Model Calculations
8.12.1 Divalent 3d$^n$ ions in alkaline earth oxides
8.12.2 Trivalent ions in alkaline earth oxides
8.13 Shell Model Calculation of Lattice Distortion
8.14 The Simple Shell Model of Ionic Crystals
8.15 Results of Shell Model Calculations
CHAPTER IX: CONCLUSIONS

9.1 Transition Metal Ions in MgTiO₃ 210
9.2 Transition Metal Ions in SrO 212

APPENDIX
| Figure 2.1       | 15  |
| Figure 4.1      | 54  |
| Figure 4.2      | 60  |
| Figure 4.3      | 63  |
| Figure 4.4      | 64  |
| Figure 4.5      | 68  |
| Figure 4.6      | 70  |
| Figure 4.7      | 71  |
| Figure 4.8      | 73  |
| Figure 4.9      | 76  |
| Figure 5.1      | 90  |
| Figure 5.2      | 105 |
| Figure 5.3      | 106 |
| Figure 5.4      | 110 |
| Figure 6.1      | 115 |
| Figure 6.2      | 119 |
| Figure 6.3      | 122 |
| Figure 6.4      | 124 |
| Figure 6.5      | 128 |
| Figure 6.6      | 130 |
| Figure 6.7      | 131 |
| Figure 6.8      | 133 |
| Figure 6.9      | 137 |
| Figure 7.1      | 145 |
| Figures 7.2 - 7.5 | 147 |
| Figure 7.6      | 149 |
| Figure 7.7      | 150 |
| Figure 7.8      | 154 |
| Figures 7.9 - 7.12 | 156 |
| Figure 7.13     | 157 |
| Figure 7.14     | 159 |
| Figure 7.15     | 161 |
| Figure 7.16     | 162 |
| Figure 7.17     | 164 |
| Figure 7.18     | 169 |
| Figure 7.19     | 170 |
| Figure 8.1      | 176 |
LIST OF FIGURES (cont'd)

| Figure 8.2 | Page 193 |
| Figure 8.3 | Page 195 |
| Figure 8.4 | Page 204 |
| Figure 8.5 | Page 205 |

* * * * *

LIST OF TABLES

| Table 1.1 | Page 6 |
| Table 4.1 | Page 55 |
| Table 4.2 | Page 57 |
| Table 4.3 | Page 65 |
| Tables 4.4 & 4.5 | Page 79 |
| Table 5.1 | Page 91 |
| Table 5.2 | Page 94 |
| Table 5.3 | Page 99 |
| Table 5.4 | Page 102 |
| Table 5.5 | Page 103 |
| Tables 7.1 & 7.2 | Page 144 |
| Tables 7.3 & 7.4 | Page 153 |
| Table 8.1 | Page 177 |
| Table 8.2 | Page 189 |
| Table 8.3 | Page 191 |
| Tables 8.4 & 8.5 | Page 197 |
| Table 8.6 | Page 207 |
CHAPTER I

INTRODUCTION
This thesis presents the results of an experimental and theoretical investigation into oxide hosts doped with transition metal ions, using electron paramagnetic resonance (EPR) as the primary experimental technique. The object of this chapter is to give a short review of the background to the present work, and to discuss the motivation for undertaking this study. The discussion may be divided into two parts on the basis of the two host materials investigated, magnesium titanate (MgTiO$_3$) and strontium oxide (SrO).

1.1 Spectroscopic Studies of Transition Metal Ions in MgTiO$_3$

Very little was hitherto known about the spectroscopic properties of transition metal ions in the MgTiO$_3$ host lattice, and only three investigations into these systems have been reported. These are reviewed in context in Chapter IV.

Magnesium titanate is a member of a series of isostructural lattices including niobates, vanadates and manganates which all crystallize with the ilmenite (FeTiO$_3$) structure. Many of the members of the series have useful dielectric or ferroelectric properties; for example, lithium niobate (LiNbO$_3$) finds practical application as a harmonic generator in laser optics. Magnesium titanate itself is used in ceramic capacitors as a low loss, high K, dielectric which has a negative temperature coefficient.

The original motivation for studying this material came from the structure, which can be visualised as that of the Al$_2$O$_3$ lattice with alternate layers of magnesium and titanium metal ions replacing the aluminium ions. It was hoped that MgTiO$_3$ containing trivalent transition metal ions would contain high concentration of pairs of these ions suitable for studying exchange interactions, since charge compensation arguments favour the replacement of a Mg$^{2+}$ - Ti$^{4+}$ nearest neighbour pair by Cr$^{3+}$ -
Cr\(^{3+}\) pair, for example. Such pairs were not in fact observed, but a considerable progress was made in understanding the substitutional behaviour of transition metal ions in MgTiO\(_3\).

Unlike Al\(_2\)O\(_3\), MgTiO\(_3\) can accommodate transition metal ions in two different sites. Both the Mg\(^{2+}\) and the Ti\(^{4+}\) sites have the point group symmetry C\(_3\), as does the Al\(^{3+}\) site in Al\(_2\)O\(_3\), but because of the different host cation charges in MgTiO\(_3\), transition metal ions can potentially be incorporated in this host in a greater variety of charge states than for Al\(_2\)O\(_3\). Furthermore, it is quite possible for transition metal ions such as Fe\(^{3+}\) and Cr\(^{3+}\) ions to simultaneously substitute for both cations in MgTiO\(_3\), rendering the site identification rather difficult.

In Chapters IV and V, an EPR and Mössbauer spectroscopy investigation of the substitutional properties of transition metal ions in MgTiO\(_3\) is described, and site structures are proposed for Ni\(^{2+}\), Co\(^{2+}\), Mn\(^{2+}\), Mn\(^{4+}\), Cr\(^{3+}\) and Fe\(^{3+}\) ions on the basis of the spectroscopic data and a crystal field calculation.

1.2 Transition Metal Ions in Alkaline Earth Oxides

Transition metal ions are important impurities in all commercially available single crystals of the alkaline earth oxide series MgO, CaO, SrO and BaO which all have the simple rocksalt structure. Transition metal ions enter the lattice substitutionally for the alkaline earth ions, and are usually found in the divalent charge state. However, the valence state of the impurity ion may be changed either by heat treatment or by irradiation.

1.2.1 Trivalent 3d\(^n\) ions in alkaline earth oxides

Trivalent transition metal ions have been observed in cubic sites in both MgO and CaO\(^{1,2}\). The mechanism of the necessary charge compensation
has been the subject of many studies. The most commonly proposed mechanism involves the association of a cation vacancy with the impurity ion\(^3\). However if the trivalent ions are randomly distributed only half of them can be compensated locally, since the vacancy concentration cannot be greater than half of that of the trivalent impurity. For trivalent impurity ions which have remote charge compensation, the effective local site symmetry is of course octahedral. However, if the cation vacancy is locally associated with the trivalent ion, the site symmetry will be lower, depending upon the position of the cation vacancy relative to the magnetic ion. Tetragonal and rhombic site spectra observed previously for Fe\(^{3+}\)\(^4\) and Cr\(^{3+}\)\(^5\)\(^6\) in addition to the octahedral site spectra were explained by assuming the presence of a cation vacancy at the nearest neighbour cation site along the \(<001>-<110>-\)type directions respectively.

1.2.2 Divalent 3d\(^n\) ions in alkaline earth oxides

In MgO and CaO, the divalent transition metal ions predominantly occupy the normal cation lattice site without any change in the local site symmetry\(^1\),\(^7\),\(^8\),\(^9\). In some cases, certain features of the spectra such as linewidths, or the intensity of nominally forbidden transitions appear to be anisotropic, but these are in general considered to be due to the influence of internal strain fields rather than to a more fundamental cause\(^7\),\(^10\). Divalent copper occupies a special place amongst the divalent transition metal ions since the \(^2\)E ground state is particularly susceptible to a Jahn-Teller effect\(^11\).

Non-octahedral spectra for divalent ions, considerably weaker in intensity than the octahedral site spectra, have been reported. For example, the orthorhombic \(V^{2+}\) spectra in MgO\(^6\) has been attributed to a nearest neighbour cation vacancy lying along the \(<110>-\)direction. The
random association of these two defects was considered to be due to the relatively large concentration of cation vacancies induced as charge compensators for the large population of $V^{3+}$ ions present in the crystal. However, such examples are unusual and it is generally found that the divalent transition metal ions occupy regular cation sites of octahedral symmetry.

In the case of MgO, the forces binding the metal ions to the on-centre sites are quite strong, whereas there is some evidence that these forces are considerably weaker in the case of CaO resulting in a localised odd-parity mode vibration\textsuperscript{12}. The large dynamic Jahn-Teller effects for CaO:Fe$^{2+}$ observed by Regnard et al.\textsuperscript{13} also supports this conclusion. In qualitative terms, this can be attributed to the mismatch in ionic radii between the Ca$^{2+}$ cation ($\sim 1\text{ Å}$)\textsuperscript{14} and divalent transition metal ions of radius 0.6 - 0.8 Å\textsuperscript{14}.

For SrO and BaO, where the ionic mismatch between the host cation and the transition metal ion is even greater, there is the possibility that the impurity ion has a lower potential energy off the regular cation site, making it susceptible to off-centre displacements.

1.2.3 Evidence for off-centre displacement in alkaline earth oxides

Alkaline earth oxides generally accommodate divalent impurity ions, and so have an advantage over monovalent lattices such as KCl in that off-centre effects may be studied using spectroscopically active open-shell divalent ions. In contrast, most monovalent ions are closed-shell systems.

The first identification of an off-centre displacement in alkaline earth oxides was for the case of BaO:Mn$^{2+}$ by Sochava et al.\textsuperscript{15}
and Weightman et al. Sochava found an EPR spectrum of trigonal symmetry below ~140 K, but a motionally averaged isotropic spectrum above 250 K. Their results were explained by assuming an off-centre potential minima along a <111>-type direction, with a potential barrier of ~0.04 eV between different equivalent <111>-type off-centre positions. However, Weightman et al. observed a quite different Mn$^{2+}$ spectrum, also of trigonal symmetry in BaO, and one of the models which they proposed to explain their results is the same <111>-type off-centre motion for the Mn$^{2+}$ ion. However, they did not observe any motional averaging effect on the spectrum.

Tolparov et al. observed a Cu$^{2+}$ EPR spectrum in SrO with orthorhombic symmetry below ~6 K, but one of tetragonal symmetry above 6 K, and interpreted their results as being due to the combined effects of a <111>-type off-centre motion and a Jahn-Teller interaction in the $^2E$ ground state. From an EPR study, Sochava et al. reported two distinct sites for Co$^{2+}$ ions in SrO. The first of these centres was tentatively identified as arising from an off-centre motion of Co$^{2+}$ along a <110> direction, whilst the second centre was thought to be due to a perturbation by a neighbouring defect on the first. However Manson and Edgar, from their EPR, MCD and optical absorption study of SrO:Co$^{2+}$, found that the dominant EPR spectrum in their samples displayed trigonal symmetry about a <111> axis.

In contrast to the non-octahedral sites observed in SrO:Cu$^{2+}$ and SrO:Co$^{2+}$, Holroyd and Kolopus and Kolopus found that V$^{2+}$ and Mn$^{2+}$ ions, which have larger ionic radii than Cu$^{2+}$ and Co$^{2+}$, occupy octahedral sites in SrO. Table 1.1 summarises the off-centre/on-centre behaviour of 3d$^n$ ions in alkaline earth oxide hosts. In summary, the situation regarding off-centre effects in the alkaline earth oxides is rather
Table 1.1

Speculated off-centre/on-centre behaviour of 3d<sup>n</sup> ions in alkaline earth oxide hosts.

<table>
<thead>
<tr>
<th>System</th>
<th>Off-centre/on-centre behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO:V&lt;sup&gt;2+&lt;/sup&gt;, Mn&lt;sup&gt;2+&lt;/sup&gt;, Fe&lt;sup&gt;2+&lt;/sup&gt;, Co&lt;sup&gt;2+&lt;/sup&gt;, Ni&lt;sup&gt;2+&lt;/sup&gt;, Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>On-centre</td>
</tr>
<tr>
<td>CaO:V&lt;sup&gt;2+&lt;/sup&gt;, Mn&lt;sup&gt;2+&lt;/sup&gt;, Fe&lt;sup&gt;2+&lt;/sup&gt;, Co&lt;sup&gt;2+&lt;/sup&gt;, Ni&lt;sup&gt;2+&lt;/sup&gt;, Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>On-centre</td>
</tr>
<tr>
<td>SrO:V&lt;sup&gt;2+&lt;/sup&gt;, Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>On-centre</td>
</tr>
<tr>
<td>SrO:Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Off-centre along $&lt;110&gt;$&lt;sup&gt;18&lt;/sup&gt;</td>
</tr>
<tr>
<td>SrO:Co&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Off-centre along $&lt;111&gt;$&lt;sup&gt;19&lt;/sup&gt;</td>
</tr>
<tr>
<td>BaO:Mn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>Off-centre along $&lt;111&gt;$&lt;sup&gt;15,16&lt;/sup&gt; (Different sites reported)</td>
</tr>
</tbody>
</table>
Two different sites in BaO:Mn$^{2+}$ have been interpreted as <111> off-centre sites, the case of SrO:Cu$^{2+}$ is complicated by the Jahn-Teller effect, and two different directions of off-centre motion have been proposed for SrO:Co$^{2+}$. Clearly investigations of other transition metal ions in these oxides are desirable, and in Chapters VI and VII the EPR spectra of SrO containing Ni$^{2+}$, Fe$^{2+}$, Mn$^{2+}$, V$^{2+}$, Fe$^{3+}$ and Cr$^{3+}$ ions are described.

1.3 Off-Centre Effects in Other Hosts

Off-centre displacements of impurity ions were first identified experimentally in the alkali halide series of crystals, and the classic example of an off-centre system is the intensively-studied case of Li$^{1+}$ doped KCl. The first suggestion of off-centre behaviour in this system came from the observation of a low-frequency resonant dip in the thermal conductivity$^{22,23,25}$, and of an increase in the low temperature polarisability$^{24,26}$. Subsequent measurements of the electrocaloric$^{26}$ and dielectric$^{27}$ properties of KCl:Li$^{1+}$ have established the existence of an electric dipole moment whose magnitude is of the order of 1 Debye (due to an off-centre displacement of the Li$^{+}$ ion). The orientation of the dipole was determined to be along a <111> direction by acoustic$^{28}$ and nuclear magnetic resonance$^{29}$ experiments. Later paraelectric resonance$^{30}$ studies agreed with this <111> dipole model. Other examples of off-centre systems are OH$^{-}$ and CN$^{-}$ in alkali halides$^{31,32}$, Ag$^{+}$ in RbCl, Cu$^{+}$ in KCl and fluorine anions in NaBr$^{33}$.

Theoretical investigations$^{33,34}$ into the off-centre systems in alkali halides, using point polarisable-ion models, have also been performed, and are in qualitative accord with experiments.
1.4 The Structure of this Work

Experimental techniques employed in the present work are discussed in Chapter II. Chapter III gives a brief review of the basic theories relating to the spectroscopy of open-shell ions used in subsequent chapters. Chapters IV and V describe the investigation of the spectroscopic properties of $3d^n$ ions in MgTiO$_3$, with experimental results being presented in the former chapter. The EPR studies of divalent and trivalent metal ions in SrO are described in Chapters VI and VII respectively, and site structure models for the sites of these ions are proposed. Chapter VIII describes a theoretical investigation, using polarisable point ion and simple shell models, of off-centre displacements of $3d^n$ ions in alkaline earth oxide hosts. Chapter IX summarizes the major results presented in this thesis and the conclusions to be drawn from them.
References on Chapter I

CHAPTER II

EXPERIMENTAL TECHNIQUES
2.1 EPR Measurements

Two EPR spectrometers were used in the present work, one operating in the Q-band (35 GHz) and the other in the X-band (9 GHz). The bulk of the measurements were made on the 35 GHz spectrometer, which was a Varian E-12 instrument. The X-band spectrometer was designed and constructed in this Department. The X-band instrument was favoured for some aspects of the work on Fe\textsuperscript{2+} and Ni\textsuperscript{2+} ions in SrO since these species have very low effective g\textsubscript{\perp} values. The X-band spectrometer is not as sensitive as the Q-band instrument, but can potentially detect resonance lines with g factors as low as 0.2.

2.2 35 GHz EPR Spectrometer

2.2.1 Specifications

The Varian E-12 35 GHz spectrometer operates in the frequency range of 34.5 GHz to 35.5 GHz, with a sensitivity of \( 5 \times 10^9 \) spins when used with the E-266 cavity for a species giving rise to a resonance line one gauss wide. The magnetic field range is 0-21 Kgauss and the DC field can be sine-wave modulated at frequencies of 100 KHz, 10 KHz, 1 KHz, 270 Hz or 35 Hz with peak-to-peak modulation amplitudes of between \( 0.5 \times 10^{-3} \) gauss and 16 gauss. The microwave bridge output power to the cavity can be varied continuously from 100 mw to 0.1 \( \mu \)W, although automatic frequency locking is not possible below about 2 \( \mu \)W.

2.2.2 Microwave bridge design

The klystron output is passed through an isolator to the reference coupler where a small portion of the signal is applied to the reference arm and the major portion of the signal is directed via an
adjustable attenuator to the sample cavity. The reference arm provides microwave bias power to both the signal detector diode and the AFC detector diode; the latter is used only in the dispersion mode of operation. The two detector diodes receive power from the reference arm with a fixed 90° phase shift from each other. When the bridge is operating in absorption mode, the reference arm power is adjusted to be in phase with the signal power coming from the cavity and both resonance and AFC information are taken from the signal detector diode. When the bridge is operating in the dispersion mode, the reference arm phase control is adjusted so that the reference arm power and the power from the sample cavity are in phase at AFC detector diode. The resonance information is taken from the signal detector diode and AFC information is taken from the AFC detector diode.

2.2.3 Cavity design

Four cavities were used for the Q-band spectrometer; two of them were supplied by Varian and the other two were designed and fabricated in the Department.

The Varian E-266 "room temperature" cavity, which can also be used at liquid nitrogen temperatures, is a right circular cylinder resonant in the TE_{011} mode, with a nominal resonance frequency of 35 GHz and an unloaded Q of 7000. The body of the cavity consists of a helix of silver wire mounted within an epoxy base for structural rigidity. This helix design allows the modulation field, provided by coils mounted in a special assembly outside the cavity, to penetrate into the cavity.

The Varian E-265 liquid helium temperature cavity is basically the same as that of the room temperature one, except that the body is made of brass which seriously attenuates the field modulation amplitude,
for high modulation frequencies. The resonant frequency of both Varian cavities can be changed within the range of 34.5 to 35.5 GHz by adjusting the base plug position. They are provided with iris controls to match the cavity impedance to that of the waveguide. With these cavities, it is possible to study spectral angular variation about the vertical axis only by rotating the static magnetic field.

The other two cavities made in the Department have facilities for rotating the sample about a horizontal axis, as required for precise angular variation studies. These cavities are right circular cylinders made of brass and resonant in the TE\textsubscript{011} mode, with the principal axes in a horizontal plane. Rotation of the sample is achieved through a cog and threaded rod arrangement. The sample is held on a PVC rod whose axis is colinear with that of the cavity; the perspex rod in turn is held by the cog. The cog for either cavity had 182 teeth cut across its rim which provides an angular resolution of approximately 0.2° when rotated in a constant direction.

Both these cavities have resonance frequencies at about 35 GHz which can be changed only by adjusting the insertion of the sample holder into the cavity. One cavity, used between room temperature and liquid helium temperatures, incorporated variable coupling. The other cavity, which was used mainly with the flow tube arrangement described later, had fixed coupling.

The flow tube cavity had 10 radial slots cut in the cavity walls (0.015" wide with 0.030" spacing) to permit entry of the modulation field. The other cavity had a single turn modulation coil inside the cavity which was driven from the console through an impedance matching transformer. It was found that the peak-to-peak modulation amplitude
obtained from the internal modulation coil was 25% of the console calibration. Both these cavities had excellent facilities for automatic temperature control as described later in this chapter.

2.3 Field Strength Measurements

The resonance field positions were measured with a Varian "Fieldial" Hall probe fluxmeter, which was accurate to within 10 gauss and reproducible to within 20 mg. This fluxmeter was then calibrated using the NMR of $^1\text{H}$ and $^7\text{Li}$ nuclei which in a field of 10 Kgauss have NMR frequencies of 42.5759 MHz and 16.546 MHz respectively.

The NMR probe is a marginal oscillator circuit. A sample coil of few turns was wound around a sealed glass tube containing a saturated solution of LiCl in water to which is added trace amounts of Fe$_2$(NO$_3$)$_3$ to shorten the relaxation times. Proton resonance is used from 2.5 to 8.3 Kgauss and Li$^7$ resonance from about 6 Kgauss to 21 Kgauss. The resonance is detected by modulating the magnetic field, using the Varian E-12 Console both as a modulation source and as a phase sensitive detector. For greatest sensitivity the oscillator should be as marginal as possible.

2.4 9 GHz Spectrometer

2.4.1 Bridge design and specifications

A block diagram of the spectrometer is shown in Figure 2.1. This spectrometer is basically of conventional homodyne design, except that a gunn diode oscillator is used rather than a klystron oscillator.

The signal is detected phase-sensitively using a Princeton Applied Research Model 126 Lock-in Amplifier whose internal oscillator drives the modulation coil through an HP 467A amplifier and provides
Fig. 2.1: Block Diagram of 9 GHz E.P.R. Spectrometer.
the reference voltage for phase sensitive detection. The AFC signal from the same microwave detector was processed by an Ithaco Dynatrac 391A Lock-in Amplifier which also generated the 70 kHz AFC carrier and AFC correction voltage.

The varactor-tuned gunn effect oscillator which was used in the present X-band machine had a mechanical tuning range of 9 - 9.5 GHz and electronic tuning range of 30 MHz with an output power in the range of 250 - 280 mW.

2.4.2 X-band cavity

A rectangular cavity, made of copper-bronze, operating in TE_{102} mode with a nominal frequency of 9 GHz was used. The coupling of the cavity to the bridge could be varied by a mechanical arrangement which changes the impedance of the waveguide component where it couples to the cavity. Modulation of the static field was achieved through a single turn loop inside the cavity. The cavity was provided with a rotating cog arrangement for rotating the sample about an horizontal axis, as described in section 2.2.3. A temperature sensor diode comprising the base-collector junction of a 2N5191 transistor and a 20Ω heater were incorporated for automatic temperature control. The temperature of the cavity could be independently determined by a 4-terminal Lakeshore Cryotronics CG-2000 porous glass carbon resistor.

2.4.3 Superconducting magnet

For static magnetic fields, an Oxford Instruments 3 Tesla split-pair superconducting magnet with a magnetic field homogeneity of better than 3 parts in 10^5 was used. The sample space has a diameter of 38 mm which is just wide enough for the X-band cavity and the waveguide components. An Oxford Instruments PS60 power supply, typically operating at a
stability of 2 gauss/hour drift was used to drive the superconducting magnet through a T20822 Electromechanical Sweep Generator. This sweep generator also drives the x-axis of the X-Y chart recorder. Magnetic field strengths were determined using the manufacturer data and the voltage drop across a standard resistance in series with the superconducting magnet. This superconducting magnet can also be used for Q-band operation in conjunction with the Varian 35 GHz E-line EPR spectrometer console and microwave bridge.

2.5 **Low Temperature Operation**

2.5.1 **Q-band flow-tube method**

The arrangement allows measurement of EPR spectra in a temperature range of 8K to 245K, and consists of a two-axis cavity and a silvered double-walled quartz tube. Cold helium gas, boiled off from a helium dewar, enters the top of the flow tube via a transfer tube and passes out to the helium return line from the bottom of the flow tube. Any temperature from 8K to 295K can be achieved and controlled to within 0.5K using an automatic temperature controller which powers an electrical heater in the gas stream. The heater wire is embedded in glass wool to ensure turbulent mixing of hot and cold gas.

2.5.2 **Varian E-265 liquid helium cryostat**

The Varian E-265 liquid helium accessory was used in conjunction with the 35 GHz spectrometer for measuring EPR spectra at liquid helium temperatures. The cavity temperature could be reduced from the (atmospheric pressure) liquid helium boiling point of 4.2K to as low as 1.8K by lowering the pressure above the liquid helium in the dewar. In this range the temperature was monitored by measuring the resistance of a standard 270Ω carbon resistor.
2.5.3 Exchange space system

One of the advantages of the Oxford Instruments superconducting magnet is that it can also be used as a variable temperature cryostat. By introducing some helium gas (~10^{-2} torr) into the exchange space the temperature of the sample can be reduced to between 5 and 8K depending upon the thermal conduction down the waveguide. With this arrangement the temperature of the sample can be also varied from 8K to greater than 90K using a resistive heating element attached to the cavity. Again the temperature can be controlled to within 0.5K using automatic temperature control.

2.5.4 Automatic temperature controller

The automatic temperature controller, constructed in the Research School, consists of a constant current source, a power supply capable of providing 30 Watts of power to the heating element, and a proportional, an integral and a differential (PID) control unit which controls the output power fed to the heater. The sensor is a Lakeshore DT-500 diode whose forward resistance at constant current is a sensitive function of the temperature. Any change in the temperature of the system changes the voltage across the sensor diode. This voltage is compared with that corresponding to the set temperature and the error signal is used to operate the proportional, integral and differential control channels. Each channel may be separately tuned to match the thermal characteristics of a particular load.

2.6 EPR Spectrum Analyses

2.6.1 Least-squares fitting methods

The EPR spectrum of a given paramagnetic species may be described by a spin-Hamiltonian (see Chapter III) appropriate to the
local symmetry of the paramagnetic ion. Usually there are more observed magnetic resonance field strengths than there are parameters, and so a least-squares fitting procedure is appropriate. In the particular procedure used here, a set of trial parameters are first used to calculate the energy level scheme at the field strength of a particular transition. The first problem is to identify the eigenstates involved in the transition, since even if the microwave photon energy matches the eigenvalue difference, the associated transition probability may be zero or so small that no significant absorption is predicted. The most reliable eigenstate identification procedure is to select the pair of eigenvalues whose energy difference matches the photon size most closely, and then evaluate the associated transition probability. If this is less than some predetermined value, the pair is rejected and a pair whose difference is next closest to the photon energy is investigated. This procedure is continued until a suitable pair is identified. Once all the transitions are identified improvements over the trial parameters are obtained by minimizing the standard deviation FSD between the photon size $hv$ and the eigenvalue difference $E_M(B_J)$, where,

$$FSD = \frac{1}{N} \sum_{M=1}^{N} (E_M(B_J) - hv)^2,$$  \hspace{1cm} (2.6.1)

where the summation is over all the observed transitions. For each parameter $B_J$ one requires,

$$\frac{\partial FSD}{\partial B_J} = 0.$$

(2.6.2)

Suppose that an improved parameter value is $B_J^0$ so that

$$B_J = B_J^0 + \Delta B_J,$$

(2.6.3)
and the corresponding eigenvalue difference $E^0_M$ is given by

$$E_M = E^0_M + \Delta E_M.$$  \hspace{1cm} (2.6.4)

Neglecting second and higher order terms in the Taylor series expansion of $E_M$ about $E^0_M$, $\Delta E_M$ is given by

$$\Delta E_M = \sum_{J=1}^{L} \left( \frac{\partial E_M}{\partial B_J} \right) \Delta B_J,$$ \hspace{1cm} (2.6.5)

where the summation runs over all the S.H. parameters. Using first order perturbation theory $\Delta E_M$ is also given by

$$\Delta E_M = \sum_{J=1}^{L} \Delta B_J (<\psi|O_J|\phi> - <\psi|O_J|\psi>),$$ \hspace{1cm} (2.6.6)

where $|\phi>$ and $|\psi>$ are the two eigenvectors involved in the transition and $O_J$ ($J=m,n$) are the operators corresponding to the different $B_J$ parameters.

Finally, a set of simultaneous equations, equal in number to the number of parameters $L$, is obtained:

$$\sum_{M=1}^{N} \frac{\partial E_M}{\partial B_J} (E_M - \nu) = \sum_{M=1}^{N} \sum_{I=1}^{L} \left( \frac{\partial E_M}{\partial B_I} \right) \left( \frac{\partial E_M}{\partial B_J} \right) \Delta B_I.$$ \hspace{1cm} (2.6.7)

The derivatives in equation (2.6.7) can be easily evaluated using equation (2.6.6). Solving these simultaneous equations the improved parameter $B_J^0$ is obtained as

$$B_J^0 = B_J - \Delta B_J.$$ \hspace{1cm} (2.6.8)

Since only first order terms have been considered the process does not converge in a single step. In practice the improvement has to be continued.
until there is no appreciable decrease in the standard deviation. For the same reason, this procedure cannot be used for parameters which do not affect the eigenvalues in first order for any of the transitions observed. In those circumstances, it is necessary to study the spectra for sufficient different orientations of the magnetic field, that all the parameters give a first-order contribution for some orientations.

A computer program to fulfil this task, originally written by Dr A. Edgar for an $S = \frac{7}{2}$ system, was adopted and converted for $S = \frac{5}{2}, \frac{3}{2}$ and 1 systems by the present author.

2.6.2 Prediction of line positions

In this procedure a set of S.H. parameters obtained from least squares fitting of the spectrum, or from published values, is used to predict the line positions and transition probabilities for an arbitrary orientation of the magnetic field. This program has been extensively used in this work for theoretical studies of the angular variation of $S = \frac{5}{2}$ and $S = \frac{3}{2}$ spin systems.

First, the S.H. is diagonalised for small equal intervals of the magnetic field over the range of interest. At each field the energy levels and the corresponding slopes are determined. The energy levels as functions of the magnetic field strength are then determined by matching the energy levels and the slopes at each point. Then a pair of energy levels is chosen in the interval $H_1$ to $H_2$ such that:

$$h\nu - \Delta E(H_1) > \delta$$

and

$$\Delta E(H_2) - h\nu > \delta,$$

where $\delta$ is a small quantity, $h\nu$ is the microwave photon energy, and
$\Delta E(H_1)$ and $\Delta E(H_2)$ are the eigenvalue differences of the two levels at magnetic fields $H_1$ and $H_2$. The transition probability is then calculated between the two levels involved in the assumed transition. If this is greater than some predetermined value, the difference $\Delta E(H)$ within this interval is fitted to a quadratic equation of the form

$$a\Delta H^2 + b\Delta H + (c - h\nu) = 0 ,$$

(2.6.10)

where $\Delta H = H - H_1$.

Once the coefficients $a, b, c$ of equation (2.6.10) are determined, the resonance position can be obtained by solution of the quadratic equation (2.6.10).

A program written by Dr. A. Edgar to perform these operations for Cr$^{3+}$ ion pairs was adopted and converted by the present author for $S = ^5/2$, $S = ^3/2$ single-ion spin systems.

2.7 Crystal Growth and Treatments

2.7.1 MgTiO$_3$ Crystals

The crystals of MgTiO$_3$ were grown by a flux growth technique. The flux was a mixture of PbO and V$_2$O$_5$ with an approximate ratio of 2:1 by weight. In the initial crystal growth experiment, the starting material comprised TiO$_2$ and MgO in the exact stoichiometric ratio, but this resulted in the formation of single crystals of MgTi$_2$O$_5$. However, the use of twice the stoichiometric amount of MgO resulted in suitable single crystals of MgTiO$_3$. The crystal structure for each titanate was checked by X-ray diffraction and the stoichiometry of the MgTiO$_3$ samples was subsequently confirmed by electron microprobe analyses as described in Chapter IV. The doping was performed with nominal molar concentration
of 0.1%, 1%, 5%, 10% and in some cases 15% of the appropriate transition metal oxides. The use of higher concentration (10% and 15%) of transition metal oxides again resulted in the formation of MgTi$_2$O$_5$ crystals.

The whole mixture was melted in a platinum crucible at 1300°C, using a Muffle furnace, and soaked at that temperature for 16 hours. The mixture was then slowly cooled, typically at a rate of 1.5°C per hour, down to a temperature of 900°C whereupon the furnace was turned off. The resulting crystals were embedded in the solid flux which was removed by dissolving it in concentrated nitric acid. The MgTiO$_3$ crystals formed in platelets, sometimes with a thickness of several millimeters and up to 1 cm$^2$ in area. Undoped samples were of light brown colour, and the doped samples were brown (Fe,Mn), green (Ni,Cr) and blue (Co).

### 2.7.2 SrO Crystals

Single crystals of SrO doped with transition metal ions were obtained from W. & C. Spicer Co., England. The mass was highly polycrystalline and only small pieces were suitable for experiment. The dopant levels and the colours of the crystals were as follows:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Typical doping level</th>
<th>As grown</th>
<th>Oxidised</th>
<th>Reduced</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped SrO</td>
<td>-</td>
<td>Colourless</td>
<td>Black</td>
<td>Transparent</td>
</tr>
<tr>
<td></td>
<td></td>
<td>transparent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SrO:Fe</td>
<td>~550 ppm</td>
<td>Brown</td>
<td>Black</td>
<td>Transparent</td>
</tr>
<tr>
<td>SrO:Ni</td>
<td>100-1200 ppm</td>
<td>Dark brown to opaque</td>
<td>Brownish transparent</td>
<td>Light pink</td>
</tr>
<tr>
<td>SrO:Co</td>
<td>~220 ppm</td>
<td>Dark brown to opaque</td>
<td>Brownish transparent</td>
<td>Light blue</td>
</tr>
</tbody>
</table>

The concentration of the dopants was determined by the manufacturer using chemical analyses.
2.7.3 **Heat treatments**

Oxidation of all samples studied was achieved by heating in atmosphere in Muffle furnaces in the temperature range of 600° - 1350°C. Reduction was done by heating the samples in vacuum (\(-10^{-5}\) torr) in a resistive heating furnace where a temperature of about 1500°C could be obtained.

---

**References for Chapter II**

CHAPTER III

THEORETICAL REVIEW:

THE ELECTRONIC ENERGY LEVELS OF TRANSITION METAL IONS IN CRYSTALLINE HOSTS
3.1 Introduction

Many of the following chapters in this thesis lean heavily on quantum mechanical formalisms describing the electronic energy levels of free ions and ions in a crystalline environment. In particular, considerable use is made of conventional crystal field theory, Newman's superposition model of crystal fields, and the spin-Hamiltonian method for describing the properties of electronic ground states. It is therefore appropriate to give a brief discussion of these topics in the present chapter to lay the foundation for the calculations and arguments presented later.

The electronic structure of neutral transition metal ions of the 3d series consists of an inert argon core, one or two electrons in the outer 4s shell and a 3d$^n$ ($n = 1, \ldots, 10$) shell which is progressively filled through the series from scandium (3d$^1$) to copper (3d$^{10}$). In the process of ionisation, the atom is first stripped of its electrons in the outer 4s shell and then successive electrons are removed from the 3d shell. The paramagnetism of the ionised transition metal ions results from this unfilled 3d shell which, unlike the situation in the lanthanide series, is an outer shell and is sensitive to the local environment of the ion. In particular, a surrounding crystal lattice can induce relatively large splittings (commonly called Stark, crystal field, or ligand field splittings) of the order of 1 eV in otherwise degenerate electronic energy levels. However, before describing the theories of these splittings in detail, it will first be necessary to summarise the quantum mechanical description of the pertinent free ion states.
3.2 The Free Ion Hamiltonian

In the non-relativistic approximation, the free ion Hamiltonian for a system of $N$ electrons with a nuclear charge $Z$ can be written as\(^2,3\),

\[
\mathcal{H} = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \frac{v_i^2}{r_i} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \xi(r_i) \mathbf{s}_i \cdot \mathbf{L}_i \tag{3.2.1}
\]

where,

\[
\xi(r_i) = \frac{\hbar^2}{2m^2c^2} \frac{1}{r_i} \frac{dU(r_i)}{dr_i}. \tag{3.2.2}
\]

In (3.2.1) and (3.2.2) $r_i$ denotes the distance between the $i^{th}$ electron and the nucleus considered as an infinite point mass, $r_{ij}$ is the inter-electronic distance, and the other quantities have their usual meanings. The first term is the total kinetic energy of all the electrons, the second is the total potential energy of all the electrons arising from their interaction with the nuclear charge $Z$, the third represents the mutual Coulombic repulsive interaction amongst the electrons, and the last term represents the spin-orbit interaction. Other magnetic interactions such as spin-spin and spin-other orbit interactions have been neglected. The presence of the Coulombic repulsive term in the Hamiltonian prevents a separation of variables. At the same time, this term is not small enough to be treated as a perturbation.

The usual method of solution is the so-called central field approximation. Each electron is considered to move independently in a spherically symmetric potential $\frac{U(r_i)}{e}$ which is composed of the nuclear field and some average field due to the rest of the electrons. Equation (3.2.1) can then be rewritten as,
\[ \mathcal{H} = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m} \nabla_i^2 + U(r_i) \right] + \left[ \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} - U(r_i) \right] \\
+ \sum_{i=1}^{N} \xi(r_i) \mathbf{s}_i \cdot \mathbf{l}_i \]  
(3.2.3)

\[ = \mathcal{H}_0^{C_F} + \mathcal{H}_{Coul} + \mathcal{H}_{SO} \]  
(3.2.4)

where,

\[ \mathcal{H}_{Coul} = \left[ \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} - U(r_i) \right] . \]  
(3.2.5)

This term will be referred to as the Coulomb term and together with \( H_{SO} \) will be treated as a perturbation on the zeroth-order central-field Hamiltonian \( H_0^{C_F} \).

The unperturbed central field Hamiltonian may be solved by separating the radial and angular variables to give normalised one-electron eigenfunction of the following form

\[ \psi(a^1) = \frac{1}{r} R_{n\ell}(r) Y_{m}^{(\ell)}(\theta, \phi) . \]  
(3.2.6)

The radial function \( R_{n\ell}(r) \) depends on the central field potential \( U(r) \) and may be approximately determined by self-consistency procedures. The spherical harmonics \( Y_{m}^{(\ell)} \) are defined by Condon and Shortley

\[ Y_{m}^{(\ell)}(\theta, \phi) = (-1)^m \frac{(2\ell+1)(\ell-m)!}{4\pi(\ell+m)!} P_{m}^{(\ell)}(\cos \theta) e^{im\phi} \]  
(3.2.7)

where

\[ P_{m}^{(\ell)}(\omega) = \frac{(1-\omega^2)^{m/2}}{2^\ell \ell!} \frac{d^{m+1}}{d\omega^{m+1}} (\omega^2-1)^\ell \]  
(3.2.8)

and \( \omega = \cos \theta \).
These one-electron wavefunctions are then combined with spin wavefunctions to form the many-electron wavefunctions. These are Slater determinants whose elements are the products of N one-electron wavefunctions which are themselves the products of an orbital wavefunction of the form (3.2.6) and a spin function.

The solution of the central field problem gives rise to a series of energy levels called configurations. A configuration is defined by the \((n,\ell)\) values of all the electrons being considered. For example, Cr\(^{3+}\) has the configuration 1s\(^2\), 2s\(^2\), 2p\(^6\), 3s\(^2\), 3d\(^3\). In general the low-lying configuration is distant from other electronic configurations so calculations for \(H_{\text{COUL}}\) and \(H_{\text{SO}}\) can be carried out within the ground configuration only. The problem is then essentially reduced to performing a degenerate perturbation calculation using the determinantal product states as the basis states. These calculations tend to be tedious because large numbers of matrix elements have to be evaluated. Furthermore, the direct determinantal state method gives no insight into the structure of the configurations and provides no simple labelling scheme for the eigenvalues. A better approach is to use the power of group-theoretical methods applied to new basis sets derived by appropriate linear transformations of the determinantal basis set. Such a transformation defines a "coupling scheme".

3.3 Classification of states and Coupling Schemes

The choice of a particular coupling scheme is usually based on the actual physical coupling exhibited by the configuration considered. However it must be emphasized that in many cases there will not be any coupling scheme which is particularly close to the actual physical coupling. Even so, the Hamiltonian matrix elements can still be conveniently
calculated in terms of the coupled basis states.

Perhaps the most commonly employed coupling scheme is the Russel-Saunders (LS) coupling in which the orbital angular momenta of all the electrons are vectorially coupled to give a resultant total orbital angular momentum \( L \), and the spins are coupled to give a total spin \( S \). The angular momenta \( L \) and \( S \) may then be coupled to give a total angular momentum \( J \). The procedure starts by forming linear combination of the determinantal states which are eigenvectors of \( L_z \) and \( S_z \) using, for example, projection techniques. Each group of states which transform amongst themselves as angular momenta states of a given \( L \) and \( S \) is called a term, denoted by \( 2S+1L \), with degeneracy \((2S+1)(2L+1)\). In some cases there may be more than one term with particular values of \( S, L \), and in these cases additional quantum numbers are required to distinguish them.

The advantage of the Russel-Saunders coupling scheme is that the Coulombic interaction is both spherically invariant and spin independent and so commutes with both \( L \) and \( S \) which are therefore good quantum numbers. Hence the Coulombic interaction is diagonal in \( L \) & \( S \) and the Coulombic interaction secular determinant is immediately solved except for the sub-determinants corresponding to cases where different terms share the same \( S \leq L \) values.

The number and form of terms arising from a given configuration are completely determined by the Pauli exclusion principle. For example, for \( d^4 \) the allowed terms are \( 5D \), \( 3H \), \( 3G \), \( 3F^1 \), \( 3F^2 \), \( 3D \), \( 3P^1 \), \( 3P^2 \), \( 1I \), \( 1G^1 \), \( 1G^2 \), \( 2F \), \( 1D^1 \), \( 1D^2 \), \( 1S^1 \) and \( 1S^2 \). All of the allowed terms for the configurations \( p^n \), \( d^n \) and \( f^n \) are given in reference [5]. The Pauli exclusion principle and the presence of electrostatic interaction requires that in any configuration, the term with lowest energy has
the maximum number of parallel spins or largest S value. Subject to
this principle the lowest term also has the largest possible orbital
angular momentum. These statements constitute Hund's rule.

3.4 Evaluation of Matrix Elements of $H_{COUL}$

The Coulomb interaction in the central-field approximation is
given by (3.2.5) and has the form

$$H_{COUL} = \left[ \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} \frac{Ze^2}{r_i} \right] - U(r_i).$$

The one-electron term $\left[ - \sum_{i=1}^{N} \frac{Ze^2}{r_i} - U(r_i) \right]$ will contribute
equally to all diagonal elements within a given configuration and
therefore only shifts the centre-of-gravity for the configuration and
has no effect on the splitting or separation of the terms. The term
structure is thus determined wholly by $Q = \sum_{i<j} \frac{e^2}{r_{ij}}$. $Q$ is a two-electron
operator and for determinantal states $|A>$, the diagonal matrix element
of $Q$ is,

$$<A|Q|A> = \sum_{a<b}^{N'} \left[ <ab|\frac{e^2}{r_{12}}|ab> - <ab|\frac{e^2}{r_{12}}|ba> \right]$$

$$= \sum_{a<b}^{N'} [J(a,b) - K(a,b)]$$

(3.4.1)

(3.4.2)

where $N'$ is the number of electrons outside the closed shell. $J$ and
$K$ denote the direct and exchange integrals of the Coulomb interaction.

The matrix elements of $Q$ may be determined by expanding $\frac{1}{r_{12}}$
in terms of spherical harmonics, followed by direct integration using
the one-electron wavefunctions. This procedure is quite lengthy and
will not be described here in detail. The end result is that the matrix
elements of $H_{\text{COUL}}$ for d-electrons between terms may be expressed as a linear combination of just three parameters $F_0$, $F_2$ and $F_4$, commonly called the Slater-Condon parameters. A more convenient form is the related set of Racah parameters $A$, $B$, $C$:

$$A = F_0 - 49F_4; \quad B = F_2 - 5F_4; \quad C = 35F_4.$$  

Complete tabulation of the electrostatic matrix elements for all the $p^n$, $d^n$ and $f^n$ configurations have been given by Neilson and Koster. The matrix elements of $H_{\text{COUL}}$ can also be evaluated by tensor operator methods developed by Racah, and a description of these methods may be found in the monographs by Racah, Judd, Wybourne and Slater.

3.5 Evaluation of Spin-Orbit Interaction Matrix Elements by Tensor Operator Methods.

The spin-orbit interaction Hamiltonian is given by:

$$H_{SO} = \sum_{i=1}^{N} \xi(r_i)(s_i \cdot \ell_i).$$  (3.5.1)

where $r_i$ is the radial coordinate, $s_i, \ell_i$ are spin and orbital angular momentum of the $i^{th}$ electron, and

$$\xi(r_i) = \frac{\hbar^2}{2m^2c^2r_i} \frac{dU(r_i)}{dr_i}.$$  (3.5.2)

$H_{SO}$ is diagonal with respect to $\ell$ but not with respect to the principal quantum number $n$. Since configurations of different $n$ are usually widely separated, configuration interaction by way of the spin-orbit
interaction can be ignored. It may be shown\(^3\) that \(H_{SO}\) commutes with \(J^2\) and \(M_J\) but not with \(L^2\) or \(S^2\). Hence its matrix elements are diagonal in \(J\) and \(M_J\).

Using tensor operator methods\(^3\), the matrix elements of \(H_{SO}\) can be obtained from,

\[
< a'S'L'J'M' | H_{SO} | a'S'L'J'M > = \zeta_{n\ell} (-1)^{S'+L+J} \delta(J,J') \delta(M_J,M'_J) \sum_{i=1}^{N} \langle \ell | \Sigma_i \ell_i | a'S'L' > ,
\]

(3.5.3)

where \(\zeta_{n\ell}\) is the radial integral,

\[
\zeta_{n\ell} = \int_0^\infty R_n^2 \xi(r) \, dr ,
\]

(3.5.4)

and is a constant in the single-configuration approximation.

It can also be shown\(^3\) that

\[
< aSLJM | H_{SO} | a'S'L' > = [\ell(\ell+1)(2\ell+1)]^{1/2} < aSL|V^{(1)}|a'S'L' > .
\]

(3.5.5)

Finally,

\[
< aSLJM | H_{SO} | a'S'L'J'M' >
\]

(3.5.6)

Neilson and Koster\(^5\) have calculated and tabulated the complete \(V^{(1)}\) matrices for all \(p^n, d^n\) and \(f^n\) configurations.

The triangle condition on the 6-j symbol gives the following
selection rules for the spin-orbit interaction,

\[
\begin{align*}
\Delta S &= 0, \pm 1 \\
\Delta L &= 0, \pm 1 
\end{align*}
\]  

(3.5.7)

3.6 The Crystal Field Interaction

The magnetic properties of a transition metal ion are considerably altered by a crystalline environment. Early attempts at understanding such phenomena as the "quenching" of orbital angular momenta centered on representing the electron-lattice interaction as that of an electron in an electrostatic field due to point charges or multipoles located at the lattice sites. However, it is now well known that covalency contributions can dominate the electrostatic contribution to the electron-lattice interaction. The electrostatic and overlap/covalency contributions are frequently referred to separately as the crystal field and the ligand field respectively especially in the chemical literature. In this work and in most of the physics literature, the interaction is called the crystal field no matter what the origin since the formal expressions for the two contributions are the same, as discussed in section 3.12. Therefore whilst the crystal field formalism developed in subsequent sections will be deduced on an electrostatic basis, its wider applicability should be noted.

The total Hamiltonian for the magnetic ion in a crystalline environment can be written as,

\[
\mathcal{H}_{\text{Tot}} = \sum_{i=1}^{N} \left[ -\frac{\hbar^2}{2m} \frac{\nabla_i^2}{V_i^2} + U(r_i) \right] + \left[ \sum_{i<j} \frac{e^2}{r_{ij}} - \sum_{i=1}^{N} \frac{Ze_i^2}{r_i} - U(r_i) \right] \\
+ \sum_{i=1}^{N} \xi(r_i) s_i \cdot s_i + \mathcal{V}_{\text{CF}}, 
\]  

(3.6.1)
where $V_{CF}$ is the crystal field interaction. The method of solution of equation (3.6.1) depends upon the relative magnitudes of $V_{CF}$, $H_{SO}$ and $H_{COUL}$. There are three common cases:

1. Weak Crystal Field $V_{CF} < H_{SO} < H_{COUL}$ for rare earth ions

2. Intermediate Crystal Field $H_{SO} < V_{CF} < H_{COUL}$ for ions of the first transition group

3. Strong Crystal Field $V_{CF} > H_{COUL} > H_{SO}$ for strongly covalent complexes.

3.7 The Weak Field Scheme

The first of the three possibilities where $V_{CF} < H_{SO} < H_{COUL}$ is called the weak field case. The free ion wavefunctions have spherical symmetry and so it is most convenient to expand $V_{CF}$ in terms of spherical harmonics or tensor operators. The electrons on the transition-metal ion experience an electrostatic potential due to the surrounding point charges. This potential at the position of transition-metal ion described by spherical coordinates $(r,\theta,\phi)$ due to a point charge $q_i$ located at the point $(R_i,\theta_i,\phi_i)$ is

$$V_{CF} = \frac{q_i}{|R_i - r|}$$

which may be expressed as a sum of Legendre Polynomials $P_n^0(\cos \omega_i)$

$$V_{CF} = \sum_{n=0}^{\infty} \frac{q_i r^n}{R_i^{n+1}} P_n^0(\cos \omega_i)$$
where $\omega_i$ is the angle subtended by $r$ and $R_i$. The Legendre Polynomials may be now expressed as the sums of products of spherical harmonics with the aid of the spherical harmonic addition theorem to give,

$$V_{CF} = \sum_i \sum_{k=0}^{\infty} \sum_{q=-k}^{k} \frac{4\pi}{(2k+1)} \frac{q_i r_i^k}{R_i^{k+1}} (-1)^q Y_{q}^{k}(\theta_i, \phi_i) Y_{q}^{k}(\theta, \phi)$$

(3.7.3)

where a summation over all the lattice points has been taken. Finally the expression (3.7.3) may be conveniently written in terms of the spherical tensor operator $C_{q}^{k}(\theta, \phi)$ defined by,

$$C_{q}^{k} = \left( \frac{4\pi}{2k+1} \right)^{1/2} Y_{q}^{k},$$

(3.7.4)

to give,

$$V_{CF} = \sum_i \sum_{k=0}^{\infty} b_{q}^{k} C_{q}^{k}(\theta, \phi),$$

(3.7.5)

where in the point charge model,

$$b_{q}^{k} = \sum_i q_i \frac{r_{i}^{k}(-1)^{q}}{R_{i}^{k+1}} C_{-q}^{k}(\theta_i, \phi_i).$$

(3.7.6)

However, in general, the coefficients $b_{q}^{k}$ will depend upon overlap and covalency contribution, and are usually regarded as parameters to be determined by experiment.

The first term in the expansion has $k = q = 0$ and is thus spherically symmetric. This term is by far the largest term in the expansion and is responsible for the greater part of the lattice energy. In the first approximation this term gives a uniform shift of all levels of the configuration and may be ignored as far as the crystal field splittings of the levels are concerned.
For $d^n$ configuration, only terms with $k \leq 4$ have non-zero matrix elements. Furthermore, all terms with odd $k$ have zero matrix elements within configurations containing solely equivalent electrons. Finally the number of terms in the expansion of equation (3.7.5) is restricted by the point group symmetry of the magnetic ion in the crystal. Prather has given the rules for determining non-vanishing terms in the expansion. For example, for $C_{3v}$, $C_{4v}$ and $C_{2v}$ symmetries, $V_{CF}$ is given by,

\[
\begin{align*}
(V_{CF})_{C_{3v}} &= B_0(2)C_0(2) + B_0(4)C_0(4) + B_3(4)(C_4(4) - C_{3}(4)) \\
(V_{CF})_{C_{4v}} &= B_0(2)C_0(2) + B_0(4)C_0(4) + B_4(4)(C_4(4) + C_{-4}(4)) \\
(V_{CF})_{C_{2v}} &= B_0(2)C_0(2) + B_2(2)(C_2(2) + C_{-2}(2)) + B_0(4)C_0(4) + B_4(4)(C_4(4) + C_{-4}(4)) \\
&\quad + B_4(4)(C_4(4) + C_{-4}(4)) .
\end{align*}
\]

Clearly, the number of $B^{(k)}_q$ parameters increases rapidly when the symmetry is reduced.

Sometimes, it is desirable to have the axis of quantisation along axes other than the z-axis, which is usually chosen as the principal axis of symmetry. In general, any other choice of quantisation axis will give a more complicated expansion in spherical harmonics and the apparent symmetry appears to be lower than that with quantisation along the z-axis. However the crystal field coefficients are not all independent. For example, a term $C_0(2)$ with quantisation along the y-axis or the x-axis may be expressed with respect to the z-axis as follows:
3.8 Evaluation of Matrix Elements of $V_{\text{CF}}$ by Tensor Operator Methods in the Weak Field Scheme

The crystal field interaction is already given in tensorial form in (3.7.5), and so it is more convenient to evaluate the matrix elements of $V_{\text{CF}}$ using tensor operator techniques, rather than the older operator-equivalent method developed by Stevens and treated in greater detail by Hutchings.

In the LS-coupling scheme, the matrix elements of $V_{\text{CF}}$ have the form,

$$
< \xi^{N_aSLJ'M} | V_{\text{CF}} | \xi^{N_a'SL'J'M'} >
$$

$$
= \sum_{k,q} B(k) < \xi^{N_aSLJ'M} | C(k) | \xi^{N_a'SL'J'M'} > \delta(S,S')
$$

$$
= \sum_{k,q} B(k) \langle \xi \| C(k) \| \xi \rangle < \xi^{N_aSLJ'M} | U(k) | \xi^{N_a'SL'J'M'} >
$$

(3.8.1)

where $U(k)$ is a unit tensor operator and is diagonal in the spin $S$.

The reduced matrix elements of $U$ have been given by Neilson and Koster.

The reduced matrix elements $\langle \xi \| C(k) \| \xi \rangle$ are given by

$$
\langle \xi \| C(k) \| \xi \rangle = (-1)^{\xi - [(2\ell+1)]} \begin{pmatrix} \ell & k & \ell \\ 0 & 0 & 0 \end{pmatrix}.
$$

(3.8.2)

The final expression for the matrix elements of $V_{\text{CF}}$ is given

\[
\begin{align*}
B_2^{0} c_0^{(2)} (y-axis) & \rightarrow B_2^{0} \left[ -\frac{1}{2} c_0^{(2)} - \frac{1}{4} \sqrt{5} (c_2^{(2)} + c_{-2}^{(2)}) \right] (z-axis) \\
B_2^{0} c_0^{(2)} (x-axis) & \rightarrow B_2^{0} \left[ -\frac{1}{2} c_0^{(2)} + \frac{1}{4} \sqrt{5} (c_2^{(2)} + c_{-2}^{(2)}) \right] (z-axis)
\end{align*}
\]
by,

\[ < a^{N_a} \alpha a^N \lambda a^N \alpha \lambda a^N \lambda | c^{(k)}_q | a^{N_a} \alpha a^N \lambda a^N \lambda | \lambda > \]

\[ = (-1)^{-M_J + S + k + L' + J + J'} (2J + 1)(2J' + 1) \delta(2\lambda + 1) \left( \begin{array}{ccc} \ell & k & \ell \\ 0 & 0 & 0 \end{array} \right) \]

\[ \times \left( \begin{array}{cc} J & k \\ -M_J & q \end{array} \right) \left( \begin{array}{cc} L & J & S \\ J' & L' & k \end{array} \right) < a^{N_a} \alpha \lambda a^N | u^{(k)} | a^{N_a} \alpha \lambda a^N \lambda > \quad (3.8.3) \]

3.9 Complete Solution of the Total Hamiltonian in a Weak Field Scheme

The total Hamiltonian for a system of N electrons with a nucleus of charge Ze subject to a crystal field \( V_{CF} \) is given by

\[ H = -\frac{\hbar^2}{2m} \sum_{i=1}^{N} \nabla_i^2 - \sum_{i=1}^{N} \frac{Ze^2}{r_i} + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + \sum_{i=1}^{N} \xi(r_i) s_i \cdot \xi + V_{CF}. \quad (3.9.1) \]

The first procedure in the weak field scheme is to determine all the states \(|a^{N_a} \alpha a^N \lambda a^N \lambda >\) of a given configuration. The number of distinct states for the \( d^n \)-configurations are 10, 45, 120, 210 and 252 for \( n=(1,9), (2,8), (3,7), (4,6) \) and (5) respectively. Evidently, the Hamiltonian matrices can be quite large, but it is possible to factorize the secular matrix by forming linear combinations of the basis states \(|a^{N_a} \lambda a^N \lambda >\) which transform according to irreducible representation of the appropriate point group. Griffith has given these symmetry adapted functions for the \( O_h \) point group up to \( J = \frac{9}{2} \). This method is very tedious and there is the problem of defining a consistent set of phase factors. An alternative procedure is to diagonalise the Hamiltonian directly within the original \(|a^{N_a} \lambda a^N \lambda >\) basis functions. However this procedure involves the diagonalisation of a \((b \times b)\) matrix for each interaction, where \( b \) is the number of basis functions in the configuration.
Fortunately, modern electronic computers can be used to both evaluate these matrix elements and to diagonalise the entire matrix. In this thesis, computer programmes were written for the complete solution of the total Hamiltonian in the weak field scheme for the d^3 and d^6 configurations.

3.10 The Strong Field Scheme

In the strong field case one has $V_{CF} > H_{Coul} > H_{SO}$. For a single d-electron, a cubic crystal field splits the fivefold degenerate d^1 orbital state into "t_{2g}" and "e_g" orbitals which transform amongst themselves according to the t_{2g} and e_g irreducible representations respectively of the cubic group. In a many electron system these orbitals are progressively filled to yield the various strong field configurations $t_{2g}^m e_g^n (m \leq 6, n \leq 4)$, and each of these is further split by $H_{Coul}$ into different terms denoted by $^{2S+1} \Gamma$, where $\Gamma$ is an irreducible representation of the cubic group. Each of these terms can be further split by $H_{SO}$ and crystal fields of lower symmetry.

Since strong field scheme calculations were not performed in the present work, the scheme will not be described in any further detail. However, transformation of parameters from strong field to weak field schemes have been required. The method of evaluating the matrix elements in the strong field scheme is described by Ballhausen, Sugano, Tanabe and Kamimura and Griffith.
3.11 The Intermediate Field Scheme

The intermediate field case when $H_{SO} < V_{CF} < H_{COUL}$ is best approached by forming the eigenstates of $L, L_z, S, S_z$ as in the weak field case without coupling $L$ and $S$ to give eigenstates of the total angular momenta $J, J_z$. The crystal field hamiltonian may then be diagonalised within these basis sets with the useful selection rule $\Delta S = 0$ since $V_{CF}$ is spin independent. If terms with the same spin are well separated, it is frequently feasible to ignore inter-term mixing. The ground terms, which are important in experiments such as EPR that depend upon thermal population of levels, are frequently treated in this approximation. For the $d^4$ and $d^6$ configurations no approximation is necessary since there is just one spin quintet term, the $^5D$ ground term.

The effect of spin-orbit coupling in the intermediate field scheme is particularly simple for a ground term which obeys Hund's rule, since the matrix elements of $H_{SO}$ are then equal to those of the operator $\lambda L \cdot S$, where $\lambda = \pm \xi/2S$. The sign is positive for a shell that is less than half-filled and negative for a shell that is more than half-filled. Thus within the ground term, the hamiltonian may be taken as,

$$\mathcal{H} = \sum_{l=0}^{\lambda} \sum_{m=-l}^{l} B^m_l C^m_l + \lambda L \cdot S \quad \text{.} \quad \text{(3.11.1)}$$

Within a given multiplet, the matrix elements of $C^m_l$ are proportional to those of the angular momentum operator equivalent $O^m_l$, defined for example by Hutchings\textsuperscript{11}, and so the hamiltonian (3.11.1) is frequently expressed as

$$\mathcal{H} = \sum_{l=0}^{\lambda} \sum_{m=-l}^{l} B^m_l O^m_l + \lambda L \cdot S \quad \text{.} \quad \text{(3.11.2)}$$
where the notation $b^{m}_k$ is unfortunately retained for the operator equivalent coefficients.

3.12 The Superposition Model of Crystal Fields

It is now well known that the crystal field interaction for open shell 3d and 4f ions is primarily due to electronic processes such as covalency and overlap, rather than to electrostatic fields generated by the ions of the crystal lattice. However Newman has shown that the crystal field Hamiltonian (3.7.5) acting within a basis set of free ion wavefunctions may still be used as an effective Hamiltonian to parametrize experimental data. However, it must be remembered that the real wavefunctions are no longer linear combinations of free ion wavefunctions and involve states of the ligands. Furthermore, the crystal field parameters can no longer be given a straightforward physical interpretation.

Whilst the crystal field Hamiltonian is therefore frequently used to summarise experimental data, comparisons of experimental with theoretically-derived parameters are rare because of the large effort which must be expended on ab-initio calculation of covalency and overlap processes. However, it is not really necessary to confront experiment with ab-initio theory for every situation since theoretical calculations have established the dominance of non-electrostatic mechanisms for several simple cases. What is of more use is a scheme whereby parameters determined for one system may be compared with those of another.

Fortunately, the superposition model of crystal fields developed by Newman fulfils this task admirably. In this empirical model, no assumption as to the underlying mechanism of the crystal field is made.
The basic premise is that the contributions of each ligand is axially symmetric about the ion-ligand axis, and that the total crystal field is simply given by the summation of the single-ligand contributions. Newman's original derivation utilizes tesseral harmonics, but in this thesis the tensor operators $C_l^m$ are used exclusively, and a derivation of the superposition model relations in this normalisation is now given.

In accordance with the basic assumptions, the crystal field for $n$ electrons is given by,

$$
V = \sum_{j=1}^{n} v_j = \sum_{j=1}^{n} B_n(R_i) C_n^0(\psi_i, 0) ,
$$

where $\psi_i$ is the angle subtended by the electronic position vector $(r_j, \theta_j, \phi_j)$ and that of the ligand nucleus $(R_i, \theta_i, \phi_i)$. Here the "intrinsic" parameters $B_n(R_i)$ describe the single-ligand interactions, and are usually assumed to follow some power law variation with ion-ligand separation:

$$
B_n(R) = \frac{B_n(R_0)}{[R_0/R]^n}
$$

where $R_0$ is a reference separation.

Using the spherical harmonic addition theorem, (3.12.1) may be rewritten as,

$$
V = \sum_j \sum_{n,m} C_n^m(\theta_j, \phi_j) \sum_i B_n(R_i)(-1)^m C_n^m(\theta_i, \phi_i)
$$

$$
= \sum_j \sum_{n,m} B_n^m C_n^m(\theta_j, \phi_j),
$$
Thus if the ligand coordinates $R_i$, $\theta_i$, $\phi_i$ are known from, for example, neutron or X-ray structure analyses, then it is possible in principle to relate the crystal field parameters of a given 3d ion-ligand system in a variety of host crystals through the four empirical parameters $B_2(R_0)$, $B_4(R_0)$, $t_2$ and $t_4$.

One simple extension of the superposition model is to include the effect of distant (non-ligand) ions using the simple electrostatic model. This is quite straightforward for point charges, since then $t_2 = 3$, $t_4 = 5$ and the intrinsic parameters $B_2$ and $B_4$ may be simply calculated. However, multipole contributions do not satisfy the requirement of axial symmetry and cannot be readily incorporated. Point charge contributions for distant ions are usually very small for fourth order parameters, but can be appreciable in the case of 2nd order parameters. This difference in relative contributions is partly due to the different distance dependences of $\frac{1}{R^3}$ and $\frac{1}{R^5}$ for $n = 2$ and $n = 4$ point charge contributions respectively.

3.13 The Spin-Hamiltonian Formalism

EPR transitions are usually only observed between energy levels within a few wavenumbers of the ground state. This is because the signal intensity is approximately proportional to the average population of the two energy levels involved in the transition, and, for moderate temperatures, this population factor is too small for EPR to be detected.
in higher excited states. Thus in EPR the properties of only a limited set of eigenstates are obtained. The full formalism of crystal field theory aims at describing the properties of a complete configuration, and is therefore a rather unwieldy framework within which to describe EPR spectra. Furthermore, extensions would be needed to include such effects as hyperfine interactions.

The spin-Hamiltonian method is an effective operator technique which is designed to describe only the properties of the set of states between which EPR is observed. (In certain situations, it may be necessary to extend this set to allow for magnetic-field induced mixing of higher levels which are not directly observed in EPR.) Quantitatively, the spin-Hamiltonian is based on equating the behaviour in a magnetic field of the $2S'+1$ experimentally observed states with that of a system with effective spin $S'$. Frequently, the effective spin $S'$ is identical to the true spin $S$ and the effective magnetic moment is approximately equal to the true spin magnetic moment, but this is by no means always the case. For example, Cr$^{3+}$ and Co$^{2+}$ have conjugate d$^3$ and d$^7$ configuration with $^4$F free ion ground states. In an octahedral crystal field, the ground state of Cr$^{3+}$ is $^4$A and hence $S'=S=3/2$, but for Co$^{2+}$ the ground state orbital triplet is split by spin-orbit coupling leaving a Kramers doublet, described by $S'=1/2$ lowest. Thus for Cr$^{3+}$ the effective magnetic moment is approximately $2\beta S'$, but for Co$^{2+}$ $\mu = 4.3\beta S'$.

The original perturbation-theory derivation of a spin-Hamiltonian by Pryce$^{17,18}$ was only applicable to orbital singlet ground states. It could not account for the splittings observed experimentally for $S$ ground states, nor could it be applied to orbital multiplet ground states. However, it did have the advantage that in cases where it could be applied it was possible to deduce explicit formulae for the parameters
appearing in the spin-Hamiltonian. More modern formulations of spin-
Hamiltonians use group theoretical \textsuperscript{19} and tensor decomposition

techniques \textsuperscript{20,21,22,23} to deduce spin-Hamiltonians appropriate for any
situation, without, however, giving any indication of the relative
magnitudes of the various terms. The group theoretical and tensor
decomposition methods are basically equivalent and utilize the symmetries
of the problem to determine which types of terms can occur.

The experimentalist utilizes the spin-Hamiltonian as a
convenient shorthand to summarize his experimental results, using physical
insight to deduce which of the many allowed terms will be largest and
including sufficient smaller terms, again selected by physical or
statistical considerations, so that an accurate representation of the
experimental data is given.

Only the tensor decomposition method will be described in
detail here, and as a specific example which will be used later in this
thesis, the spin-Hamiltonian (S.H.) for the \( ^6S \) ground state of the Fe\(^{3+} \)
ion at site of orthorhombic symmetry will be deduced.

The spin tensor operators \( T^M_S(S) \), defined for example by
Buckmaster\textsuperscript{24}, form a complete set of linearly independent operators
within any spin angular momentum basis set \( |S'\rangle, |S'-1\rangle, \ldots, |-S'\rangle \).
Hence any Hamiltonian matrix within a \( 2S'+1 \)-fold set of states may be
represented by an appropriate linear combination of operators \( T^M_S(S) \)
acting within the basis set \( |S\rangle, \ldots, |-S\rangle \). Furthermore, the
variation of the matrix elements with magnetic field strength may be
represented with complete generality by writing the effective Hamiltonian
as a power series in field tensors \( T^M_H(H) \);
\[ \mathcal{H} = \sum_{L_s, M_s} A_{L_s}^{M_s} T_{L}^{M_s} (S) + \sum_{L_s, M_s, M_H} B_{L_s}^{M_s} T_{L}^{M_s} (S) T_{L}^{M_H} (H) \]
\[ + \sum_{L_s, M_s, M_H} C_{L_s}^{M_s} T_{L}^{M_s} (S) T_{L}^{M_H} (H) . \]  
(3.13.1)

The terms in this equation may be rewritten in terms of the tensor products \( T_{L}^{M}(S,H) \) of field and spin tensors provided the triangle rule holds:

\[ |L_s - L_H| \leq L \leq |L_s + L_H| \]

One then obtains,

\[ \mathcal{H} = \sum_{L_s, M} (0 \alpha_L^M T_{L}^{M} + 1 \alpha_L^{M_1} T_{L}^{M_1} + 2 \alpha_L^{M_2} T_{L}^{M_2} + \ldots . ) \]  
(3.13.3)

where the prefix denotes the field tensor rank parentage.

There are several conditions which impose constraints on the values of the coefficients \( n_L^M \):

(1) The S.H. must be Hermitian, so that

\[ (a_L^M T_{L}^{M})^\dagger = (-1)^M (a_L^M)^* T_{L}^{M} \]  
(3.13.4)

\[ \therefore a_L^{-M} = (-1)^M (a_L^M)^* . \]  
(3.13.5)

(2) Time reversal, represented by the Kramers operator \( K \), requires,
and it can be shown that\textsuperscript{20}

\[ KHK^{-1} = H \quad (3.13-6) \]

Hence terms with \( L \) odd are forbidden.

(3) The spin-Hamiltonian must be invariant under the operations of the local point group symmetry. For the present example, the linear combination of the which remains invariant under the \( C_{2v} \) point group and satisfies the previous conditions is,

\[
\begin{align*}
\sum a^0 T^0_0 + a^0_a T^0_a + a^2_a [T^2_a + T^{-2}_a] + a^4_a [T^4_a + T^{-4}_a] + & a^4_a [T^4_a + T^{-4}_a] \\
& + a^4_a [T^4_a + T^{-4}_a] \\
\end{align*}
\]

(3.13.8)

where \( T^M_L = T^M_L(S,H) \).

In the next stage, the tensors of equation (3.13.8) have to be decomposed into products of operators, according to equation (3.13.2). The factors in these products are functions of the magnetic field only or of the spin only. The decomposition of equation (3.13.2) is not unique, since for any given \( L \), an infinite number of \( L_S \) and \( L_H \) combinations are possible as long as the triangle rule is obeyed. However the following physical restrictions limit the allowable modes of decomposition:

(1) The triangle rule on the \( 3J \) symbol requires that:

\[
M_S + M_H = M \quad \text{and} \quad |L_S - L_H| \leq L \leq |L_S + L_H| .
\]

(2) Odd parity products do not satisfy time reversal invariance, i.e. \( L_H + L_S \) must be even.
(3) Spin tensors of rank greater than $2S$ (5 in the case of $\text{Fe}^{3+}$) can be neglected, since their matrix elements necessarily vanish within an $S = \frac{5}{2}$ basis set. This again is an immediate consequence of the triangle rule.

(4) Field tensors of rank $L_H$ imply terms in the field of the form $H^{L_H}$. Usually quadratic and higher order terms are negligible and so we assume that $L_H$ is zero or one.

The decomposition of tensors in equation (3.13.8) into products of field-only or spin-only tensors are as follows:

$$T^0_0 \rightarrow \frac{1}{\sqrt{3}} \left[ T^{-1}(S)T^{1}(H) + T^{1}(S)T^{-1}(H) - T^0(S)T^0(H) \right]$$

$$T^0_2 \rightarrow \frac{1}{\sqrt{30}} \left[ T^{-1}(S)T^{1}(H) + T^{1}(S)T^{-1}(H) + 2T^0(S)T^0(H) \right].$$

Thus the decomposition of the $T^0_0$ operator results in an isotropic Zeeman interaction, whilst the $T^0_2$ operator gives an axially symmetric interaction. Similarly, the $T^{\pm 2}_2$ operators give rise to a Zeeman interaction of orthorhombic symmetry. The zero-field tensor decompositions are as follows:

$$T^0_2(S,H) + T^0_2(S)$$

$$[ T^2_2(S,H) + T^{-2}_2(S,H) ] \rightarrow [ T^2_2(S) + T^{-2}_2(S) ]$$

$$T^0_4(S,H) + T^0_4(S)$$

$$[ T^2_4(S,H) + T^{-2}_4(S,H) ] \rightarrow [ T^2_4(S) + T^{-2}_4(S) ]$$

$$[ T^{-4}_4(S,H) + T^4_4(S,H) ] \rightarrow [ T^{-4}_4(S) + T^4_4(S) ].$$
The tensor operators $T^M_L(S)$ have been tabulated by Buckmaster et al.\textsuperscript{25}. Using their tables, the spin-Hamiltonian may finally be written as

\[ H = g_x H x x + g_y H y y + g_z H z z + a^{00}_2 T^0_2(S) + a^{22}_2 [T^2_2(S) + T^{-2}_2(S)] \\
+ a^{01}_4 T^1_4(S) + a^{21}_4 [T^2_4(S) + T^{-2}_4(S)] + a^{42}_4 [T^4_4(S) + T^{-4}_4(S)] . \quad (3.13.9) \]

The tensor operator notation used here is still not widely used in EPR literature. Instead the S.H. operators are usually expressed in terms of Stevens operator equivalents $O^M_L$ which are related to $T^M_L$ according to the following relation:

\[ O^M_L(S) = N [T^M_L(S) + (-1)^M T^{-M}_L(S)] , \quad (3.13.10) \]

where $N$ is a normalisation constant. In terms of these operators the S.H. for Fe$^{3+}$ in $C_{2v}$ point group symmetry becomes

\[ H = \beta H g S_x + B^0_{200} + B^2_{202} + B^0_{400} + B^2_{402} + B^4_{404} . \quad (3.13.11) \]

Whilst this derivation has not included any hyperfine terms, the incorporation of same terms through the nuclear spin tensor operator $T^M_L(I)$ is quite straightforward.
References on Chapter III

CHAPTER IV

GROUND STATE SPECTRA AND SUBSTITUTIONAL CHARACTERISTICS OF \(3d^n\) TRANSITION METAL IONS IN MAGNESIUM TITANATE
4.1 Introduction

As far as is known, only three investigations of MgTiO$_3$ containing transition metal ion impurities have been hitherto performed. Schimitschek$^1$ reported the EPR spectra of MgTiO$_3$:Cr$^{3+}$. He found a single, trigonally symmetric spectrum characteristic of Cr$^{3+}$ ions which could be described by an $S = \frac{3}{2}$ spin-Hamiltonian with parameters, $g_\parallel = 1.976 (2)$, $g_\perp = 1.981 (2)$ and $|D| = 15.05 (3)$ GHz. Neither the site location of the chromium ions nor the sign of the zero field splitting was determined.

Louat et al.$^2$ described the R-line emission spectra of Cr$^{3+}$ and Mn$^{4+}$ ions in polycrystalline samples of MgTiO$_3$, and Villela et al.$^3$ reported the emission spectra of MgTiO$_3$:Mn$^{4+}$ powders. The two sharp intense emission lines, labelled $R_1$ and $R_2$ by analogy with the case of ruby, were interpreted as transitions to the $^4A_2$ ground state from the $^2E$ state which is split into two Kramers doublets by the trigonal component of the crystal field. For MgTiO$_3$:Cr$^{3+}$, the R lines occur at 13645 and 13663 cm$^{-1}$, and for Mn$^{4+}$ these lines lie at 14300 cm$^{-1}$ and 14339 cm$^{-1}$. Two significant differences between the Cr$^{3+}$ and Mn$^{4+}$ spectra are that no vibronic sidebands are observed for Cr$^{3+}$, and, in contrast to the case for Mn$^{4+}$, the temperature dependence of the frequency of the $R_1$ transition for Cr$^{3+}$ is negligible. The origin of these differences, and the question of whether Cr$^{3+}$ ions are located at the Mg$^{2+}$ site, or the Ti$^{4+}$ site, or both, was not resolved.

In this chapter the EPR spectra of Co$^{2+}$, Ni$^{2+}$, Mn$^{2+}$ and Mn$^{4+}$ at single sites and Fe$^{3+}$ and Cr$^{3+}$ at two lattice sites in MgTiO$_3$ are reported. The angular dependences of the spectra are described, and spin-Hamiltonian parameters determined by least-squares fittings are presented. Finally the location of substitutional 3d$^n$ ions in the MgTiO$_3$ lattice and the mechanisms of charge compensation are discussed.
4.2 Crystal Structure

Magnesium titanate (MgTiO$_3$) is a member of an isostructural family of titanates, manganates, vanadates and niobates which all crystallize with the ilmenite (FeTiO$_3$) structure. The packing arrangement may be described by the space group $C_{31}^2$ and is based on a non-primitive hexagonal unit cell containing six formula units. The ilmenite structure, illustrated in Fig. 4.1, is very similar to that of alumina (Al$_2$O$_3$) and differs only in having half the metallic atoms unlike the other half and in the lower symmetry this entails. There are six hexagonal close-packed layers of oxygen ions in the unit cell with the layer planes aligned normal to c axis. Between these layers there are distorted octahedrally-coordinated spaces. Proceeding in the direction of the c axis, these spaces are occupied by a metallic ion or are vacant according to the scheme,

\[ \text{Ti}^{4+} \quad \text{Mg}^{2+} \quad \text{vacant} \quad \text{Mg}^{2+} \quad \text{Ti}^{4+} \quad \text{vacant} \]

The hexagonal unit cell edges for MgTiO$_3$ have been measured as $a'_0 = 5.054 \, \text{Å}, \, c'_0 = 13.898 \, \text{Å}$ (Wyckoff$^5$), but in contrast to FeTiO$_3$ and NiTiO$_3$ the exact positions of the atoms within the unit cell have not been determined. However it is reasonable to assume that the internal structure is similar to that of NiTiO$_3$ in view of the proximity of the lattice parameters for NiTiO$_3$ ($a'_0 = 5.044 \, \text{Å}, \, c'_0 = 13.819 \, \text{Å}$) and those for MgTiO$_3$, and of the ionic radii for Ni$^{2+}$ and Mg$^{2+}$. ($0.70 \, \text{Å}$ and $0.72 \, \text{Å}$ respectively$^6$).

Both the Mg$^{2+}$ and Ti$^{4+}$ ion sites in MgTiO$_3$ are octahedrally coordinated and satisfy the point group $C_3$. The geometries of the ligand cages surrounding the divalent and tetravalent metal ions are given in Table 4.1 for a representative sample of ilmenite structure hosts,
Fig 4.1: The structure of MgTiO$_3$, showing the rhombohedral unit cell.
Table 4.1

Characteristics of different ilmenite-structure crystals. (For comparison the structural values of \( \text{Al}_2\text{O}_3 \) are also included.) Distances are given in angström units and \( (\text{C}, \text{Me-O}) \) represents the angle between the c axis and the metal-oxygen bond.

<table>
<thead>
<tr>
<th></th>
<th>MnTiO₃</th>
<th>FeTiO₃</th>
<th>NiTiO₃</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_0 ) in Å</td>
<td>5.13</td>
<td>5.082</td>
<td>5.044</td>
<td>4.759</td>
</tr>
<tr>
<td>( C_0 ) in Å</td>
<td>14.283</td>
<td>14.026</td>
<td>13.819</td>
<td>12.991</td>
</tr>
<tr>
<td>Me-Me distance in Å</td>
<td>4.09</td>
<td>3.98</td>
<td>4.06</td>
<td>6.79</td>
</tr>
<tr>
<td>Ti-Ti distance in Å</td>
<td>4.09</td>
<td>3.98</td>
<td>4.06</td>
<td>-</td>
</tr>
<tr>
<td>Me-O distance in Å</td>
<td>2.26; 2.10</td>
<td>2.14; 2.02</td>
<td>2.10; 2.04</td>
<td>1.97; 1.86</td>
</tr>
<tr>
<td>Ti-O distance in Å</td>
<td>2.12; 1.86</td>
<td>2.14; 1.92</td>
<td>2.06; 1.92</td>
<td>-</td>
</tr>
<tr>
<td>( (\text{C}, \text{Me-O}) ) in degrees</td>
<td>136.0; 63.1</td>
<td>135.0; 66.0</td>
<td>133.7; 63.5</td>
<td>132.4; 63.1</td>
</tr>
<tr>
<td>( (\text{C}, \text{Ti-O}) ) in degrees</td>
<td>47.8; 113.8</td>
<td>45.0; 115.0</td>
<td>47.4; 116.3</td>
<td>-</td>
</tr>
</tbody>
</table>
including NiTiO$_3$.

4.3 Crystal Growth and Characterisation

The preparation of samples of MgTiO$_3$ doped with transition metal ions by flux-growth techniques has been described in Chapter II. The advantage of flux growth methods is that it is not necessary to attain temperatures close to the melting point, approximately 2000°C in the case of MgTiO$_3$. However a major disadvantage is that it is possible to have small inclusions of the flux trapped in the grown crystals. Furthermore, metallic ions from the flux constituents may be dispersed throughout the crystals in concentrations comparable with those of the deliberate dopants. Evidently it is desirable to analyse flux-grown crystals for both deliberate and flux-induced impurities.

The doped and nominally pure samples of MgTiO$_3$ studied here were analysed by Mr N. Ware of the Research School of Earth Sciences, ANU, using the electron microprobe technique, and the results for several samples are presented in Table 4.2. The first major point to be noted is that the stoichiometry of the samples, as given by the MgO and TiO$_2$ analyses, is correct. Powder and Laue X-ray investigations provided further confirmation that the samples were indeed single crystals of MgTiO$_3$. These checks are important since, as far as is known, this is the first time that single crystals of MgTiO$_3$ have been produced by flux methods.

The sample analyses show that the lead content is below the detection limit of 0.1 weight%, but Vanadium is present in all samples in significant concentrations of between 0.29% and 1.92% V$_2$O$_3$ by weight. Most samples also contained small concentrations, typically $\approx$0.1% by weight, of SiO$_2$ and ZrO$_2$ which were probably present in the TiO$_2$ starting material.
Table 4.2

Microprobe analyses of MgTiO₃ crystals. The concentrations are quoted in weight percent.

<table>
<thead>
<tr>
<th>Deliberate dopants with nominal concentration</th>
<th>Nominally undoped</th>
<th>0.1% of Cr</th>
<th>1% of Mn</th>
<th>0.1% Fe</th>
<th>0.1% Ni</th>
<th>1% Co</th>
<th>0.5% Cu</th>
<th>0.5% Gd</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>66.15</td>
<td>64.74</td>
<td>65.46</td>
<td>64.35</td>
<td>64.4</td>
<td>65.09</td>
<td>63.81</td>
<td>64.72</td>
</tr>
<tr>
<td>MgO</td>
<td>33.86</td>
<td>33.59</td>
<td>33.24</td>
<td>33.45</td>
<td>33.04</td>
<td>32.73</td>
<td>32.55</td>
<td>32.76</td>
</tr>
<tr>
<td>V₂O₃</td>
<td>&lt;.12</td>
<td>0.80</td>
<td>.29</td>
<td>1.92</td>
<td>.56</td>
<td>1.03</td>
<td>2.03</td>
<td>1.44</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&lt;.1</td>
<td>&lt;.1</td>
<td>&lt;.1</td>
<td>&lt;.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>&lt;.08</td>
<td>.35</td>
<td>&lt;.08</td>
<td>&lt;.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>MnO</td>
<td>&lt;.08</td>
<td>&lt;.08</td>
<td>.58</td>
<td>&lt;.08</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&lt;.08</td>
<td>&lt;.08</td>
<td>&lt;.08</td>
<td>.27</td>
<td>&lt;.03</td>
<td>&lt;.03</td>
<td>&lt;.03</td>
<td>&lt;.03</td>
</tr>
<tr>
<td>NiO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>.18</td>
<td>&lt;.04</td>
<td>.22</td>
<td>.08</td>
</tr>
<tr>
<td>CoO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;.04</td>
<td>1.08</td>
<td>&lt;.04</td>
<td>&lt;.04</td>
</tr>
<tr>
<td>CuO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;.05</td>
<td>&lt;.05</td>
<td>.45</td>
<td>&lt;.05</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;.04</td>
<td>&lt;.04</td>
<td>&lt;.04</td>
<td>&lt;.04</td>
</tr>
<tr>
<td>Ratio of numbers of Ti⁴⁺ ions to Mg²⁺ ions</td>
<td>.977</td>
<td>.964</td>
<td>.984</td>
<td>.962</td>
<td>.975</td>
<td>.994</td>
<td>.985</td>
<td>.988</td>
</tr>
</tbody>
</table>

In addition to these contents all samples contain trace amounts of SiO₂ & ZrO₂.
All of the samples which were deliberately doped with transition metal ions were found to contain detectable concentration of the appropriate oxide, with the exception of gadolinium-doped samples. The measured concentrations are not simply related to the nominal dopings, which is not unexpected since the different ions will have different solubilities in the flux. The absence of any detectable gadolinium content is also not surprising since the ionic radius of the Gd$^{3+}$ ion is much greater than that of either Mg$^{2+}$ or Ti$^{4+}$, and its accommodation in the MgTiO$_3$ lattice is therefore unlikely.

EPR spectra of the nominally undoped samples revealed the presence of small concentrations of Mn$^{2+}$, Cr$^{3+}$ and Fe$^{3+}$ ions. These spectra are described in section 4.4. More importantly, no spectrum which could be attributed to V$^{2+}$ was observed in undoped or doped samples, despite the high vanadium concentration found in the electron microprobe analyses. However, heating undoped samples in a vacuum ($\approx 10^{-5}$ torr) at 1300°C resulted in the appearance of an isotropic 8-line EPR spectrum characteristic of V$^{2+}$ which could be described by an $S = 3/2$, $I = 7/2$ spin-Hamiltonian with $g = 1.97(1)$ and $A = 74(1) \times 10^{-4}$ cm$^{-1}$. An identical treatment given to one of the MgTi$_2$O$_5$ samples produced during crystal growth experiments resulted in an identical EPR spectrum. The spectral parameters are very similar to those measured for MgO:V$^{2+}$ ($g = 1.9803 (5)$, $A = 74.3 (2) \times 10^{-4}$ cm$^{-1}$), and it is concluded that the spectrum most likely arises from V$^{2+}$ ions in flux or MgO inclusions in the samples. Certainly the isotropic spectrum cannot arise from V$^{2+}$ ions located at regular lattice sites in MgTiO$_3$, and no evidence of V$^{2+}$ ions at such sites was obtained.

It is reasonable to conclude that vanadium does not therefore occupy the magnesium site in significant concentration, since the most plausible charge state at this site, V$^{3+}$, should be readily reducible to
$V^{2+}$ as in the case in MgO. However, the possibility remains that there
is a significant concentration of vanadium ions at the titanium site
since it would be difficult to reduce $V^{4+}$ or $V^{5+}$ at this site to $V^{2+}$.
In view of the oxidising condition under which the crystals were grown,
it is likely that any vanadium ions at this site are in the pentavalent
charge state.

4.4 Experimental Measurements

4.4.1 EPR spectra of Cr$^{3+}$ ions in MgTiO$_3$

Trivalent chromium has the electronic configuration 3d$^3$ with
a $^4$T ground term for the free ion. An octahedral crystal field splits
this term, leaving a $^4$A state lowest which may be further split into two
Kramers doublets by the combined effects of a trigonal crystal field
component and spin-orbit interaction. EPR is observed within and between
these doublets, whose energies may be described by the following spin-
Hamiltonian appropriate for a site with trigonal symmetry,

$$\mathcal{H} = g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + B^0_{20}, \quad (4.4.1)$$

where $S = 3/2$ and the terms have their usual meaning$^7$. The z-axis lies
parallel with the symmetry axis, but since the spin-Hamiltonian (4.4.1)
displays cylindrical symmetry, there is no preferred direction of the
x,y axes in the basal plane. The zero field splitting between the two
Kramers doublets is $6B^0_{2} = 2D$.

It is immediately apparent from the experimental EPR spectra
of MgTiO$_3$:Cr$^{3+}$ that Cr$^{3+}$ ions are present in two distinct sites, rather
than the single site reported by Schimitschek$^1$. Figure 4.2 shows the
spectra for the particular field orientation $H \parallel c$. The EPR spectrum for
Fig. 4.2: EPR spectra of Cr$^{3+}$ ions in MgTiO$_3$ for H || c at 35 GHz. The EPR spectra from Fe$^{3+}$ and Mn$^{2+}$ ions are also visible.
one site (with larger $B_2^0$), which will hereafter be called site #1, is in agreement with that reported by Schimitscheck\(^1\), but the second site has not hitherto been reported. Possibly the second site spectrum was overlooked in the earlier work because the peak-to-peak intensities on a first-derivative recording are smaller, and the linewidths are larger, than for site #1. For example, with $H \parallel c$, the linewidths of the $M_s = 3/2 \leftrightarrow 1/2$ transition are -100 gauss and -30 gauss for sites #2, #1 respectively. However the integrated intensities are comparable, and the ratios $I_1/I_2$ of the $\pm 3/2 \leftrightarrow \pm 1/2$ lines for the two sites were found to be 2.0, 1.8, 1.4 and 2.1 for crystals containing nominal chromium concentrations of zero, 0.1, 1.0 and 5 at% respectively. For both sites the linewidths prevented observation of hyperfine structure due to the $\text{Cr}^{53}$ isotope which is 9% abundant in nature. All the other naturally abundant isotopes of chromium have no nuclear spin.

The marked differences in the spectral characteristics of the two sites, and the absence of any report of site #2 in the work on $\text{MgTiO}_3:\text{Cr}^{3+}$ by Schimitschek\(^1\), resulted in an initial tentative assignment of the 2nd site spectrum to $\text{V}^{2+}$ ions rather than to $\text{Cr}^{3+}$ ions. Divalent vanadium has the same electronic configuration and ground state as $\text{Cr}^{3+}$, the presence of vanadium was confirmed by the electron microprobe analyses, and the absence of any apparent hyperfine structure due to the 100% abundant $\text{V}^{51}$ ($I = 7/2$) could be attributed to the large linewidth. However, the site #2 spectrum was virtually unchanged by X-ray irradiation at room temperature, or by heating in air for several hours at 1300°C, whereas it might be expected that the $\text{V}^{2+}$ would be oxidised to $\text{V}^{3+}$. Finally, there was no correlation of the spectral intensity with vanadium content, whereas a definite correlation with the nominal chromium content over a dopant concentration range of 0.1% to 5%
was observed. Thus it is concluded that the second site spectrum is indeed due to Cr\(^{3+}\) ions and is not associated with vanadium.

Parameters in the spin-Hamiltonian (4.4.1) were fitted in the least-squares sense to the observed spectra for H \(\parallel c\) and H \(\perp c\), and the resulting values for sites #1 and #2 are listed in Table 4.3. The absolute sign of the parameters was determined by comparing the relative intensities of the spectral lines at 77.4, 4.2 and 2K. As a check on the best-fit parameters, the angular variation of the site #1 spectrum between the parallel and perpendicular orientations of the field with respect to the c-axis was measured, and is confronted with predictions based on the best-fit parameter values in Figure 4.3. The excellent agreement obtained supports confidence in the parameter values.

### 4.4.2 EPR spectra of Mn\(^{2+}\) and Mn\(^{4+}\) ions in MgTiO\(_3\)

The EPR spectrum of MgTiO\(_3\):Mn, shown in Figure 4.4, reveals the presence of both Mn\(^{2+}\) ions and Mn\(^{4+}\) ions at single lattice sites. The spectrum of Mn\(^{2+}\) ions was also observed in nominally undoped samples.

Tetravalent manganese is isoelectronic with Cr\(^{3+}\), and it is only necessary to add a hyperfine interaction term to the spin-Hamiltonian (4.4.1) to describe the spectrum:

\[
\mathcal{H} = g_\| \beta H S_z + g_\perp \beta \left( H S_x + H S_y \right) + B_0^2 + A_\| S_I z + A_\perp \left( S_I x + S_I y \right) \]

where S = \(3/2\) and the nuclear spin I has the value \(5/2\) appropriate to the isotope Mn\(^{55}\) which has a natural abundance of 100%. However, the hyperfine structure was not completely resolved in the outer \(M_s = \pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}\) transitions, and the inner \(M_s = \pm \frac{1}{2} \leftrightarrow - \frac{1}{2}\) transition could not be clearly resolved from the much stronger spectrum due to Mn\(^{2+}\) ions. For
Fig. 4.3: The angular variation of site #1 Cr$^{3+}$ ion EPR spectra at 35 GHz with the magnetic field lying in a plane containing the c-axis with H∥c at θ = 0°. The curves marked a, b and c are for the $M_s = -3/2 \rightarrow -1/2$, $-1/2 \rightarrow 1/2$, and $1/2 \rightarrow 3/2$ transitions respectively. The other lines are nominally forbidden.
Fig. 4.4: The EPR spectra of MgTiO$_3$:Mn for H || c at 35 GHz.
<table>
<thead>
<tr>
<th>Ion</th>
<th>$g_{\perp}$</th>
<th>$g_{\parallel}$</th>
<th>$B_{2}^{0}$</th>
<th>$B_{4}^{0}$</th>
<th>$B_{2}^{3}$</th>
<th>$B_{4}^{3}$</th>
<th>$A_{\perp}$</th>
<th>$A_{\parallel}$</th>
<th>No. of transitions fitted</th>
<th>Overall standard deviation (gauss)</th>
<th>Site no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr$^{3+}$</td>
<td>1.9761</td>
<td>1.9772</td>
<td>-1672.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td>Mn$^{4+}$</td>
<td>1.9752</td>
<td>1.9726</td>
<td>364.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6</td>
<td>6</td>
<td>-</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>1.9757</td>
<td>1.9491</td>
<td>-1768.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>8</td>
<td>8</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>2.0044</td>
<td>2.0037</td>
<td>281.65</td>
<td>-0.64</td>
<td>11.90</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>2.0037</td>
<td>2.0033</td>
<td>262.1</td>
<td>-0.76</td>
<td>12.28</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>14</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>2.2611</td>
<td>2.2523</td>
<td>-1370</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.1

Spin-Hamiltonian parameters for different transition metal ions in MgTiO$_{3}$, measured at 295 K and 4.2 K. The parameters $B_{2}^{0}$ and hyperfine interaction parameters are in units of 10$^{-4}$ cm$^{-1}$.
these reasons the hyperfine parameters could not be accurately determined. Table 4.3 lists all of the spin-Hamiltonian parameters determined for Mn$^{4+}$ ions in MgTiO$_3$ determined by least-squares fitting to the experimental spectra for H $\parallel$ c and H $\perp$ c. The sign of $B_2^0$ was determined as in the case of MgTiO$_3$:Cr$^{3+}$ by thermal depopulation experiments.

Divalent manganese has a $^6$S ground term which is not split in first order by a crystal field. However, higher order processes involving the combined effects of the spin-orbit coupling and the crystal field may induce small splittings, usually of magnitude less than 1 cm$^{-1}$. For the case of a trigonally symmetric crystal field, the spin-Hamiltonian which describes these splittings may be written,

$$H = g_i \beta (H_S + H_I) + B_{2z}^0 I_z + B_{4z}^0 I_x + B_{4y}^0 I_y + A_{zz}^2 S_z^2 + A_{44}^3 S_x I_z + A_{44}^3 S_y I_z,$$

(4.4.2b)

where $S = \frac{5}{2}$ and $I = \frac{5}{2}$ for the Mn$^{55}$ isotope. The z-axis lies parallel to the axis of trigonal symmetry, but the location of the x,y axes in the basal plane depends upon the particular trigonal point group in question. If there are vertical reflection planes, the axes are fixed with respect to these planes. In the absence of such symmetry elements, as in the present case where the appropriate point group is C$_3$, the location of the x,y axes is determined by the crystal field. However, the deviation from C$_{3v}$ symmetry is slight, and it could be expected that the x-axis will be aligned closely with one of the pseudo reflection planes of the surrounding O$^{2-}$ ligand octahedron. This point is discussed further in Chapter V.

The spin-Hamiltonian (4.4.2b) was initially fitted to the observed spectrum for H $\parallel$ c and an arbitrary choice of H $\perp$ c, but it was apparent from the calculated uncertainties that the parameter $B_{4z}^3$ could not be
accurately determined from these spectra alone. The problem is that the term $B_{40}^{3}$ only contributes in second order to the eigenvalues of the spin-Hamiltonian for $H \parallel c$ and $H \perp c$, as will be shown in section 4.7. For this reason, it was necessary to measure the spectra at intermediate orientation, and Figure 4.5 shows a polar plot of the field strengths of the $M_s = -3/2 \leftrightarrow -1/2$ transition as the magnetic field describes a cone about the c-axis. The three-fold symmetry is readily apparent, and is due to a first order contribution to the eigenvalues from the term $B_{40}^{3}$. The spectra corresponding to the maxima and minima of the angular variation were accordingly included in the least-squares fitting procedure. The x axis in the basal plane was taken to coincide with the minima of the polar plot. Hyperfine structure parameters were not determined by least squares fitting but were measured directly from the spectra, and the centres of the hyperfine patterns were then used in the least-squares fitting procedure to deduce the electronic parameters. In both cases, appropriate corrections deduced by perturbation theory (Abragam and Bleaney) were made to correct for second order admixtures of nuclear and electronic states. The resulting parameters are given in Table 4.3.

4.4.3 EPR spectra of $Fe^{3+}$ ions in MgTiO$_3$

Trivalent iron has the same electronic structure as divalent manganese, and so the spin-Hamiltonian (4.4.2b) may be used. However the hyperfine terms may be omitted since 98% of naturally occurring iron has no nuclear spin and hyperfine structure due to the Fe$^{57}$ isotope with $I = 1/2$ could not be resolved.

The EPR spectrum of MgTiO$_3$:Fe$^{3+}$ shown in Figure 4.2 indicates the presence of Fe$^{3+}$ ions in two distinct lattice sites, as observed for MgTiO$_3$:Cr$^{3+}$. No spectrum which could be attributed to Fe$^{2+}$ ions was
Fig. 4.5: Polar plot of the resonance field strengths of the $M_s = -3/2 \to -1/2$ transitions for the EPR spectra of Mn$^{2+}$ ion and Fe$^{3+}$ ions at sites #1, #2 in MgTiO$_3$. The field strengths are plotted as a function of azimuthal angle $\phi$ when the magnetic field makes an angle $\theta = 80^\circ$ with the $c$-axis. The separating of the extrema are 142 and 13 gauss for the site #1 Fe$^{3+}$ and Mn$^{2+}$ ion spectra respectively.
observed, even at liquid helium temperatures. The same difficulties in determining the spin-Hamiltonian parameter $B_4^3$ for the case of MgTiO$_3$:$Mn^{2+}$ were again encountered, and it was once more necessary to record the spectra at magnetic field orientations intermediate between $H \parallel c$ and $H \perp c$. The angular variation of the $-{3/2} \leftrightarrow {1/2}$ transition as the magnetic field describes a cone about the c-axis is shown in Figure 4.5 and reveals the interesting point that the $x,y$ axes for one site are rotated relative to those for the other site by $\approx 60^\circ$. The $x$ axes for the two sites were consistently chosen to coincide with the minima of the polar plot as in the case of $Mn^{2+}$. The spin-Hamiltonian parameters for both sites given in Table 4.3 were determined by least-squares fittings to the observed spectra for $H \parallel c$, $H \perp c$ and for the two intermediate orientations corresponding to $H$ in the zx plane and a plane $60^\circ$ away from this plane. As a check on these parameters, the predicted and observed angular variations of the spectra were determined for $H$ in the zx plane and are confronted in Figures 4.6 and 4.7.

The relative intensities of the two sites were determined by double integration of the recorded lineshape for the $5/2 \leftrightarrow 3/2$ transitions for $H \parallel c$ using numerical techniques. Denoting the site with the largest value of $B_2^0$ as site 1, the relative intensities $I_1/I_2$ for crystals containing nominal concentrations of zero, 0.1%, 1% and 5% iron were found to be 2.0, 2.2, 1 and 0.1 ($\pm 10\%$) respectively.

4.4.4 Mössbauer spectra of MgTiO$_3$:Fe

Mössbauer spectroscopy of Fe$^{57}$ nuclei is a very useful technique which can potentially identify the charge states and, in some cases, the site occupancy of iron ions in solids. In this work, the major interest lay in the distribution of Fe$^{2+}$ ions, since this ion is usually very
Fig. 4.6: The angular variation of site #1 Fe$^{3+}$ ion EPR spectra at 35 GHz, with the magnetic field in a plane containing the c-axis, with $H \parallel c$ at $\theta = 0$. The curves marked a, b, c, d, e are the $M_s = 3/2 \rightarrow 5/2$, $1/2 \rightarrow 3/2$, $-1/2 \rightarrow 1/2$, $-3/2 \rightarrow -1/2$ and $-5/2 \rightarrow -3/2$ transitions.
Fig. 4.7: The angular variation of site #2 Fe$^{3+}$ ion EPR spectra at 35GHz. The plane of rotation of the magnetic field and the transitions are the same as in Fig. 4.6.
difficult to detect by EPR techniques due to its even-electron valence state and strong spin-lattice coupling. However, additional information on the Fe$^{3+}$ sites observed by EPR would also be useful for the purposes of site identification.

The Mössbauer spectra of as-grown single crystals of MgTiO$_3$ containing a nominal concentration of 1% unenriched iron were kindly recorded by Dr D.C. Price of this Department using the spectrometer system described by Window et al. Spectra were taken with the $\gamma$-ray beam direction parallel to the crystal $c$ axis, and at sample temperatures of 295, 80 and 4.2K. However, no significant temperature dependence of the spectrum was observed. The measurements reported here refer to the 80K spectrum.

Figure 4.8 shows a typical absorption spectrum for MgTiO$_3$:Fe. There are two absorption lines, one at 0.20 mm/sec and a more intense line at 0.78 mm/sec which may be simply interpreted as transitions from the I = $\frac{1}{2}$ nuclear ground state to the I = $\frac{3}{2}$ excited state which is split by a quadrupolar field into $I_z = \pm \frac{1}{2}, \pm \frac{3}{2}$ doublets. For the geometry used here the theoretical intensity ratio of the lines is 3:1 with the $\pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}$ line being more intense. Hence the quadrupolar splitting $E(\pm \frac{3}{2}) - E(\pm \frac{1}{2})$ is positive, and a direct determination from the spectra gives a splitting magnitude of 0.58 (4) mm/sec.

The isomer shift, which is just the shift of the centroid of the two absorption lines relative to Fe$^{57}$ nuclei in some host material, depends upon the valence state of the ion. Bancroft quotes isomer shifts relative to iron foil in the ranges ~0.3 to 0.6 mm/sec for Fe$^{3+}$ and ~0.9 to 1.3 mm/sec for Fe$^{2+}$ high-spin ions in octahedral coordination. In the present case an isomer shift of 0.48 (4) mm/sec indicates that the iron is in the
Fig. 4.8: Mössbauer spectrum of a single crystal sample of MgTiO$_3$ containing 1% of iron, recorded at 80 K.
trivalent state in MgTiO$_3$. Divalent iron ions would be expected to give rise to a doublet close to the positions found for Fe$^{2+}$ ions in FeTiO$_3$, for which Grant et al.$^1$ report on isomer shift of 1.22 mm/sec and a quadrupole splitting of 1.14 mm/sec. No absorption was observed in this region.

One possible origin of the Fe$^{3+}$ spectrum which can and should be eliminated is inclusions of Fe$_2$O$_3$. First, sufficiently large particles of Fe$_2$O$_3$ are antiferromagnetic at the temperatures investigated and should show magnetic hyperfine structure, contrary to observation. Secondly, small particles of Fe$_2$O$_3$ which may be superparamagnetic would be expected to show a quadrupole splitting similar to that observed for Fe$_2$O$_3$ in its paramagnetic state. However the quadrupole splittings of .98 mm/sec reported by Ono et al.$^1$ for Fe$_2$O$_3$ above the Néel point discounts this possibility.

In contrast, the Mössbauer spectrum reported here closely resembles that found for Fe$^{3+}$ ion in Al$_2$O$_3$, where Blide et al.$^{12}$ report a quadrupole splitting of .50 mm/sec and an isomer shift of .396 mm/sec. There is also a close relation to the spectrum of isolated Fe$^{3+}$ ions in solid solutions of Fe$_2$O$_3$ in FeTiO$_3$ for which Shirane et al.$^{13}$ find quadrupole shifts of between 0.4 and 0.5 mm/sec and isomer shifts of 0.45 to 0.35 mm/sec, depending upon the relative concentration of Fe$_2$O$_3$.

It is therefore concluded that the Mössbauer spectra of MgTiO$_3$:Fe may be attributed to Fe$^{3+}$ ions at isolated lattice sites. Although a rigorous least-squares fitting to the Mössbauer spectra has not been attempted, it seems clear that the observed spectra must in fact be a superposition of two sets of absorption lines since two distinct Fe$^{3+}$ EPR spectra are observed. Shirane et al.$^{13}$ also assumed that this must be the case for Fe$_2$O$_3$(1-x)FeTiO$_3(x)$ since Fe$^{3+}$ ions were considered to
occupy both cation sites. The EPR and Mössbauer data combined strongly suggest that the two Fe$^{3+}$ sites in MgTiO$_3$ are closely related. Specific site models will be discussed in section 4.7.

4.4.5 EPR spectrum of MgTiO$_3$:Ni$^{2+}$

The $^3F$ free ion ground term of the $d^9$ configuration of Ni$^{2+}$ is split by an octahedral crystal field, leaving a $^3A_2$ ground state lowest. The threefold spin degeneracy of this state may be further split by an axially symmetric crystal field, and in this situation the magnetic properties may be described with an $S=1$ spin-Hamiltonian,

$$
\mathcal{H} = g \beta z \mathbf{S} z + g_1 \beta (x \mathbf{S} + y \mathbf{S}) + B_2^0 \mathbf{S} z \mathbf{S} z + B_0^0 z \mathbf{S} z + B_0^0 z \mathbf{S} z .
$$

The EPR spectrum of MgTiO$_3$:Ni$^{2+}$, shown in Figure 4.9 indicates the presence of Ni$^{2+}$ ions at a single site. The spin-Hamiltonian parameters were again determined by least-squares fitting at room temperature and 4.2K and are presented in Table 4.3.

4.4.6 EPR spectrum of MgTiO$_3$:Co$^{2+}$

The $^4F$ free ion ground term of Co$^{2+}$, which has a $d^7$ electronic configuration, is split by an octahedral crystal field, leaving an orbital triplet lowest. Spin-orbit interaction further splits this triplet, leaving a Kramers doublet as the ground state. In an axial crystal field this doublet may be described by the spin-Hamiltonian,

$$
\mathcal{H} = g \beta z \mathbf{S} z + g_1 \beta (x \mathbf{S} + y \mathbf{S}) + A_2^0 \mathbf{S} z + A_0^0 (x \mathbf{S} + y \mathbf{S}),
$$

where $I = \frac{7}{2}$ for the Co$^{59}$ isotope which is 100% abundant in nature. A single Co$^{2+}$ spectrum was observed below $\approx 30$K and the associated
Fig. 4.9: The EPR spectrum of MgTiO$_3$:Ni$^{2+}$ for $H \parallel c$ at 35 GHz. The two transitions due to Ni$^{2+}$ ions are marked. The other lines arise from Fe$^{3+}$, Cr$^{3+}$ and Mn$^{2+}$ transitions.
spin-Hamiltonian parameters are given in Table 4.3. There is a relatively large uncertainty associated with $A_\perp$ since the hyperfine structure was only partially resolved for $H \perp c$. Only an upper limit can be given for $A_\parallel$ since no hyperfine structure could be resolved with $H \parallel c$.

### 4.4.7 EPR spectrum of MgTiO$_3$:Cu

Electron microprobe analyses indicated the presence of copper in appropriately doped samples, but no EPR spectrum attributable to copper could be obtained although the spectrum of Mn$^{2+}$ and Fe$^{3+}$ was clearly observed.

### 4.5 Oxidation and Reduction Effects for MgTiO$_3$ Containing Cr$^{3+}$, Fe$^{3+}$ and Mn$^{4+}$ Ions

In an attempt to gain further information which may shed light on the site occupancy of Fe$^{3+}$ and Cr$^{3+}$ ions in MgTiO$_3$, a series of oxidation and reduction experiments were performed. It was expected that Cr$^{3+}$ and Fe$^{3+}$ ions occupying the Mg$^{2+}$ site should be more readily reducible to the divalent state than the same ions occupying the Ti$^{4+}$ site, giving a simple way of assigning the observed spectra. In practice, the interpretation of the observed oxidation and reduction effects is not straightforward.

Reductions were achieved by heating in a vacuum of $\approx 10^{-5}$ torr for 5 hours over a temperature range of 1000°C to 1400°C. The samples were subsequently oxidised by heating in air for 6 hours at a temperature of 1350°C. In all cases, EPR spectra were recorded before and after the treatments under identical conditions. It is possible to analyse
the results of these experiments in two different ways. First, the relative intensities of lines within the spectrum of a given sample may be compared before and after treatment. Secondly, the intensities of a particular line before and after treatment may be compared. Whilst the first comparison involves no approximation or assumptions other than those involved in the necessary double numerical integration, the second method of analysis implicitly assumes that the spectrometer and sample characteristics are identical before and after the treatment. The major source of error in this type of comparison is a different microwave field intensity in the before and after treatment recordings due to different sample placements, microwave power fluctuations, or changes in the dielectric loss of the sample. However, reproducibility tests showed that the first two factors gave rise to an uncertainty of less than 10% in the measured line intensities. Any changes in the dielectric loss of the sample are not expected to change the Q factor of the resonant cavity appreciably since the overall Q is dominated by microwave losses in the much more massive PVC sample holder. Overall, the uncertainties are estimated to be ±10% in the first method and ±20% in the second method. The results of the analyses are presented in Tables 4.4 and 4.5.

It is first noted that the intensity of the Mn$^{2+}$ spectrum is not significantly affected by oxidation or reduction except in the case of a reduction at 1450°C. This stability reflects the chemical stability of divalent manganese; the apparent drop in intensity on reduction at 1450°C may be due to an increasing Ti$^{3+}$ concentration resulting in associated Mn$^{2+}$ - Ti$^{3+}$ pairs. In contrast the intensity of the tetravalent manganese spectrum is strongly diminished on reduction, and the spectrum disappears on reduction at or above 1250°C. Subsequent oxidation does not restore the spectrum.
Table 4.4

Effects of oxidation and reduction treatments on the intensity of the EPR spectra for different transition metal ions in MgTiO₃. All subsequent oxidation treatments were done at 1350°C. Reduction treatments were done at the quoted temperatures. The intensities are normalised to their untreated values. No entry implies that the spectrum was not visible after the corresponding treatment. The uncertainties in the ratios are ±20%.

<table>
<thead>
<tr>
<th>Ion</th>
<th>Reduction (1000°C)</th>
<th>Reduction (1100°C)</th>
<th>Subs. oxidation</th>
<th>Reduction (1250°C)</th>
<th>Reduction (1450°C)</th>
<th>Subs. oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn⁴⁺</td>
<td>.57</td>
<td>.23</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>.96</td>
<td>1.29</td>
<td>1.03</td>
<td>.85</td>
<td>.46</td>
<td>.98</td>
</tr>
<tr>
<td>Cr³⁺ at site #1</td>
<td>1.05</td>
<td>1.06</td>
<td>.214</td>
<td>1.06</td>
<td>.668</td>
<td>.93</td>
</tr>
<tr>
<td>Cr³⁺ at site #2</td>
<td>.92</td>
<td>1.1</td>
<td>1.2</td>
<td>.73</td>
<td>.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe³⁺ at site #1</td>
<td>.90</td>
<td>.70</td>
<td>1.44</td>
<td></td>
<td></td>
<td>2.00</td>
</tr>
<tr>
<td>Fe³⁺ at site #2</td>
<td>1.42</td>
<td>1.85</td>
<td>.5</td>
<td></td>
<td></td>
<td>.20</td>
</tr>
</tbody>
</table>

Table 4.5

Comparison of intensities of spectra at different sites in MgTiO₃ after oxidation and reduction treatments. For manganese the ratios of intensity of Mn⁴⁺ to Mn²⁺ ions are shown. All the ratios are normalised to their values determined before treatment. The uncertainties in the ratios are ±10%.

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Reduction (1000°C)</th>
<th>Reduction. (1100°C)</th>
<th>Subs. oxidation</th>
<th>Reduction (1250°C)</th>
<th>Reduction (1450°C)</th>
<th>Subs. oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺ (#2) / Fe³⁺ (#1)</td>
<td>1.57</td>
<td>2.64</td>
<td>.35</td>
<td></td>
<td></td>
<td>.1</td>
</tr>
<tr>
<td>Cr³⁺ (#2) / Cr³⁺ (#1)</td>
<td>.68</td>
<td>1.04</td>
<td>5.60</td>
<td>.69</td>
<td>.75</td>
<td>1.29</td>
</tr>
<tr>
<td>Mn⁴⁺ / Mn²⁺</td>
<td>.59</td>
<td>.18</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The intensity changes of the two Cr$^{3+}$ spectra do not show very clear trends. For the site #2 spectrum, oxidation treatments generally increase the spectral intensity, whilst reduction diminishes the intensity, but in most cases the effects are comparable with the uncertainties. In the case of the site #1 spectrum, the intensity was initially unchanged by reduction but a sharp decrease was observed for subsequent oxidation after reducing at 1100°C. Reducing treatments almost doubled the linewidths, while subsequent oxidation restored the widths almost to the previous values.

The pattern for the two Fe$^{3+}$ spectra is much more clear. Reduction treatments about 1100°C diminish the intensity of the spectrum #1 and increase that of spectrum #2, but both spectra vanish on treatment at higher temperature. Oxidation treatments increase the intensity of spectrum #1 and decrease the intensity of spectrum #2.

These intensity variations will be discussed further in Section 4.7 and Chapter V in the context of site models for the various ions.

4.6 Site Location of Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ Ions in MgTiO$_3$

The compounds CoTiO$_3$, NiTiO$_3$ and MnTiO$_3$ are all iso-structural with MgTiO$_3$ and since single EPR spectra were observed here for these ions it is deduced that Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ ions occupy the magnesium ion site in MgTiO$_3$.

4.7 Site Determination for Fe$^{3+}$ Ions in MgTiO$_3$

It is proposed here that the spectrum #1 for Fe$^{3+}$ ions in MgTiO$_3$ arises from a site of structure $[\text{Fe}^{3+}]_{\text{Mg}^{2+}} - [\text{Mg}^{2+}]_{\text{Ti}^{4+}}$, whereas the
site #2 spectrum arises from a site with the structure \([\text{Mg}^{2+}]_{\text{Mg}}^{2+} - [\text{Fe}^{3+}]_{\text{T}_{i}}^{4+}\). Here the notation \([X]_{\text{Mg}}^{2+} - [Y]_{\text{T}_{i}}^{4+}\) implies a species X located at a \(\text{Mg}^{2+}\) lattice site with a species Y located at the closest \(\text{T}_{i}^{4+}\) site along a direction parallel to the c-axis.

The first and most important part of the argument for these assignments comes from the angular variation studies for \(\text{Fe}^{3+}\) and \(\text{Mn}^{2+}\) ion spectra reported in 4.4.3 and 4.4.2. Both \(\text{Fe}^{3+}\) and \(\text{Mn}^{2+}\) ions have a \(6S\) ground state with spin \(S = \frac{5}{2}\) and so the spin-Hamiltonian for both ions contains fourth order operators \(0^4_0\) with non-zero matrix elements. In the present case, the only two symmetry-allowed fourth order operators are \(0^0_4\) and \(0^3_4\). The latter operator is of particular interest, since it is the only one in the spin-Hamiltonian which displays threefold rather than cylindrical symmetry, and is thus responsible for the threefold symmetry in the polar angular variation plots for \(\text{Fe}^{3+}\) and \(\text{Mn}^{2+}\) ions shown in Figure 4.5.

In order to deduce the theoretical polar angular variation of the EPR spectra, it is useful to transform from the coordinate system defined by the crystal to a magnetic system in which the new z-axis lies along the magnetic field direction. Buckmaster\(^{14}\) has given transformation formulae for the tensor operators \(T_{l m}\) for an arbitrary rotation of the coordinate system by angles \((\theta, \phi)\). For \(T_{4+3}\), neglecting the off-diagonal elements in first order approximation,

\[
T_{4+3}(S) = e^{i3\phi} \left\{ \frac{\sqrt{15}}{4} \sin^3 \theta \cos \theta T_{40}(S') \right\} .
\]  

(4.7.1)

It was pointed out in Chapter III that there is a relationship between the \(T_{l m}\) operators of Buckmaster and the Stevens operator equivalents \(O^m_4\). In particular, \(O^0_4\) and \(O^3_4\) are related to the corresponding tensor operators.
Using equations (4.7.1) and (4.7.2), the term $B_{4}^{3}O_{4}^{3}$ in the spin-Hamiltonian (4.4.2b) transforms as:

$$B_{4}^{3}O_{4}^{3} \Rightarrow (B_{4}^{3})' (O_{4})'$$  \hspace{1cm} (4.7.3)

where

$$(B_{4}^{3})' = \frac{B_{4}^{3}}{8} \sin^{3} \theta \cos \theta \cos 3\phi.$$  

Thus for $\theta = 0^\circ$ or $90^\circ$, $(B_{4}^{3})'$ vanishes, and the operator $O_{4}^{3}$ does not affect the spectrum in first order for these orientations. The polar plots of the angular variation of the $-3/2 \leftrightarrow -1/2$ transition for Fe$^{3+}$ and Mn$^{2+}$ ions in Figure 4.5 clearly shows the threefold symmetry predicted by (4.7.3). The differences in resonance positions between $\phi = 0^\circ$ and $\phi = 60^\circ$ for the $-3/2 \leftrightarrow -1/2$ transition for Fe$^{3+}$ ions at site #1 and Mn$^{2+}$ ions are predicted to be 162 gauss and 16 gauss respectively on the basis of the best-fit parameter values. These compare well with experimental values of 142 and 13 gauss, providing a useful self-consistency check on the determination of the values of $B_{4}^{3}$.

First considering the polar plots for the Fe$^{3+}$ spectra only, the most striking feature is that the two patterns show a relative angular displacement of $\approx 60^\circ$. This immediately demonstrates that the two spectra cannot arise from Fe$^{3+}$ ion at the same lattice site, since the patterns reflect the orientation of the surrounding ligand cage. However, the ligand cages of the Mg$^{2+}$ and Ti$^{4+}$ sites are rotated by almost $60^\circ$ from each other, as are those of the octahedrally coordinated vacant spaces. It is unlikely
that Fe$^{3+}$ ions occupy the interstitial sites in preference to the regular lattice cation sites, and so it is concluded that the Fe$^{3+}$ EPR spectra reported here arise from Fe$^{3+}$ ions located at both the Mg$^{2+}$ and Ti$^{4+}$ ion sites in MgTiO$_3$.

Further progress can be made by comparing the polar plots for the Mn$^{2+}$ EPR spectra with those for the Fe$^{3+}$ spectra; evidently the patterns for Mn$^{2+}$ ions and the site #1 Fe$^{3+}$ spectra show no relative angular displacement. The signs of B$^3$, as determined by the least squares fitting, are positive in both cases, and so it is concluded that these spectra are due to ions at the same lattice site. Since Mn$^{2+}$ ions substitute for Mg$^{2+}$ ions, the site #1 spectrum for Fe$^{3+}$ ions results from a substitution for Mg$^{2+}$ by Fe$^{3+}$ ion in MgTiO$_3$. The site location for the Fe$^{3+}$ ions giving rise to spectrum #2 must therefore be the Ti$^{4+}$ lattice site.

Ferric ions substituting for host cations in MgTiO$_3$ produce a charge imbalance which requires either local or remote charge compensation. Since the spectral symmetry is axial in both cases, the local charge compensating agent, if any, must be located along a direction parallel to the c axis.

The intensity of the site #2 Fe$^{3+}$ EPR spectrum increases almost linearly with nominal iron concentration. This behaviour is consistent with Fe$^{3+}$ ions at the Ti$^{4+}$ site being located in a regular crystal environment not associated with a local lattice defect; i.e., a [Mg$^{2+}$]$_{Mg^{2+}}$-[Fe$^{3+}$]$_{Ti^{4+}}$ site. In contrast the intensity of the Fe$^{3+}$ spectrum from site #1 saturates in intensity at high nominal concentrations of iron: this observation supports a site model involving the association of an intrinsic lattice defect with the Fe$^{3+}$ ion at the Mg$^{2+}$ site. In this case a saturation effect in the intensity of the site #1 spectrum with concentration would be expected as the concentration of intrinsic defects.
in the lattice does not necessarily depend upon the concentration of a particular dopant.

It is known that S ground states are sensitive mainly to the local environment\textsuperscript{15,16}. The very similar EPR and M"ossbauer spectra for the two sites of Fe\textsuperscript{3+} ions in MgTiO\textsubscript{3} therefore suggests that these sites have related structures.

If the model of \([\text{Mg}^2+]\text{Mg}^{2+} - [\text{Fe}^3+]\text{Ti}^{4+}\) proposed above is adopted for site \#2, then the structure which most closely resembles this but has Fe\textsuperscript{3+} ions at Mg\textsuperscript{2+} ion site is simply \([\text{Fe}^3+]\text{Mg}^{2+} - [\text{Mg}^2+]\text{Ti}^{4+}\). This model for site \#1 is supported indirectly by the neutron diffraction measurements of Shirane et al.\textsuperscript{17} who reported a disorder of 6\% in the cation sublattice of NiTiO\textsubscript{3} and FeTiO\textsubscript{3}. The presence of Mg\textsuperscript{2+} ions in the Ti\textsuperscript{4+} sublattice in MgTiO\textsubscript{3} is therefore quite feasible. In addition, the samples were grown from a melt which contained twice the stoichiometric ratio of MgO and so an excess of Mg\textsuperscript{2+} ions in the MgTiO\textsubscript{3} samples studied here is plausible.

Prolonged reduction would eventually result in divalent iron occupying both sites, in agreement with experimental results for reducing temperatures greater than 1250°C. On reduction at lower temperatures, the relative intensity of the site \#1 Fe\textsuperscript{3+} spectra was virtually unaffected and the intensity of the second site increased. On the site model proposed here it would be easier to reduce Fe\textsuperscript{3+} ions at the Mg\textsuperscript{2+} sites than Fe\textsuperscript{3+} ions at the Ti\textsuperscript{4+} sites since the Madelung energy favours divalent iron at the Mg\textsuperscript{2+} site. However this will be partially counterbalanced by the presence of a Mg\textsuperscript{2+} ion at the Ti\textsuperscript{4+} site. Since the effects of the Madelung energy and presence of the Mg\textsuperscript{2+} ions at the Ti\textsuperscript{4+} site act in opposition to each other, the intensity of site \#1 may not be strongly affected by reduction, as was observed.
The increase in relative intensity of the spectrum of $\text{Fe}^{3+}$ ions at the Ti$^{4+}$ site can be attributed to the reduction of $\text{Fe}^{4+}$ ions at the Ti$^{4+}$ site. The reduction of the relative intensity of this spectrum on oxidation can be understood by the reverse reaction.

In conclusion, all of the evidence which has been obtained is consistent with the models proposed for the two sites, viz., $[\text{Fe}^{3+}]_{\text{Mg}^{2+}} - [\text{Mg}^{2+}]_{\text{Ti}^{4+}}$ and $[\text{Mg}^{2+}]_{\text{Mg}^{2+}} - [\text{Fe}^{3+}]_{\text{Ti}^{4+}}$. 
References on Chapter IV

CHAPTER V

CALCULATIONS OF THE GROUND STATE SPLITTING AND SITE STRUCTURES FOR Cr$^{3+}$ IONS IN MgTiO$_3$. 
5.1 Introduction

In the preceding chapter, site structures were proposed to account for the two Fe$^{3+}$ EPR spectra observed in MgTiO$_3$. The experimentally measured zero-field splittings of the $^6S$ ground state were only used indirectly in the arguments presented there since a direct calculation based on a crystal field estimate, followed by diagonalisation of the $d^5$ crystal field Hamiltonian, was considered unlikely to yield definitive results in view of the small difference of only 7% in the zero-field splittings.

This approach is much more promising for the case of the two Cr$^{3+}$ ion spectra observed in MgTiO$_3$, since the experimentally observed ground state splittings for the two sites differ by a factor of ~4 in magnitude and are opposite in sign. Macfarlane$^1$ has shown that the zero-field splitting for the $^4A$ ground state of Cr$^{3+}$ ions in octahedral coordination can be reliably calculated for a given crystal field provided the entire set of $d^3$ configuration states is taken into account. A crystal field calculation can thus provide a useful basis for testing models of the site structures.

At the same time, such calculations are of intrinsic interest because of the parallels between MgTiO$_3$:Cr$^{3+}$ and Al$_2$O$_3$:Cr$^{3+}$ which has long been a testing ground for theories of crystal field interactions. Feher and Sturge$^2$ and Stedman$^{3,4}$, using the same experimental data, have arrived at quite different conclusions regarding the crystal field interactions in Al$_2$O$_3$:Cr$^{3+}$, commonly known as ruby. In this chapter the crystal field at Mg$^{2+}$ and Ti$^{4+}$ sites in MgTiO$_3$ is estimated using the experimental data provided by Feher and Sturge$^2$ for ruby, but using a variant of the crystal field model proposed by Stedman rather than
that of the former authors. Before describing the calculation for MgTiO₃:Cr³⁺ in detail in Section 5.3, it is worthwhile to first briefly review the work of Feher and Sturge and Stedman which lay the foundation for these calculations.

5.2 Crystal Field Calculations for Ruby

Both Feher and Sturge and Stedman based their discussions on the former authors experimental determination of the strong-field crystal field parameters \( v, v' \) and \( D_q \) for Al₂O₃ containing the isoelectronic series of ions \( V^{2+}, Cr^{3+} \) and \( Mn^{4+} \). Figure 5.1 illustrates the meaning of these parameters for the \(^4F\) ground term of the \( d^3 \) configuration; \( 18 \ D_q \) is the total cubic crystal field splitting of the term and \( v, v' \) are trigonal field coefficients with diagonal and off-diagonal matrix elements respectively in the strong field scheme. Table 5.1 gives the experimental values of these parameters.

It is obvious from the table that \( v \) increases whereas \( v' \) decreases along the series \( V^{2+}, Cr^{3+} \) and \( Mn^{4+} \). McClure has calculated \( v \) and \( v' \) for the Al₂O₃ lattice from the point charge model. His formulae can be written as,

\[
\begin{align*}
v &= b_2 \langle r^2 \rangle + b_4 \langle r^4 \rangle \\
v' &= -\frac{1}{3} \sqrt{2} b_2 \langle r^2 \rangle + \frac{1}{4} \sqrt{2} b_4 \langle r^4 \rangle .
\end{align*}
\]

The values of \( b_2 \) and \( b_4 \) calculated by McClure for an undistorted Al₂O₃ lattice with an impurity ion exactly on the \( Al^{3+} \) site are respectively -540 cm⁻¹ and 20 cm⁻¹. Using Watson's values for \( \langle r^2 \rangle \) and \( \langle r^4 \rangle \) and equation (5.2.1) Feher and Sturge obtained the point charge model values of \( v \) and \( v' \), given in Table 5.1. The absolute values of \( v \) and \( v' \) depend
Fig. 5.1: The meaning of Dq, v, and v' in terms of the splitting of the \( ^4F \) ground term of \( d^3 \) ion in trigonal crystal field.
Table 5.1

Values of strong-field crystal field parameters (cm\(^{-1}\)) for \(\text{V}^{2+}\), \(\text{Cr}^{3+}\) and \(\text{Mn}^{4+}\) ions in \(\text{Al}_2\text{O}_3\) *.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>(\text{V}^{2+})</th>
<th>(\text{Cr}^{3+})</th>
<th>(\text{Mn}^{4+})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental values</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DQ</td>
<td>1500</td>
<td>1800</td>
<td>2100</td>
</tr>
<tr>
<td>(v)</td>
<td>420</td>
<td>830</td>
<td>2100</td>
</tr>
<tr>
<td>(v')</td>
<td>1100</td>
<td>840</td>
<td>570</td>
</tr>
<tr>
<td>Point charge model values calculated by Feher and Sturge(^2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(v)</td>
<td>-1290</td>
<td>-870</td>
<td>-650</td>
</tr>
<tr>
<td>(v')</td>
<td>590</td>
<td>400</td>
<td>300</td>
</tr>
</tbody>
</table>

* Taken from reference 2.
on the details of the model, particularly on the ionic positions, and no great significance can be attached to them. However, the trend from ion to ion, on the other hand, is determined almost entirely by the variation of $<r^2>$ and may be a significant test of the point charge model. Feher and Sturge did not include a point dipolar contribution but considered that it would show the same trends as the point charge term. Thus they concluded that $v'$ was primarily determined by long-range electrostatic effects. The apparently anomalous variation of $v$ was not thought to be due to covalency but rather to local distortion effects, such as those proposed by Artman and Murphy, or to local charge compensation. The elimination of covalency as a possible mechanism was based on the success of the point charge model in explaining stress-induced splittings characterized by $\Delta v$, $\Delta v'$ in the spectrum of a similar system, MgO:Cr$^{3+}$.

Stedman pointed out several deficiencies in the crystal field analyses of Feher and Sturge. First, and most important, the electrostatic model cannot explain the magnitude of $Dq$. Second, the success of the electrostatic model for MgO:Cr$^{3+}$ depends upon the choice of two quite different sets of experimental results. Thirdly, the 'long-range' description of the contribution to $v'$ is not valid even in the point charge model since the distant (non-ligand) ion contribution is less than that of the ligands and of opposite sign to the experimental value.

Stedman considered the crystal field to be the sum of three components, a distant ion contribution calculated on the point charge model, a ligand contribution dominated by overlap mechanisms and calculated using the superposition model, and finally a dipolar contribution from all ions. For this calculation, it is more convenient to work in the weak field scheme. The relationship between the parameters in the two schemes
is given by,

\[ B_0^2 = v - 2\sqrt{2} v' \]
\[ B_0^4 = \frac{4}{3} v + 2\sqrt{2} v' - 14 Dq \]
\[ B_3^4 = \frac{1}{2\sqrt{10}} \left( \frac{4}{3} v + 2\sqrt{2} v' \right) + 14\sqrt{\frac{10}{7}} Dq. \]  

(5.2.2)

Sometimes it is more convenient to express the fourth order terms as the sum of a cubic term and a cylindrically symmetric term \( B_4^t \). In this case,

\[ B_4^t = \frac{27}{20} \left( \frac{4}{3} v + 2\sqrt{2} v' \right). \]  

(5.2.3)

Table 5.2 gives the non-cubic parameters \( B_0^2, B_4^t \) for the electrostatic contributions to the crystal field and for the ligand-superposition contribution. The latter are simply calculated as the residual of the experimental values and do not of course form a test of the model. However Stedman \(^4\) was able to deduce the intrinsic superposition model parameters from these residuals and use them to satisfactorily account for stress-induced splittings in ruby. Further evidence for the success of this type of crystal field model for 3d\(^n\) ions has come from applications in the case of Co\(^{2+}\) ions in a variety of chloride hosts \(^9\) and for Fe\(^{2+}\) ions in garnets \(^10\).

Stedman \(^3\) has attributed the trends in \( v \) and \( v' \) in the case of ruby to an increase in the fourth order parameters consequent on an increase in overlap induced by contraction of the ligands on the more highly ionised species. He further states that the \( n=4 \) parameters contribute negatively to \( v' \) and positively to \( v \), thus giving rise to the opposite trends in these parameters. However this appears to be at variance with equation (5) of reference 4, which are compatible, with
Table 5.2

Axial crystal field parameters in the weak field scheme for $3d^3$ ions in Al$_2$O$_3$ deduced from the work of Stedman. Parameter values are in wave-number units.

<table>
<thead>
<tr>
<th>Contribution</th>
<th>Parameter</th>
<th>$V^{2+}$</th>
<th>$Cr^{3+}$</th>
<th>$Mn^{4+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total experimental</td>
<td>$B_0^2$</td>
<td>-2691</td>
<td>-1546</td>
<td>488</td>
</tr>
<tr>
<td></td>
<td>$B_4^t$</td>
<td>4956</td>
<td>4701</td>
<td>5956</td>
</tr>
<tr>
<td>Point dipolar + distant ion point charge</td>
<td>$B_0^2$</td>
<td>1724</td>
<td>1272</td>
<td>1002</td>
</tr>
<tr>
<td></td>
<td>$B_4^t$</td>
<td>-2447</td>
<td>-1096</td>
<td>-638</td>
</tr>
<tr>
<td>Ligand superposition model</td>
<td>$B_0^2$</td>
<td>-4415</td>
<td>-2818</td>
<td>-514</td>
</tr>
<tr>
<td></td>
<td>$B_4^t$</td>
<td>7403</td>
<td>5797</td>
<td>6594</td>
</tr>
</tbody>
</table>
due regard for a different normalization, with the parameter relations (5.2.2), (5.2.3) given here. From Table 5.2 it would appear that the second order parameters show much more variation with the ionic species than the fourth order ones and as in equation (5) of reference 4 in fact contribute in opposite senses to \( v \) and \( v' \). Despite these questions of interpretation, the model is clearly a substantial improvement over earlier electrostatic models, and has been found to give an adequate description of the relatively few \( 3d^n \) systems to which it has been applied. A considerably larger literature is available which demonstrates its applicability for rare earth systems\(^1\text{1,12,13}\).

5.3 Crystal Field Model for \( \text{MgTiO}_3 \)

The model of the crystal field used here for \( \text{MgTiO}_3:Cr^{3+} \) is similar to that of Stedman\(^3\) described in 5.2, and identical to that used by Edgar\(^9\) for \( \text{Co}^{2+} \) ions in chloride hosts. The contribution from the ligands is calculated using the superposition model with intrinsic parameters deduced from the case of ruby, and the distant ion contribution is calculated on a point charge model. There are two approximations in this calculation. The first is that local distortions of the ligand cage around the \( \text{Cr}^{3+} \) ion are not included, although the calculation does permit displacement of the \( \text{Cr}^{3+} \) ion along the c-axis. Some distortion of the ligand cage is expected since a \( \text{Cr}^{3+} \) ion is replacing a \( \text{Mg}^{2+} \) or \( \text{Ti}^{4+} \) ion, but the magnitude of this distortion is difficult to estimate. Such distortions were also neglected in the case of ruby\(^3\).

The second approximation is that the contribution of point dipoles has been neglected, although it has been estimated\(^{14}\) that this contribution can be as large as that of point charges for \( \text{Al}_2\text{O}_3 \). However, this contribution has probably been overestimated, since weak field values
of the $O^{2-}$ polarisibility were used. The electric field at the oxygen site has been calculated here and has been found to be in the region of $10^8 V cm^{-1}$ for both $Al_2O_3$ and $MgTiO_3$ lattices. This is much larger than the field strength of the optical electromagnetic waves involved in refractive index measurements. Electronic polarisibilities of ions in solids are calculated (Tessman et al.\textsuperscript{15}) from the refractive indices of the cubic crystals, and so they apply to weak fields for which the induced dipole moments are proportional to the field strengths. The generalisation of this proportionality does not necessarily hold for high field strengths. Böttcher\textsuperscript{16} has shown that relationship between dipole moments and electric fields for molecules is certainly nonlinear when the electric field is very high and that the dipole moment can saturate. The situation is similar for ions in solids, since the distortion of the electronic shells will be limited by overlap-induced repulsion with neighbouring ions.

The second reason for omitting dipolar contribution is that the superposition model automatically incorporates a contribution from these components of the ligand dipoles which are parallel with the ligand-ion axis. Non-axial components and contributions from more distant ions are neglected, but the latter should be relatively small since the convergence of dipolar sums is faster than for monopolar sums by a factor of $1/R$.

5.3.1 Point charge contribution from distant ions

Sharma\textsuperscript{17} has given expressions for a crystal field generated by external point charges $q_j|e|$ located at $(X_j, Y_j, Z_j)$ with the magnetic ion at the origin:
\[ B^2_0 = \left< r^2 \right> \sum_j q_j (3Z^2_j - R^2_j)/R^5_j \]
\[ B^4_0 = \left< r^4 \right> \sum_j q_j (35Z^4_j - 30Z^2_j R^2_j + 3R^4_j)/R^8_j \]  
\[ B^4_3 = \left< r^4 \right> \frac{35}{2} \sum_j q_j Z_j X_j (X^2_j - 3Y^2_j)/R^8_j . \]  

Here \( X_j, Y_j, Z_j \) and \( R_j \) are in units of \( a_0 \), the Bohr radius. The parameter \( B^2_0 \) is in units of \( \frac{e^2}{2a_0^4} \), and the fourth order parameters are in units of \( \frac{e^2}{2a_0^8} \) and charges are expressed in electrostatic units. In this calculation the radial averages \( \left< r^2 \right> = 1.447 \) a.u. and \( \left< r^4 \right> = 4.297 \) a.u. for \( \text{Cr}^{3+} \) ion have been taken from Abragam and Bleaney. The program for this part of the calculation was tested by comparing with the results of Artman and Murphy for an \( \text{Al}_2\text{O}_3 \) lattice and with the results of Edgar for a \( \text{CdCl}_2 \) lattice. Satisfactory agreement was obtained in both cases provided that sufficient numbers of ions were included to ensure convergence.

5.3.2 Superposition model contribution from the ligands

In the superposition model, the effective crystal field from each neighbour is assumed to be axially symmetric with respect to that neighbour and contributes additively to the crystal field.

\[ B^2_0 = \sum_j \bar{B}^2_j(r_0) \left( \frac{r_0}{R_j} \right)^2 c^2_0(\theta_j, \phi_j) \]
\[ B^4_0 = \sum_j \bar{B}^4_j(r_0) \left( \frac{r_0}{R_j} \right)^4 c^4_0(\theta_j, \phi_j) \]  
\[ B^4_3 = \sum_j \bar{B}^4_j(r_0) \left( \frac{r_0}{R_j} \right)^4 \left\{ c^4_3(\theta_j, \phi_j) - c^4_{-3}(\theta_j, \phi_j) \right\} , \]  

where the summation is over all the coordinated ligands. Here the
$B_n(r_0)$ \((n = 2 \text{ and } 4)\) are 'intrinsic' parameters which describe the interactions of a single ligand with the magnetic ion for an ion-ligand separation of \(r_0\). The power law exponents \(t_2, t_4\) account for the variation of the intrinsic parameters with distance. The superposition model calculation of the crystal field parameters was checked by comparing with the results of Edgar\(^9\) for the CdCl\(_2\).Co\(^{2+}\) system.

### 5.3.3 Evaluation of superposition model parameters

The crystal field parameters \(D_q, v\) and \(v'\) for ruby deduced by Feher and Sturge\(^2\) have been used in this work to evaluate the superposition model parameters $B_2$, $B_4$ and $t_4$. Consistent with the crystal field model described earlier, the point charge contribution from distant ion was first subtracted from the experimental values. Table 5.3 gives the parameters in the weak field parameterisation. The residuals are then the ligand contributions which may, in principle, be used to determine $t_2$, $t_4$, $B_2$ and $B_4$. However, there are two second-order parameters to be deduced from a single experimental value, and so either $t_2$ or $B_2$ must be held fixed. Following Stedman\(^3\), the value of $t_2$ is chosen to be 3. By solving the simultaneous equations (5.3.2) for the intrinsic parameters using the structural data for Al\(_2\)O\(_3\)\(^19\), the intrinsic parameter values are found to be $t_4 = 8.1$, $B_2 = 12,200 \text{ cm}^{-1}$ and $B_4 = 11,500 \text{ cm}^{-1}$, where the intrinsic parameters are quoted at an ion-ligand separation of 1.915 Å. The value of $t_4$ is close to the theoretical value $t_4 = 8.6$ found for the same system by Stedman\(^3\), the difference being due to the differing treatments of dipolar contribution. The intrinsic parameter $B_2$ is similar in magnitude to the value of $B_2 = 11,000 \text{ cm}^{-1}$ but $B_4$ is more than twice the value of $B_4 = 4,060 \text{ cm}^{-1}$ found for chloride ligands\(^9\). The latter effect is of course expected as a reflection of the widely different values of $D_q$ for the two systems.
Table 5.3

Crystal field parameters in the weak field scheme for Cr$^{3+}$ ions in Al$_2$O$_3$. Parameter values are in wavenumber units.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Experimental total</th>
<th>Point charge distant ions</th>
<th>Residual</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_0^2$</td>
<td>-1546</td>
<td>20</td>
<td>-1565</td>
</tr>
<tr>
<td>$B_0^4$</td>
<td>-21717</td>
<td>-872</td>
<td>-20845</td>
</tr>
<tr>
<td>$B_3^4$</td>
<td>31577</td>
<td>19</td>
<td>31558</td>
</tr>
</tbody>
</table>
5.3.4 Crystal field Hamiltonian

The zero-field splitting of $^4A_2$ ground state can be calculated by diagonalising the Hamiltonian,

$$
\mathcal{H} = \mathcal{H}_{\text{ele}} + \mathcal{H}_{\text{SO}} + \mathcal{H}_{\text{CF}}.
$$  \hspace{1cm} (5.3.3)

The first term on the right represents the electrostatic interaction between electrons in the unfilled d shell, whilst the second and third terms are the spin-orbit and crystal field interaction terms respectively. The matrix elements of the total Hamiltonian in equation (5.3.3) were evaluated in the weak field scheme using the complete set of 120 states of the $d^3$ configuration.

Both of the cation sites in MgTiO$_3$ have $C_3$ point group symmetry, and the appropriate crystal field Hamiltonian has, in general, the following terms.

$$
\mathcal{H}_{\text{CF}} = \sum_{i=1}^{3} \left[ B_i^2 c_i^2 + B_i^4 c_i^4 + B_i^6 (c_{-3}^6 - c_3^6) + iB_i^4 (c_{-3}^6 + c_3^6) \right], \hspace{1cm} (5.3.4)
$$

where $C_i^m(\theta, \phi)$ are Racah spherical tensors, $B_i^m$ are real crystal field parameters, and the summation is over the three electrons in the unfilled 3d shell. The imaginary coefficient $iB_{-3}^4$ can be made equal to zero by rotating the coordinate system about the z-axis by an angle $\alpha$, where,

$$
\alpha = \frac{1}{3} \tan^{-1} \frac{B_{-3}^4}{B_3^4}. \hspace{1cm} (5.3.5)
$$

The electrostatic interaction was expressed in terms of Racah parameters $B$ and $C$ using the values adopted by Macfarlane for Al$_2$O$_3$:Cr$^{3+}$. The spin-orbit coupling parameter was also taken from his work. A computer
program was written to diagonalise the Hamiltonian of equation (5.3.3), and was checked by comparing the eigenvalues with the calculated energy levels of Cr$^{3+}$ in Al$_2$O$_3$ (Macfarlane$^{20}$) and Cr$^{3+}$ in K$_2$NaGaF$_6$ (Wong$^{21}$). In the former case the energy levels calculated by the program agreed with the published values to within five wave numbers and in the latter case the overall argument was better than 1 wave number. The larger discrepancy in the former case is attributed to lower numerical precision in Macfarlane's work$^{20}$.

Table 5.4 summarizes the data base used for the analysis of the Al$_2$O$_3$:Cr$^{3+}$ crystal field.

5.3.5 Crystal fields for MgTiO$_3$:Cr$^{3+}$

The intrinsic parameters for Al$_2$O$_3$:Cr$^{3+}$ derived in the preceding sections may be combined with the structural data for NiTiO$_3$ presented in Chapter IV to deduce ligand superposition model crystal field parameters for the Mg$^{2+}$ site and the Ti$^{4+}$ site in MgTiO$_3$. The use of nickel titanate structural data is dictated by the absence of equivalent data for MgTiO$_3$, as discussed earlier in Section 4.2. This data has also been used to calculate the point charge contribution from distant ions, and the various contributions and the total crystal field for the two sites are given in Table 5.5. Trivalent chromium substituting for either of Mg$^{2+}$ or Ti$^{4+}$ will result in local distortion effects which are difficult to estimate, particularly for the ligand cage. The simplest distortion which preserves the C$_3$ symmetry of the site is a displacement of the Cr$^{3+}$ ion along the c-axis. Accordingly the crystal field has been calculated for a range of the structural parameters u and v, corresponding to translation of the Cr$^{3+}$ ion away from the Mg$^{2+}$ or Ti$^{4+}$ lattice sites along the c-axis.
Table 5.4

Values of the crystal field parameters $D_Q$, $v$ and $v'$, electrostatic parameters $B$ and $C$ and spin-orbit coupling $\xi_i$ used in the superposition model analysis. Values are in cm$^{-1}$ units.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value in cm$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_Q$</td>
<td>1800</td>
<td>2</td>
</tr>
<tr>
<td>$v$</td>
<td>830</td>
<td>2</td>
</tr>
<tr>
<td>$v'$</td>
<td>840</td>
<td>2</td>
</tr>
<tr>
<td>$B$</td>
<td>650</td>
<td>1</td>
</tr>
<tr>
<td>$C$</td>
<td>3120</td>
<td>1</td>
</tr>
<tr>
<td>$\xi_i$</td>
<td>170</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 5.5

Calculated contributions to the weak field parameters for Cr$^{3+}$ ions at the regular lattice sites of Mg$^{2+}$ and Ti$^{4+}$ ions in MgTiO$_3$. Parameter values are in wave-numbers. Ligand point charge estimates are listed for comparative purposes only and are not included in the estimate of the total crystal field.

<table>
<thead>
<tr>
<th>Site</th>
<th>Contribution</th>
<th>$B_0^2$</th>
<th>$B_0^4$</th>
<th>$B_3^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>Ligand + point charge</td>
<td>-17</td>
<td>-3711</td>
<td>-5338</td>
</tr>
<tr>
<td></td>
<td>Ligand + superposition model</td>
<td>-38</td>
<td>-10860</td>
<td>15990</td>
</tr>
<tr>
<td></td>
<td>Distant ion - ligand point charge</td>
<td>-3338</td>
<td>-242</td>
<td>231</td>
</tr>
<tr>
<td></td>
<td>Total (ligand sup. + distant ion</td>
<td>-3376</td>
<td>-11102</td>
<td>16221</td>
</tr>
<tr>
<td></td>
<td>point charge)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>Ligand + point charge</td>
<td>-1946</td>
<td>-4349</td>
<td>6477</td>
</tr>
<tr>
<td></td>
<td>Ligand + superposition model</td>
<td>-1796</td>
<td>-14141</td>
<td>-22282</td>
</tr>
<tr>
<td></td>
<td>Distant ion - ligand point charge</td>
<td>3642</td>
<td>-564</td>
<td>-138</td>
</tr>
<tr>
<td></td>
<td>Total (ligand sup. + distant ion</td>
<td>1846</td>
<td>-14705</td>
<td>-22420</td>
</tr>
<tr>
<td></td>
<td>point charge)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5.4 Results of the Calculations

The calculations yield the entire spectrum of eigenvalues of the d^3 configuration, but only the splittings 2D of the ^4A ground state and ^2A of the ^2E excited state will be presented here since experimental data for the other levels are not available. Figure 5.2 shows the predicted splitting of the ^4A ground state as a function of cation displacement for Cr^{3+} ions occupying both the Mg^{2+} and Ti^{4+} sites in MgTiO_3, and the experimental values are also shown for comparison. The predicted values for the Mg^{2+} site and Ti^{4+} sites at zero displacement closely match the experimental observations for the site #1 spectrum and site #2 spectrum respectively.

Crude calculations of the magnitude of the displacements were made using Born-Mayer repulsive forces and the calculated electric field strengths at each site determined by a point charge model. The calculated displacements were found to be relatively small, less than 0.05 Å, primarily because the strong repulsive forces limit the effects of any change in the electro-static force due to a change in the ionic charge. Thus whilst the degree of agreement obtained here between experimental and theoretical values of the ^4A splittings is probably fortuitous, it may nonetheless be concluded that for a range of impurity cation displacements which is physically reasonable, the sign and approximate magnitudes of the zero-field splittings for Cr^{3+} ions occupying the Mg^{2+} and Ti^{4+} sites are in agreement with experimental values for the site #1 spectrum and the site #2 spectrum respectively.

The splittings ^A of the ^2E excited states are shown in Figure 5.3. The plots do not show smooth variations as for the ground state splitting because of wavefunction admixture effects resulting from level
Fig. 5.2: The calculated values of the splitting of the $^4A_2$ ground state of Cr$^{3+}$ ions as functions of the displacements of the magnetic ion along the c-axis from the normal Mg$^{2+}$ and Ti$^{4+}$ lattice sites, shown by solid and broken lines respectively. The corresponding horizontal lines indicate the experimental values of 2D. The displacements are in units of $C_0$. 
Fig. 5.3: The calculated splitting of the $^2E$ excited state of Cr$^{3+}$ ions. The closed and open circles correspond to Cr$^{3+}$ ions at Ti$^{4+}$ and Mg$^{2+}$ ion sites in MgTiO$_3$ respectively. The displacements of the central ion are the same as in Fig. 5.2.
crossing of the $^2E$ states with the $^4T_2$ states. The best agreement for small displacements with the experimentally observed splitting of 18 cm$^{-1}$ is obtained for Cr$^{3+}$ ions in Mg$^{2+}$ site for which $\Delta \sim -30$ cm$^{-1}$ at zero displacement; in contrast $\Delta$ for Cr$^{3+}$ ions at the Ti$^{4+}$ site is approximately +55 cm$^{-1}$ under the same conditions. However this association is not as firmly based as that made from the ground state splittings since the calculated values are quite sensitive to the level-crossing effect. Indeed, it is shown later in Section 5.5 that the opposite assignment can explain the observation of a single fluorescence spectrum.

It may be useful for future work to comment on the accuracy of perturbation expressions which have been proposed by Macfarlane$^{22}$ to describe the $^4A_2$ and $^2E$ splittings. For the $^4A$ splitting, it was found that Macfarlane's expressions were accurate to within ±15% of the values obtained by diagonalising the complete $d^3$ configuration, but for the $^2E$ state Macfarlane's expressions were in error by as much as several hundred percent. The latter discrepancy is probably related to the level-crossing problem.

5.5 Site Structures for MgTiO$_3$:Cr$^{3+}$

The preceding section of this chapter has shown that the zero-field splittings of the $^4A$ ground state of Cr$^{3+}$ ions in MgTiO$_3$ are consistent with sites #1 and #2 having the structures $[\text{Cr}^{3+}]_{\text{Mg}^{2+}} - [\text{Ti}^{4+}]_{\text{T}_1}$ and $[\text{Mg}^{2+}]_{\text{T}_1} - [\text{Cr}^{3+}]_{\text{Ti}^{4+}}$ respectively. These are the simplest possible substitutional sites and no local charge compensation is involved, in contrast to site #1 for MgTiO$_3$:Fe$^{3+}$. To check on the possibility of local charge compensation through disorder in the cation sublattice, the zero-field splittings of the $^4A_2$ state for the sites $[\text{Cr}^{3+}]_{\text{Mg}^{2+}} - [\text{Mg}^{2+}]_{\text{T}_1}$ and $[\text{Ti}^{4+}]_{\text{Mg}^{2+}} - [\text{Cr}^{3+}]_{\text{Ti}^{4+}}$ have been
calculated with the results of $2D = -0.06 \text{ cm}^{-1}$ and $-0.54 \text{ cm}^{-1}$ respectively. Neither possibility is in as good agreement with the experimental results as the simple substitutional sites. There is also no evidence for such sites from the concentration dependence of the spectral intensities.

The oxidation and reduction experiments described in Chapter IV do not show any well defined trends which may be used to support or refute a particular site structure model. However, the $\text{Mn}^{4+}$ spectrum, whose zero-field splitting is very close to that of the $\text{Cr}^{3+}$ spectrum, disappeared on reduction and could not be restored by oxidation treatments. At first sight this result and the resemblance between the two spectra suggests that the model proposed here as site #1, viz. $[\text{Cr}^{3+}]_{\text{Mg}}^2 - [\text{Ti}^{4+}]_{\text{Ti}}^2$ is incorrect since $\text{Mn}^{4+}$ ions may reasonably be expected to occupy the $\text{Ti}^{4+}$ site. This may well be so, but the ease with which $\text{Mn}^{4+}$ spectrum may be eliminated by reduction and the inability to restore it by oxidation treatments argues against the observed spectrum due to $\text{Mn}^{4+}$ ions at the $\text{Ti}^{4+}$ site. It is proposed here that the observed $\text{Mn}^{4+}$ spectrum arises from a small percentage of the much larger population of $\text{Mn}^{2+}$ ions at the $\text{Mg}^2+$ site being converted into $\text{Mn}^{4+}$ ions by the strongly oxidising conditions of crystal growth. Such ions are then in a metastable state and can readily be reduced, as observed, but may be difficult to re-oxidise except under the strongest conditions. It is possible that there are also $\text{Mn}^{4+}$ ions at the $\text{Ti}^{4+}$ site, but on the evidence of the crystal field calculation described here it would be expected that they would give rise to a broad EPR spectrum analogous to that of the $\text{Cr}^{3+}$ site #2 spectrum. The low peak to peak height of such a spectrum, consequent on the small population of ions at this site and the large linewidth, would render its observation in a region of the spectrum containing many other resonance lines rather difficult.
As a check on the self-consistency of the arguments presented here, the zero-field splitting of the \( ^4A \) ground state for \( \text{Mn}^{4+} \) in the \( [\text{Mn}^{4+}]_{\text{Mg}^{2+}} - [\text{Ti}^{4+}]_{\text{Ti}^{4+}} \) site was calculated, using Feher and Sturges data to derive the intrinsic superposition model parameters. The calculated splitting of \(-0.91 \text{ cm}^{-1}\) is in good agreement with the experimental value of \(-1.06 \text{ cm}^{-1}\). In contrast, the calculated splitting for the \( [\text{Mg}^{2+}]_{\text{Mg}^{2+}} - [\text{Mn}^{4+}]_{\text{Ti}^{4+}} \) site was \(+0.24 \text{ cm}^{-1}\).

One puzzling feature which remains is that only a single \( \text{Cr}^{3+} \) site was observed in the optical fluorescence spectrum reported by Louat et al. (see Section 4.1), whereas two \( \text{Cr}^{3+} \) EPR spectra of comparable intensity have been reported here. A single \( \text{Mn}^{4+} \) optical emission spectrum was also observed, and although a single \( \text{Mn}^{4+} \) EPR spectrum was found here, it was suggested here that spectrum from a \( [\text{Mg}^{2+}]_{\text{Mg}^{2+}} - [\text{Mn}^{4+}]_{\text{Ti}^{4+}} \) site would be difficult to detect. The resolution of these difficulties lies in the relative strength of the cubic component of the crystal field for the two types of sites. Figure 5.4 shows the energy levels of the \( d^3 \) configuration as a function of the strength of the cubic field. Above a value of \( Dq/B = 2.1 \), the first excited state is a \( ^2E \) state which shows sharp line fluorescence since it is only weakly coupled to the lattice. However for \( Dq/B \leq 2.1 \), the lowest excited state is a \( ^4T_2 \) triplet which is strongly coupled to the lattice. Excited \( \text{Cr}^{3+} \) ions will then decay into this level which does not show strong radiative emission behaviour. Thus an explanation for the appearance of only a single site in the optical fluorescence spectra is that the \( ^4T_2 \) level for the \( [\text{Cr}^{3+}]_{\text{Mg}^{2+}} \) site lies below the \( ^2E \) state, whereas for the \( [\text{Cr}^{3+}]_{\text{Ti}^{4+}} \) site the ordering of the levels is reversed. These orderings reflect the strength of the cubic crystal field for the two sites, which in turn reflects the smaller ion-ligand separation for the \( \text{Ti}^{4+} \) site compared with the \( \text{Mg}^{2+} \) site.
$d^3$ Cr$^{3+}$, $\gamma = 4.502$, $B = 918$ cm$^{-1}$

Fig 5.4: Energy level diagram for $d^3$ ion in cubic crystal field.
Numerically, the $^4T_2$ and $^2E$ levels are calculated to lie at 12,540 and 13,570 cm$^{-1}$ respectively for the $[\text{Cr}^{3+}]_{\text{Ti}^4+}$ site and 9,320 and 13,850 cm$^{-1}$ for the $[\text{Cr}^{3+}]_{\text{Mg}^2+}$ site. Whilst these values suggest that the $^4T_2$ level already lies lowest for $[\text{Cr}^{3+}]_{\text{Ti}^4+}$, this result is sensitive to the choice of electrostatic parameters and the power law exponent $t_4$. Of more importance is the trend from one site to the other; the cubic crystal field is 35% larger for the $[\text{Cr}^{3+}]_{\text{Ti}^4+}$ site than for the $[\text{Cr}^{3+}]_{\text{Mg}^2+}$ site which supports the explanation given here for the single optical emission spectrum observed by Louat et al.

In conclusion, all of the evidence presented here is consistent with $\text{Cr}^{3+}$ ions occupying the two site structures $[\text{Cr}^{3+}]_{\text{Mg}^2+} - [\text{Ti}^4+]_{\text{Ti}^4+}$ and $[\text{Mg}^{2+}]_{\text{Mg}^2+} - [\text{Cr}^{3+}]_{\text{Ti}^4+}$ in MgTiO$_3$. 
References on Chapter V

CHAPTER VI

ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF
DIVALENT $3d^n$ IONS IN STRONTIUM OXIDE
6.1 Introduction

Strontium oxide is one member of the alkaline earth oxide series of crystals MgO, CaO, SrO and BaO which have a face centered cubic structure identical to that of NaCl. The cubic non-primitive unit cell contains four formula units and has an edge length of \(5.16 \, \text{Å}^1\). The point group symmetry of the cation site is \(O_h\), and each cation is octahedrally coordinated to six oxygen ligands. The \(\text{Sr}^{2+} - \text{O}^{2-}\) separation is \(2.58 \, \text{Å}\).

Single crystals of SrO doped with iron, nickel, manganese, chromium and vanadium have been studied in this work. All of these samples, and the nominally undoped crystals, showed a spectrum due to Mn\(^{2+}\) ions at sites of octahedral symmetry in addition to spectra characteristic of the deliberate dopants. The undoped samples also showed a very weak spectrum characteristic of Gd\(^{3+}\) ions\(^7\). In the present chapter, the EPR spectra of the divalent ions are reported; the spectra of trivalent ions are discussed in Chapter VII.

6.2 The EPR Spectrum of Fe\(^{2+}\) Ions in Strontium Oxide

6.2.1 Experimental observation

Single crystal samples of SrO:Fe were cleaved from boules obtained from W.C. Spicer Ltd. The concentration of iron oxide added to the strontium carbonate starting material was 1% by weight, but chemical analyses of the resulting single crystals of SrO showed typical dopant concentration of 500 ppm of iron. The iron doped single crystals exhibited EPR spectra typical of both divalent and trivalent iron at temperatures below about 80 K and 150 K respectively.
Below ≈80 K a spectrum comprising single resonance lines from four magnetically inequivalent sites of trigonal symmetry appeared. Each resonance line reached a minimum field strength of ≈0.6 T, corresponding to an effective g-value of about 4, along one of the four <111>-type axes, which are body diagonal of the unit cube. For \( H \parallel <111> \), the spectrum comprised this single resonance line plus three degenerate lines at ≈1.8 T from the remaining three sites for which the magnetic field makes an angle \( \theta = 109.5^\circ \) with the symmetry axis. The general appearance of the spectrum is shown in Figure 7.1. The shape of the singlet line was asymmetric, being broader on the low field side, and below 20 K this line was sufficiently narrow that two hyperfine satellite lines could be resolved with total intensity ≈2% of that of the parent line. In Figure 6.1 the hyperfine lines of Fe\(^{2+}\) in SrO recorded using second derivative detection are shown. When the magnetic field was rotated away from the threefold axis by an angle \( \theta \), the low field resonance line shifted to higher field strength with an effective g-value given by \( g_{||} \cos \theta \) as shown in Figure 6.2 until the line moved above the maximum field of the electromagnet.

6.2.2 Interpretation of the spectra

Asymmetric lineshapes of the type observed in this case are typical of transitions between eigenstates of the form \( |\pm M_s \rangle \) with \( M_s \) integral, which occur only in even-electron systems. The weak hyperfine pattern arises from the isotope Fe\(^{57}\) which has a nuclear spin \( \frac{1}{2} \) and is 2.2% naturally abundant; other naturally occurring isotopes of iron all have zero nuclear spin. The most plausible even-electron valence state for iron in the present case is Fe\(^{2+}\), and the following discussion is based on this assignment.
Fig. 6.1: The EPR spectra at 35 GHz for Fe\textsuperscript{2+} ions in SrO with $H \parallel \langle 111 \rangle$. The positions of the two hyperfine components due to Fe\textsuperscript{57} are indicated.
Divalent iron has a $d^6$ electronic configuration with $^5D$ as the ground term. In an intermediate cubic crystal field this term is split into a $^5T_{2g}$ ground state and an excited $^5E_g$ state. A trigonal field splits the orbital triplet into a doublet and a singlet and in the present case the results are consistent with the singlet being lowest. Spin-orbit coupling, together with the trigonal component of the crystal field, removes the 5-fold spin degeneracy of the ground orbital singlet, leaving a spin singlet $|M_S = 0>$ and two non-Kramers doublets $|\pm 1>$ and $|\pm 2>$. 

The properties of this ground state orbital singlet can be described using an $S=2$ spin-Hamiltonian with the trigonal crystal field effects represented by a term $D(S^2 - \frac{1}{3}S(S+1))$, where $D = 3B_2^0$. If a magnetic field $H$ is applied at an angle $\theta$ to the symmetry axis in the $zx$ plane, the spin-Hamiltonian, neglecting the hyperfine interaction term, is:

$$\mathcal{H} = D\left(S^2 - \frac{1}{3}S(S+1)\right) + g_\beta H S_z \cos \theta + g_\beta H S_x \sin \theta.$$  \hspace{1cm} (6.2.1)

In the limit of $g_\beta H \ll D$, the energy levels and states are in first order:

$$|\pm 2> \quad W_{\pm 2} = 2D \pm 2g_\parallel H \cos \theta$$

$$|\pm 1> \quad W_{\pm 1} = -D \pm g_\parallel H \cos \theta$$  \hspace{1cm} (6.2.2)

$$|0> \quad W_0 = -2D,$$

with no allowed transition in either doublet. In second-order perturbation theory the calculation is complicated because the operator $g_x H S_x \sin \theta$ mixes the $|\pm 1>$ states with the $|0>$ state, and the $|\pm 2>$ states with the $|\pm 1>$ states.
The presence of a small rhombic term $E(S_x^2 - S_y^2)$ due to such effects as random strains introduces a similar problem in that it not only splits the $|\pm 1\rangle$ states in first order, but also splits the $|\pm 2\rangle$ states in second order through matrix elements linking them to the state $|0\rangle$. Abragam and Bleaney have calculated the energy levels and the eigenstates for an $S=2$ system subject to a strong axial and weaker rhombic perturbation correct up to second order of perturbation theory, for an arbitrary orientation of the magnetic field. The $|\pm 1\rangle$ and $|\pm 2\rangle$ doublets are no longer degenerate but show zero-field splittings given by $\Delta_1 = 6E$, $\Delta_2 = 12E^2/(E_2 - E_0)$, where $E_M$ is the unperturbed energy of the state $|M\rangle$. In a magnetic field these levels split up as

$$E_{\pm M} = \pm \frac{1}{2} \left( (\tilde{g}_|| \beta H \cos \theta)^2 + \Delta^2 \right)^{1/2},$$  

(6.2.3)

where $\tilde{g}_|| = 2g_||$ for the $|\pm 1\rangle$ states and $\tilde{g}_|| = 4g_||$ for the $|\pm 2\rangle$ states. Thus the resonance line position for each doublet is given by,

$$H = \frac{\left( (\hbar \omega)^2 - \Delta^2 \right)^{1/2}}{\tilde{g}_|| \beta \cos \theta},$$  

(6.2.4)

and Abragam and Bleaney show that the transition within the doublet occurs for an RF field parallel to the z-axis with transition probability,

$$|\nu_{ij}|^2 = \frac{1}{4} \tilde{g}_||^2 \beta^2 \frac{\Delta^2}{(\hbar \omega)^2}.$$

(6.2.5)

These results provide a useful framework for interpreting the spectrum described here. The observed transition occurs between the $|\pm 1\rangle$ states and is only allowed through the presence of non-axial strains or electric fields in the crystal which give rise to a finite value of $\Delta$ in equations.
(6.2.3)-(6.2.5). Assuming that these perturbations have a symmetrical distribution about a most probable value of zero, equation (6.2.4) shows that the predicted resonance line will be asymmetric, being broadened on the low field side by the tail in the distribution, in accord with experiment.

In the present case, a transition is only observed between the \( |\pm 1 \rangle \) states. No transition between the \( |\pm 2 \rangle \) states was observed despite an intensive search for such a resonance around the \( g \approx 8 \) region. The absence of this transition can be ascribed to two effects. Firstly, from equation (6.2.5) the intensity of the transition between \( |\pm 1 \rangle \) states is proportional to \( E^2 \), whereas for the \( |\pm 2 \rangle \) transition it is proportional to \( E^4 \). Since \( E \) is very small, the intensity of the transition between the \( |\pm 2 \rangle \) states will be much reduced compared to that for the \( |\pm 1 \rangle \) states. Secondly, the \( |\pm 1 \rangle \) and \( |\pm 2 \rangle \) states lie above the non-magnetic ground state \( |0 \rangle \) by energies \( D \) and \( 4D \) respectively. The EPR signal intensity is approximately proportional to the average population of the two energy levels involved in the transition. From the Maxwell-Boltzman distribution law, the ratio of the average population of the \( |\pm 2 \rangle \) and \( |\pm 1 \rangle \) states for zero field is given by,

\[
\frac{N_{\pm 2}}{N_{\pm 1}} = \frac{e^{-4D/kT}}{e^{-D/kT}} = e^{-3D/kT} .
\] (6.2.6)

In the present case, the value of the axial field splitting parameter \( D \) is \( \sim 12 \text{ cm}^{-1} \) (see Section 6.2.3) and so far a typical temperature of \( 20 \text{ K} \), the ratio in equation (6.2.6) is only 0.07.

The theoretical angular variation of the observed resonance line is just that predicted by equation (6.2.4). In Figure 6.2, the
Fig. 6.2: The position of the EPR line at 35 GHz for Fe$^{2+}$ ions in SrO as a function of the reciprocal of cosθ, where θ is the angle between H and the $<111>$-type direction.
line position is plotted against the reciprocal of $\cos \theta$. The circles indicate the experimental points and the firm line is a plot of equation (6.2.4), taking $\Delta = 0$. The fit between the experimental points and the theoretical solid line is very good, providing further confirmation of the assignment proposed here.

### 6.2.3 Determination of spin-Hamiltonian parameters

The single observed transition between $|\pm 1>$ states can be described with a simplified spin-Hamiltonian of the form

$$
\mathcal{H} = \tilde{g}_{||} \beta H_z S'_z + A_{||} I_z S'_z ,
$$

(6.2.7)

where the effective spin is $S' = \frac{1}{2}$, the nuclear spin is $I = \frac{1}{2}$, and the $z$-axis is chosen to lie parallel to the symmetry axis. The parameters have the values:

$$
\tilde{g}_{||} = 3.992 \pm 0.005; \quad A_{||} (\text{Fe}^{57}) = (30.2 \pm 0.6) \times 10^{-4} \text{ cm}^{-1}.
$$

These parameters were measured at a temperature of 8 K, where the linewidth of the transition was $\approx 2$ gauss.

Generally, the linewidth of a divalent iron EPR line prevents the resolution of Fe$^{57}$ hyperfine lines, and the observation of hyperfine structure reported here is quite unique. The narrow linewidth of only 2 gauss for $H \parallel <111>$ may be attributed partly to the low concentration of electron and nuclear spins in the sample. However, the major factor is that a large trigonal component of the crystal field leaves an isolated orbital singlet state lowest. This has the effect of reducing the sensitivity of the line position to small variations in the crystal field.
since such shifts involve admixtures of other orbital states.

The separation $D$ of the $|\pm 1\rangle$ doublet from the ground state singlet $|0\rangle$ cannot be directly determined from an allowed $\Delta M = \pm 1$ transition since this separation appears to be much larger than the microwave quantum of $\approx 1.1 \text{ cm}^{-1}$ up to the maximum field strength used here of 3T. In this situation, the temperature dependence of the spectral intensity may be used to determine $D$.

Suppose the population of the $|\pm 1\rangle$ states in the presence of a magnetic field applied parallel to the $z$-axis is $P_+$ and $P_-$. Then from the Maxwell-Boltzman distribution function,

$$P_+ \propto e^{-\frac{D + \frac{1}{2}g_\| \beta H}{kT}}$$

$$P_- \propto e^{-\frac{D - \frac{1}{2}g_\| \beta H}{kT}}.$$  \hfill (6.2.8)

The intensity $I$ of the transition between the $|\pm 1\rangle$ states is proportional to their population difference and so,

$$I \propto e^{-\frac{D}{kT}} \sinh\left(\frac{g_\| \beta H}{kT}\right).$$ \hfill (6.2.9)

The intensity of the Fe$^{2+}$ resonance line relative to that of a standard powder sample of dpph between 1.8 K to 4.2 K was measured and fitted to equation (6.2.9) in the least squares sense. Figure 6.3 shows the comparison between the experimental points and equation (6.2.9), plotted using the experimentally determined value of $g_\|$ and the best fit value of $D$ of $12 \pm 5 \text{ cm}^{-1}$.
Fig. 6.3: Temperature dependence of the intensity of the $\Delta M_s = 2$ EPR line for Fe$^{2+}$ ions in SrO with $H \parallel <111>$ at 35 GHz. The solid line represents the least-squares fit to the experimental data (points) using the expression given in the text.
6.2.4 Temperature dependence of linewidth

The linewidth, defined as the separation of the extreme values on a first derivative recording, was measured as a function of temperature over the range of 6 K to 56 K. Special care was taken to eliminate instrumental broadening due to such effects as overmodulation or saturation. The results, shown in Figure 6.4, may be fitted with a temperature variation of the form,

\[ \Delta H = \Delta H_0 + \Delta H(T), \quad (6.2.10) \]

where \( \Delta H_0 \) is the low temperature linewidth and \( \Delta H(T) \) represents a temperature induced broadening. The form of equation (6.2.10) implicitly assumes that the observed line is a convolution of a Lorentzian lineshape, whose width is temperature dependent due to lifetime broadening induced by relaxation processes, with a temperature independent Lorentzian line. The latter assumption is incorrect in the present case since the low temperature line is asymmetric, but a detailed numerical study of the convolution of a skewed lineshape with a Lorentzian broadening function was not considered to be warranted. The errors introduced by this assumption are not expected to be serious since the ratio of the linewidths at the extremes of the temperature range studied was ~25.

The experimentally observed temperature dependence of the spectrum suggest that an Orbach relaxation mechanism (Abragam and Bleaney\textsuperscript{2}) is operative, which may be accounted for with a temperature dependent linewidth of the form,

\[ \Delta H(T) = \Delta H'(\exp(\Delta E/kT) - 1)^{-1}, \quad (6.2.11) \]
Fig. 6.4: Linewidth for the $\Delta M_s = 2$ EPR line of Fe$^{2+}$ ion in SrO at 35 GHz for $H || <111>$ as a function of temperature. The solid line represents the least-squares fit to the experimental data (points) using the expression given in the text.
where $E$ is the energy of the excited state involved in the relaxation. A least squares fitting yielded a value of $\Delta E = 64 \pm 6 \text{ cm}^{-1}$. It is unlikely that this state is the $|\pm 2\rangle$ doublet since matrix elements of the orbit-lattice interaction are diagonal in the electron spin. Possibly the excited state is a vibronic level involving admixtures of the orbital doublet state.

6.3 The EPR Spectra of Ni$^{2+}$ Ions in Strontium Oxide

6.3.1 Experimental observation

Most of the samples used in this study contained about 1000 ppm of NiO. At room temperature, only the cubic Mn$^{2+}$ EPR spectra described in Section 6.5.1 could be observed, but at about liquid nitrogen temperature a spectrum comprising single resonance lines from four magnetically inequivalent sites of trigonal symmetry appeared. This spectrum showed many features similar to those of the Fe$^{2+}$ ion spectrum. Each line reached a minimum field strength of $\approx 0.5 \text{ T}$ for $H$ parallel to a $\langle 111 \rangle$-type direction, corresponding to an effective $g$-value of $\approx 5$, and the singlet line again showed the asymmetric lineshape typical of a transition within a doublet of a non-Kramers ion. For temperatures below $\approx 30 \text{ K}$, the singlet resonance line for $H \parallel \langle 111 \rangle$ was sufficiently narrow that four distinct hyperfine lines could be resolved with total intensity $\approx 1\%$ of the parent line. The weak hyperfine pattern arises from the isotope Ni$^{61}$, which has a nuclear spin $I = \frac{3}{2}$ and is 1.1% abundant in nature. The other naturally occurring isotopes of nickel all have zero nuclear spin.

6.3.2 Interpretation of the spectrum

The most plausible even-electron valence state of nickel consistent with all the observed spectral characteristics is Ni$^{2+}$. The $^3A_2$
orbital singlet ground state of Ni$^{2+}$ ions in an octahedral field is split into a ground state spin doublet and an excited non-magnetic spin singlet by the combined effects of spin-orbit coupling and a trigonal component of the crystal field. If a magnetic field is applied in the zx plane, z being the threefold axis of symmetry, the spin Hamiltonian can be written as,

$$\mathcal{H} = D\left(S_z^2 - \frac{1}{3} S(S+1)\right) + g_\| \beta H S_z \cos \theta + g_\perp \beta H S_x \sin \theta \quad (6.3.1)$$

Since an allowed transition of the type $\Delta M_S = \pm 1$ was not observed the magnitude of $D$ must be such that $|D| >> \hbar \nu$. In this limit, the energy levels and states correct to first order are,

$$|\pm 1 > > W_\pm = \frac{1}{3} D \pm g_\| \beta \nu \cos \theta$$

$$|0 > > W_0 = -\frac{2}{3} D \quad (6.3.2)$$

with no allowed transition between the $|\pm 1 >$ doublet. However a transition is weakly allowed, except when $H$ is along the z-axis, through the second order Zeeman effect, since for $\theta \neq 0$, each of the $|\pm 1 >$ doublets is an admixture of the form $|+1, 0, -1 >$. The transition between the $|\pm 1 >$ states can only be induced through a rhombic component of the crystal field which will introduce a term $E(S_x^2 - S_y^2)$ in the spin-Hamiltonian. This term has matrix elements connecting the $|\pm 1 >$ states and these states are split in first order by an amount $\Delta = 2E$. A transition between the states is now allowed for the RF field parallel with the z-axis with a probability and field strength for $E << D$ given by equations (6.2.5) and (6.2.4) respectively, with $\Delta = 2E$ and $g_\| = 2g_\|$. In the present case, a rhombic component of the crystal field is introduced through random strain and electric fields and so a transition between the $|\pm 1 >$ levels of
asymmetric lineshape is expected even for $H \parallel z$, in the same way as for $\text{Fe}^{2+}$ ions. Further support for the assignment of the observed resonance line to a $|±1>$ level comes from the angular variation of the spectrum shown in Figure 6.5. The predicted angular variation is just that given by equation (6.2.4), neglecting $\Delta$, and as may be seen from Figure 6.5, is in excellent agreement with experiment.

6.3.3 Determination of the spin-Hamiltonian parameters

The transition observed within the $|±1>$ doublet can be described by the spin-Hamiltonian,

$$\mathcal{H} = g_\parallel S_z^z \cos \theta + A_\parallel S_z I_z,$$

where $S=1$ and $I=3/2$ for Ni$^{61}$. The measured parameters, determined directly from the spectra have values $g_\parallel = 2.58 \pm 0.02$ and $A_\parallel (\text{Ni}^{61}) = (28.0 \pm 0.5) \times 10^{-4}$ cm$^{-1}$ at 4.2K.

From the Maxwell-Boltzman distribution law, the intensity of the transition between $|±1>$ states as function of temperature is given by,

$$I = \frac{K_{\text{Ni}} (e^{-\frac{1}{2}g_\parallel \beta H/kT} - e^{\frac{1}{2}g_\parallel \beta H/kT})}{Z},$$

where $K_{\text{Ni}}$ is a proportionality constant and

$$Z = e^{-\frac{1}{2}g_\parallel \beta H/kT} + e^{\frac{1}{2}g_\parallel \beta H/kT} + e^{-D/kT}$$

is the partition function. Comparing the intensity of Ni$^{2+}$ line relative to that of a standard sample, the ratio of the intensities at a temperature
Fig. 6.5: The position of the EPR line at 35 GHz for Ni$^{2+}$ ions in SrO as a function of the reciprocal of $\cos \theta$, where $\theta$ is the angle between $\mathbf{H}$ and the $<111>$-type direction.
The experimental ratios of intensities measured between 5 K and 50 K were fitted to the above equation in the least squares sense and are shown in Figure 6.6. The value of $D$ obtained from this fit was $D = -20 \pm 6$ cm$^{-1}$.

From an optical spectroscopy depopulation experiment, Brunskill determined the value of this zero field splitting to be $-17 \pm 5$ cm$^{-1}$, in good agreement with that determined here.

### 6.3.4 Temperature dependence of the linewidth

The linewidth for $H$ parallel to the threefold symmetry axis was measured as a function of temperature over the range of 5-50 K, and the results are shown in Figure 6.7. The data was fitted to an Orbach relaxation mechanism as in the case of Fe$^{2+}$ ion, with the result that the energy of the excited state involved in the relaxation was determined to be $46 \pm 2$ cm$^{-1}$. The comparison between the experimental measurements and the predicted variation based on this value is shown in Figure 6.7. As in the case of Fe$^{2+}$, it is unlikely that this excited state reflects the spin singlet $|0\rangle$ but instead is thought to be a low-lying vibronic level containing admixtures of the higher orbital multiplet states.

### 6.4 Effective Perpendicular $g$-Value for Fe$^{2+}$ and Ni$^{2+}$ Ions in SrO

In first-order approximation the effective $g$-value of the $\Delta M = \pm 2$ transition for Fe$^{2+}$ and Ni$^{2+}$ was shown in sections 6.2.2 and 6.3.2.
Fig. 6.6: Temperature dependence of the intensity of the $\Delta m_s = 2$ EPR line for Ni$^{2+}$ ions in SrO with $H \parallel <111>$ at 35 GHz. The solid line represents the least-squares fit to the experimental data (points) using the expression given in the text.
Fig. 6.7: Linewidth for the $\Delta M_s = 2$ EPR line of Ni$^{2+}$ ion in SrO at 35 GHz for $H \parallel <111>$ as a function of temperature. The solid line represents the least-squares fit to the experimental data (points) using the expression given in the text.
to be given by $2g_\| \cos \theta$. So in first-order approximation $\tilde{g}_\perp$ for both ions is zero. However in a second-order theory, $\tilde{g}_\perp$ is non-zero for both ions due to Zeeman mixing. Since the $\Delta M = \pm 2$ transition for both the ions moved beyond the range of the electromagnet for the 35 GHz spectrometer, it was considered worthwhile to use the 9-GHz spectrometer and the 3T superconducting magnet in an attempt to estimate $\tilde{g}_\perp$ for both ions. However, pronounced line broadening occurred for both Fe$^{2+}$ and Ni$^{2+}$ ions for large values of $\theta$, resulting in a reduced line intensity. For this reason, the line could not be followed above about $\theta = 70^\circ$ with the 9-GHz spectrometer, which is not as sensitive as the Q-band instrument.

6.5 The EPR Spectra of Mn$^{2+}$ and V$^{2+}$ Ions in Strontium Oxide

The EPR spectra of divalent manganese$^5,6,9$ and divalent vanadium$^7$ in single crystals of SrO have been investigated previously. Nonetheless, in view of the trigonal site found for Fe$^{2+}$ and Ni$^{2+}$ ions in the present work, and for Co$^{2+}$ ions (Manson and Edgar)$^8$ in SrO, it was considered worthwhile to check the site symmetries of Mn$^{2+}$ and V$^{2+}$ in this lattice.

6.5.1 The EPR spectra of Mn$^{2+}$ ions in SrO

The trace amount of manganese present in all samples of SrO, even those which were nominally undoped, was sufficient for the EPR spectra of Mn$^{2+}$ ions to be detected using the Q-band spectrometer. The EPR spectra of Mn$^{2+}$ ions in SrO consists of six well resolved hyperfine lines corresponding to the nuclear spin of $I = \frac{5}{2}$ for Mn$^{55}$. The fine structure lines due to the $S = \frac{5}{2}$ electronic spin could not be fully resolved for arbitrary orientations of the magnetic field. However, with $H \parallel <111>$ all five lines are clearly resolved as shown in Figure 6.8, but on rotation
containing trace amounts of manganese. The fine structure is best resolved on the low field pentad; the two unresolved pentads at high fields are not shown.

Fig. 6.8: EPR spectrum at 35 GHz with $\mathbf{H} \parallel <111>$ for nominally undoped samples of SrO containing trace amounts of manganese. The fine structure is best resolved on the low field pentad; the two unresolved pentads at high fields are not shown.
in the (110) plane through to the <001> direction the \(M_\parallel = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}\) lines rapidly broadened, and they could not be resolved for \(H \parallel (001)\). The \(\pm \frac{3}{2} \leftrightarrow \pm \frac{1}{2}\) lines were also broadened, but could still be observed along the <001> axis, although with reduced intensity.

The \(g\)-value, the fine structure splitting term \(a\), and the hyperfine interaction parameter have the values \(g = 2.001 \pm 0.001\), \(a = (2.5 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}\) and \(|A(\text{Mn}^{55})| = (78.2 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}\), measured at room temperature. These parameter values are in reasonable agreement with the values \(g = 2.0012 \pm 0.0005\), \(a = (4.3 \pm 0.8) \times 10^{-4} \text{ cm}^{-1}\) and \(|A(\text{Mn}^{55})| = (-78.7 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}\) as reported by Holroyd and Kolopus, and with the values \(g = 2.001 \pm 0.001\), \(a = (3.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}\), \(A = (80.5 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}\) reported by Sochava et al., and with the values \(g = 2.0010 \pm 0.0003\), \(a = (3.0 \pm 0.2) \times 10^{-4} \text{ cm}^{-1}\), \(A = (-78.3 \pm 0.1)\) reported by Rubio et al.

Samples of single crystals of SrO deliberately doped with manganese showed an axial site spectrum for Mn\(^{2+}\) ions in addition to the cubic site spectrum. From an angular variation study with the magnetic field in the (100) plane, the spectrum was found to exhibit tetragonal symmetry about an <001>-type axis. The axial field splitting, and the hyperfine constant parameter, were determined from the spectrum with \(H \parallel (001)\) at 85 K to be \(|D| = 494(5) \times 10^{-4} \text{ cm}^{-1}\) and \(A_{\parallel}(\text{Mn}^{55}) = 78(4) \times 10^{-4} \text{ cm}^{-1}\). These values agree reasonably with the values \(|D| = (454.8(8)) \times 10^{-4} \text{ cm}^{-1}\) and \(A_{\parallel}(\text{Mn}^{55}) = (-80.2(1)) \times 10^{-4} \text{ cm}^{-1}\), reported by Rubio et al., for Mn\(^{2+}\) ions at a \(C_{4v}\) site in SrO. It was concluded that the axial spectrum reported here is identical with that reported by Rubio et al. and the spectrum was not studied in any further detail.

The nominally undoped samples of SrO exhibited, in addition to the cubic Mn\(^{2+}\) spectrum, another manganese spectrum which appears below
The spectrum for $H \parallel <111>$ between $\approx 100$ K and 70 K comprises six well resolved hyperfine lines which split up into several components when the magnetic field is rotated away from this direction. However the site symmetry, and even the charge state of the manganese ion has not been identified, since the spectrum shows an unusual temperature dependence and the very weak intensity prevents detailed angular dependence studies. The spectrum was not observed in deliberately doped samples. The following treatments were given to the samples in an attempt to increase the spectral intensity relative to that of the regular cubic site. In the first treatment the samples were heat treated in air at 1100°C and then quenched. The second type of treatment was identical except that the samples were annealed, rather than quenched, by turning the furnace off to permit slow cooling. No appreciable change of the spectrum was obtained after the first treatment, but after the second treatment, the intensities of the lines from this site were very much reduced, with a corresponding increase in the intensity of the cubic site spectrum. These treatments suggest that a manganese ion associated with a defect or an interstitial manganese ion is responsible for the new site spectrum.

The samples were also treated at the same temperature with a mixture of powders of $\text{Li}_2\text{CO}_3$ and SrO with the intention of diffusing $\text{Li}^+$ ions into the lattice. This treatment increased the intensity of the new site at the expense of the intensity of the cubic site spectrum. This observation suggests that the charge state of the manganese ion responsible for the new spectrum is tetravalent since $\text{Li}^{1+}$ ions incorporated in the lattice act as charge compensators. Tetravalent manganese has previously been observed in lithium and manganese doped MgO and CaO$^{10,12,13}$. The hyperfine interaction constant for manganese in the new site was measured to be $68 \times 10^{-4}$ cm$^{-1}$. The smallest value of the
hyperfine interaction parameter previously reported for manganese ions in any site or charge state in SrO is \(75 \times 10^{-4} \text{ cm}^{-1}\) for Mn\(^{4+}\) ions in a cubic site.

A temperature variation study of the spectrum is shown in Figure 6.9 for the \(H \parallel \langle 111 \rangle\) orientation of the magnetic field. The six line pattern which appears below about 100 K first broadens as the temperature is lowered and then at \(-64\) K a multitude of resonance lines appears. A few degrees below this the resonance lines disappear altogether and cannot be observed at lower temperatures. This highly unusual behaviour is very interesting and merits further studies if by some method the intensity of the signal can be further increased.

6.5.2 The EPR spectra of \(V^{2+}\) ions in SrO

The as-grown crystals of SrO doped with vanadium did not show any spectrum which could be attributed to vanadium ions. However, samples reduced in a vacuum at 1300°C showed a spectrum with 8 well-defined hyperfine lines typical of \(V^{2+}\) ions at an octahedral site. The angular variation of the spectrum did not reveal any measurable anisotropy in the \(g\)-value or in the hyperfine interaction parameter and so the spectrum can be described with a spin-Hamiltonian of the form,

\[
\mathcal{H} = g \mathbf{H} \cdot \mathbf{S} + A \mathbf{I} \cdot \mathbf{S},
\]

with \(S = \frac{3}{2}\) and \(I = \frac{7}{2}\) for \(V^{51}\) which is 99.76% abundant in nature.

The measured parameters are \(g = 1.957(2)\) and \(A(V^{51}) = 79(1) \times 10^{-4} \text{ cm}^{-1}\). These values of the spin-Hamiltonian parameters agree very well with those reported previously by Kolopus et al.\(^7\) for a cubic \(V^{2+}\) spectrum in SrO. Their measured parameter values are \(g = 1.9592(6)\) and \(A(V^{51}) = (79.7 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}\).
Fig. 6.9: The EPR spectra at 35 GHz of nominally undoped SrO at various temperatures. The EPR lines from the new Mn$^{2+}$ ion site are indicated by x.
6.6 Site Structure for Divalent Ions in SrO

6.6.1 Mn$^{2+}$ and V$^{2+}$ ions

Mn$^{2+}$ and V$^{2+}$ ions have the same charge state as that of Sr$^{2+}$ ions in SrO, and there is no reason to suppose that they do not simply substitute for Sr$^{2+}$ ions. The only change in the local crystal structure would then be a breathing mode contraction centered on the magnetic ion.

The tetragonal spectrum for Mn$^{2+}$ ions reported here and also observed by Rubio et al.\textsuperscript{9} may result from a defect-associated centre. Rubio et al. did not propose a site structure for this spectrum.

6.6.2 Fe$^{2+}$ and Ni$^{2+}$ ions in SrO

It is evident from the EPR measurements on SrO:Fe$^{2+}$ and SrO:Ni$^{2+}$ reported here that there is a marked contrast in the behaviour of these ions when incorporated in MgO or CaO as compared with SrO. In the former two hosts these ions exhibit spectra of octahedral symmetry characteristic of simple substitutional site.

There are several possible models which, in principle, could explain the occurrence of trigonally symmetric sites for Fe$^{2+}$ and Ni$^{2+}$ ions in SrO. The first of these models is that of an interstitial site for the magnetic ion in SrO. The ionic radii of Fe$^{2+}$ and Ni$^{2+}$ are respectively 0.77 Å and 0.70 Å, and so an interstitial site can accommodate these ions, since on a hard sphere argument, any ion with ionic radius less than 0.82 Å can be accommodated in the interstitial site. A possible model of the site structure therefore comprises an interstitial divalent magnetic ion (Fe$^{2+}$ or Ni$^{2+}$), charge compensated by a defect or defects whose net charge is $-2|e|$ and whose distribution is trigonally symmetric about a $<111>$ axis. However, the Madelung constant for an interstitial
site in a perfect rocksalt lattice is zero, and even in the case of charge compensation by a nearest neighbour cation vacancy the stabilizing electrostatic energy for such a site is less than that of the regular cation site. Furthermore, it would be expected that some of these interstitial sites would have remote charge compensation. These remotely-compensated interstitial sites should exhibit a spectrum with effectively tetrahedral symmetry, particularly the samples which were heated and subsequently quenched. This treatment would have been expected to disassociate the centres. Finally, the cubic component of the crystal field for an interstitial site is expected to have a sign appropriate to tetrahedral coordination of the oxygen ligands, whereas the EPR spectra of both Ni$^{2+}$ and Fe$^{2+}$ ions in SrO can be satisfactorily predicted with a crystal field whose cubic component has a sign corresponding to octahedral coordination. These arguments do not support an interstitial site location for Fe$^{2+}$ and Ni$^{2+}$ ions in SrO.

The other possible models involve a substitutional site. The octahedral site symmetry of a substitutional divalent $3d^n$ ion may be effectively lowered by neighbouring defects, a static Jahn-Teller interaction, or an off-centre displacement of the impurity ion. No charge compensation is required for substitutional divalent ions. Furthermore, if a neighbouring defect is responsible for the reduction of the local site symmetry, there should be other sites with symmetries different from trigonal, corresponding to different locations of the defect relative to the magnetic ion. More important, some of the substitutional sites would be expected to be remotely charge compensated, in which case a cubic site spectrum should have been observed for Ni$^{2+}$ and Fe$^{2+}$ ions in SrO.

Manson and Edgar$^8$ have also reported trigonally symmetric sites for Co$^{2+}$ ions in SrO. An even-mode static Jahn-Teller effect would not
provide a consistent explanation for all the three ions (Fe$^{2+}$, Ni$^{2+}$ and Co$^{2+}$) in either substitutional or interstitial sites, since Ni$^{2+}$ and Co$^{2+}$ have orbital singlets lowest in octahedral and tetrahedral environments respectively. Furthermore, from electric field modulation studies of the optical spectra of Ni$^{2+}$ and Co$^{2+}$ ions in SrO, Brunskill$^4$ has observed that the trigonal Co$^{2+}$ and Ni$^{2+}$ sites lack inversion symmetry. The lack of inversion symmetry for trigonal Co$^{2+}$ ions was also observed by Manson and Edgar$^8$ and is contrary to the even-mode coupling expected for a static Jahn-Teller effect.

It is therefore concluded that the site structure model which is most consistent with all experimental evidence is that of a substitutional ion (Fe$^{2+}$, Ni$^{2+}$ or Co$^{2+}$) displaced from the regular cation site along a $<111>$-type direction of the cubic axis, i.e. an off-centre displacement analogous to that found for the classic off-centre system KCl:Li$^+$. A theoretical study of the off-centre/on-centre behaviour of the 3d$^n$ ions in alkaline earth oxides which supports this assignment is presented in Chapter VIII.
References for Chapter VI

CHAPTER VII

ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF Fe$^{3+}$

AND Cr$^{3+}$ IONS IN STRONTIUM OXIDE
7.1 Introduction

Transition metal ion dopants usually enter alkaline earth oxides host lattices in the divalent state, but higher charge states may be produced by irradiation or charge compensation mechanisms. The latter may be induced either during crystal growth, or by subsequent thermal treatments.

In this Chapter, the EPR spectra of Fe$^{3+}$ and Cr$^{3+}$ ions in both as-grown and thermally treated samples of SrO are reported. In the case of Cr$^{3+}$ ions, the dominant spectrum exhibited octahedral symmetry, but for Fe$^{3+}$ ions, two low-symmetry sites were observed and an octahedral site could not be detected.

7.2 EPR Spectra of Fe$^{3+}$ Ions in SrO

7.2.1 Spectral characteristics and identification of an orthorhombic Fe$^{3+}$ EPR spectrum.

The room temperature EPR spectrum of as-grown single crystals of SrO doped with iron showed only the cubic Mn$^{2+}$ ion EPR spectrum described earlier. However, below -140 K, a complex spectrum comprising many resonance lines appeared, including the trigonal Fe$^{2+}$ spectrum described earlier. By studying the degeneracies $<001>$, $<111>$ and $<110>$, and also by measuring the angular variation of the spectrum in the (110) plane, it was determined that the new spectrum was due to Fe$^{3+}$ ions at six magnetically inequivalent sites of orthorhombic ($C_{2v}$) symmetry. The number of possible orientations of the paramagnetic centres relative to the crystal axes is equal to the ratio of the order of the symmetry group ($O_h$), of the perfect lattice cation site to the order of the symmetry group ($C_{2v}$) of the paramagnetic centre. This ratio is 12, but because EPR
spectra are invariant to a reversal of the magnetic field direction, the paramagnetic centres are equivalent in pairs resulting in a total of six magnetically inequivalent sites. The EPR spectrum of Fe$^{3+}$ ions at this site is shown in Figure 7.1 for the magnetic field aligned along a $<111>$-type direction. No hyperfine components could be observed and so the EPR spectrum of Fe$^{3+}$ ions in this orthorhombic site may be described by the following spin-Hamiltonian,

$$\mathcal{H} = \beta (g_x S_x + g_y S_y + g_z S_z) + B_0^0 + B_2^0 + B_4^0 + B_4^4$$  \hspace{1cm} (7.2.1)

with $S = \frac{5}{2}$. The axes $x$, $y$ and $z$ were chosen to be parallel to $<001>$, $<110>$ and $<110>$ directions of the cubic axes. A total of 41 transitions were fitted to the above spin-Hamiltonian using a least-squares fitting program. The resonance line positions predicted from the best fit parameters, given in Table 7.1, closely match the experimental values with a standard deviation of less than 4 gauss. The overall signs of the parameters were determined in depopulation experiments at 4.2 and 2 K.

Some additional weak lines in the spectrum could not be assigned to this orthorhombic site, but were not studied in detail. However, their angular variation indicated that they did not arise from an Fe$^{3+}$ site of cubic symmetry and no evidence of such a site could be found.

7.2.2 Energy levels diagrams

The energy levels of Fe$^{3+}$ ions in the orthorhombic site in SrO as function of magnetic field strength for different field orientations are shown in Figures 7.2 - 7.5. The nominally $\Delta M = \pm 1$ transitions are shown by double arrowed lines.

All these figures clearly show strong magnetic field mixing of the crystal field levels, particularly at low field strengths. The energy
Table 7.1
Spin-Hamiltonian parameters for Fe$^{3+}$ ions at a site of orthorhombic symmetry in strontium oxide. Forty-one field strengths were used in the fitting from spectra recorded at 90 K, and the standard deviation of observed and predicted field strengths was 2.7 gauss. The parameter values of $B_i$ are given in units of $10^{-4}$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$B^0_2$</th>
<th>$B^2_2$</th>
<th>$B^0_4$</th>
<th>$B^2_4$</th>
<th>$B^4_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0060</td>
<td>2.0058</td>
<td>2.0062</td>
<td>884.7</td>
<td>-422.0</td>
<td>0.31</td>
<td>-1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>±0.005</td>
<td>±0.005</td>
<td>±0.005</td>
<td>±0.3</td>
<td>±0.5</td>
<td>±0.02</td>
<td>±0.09</td>
<td>±0.09</td>
</tr>
</tbody>
</table>

Table 7.2
Axis systems for the six magnetically inequivalent Fe$^{3+}$ centres of orthorhombic symmetry in SrO.

<table>
<thead>
<tr>
<th>Centre no.</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>&lt; 001 &gt;</td>
<td>&lt; 110 &gt;</td>
<td>&lt; 110 &gt;</td>
</tr>
<tr>
<td>2</td>
<td>&lt; 001 &gt;</td>
<td>&lt; 110 &gt;</td>
<td>&lt; 110 &gt;</td>
</tr>
<tr>
<td>3</td>
<td>&lt; 100 &gt;</td>
<td>&lt; 011 &gt;</td>
<td>&lt; 011 &gt;</td>
</tr>
<tr>
<td>4</td>
<td>&lt; 100 &gt;</td>
<td>&lt; 011 &gt;</td>
<td>&lt; 011 &gt;</td>
</tr>
<tr>
<td>5</td>
<td>&lt; 010 &gt;</td>
<td>&lt; 101 &gt;</td>
<td>&lt; 101 &gt;</td>
</tr>
<tr>
<td>6</td>
<td>&lt; 010 &gt;</td>
<td>&lt; 101 &gt;</td>
<td>&lt; 101 &gt;</td>
</tr>
</tbody>
</table>
Fig. 7.1: The 35 GHz EPR spectrum of iron-doped strontium oxide crystals. The lines marked A, B, C and D arise from Fe$^{3+}$ ions in C$_{2v}$ sites, Fe$^{2+}$ ions in C$_{3v}$ sites, Mn$^{2+}$ ions in cubic sites and from dpph respectively.
level diagrams for $H \parallel x$ and $H \parallel y$ (Figs. 7.4 and 7.5) are very different, reflecting the relatively large magnitude of the rhombic component in the spin-Hamiltonian. The effect of rotating the magnetic field away from $H \parallel z$ to some intermediate orientation in the $zx$ plane is obvious from Figures 7.2 and 7.3.

7.2.3 Angular variation of the spectrum

The angular variation of the spectrum was studied with the aid of a stereographic projection using a cavity which permitted sample rotations. The crystal was mounted on a PVC sample holder, terminated in a precision-cut $45^\circ$ wedge, which could be rotated about the horizontal cavity axis. The magnetic field, which could be rotated about a vertical axis, was aligned at an angle $\theta = 90^\circ$ with the crystal rotation axis. This arrangement was suitable for studying the angular variation of the spectrum in the (110) plane. Rotation in other planes could be achieved by using different sample holders with wedge angles of $35.3^\circ$ or $54.7^\circ$.

The theoretical calculation of the angular variation of the spectrum was performed using the best fit spin-Hamiltonian parameters obtained from the least squares fitting of the spectrum. Because of the high number of inequivalent sites, a systematic method of performing the calculation is essential. A short description of the method adopted here is given below.

The plane of rotation of the magnetic field is kept fixed and the spectra from the 6 possible inequivalent sites, listed in Table 7.2, are generated. When $H$ is rotated in the (110) plane from the $<110>$ direction to the $<001>$ direction, the magnetic field vector, in terms of the cubic crystal axes, is given by
Figs. 7.2 to 7.5: Ground state energy levels of Fe$^3+$ ions at C$_2v$ site in SrO as a function of magnetic field strength. The direction of the magnetic field with respect to the magnetic axes defined in the text are specified by the angles (θ, φ) = (0, 0), (35.26, 0), and (90, 90) for Figures 7.2 through 7.5 respectively.
where $\phi$ is the angle between the $<110>$ direction and $\vec{H}$. The polar and azimuthal angles of the magnetic field with respect to each paramagnetic centre are then calculated and used in the program.

The angular variation of the spectrum in the $<110>$ plane is shown in Figures 7.6 and 7.7. The solid lines represent the calculated angular variation of the spectrum, and the circles represent the experimental points. Because a large number of resonance lines are involved, the angular variation data has been divided into two parts, depending on whether a particular line is a component of a degenerate doublet or quartet for $\vec{H} \parallel <001>$.

Figure 7.6 shows the splitting of the doublet lines arising from paramagnetic centres 1 and 2 of Table 7.2, as the magnetic field is rotated away from the $<001>$-type direction. Neglecting the fourth order terms, the splitting of the doublet lines is due to the term $B_{202}^2$ present in the spin-Hamiltonian.

The angular variation of the 4-fold degenerate lines, for $\vec{H} \parallel <001>$ or $\vec{H} \parallel <110>$, originating from paramagnetic centres 3, 4, 5 and 6 are shown in Figure 7.7. For intermediate orientations of the magnetic field the centres 3 & 6 and 4 & 5 remain magnetically equivalent in pairs so the quadruplet lines split up into pairs of doublets. For $\vec{H} \parallel <111>$ each doublet becomes degenerate with a singlet arising from the $\vec{H} \parallel <001>$ doublets, and results in two sets of triply degenerate lines.
Fig. 7.6: The angular variation of part of the 35 GHz EPR spectrum for Fe$^{3+}$ ion at the $C_{2v}$ site in SrO when the magnetic field is rotated in a (110) plane. The curves labelled a, b, c, d & e correspond to the transition between the $M_s = 3/2 \rightarrow 5/2$; $1/2 \rightarrow 3/2$; $-1/2 \rightarrow 1/2$; $-3/2 \rightarrow -1/2$, and $-5/2 \rightarrow -3/2$ states respectively. The lines marked z and y for $\mathbf{H} \parallel \langle 110 \rangle$ correspond to centres 1 and 2 of table 7.2.
Fig. 7.7: The angular variation of the remaining resonance lines originating from centres 3 to 6 of table 7.2 omitted in figure 7.6. The labelling scheme of the transitions is identical with that in figure 7.6.
The intensity of some of the experimentally observed resonance lines rapidly decreased away from the high symmetry direction and disappeared for some ranges of θ. However, this is entirely in agreement with the predicted intensity variation and is due to a transfer of intensity to new resonance lines which are predicted, and observed, in these ranges.

The excellent agreement obtained between the theoretically predicted and experimentally observed angular variation of the spectrum provides convincing confirmation that the spin-Hamiltonian (7.2.1) with the best fit values of the parameters is an accurate description of the electronic ground state of this Fe$^{3+}$ ion site.

7.2.4 EPR spectrum of Fe$^{3+}$ ion in a C$_{1h}$ site in SrO

Treating the iron-doped samples in air at ~1350°C for several hours produced a spectrum with a local symmetry even lower than orthorhombic. For treatments at lower temperatures, at 1350°C or for shorter times, the total spectrum comprised both the new Fe$^{3+}$ spectrum and that from Fe$^{3+}$ ions at the orthorhombic site described in the preceding section. The new site spectrum could be observed at much higher temperatures, up to ~250 K, than for the C$_{2v}$ site spectrum which disappeared due to broadening effects above ~140 K. However, the treated sample did not show the Fe$^{2+}$ spectrum which was observed in untreated samples.

The degeneracies of the lines arising from the new site along high symmetry directions, as well as their angular variation in (110) and (100) plane were studied. It was concluded that the new spectrum was due to Fe$^{3+}$ ions at 12 magnetically inequivalent sites of C$_{1h}$ symmetry. The C$_{1h}$ point group has only two symmetry elements, the identity element and
one reflection plane. This results in 24 paramagnetic centres in the
crystal, which are magnetically equivalent in pairs. The EPR spectrum
for this site for the $H \parallel <110>$ direction is shown in Figure 7.8. If
the $xz$ plane is chosen as the plane of reflection symmetry, the spin-
Hamiltonian describing the spectrum involves only real parameters:

\[
\mathcal{H} = \beta(g_x \mathbf{H}_x \mathbf{S}_x + g_y \mathbf{H}_y \mathbf{S}_y + g_z \mathbf{H}_z \mathbf{S}_z) + B_{22}^0 \mathbf{O}_2^0 + B_{22}^1 \mathbf{O}_2^1 + B_{22}^2 \mathbf{O}_2^2 + B_{44}^0 \mathbf{O}_4^0 + B_{44}^1 \mathbf{O}_4^1 + B_{44}^2 \mathbf{O}_4^2 +
\]

\[
B_{44}^3 \mathbf{O}_4^3 + B_{44}^4 \mathbf{O}_4^4 ,
\]  

(7.2.4)

with $S = \frac{5}{2}$. The $x, y$ and $z$ axes were chosen to be parallel to the
$<\bar{1}12>$, $<110>$ and $<111>$ directions of the cubic axes. The sites
show some degeneracies when the magnetic field is applied along high
symmetry axes according to the following scheme:

\[
\begin{align*}
H \parallel <111> & \quad 3:3:6 \\
H \parallel <110> & \quad 2:2:4:4 \\
H \parallel <100> & \quad 4:8 ,
\end{align*}
\]

where the numbers indicate the order of the degeneracies.

A total of 44 nominally $\Delta M = \pm 1$ transitions were fitted to the
spin-Hamiltonian (7.2.4), in the least-squares sense. The best fit spin-
Hamiltonian parameters, listed in Table 7.3, predicted the line positions
with an overall standard deviation of 5 gauss. Some of the more
degenerate lines had individual deviations of up to 9 gauss, which is
attributed to a higher uncertainty in the recorded resonance field due
to the broad line width resulting from a slight misalignment of the
crystal. The overall sign of the spin-Hamiltonian parameters was determined
by depopulation experiments at 4.2 K and 2 K. Here again, some additional
Spin-Hamiltonian parameters for Fe$^{3+}$ ions with C$_{1h}$ point group symmetry in SrO. 44 transitions were fitted to the S.H. of equation (7.2.4). The spectra were recorded at ~90 K. The overall standard deviation of observed and predicted field strengths was 5 gauss. The parameters $B_m^m$ are given in units of $10^{-4}$ cm$^{-1}$.

<table>
<thead>
<tr>
<th>$g_x$</th>
<th>$g_y$</th>
<th>$g_z$</th>
<th>$B_0^2$</th>
<th>$B_1^2$</th>
<th>$B_2^2$</th>
<th>$B_0^4$</th>
<th>$B_1^4$</th>
<th>$B_2^4$</th>
<th>$B_3^4$</th>
<th>$B_4^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0067</td>
<td>2.0061</td>
<td>2.0071</td>
<td>661.5</td>
<td>-538.2</td>
<td>250.3</td>
<td>-0.10</td>
<td>-2.4</td>
<td>0.4</td>
<td>0.9</td>
<td>-0.3</td>
</tr>
<tr>
<td>±0.005</td>
<td>±0.005</td>
<td>±0.005</td>
<td>±0.3</td>
<td>±0.4</td>
<td>±0.6</td>
<td>±0.02</td>
<td>±0.08</td>
<td>±0.05</td>
<td>±0.03</td>
<td>±0.07</td>
</tr>
</tbody>
</table>

Table 7.4

Inequivalent (110) planes of rotation of the magnetic field used in generating the entire spectrum for the angular variation study of Fe$^{3+}$ ions at a C$_{1h}$ site in SrO. The paramagnetic centre had magnetic x, y and z axes along the $<\overline{112}>$, $<\overline{110}>$ and $<111>$ directions. The planes are specified by the initial and final directions of the magnetic field.

<table>
<thead>
<tr>
<th>System no.</th>
<th>Initial direction of H</th>
<th>Final direction of H</th>
<th>System no.</th>
<th>Initial direction of H</th>
<th>Final direction of H</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$&lt;\overline{110}&gt;$</td>
<td>$&lt;\overline{001}&gt;$</td>
<td>7</td>
<td>$&lt;\overline{0\overline{1}}&gt; &gt;$</td>
<td>$&lt;100&gt;$</td>
</tr>
<tr>
<td>2</td>
<td>$&lt;\overline{110}&gt;$</td>
<td>$&lt;\overline{001}&gt;$</td>
<td>8</td>
<td>$&lt;\overline{01\overline{1}}&gt; &gt;$</td>
<td>$&lt;100&gt;$</td>
</tr>
<tr>
<td>3</td>
<td>$&lt;\overline{110}&gt;$</td>
<td>$&lt;\overline{001}&gt;$</td>
<td>9</td>
<td>$&lt;\overline{101}&gt; &gt;$</td>
<td>$&lt;010&gt;$</td>
</tr>
<tr>
<td>4</td>
<td>$&lt;\overline{110}&gt;$</td>
<td>$&lt;\overline{001}&gt;$</td>
<td>10</td>
<td>$&lt;\overline{10\overline{1}}&gt; &gt;$</td>
<td>$&lt;010&gt;$</td>
</tr>
<tr>
<td>5</td>
<td>$&lt;\overline{011}&gt;$</td>
<td>$&lt;100&gt;$</td>
<td>11</td>
<td>$&lt;\overline{1\overline{1}}&gt; &gt;$</td>
<td>$&lt;010&gt;$</td>
</tr>
<tr>
<td>6</td>
<td>$&lt;\overline{011}&gt;$</td>
<td>$&lt;100&gt;$</td>
<td>12</td>
<td>$&lt;\overline{1\overline{1}}&gt; &gt;$</td>
<td>$&lt;010&gt;$</td>
</tr>
</tbody>
</table>
Fig. 7.8: The 35 GHz EPR spectrum of Fe$^{3+}$ ions at $C_{\text{th}}$ site in SrO. The lines marked x are not associated with this Fe$^{3+}$ ion spectra, but were not studied in detail. The line D corresponds to a standard g-marker.
weak lines could not be assigned to $C_{1h}$ site but were not examined in detail. However, they did not arise from a hypothetical cubic, or the observed orthorhombic site of Fe$^{3+}$ ions in SrO.

7.2.5 *Ground state energy levels of Fe$^{3+}$ ions in the $C_{1h}$ site*

The energy levels for Fe$^{3+}$ ions in the $C_{1h}$ site as a function of the magnetic field strength for different orientations of the magnetic field is shown in Figures 7.9 - 7.12. The nominally $\Delta M = \pm 1$ transitions are shown by double arrowed lines.

7.2.6 *Angular variation of the spectrum*

The angular variation of the spectrum was studied with magnetic field in the (001)- and (110)-type planes, according to the procedure described in section 7.2.3.

A theoretical calculation of the angular variation of the spectra was performed using the best-fit spin-Hamiltonian parameters. Since the number of inequivalent sites was much higher than that for $C_{2v}$ site, a different approach was adopted here. In this method a single paramagnetic centre was considered and the magnetic field was rotated in different planes of the type (110) as listed in Table 7.4, to generate the entire spectrum from all possible magnitically inequivalent sites. As for the $C_{2v}$ site, the large number of resonance lines for an arbitrary direction of the magnetic field makes it useful to partition the discussion of the spectrum into separate groups of lines.

The angular variation of the spectrum resulting from systems 1, 2, 3 and 4 of Table 7.4 is shown in Figure 7.13. All of these systems are equivalent for a magnetic field aligned along a $<001>$-type direction,
Figs. 7.9 to 7.12: Ground state energy levels for Fe$^{3+}$ ions at the $C_{1h}$ site in SrO as a function of magnetic field strength. The magnetic field makes angles $(\theta, \phi)$ with the spin-Hamiltonian axes defined in the text, and the values are $(\theta, \phi) = (0,0), (90,90), (54.736,0)$ and $(90,30)$ for figures 7.9 through 7.12 respectively.
Fig. 7.13: The angular variation for part of the $C_{1h}$ site Fe$^{3+}$ ion 35 GHz EPR spectrum when the magnetic field is rotated in a (110) plane. The curves labelled a, b, c, d and e correspond to the transitions between $M_S = 3/2 \rightarrow 5/2$; $1/2 \rightarrow 3/2$; $-1/2 \rightarrow 1/2$; $-3/2 \rightarrow -1/2$ and $-5/2 \rightarrow -3/2$ states respectively. This angular variation corresponds to systems 1 to 4 of table 7.4.
resulting in a single set of 4-fold degenerate lines. For a magnetic field along a $<110>$-type direction, the pairs 1 & 3 and 2 & 4 are magnetically equivalent. The systems 2 and 4 remain degenerate for any intermediate orientation of the magnetic field between $<110>$- and $<001>$-type directions in the (110) plane but the doublet originating from systems 1 & 3 splits up due mainly to the term $B_2^1$ in the spin-Hamiltonian.

In Figure 7.14 the angular variation of the spectrum generated by systems 5 to 12 of Table 7.4 is shown. For $H$ along a $<001>$-type direction, all these sites are all equivalent, resulting in eightfold degenerate lines. As the magnetic field is rotated away from the $<001>$ direction, each of the eightfold degenerate lines splits up into 4 doublets corresponding to systems 5 & 9, 7 & 11, 6 & 12 and 8 & 10. These four doublets become degenerate in pairs for the $<110>$ direction, resulting in 2 sets of 4-fold degenerate lines. For $H \parallel <111>$ the singlets corresponding to systems 1 and 3 become degenerate with doublets arising from systems 5 & 9 and 8 & 10 respectively. Two sets of triply degenerate lines result. The unsplit doublet resulting from 2 and 4 becomes degenerate with doublets from systems 7 & 11 and 6 & 12 resulting in an additional set of 6-fold degenerate lines for this orientation of the magnetic field.

7.3 The EPR Spectrum of Cr$^{3+}$ Ions in SrO

Low$^2$ reported an EPR spectrum of octahedral symmetry for Cr$^{3+}$ ions in SrO. However, since a cubic site spectrum for Fe$^{3+}$ ions in SrO was not found here, it was considered worthwhile to check the site symmetry for Cr$^{3+}$ ions.

As-grown single crystals of SrO doped with chromium did not show any EPR spectrum which could be attributed to chromium, but for samples
resulting from systems 5 to 12 in table 7.4 are shown.

Fig. 7.14: The angular variation of the remainder of the EPR spectra for the C_{1h} Fe^{3+} site omitted from figure 7.13. The labelling scheme of the transitions is identical with that in figure 7.13. The lines resulting from systems 5 to 12 in table 7.4 are shown.
reduced at 1400°C an intense spectrum appeared similar to that reported by Low\(^2\), together with a much weaker spectrum. The site symmetry for this second spectrum was not ascertained but appeared to be lower than axial or orthorhombic and this spectrum was not studied in any further detail. The cubic site spectrum was characterised by the following spin-Hamiltonian parameters,

\[
g = 1.97(1); \quad A = 16.95(5) \times 10^{-4} \text{ cm}^{-1} \quad \text{at } 90 \text{ K},
\]

and

\[
g = 1.97(1); \quad A = 17.20(5) \times 10^{-4} \text{ cm}^{-1} \quad \text{at } 4.2 \text{ K},
\]

these compare well with the values of \(g = 1.9683(6), A = 17.2(5)\) \& \(g = 1.9686(5)\) and \(A = 17.3(4)\) measured at 77 K and 4.2 K respectively by Low\(^2\).

7.4.1 Heat treatments of Iron-doped SrO crystals

Oxidation treatments were effected by heating the iron-doped samples in air followed by quenching in an oil bath to room temperature. Two effects were observed. First, the divalent iron spectrum disappeared for oxidising treatments above 1100°C and second, the \(C_{1h}\) site Fe\(^{3+}\) ion spectrum appeared above about 1000°C. The intensity of \(C_{1h}\) site spectrum relative to the \(C_{2v}\) site spectrum was monitored after 3 hours treatment at various temperatures. The relative intensity of \(C_{1h}\) site was virtually zero for oxidation at 950°C, increased rapidly at about 1150°C and reached a saturation value at about 1350°C, as shown in Figure 7.15. In Figure 7.16 the relative intensity of the \(C_{1h}\) site as function of oxidation time for a constant temperature of 1350°C is shown. It was not possible to estimate the rate of conversion from the \(C_{2v}\) to the \(C_{1h}\) site because of the indeterminate contribution of divalent iron. Whilst it is possible to calculate
Fig. 7.15: The ratio of intensity of the $C_{1h}$ site to $C_{2v}$ site spectra for Fe$^{3+}$ ions in SrO as a function of oxidation temperature. Each treatment was of 3 hours duration.
Fig. 7.16: The ratio of intensity of the $C_{1h}$ site to $C_{2v}$ site spectra for Fe$^{3+}$ ions in SrO as functions of duration of oxidation treatment. The temperature was kept constant at 1350°C.
the relative numbers of spins giving rise to the \( C_{2v} \) and \( C_{1h} \) EPR spectra from the theoretical transition probabilities, it is impossible to do so for \( \text{Fe}^{2+} \) since the transition is induced by random strain.

Reduction treatments were effected by heating the sample in a vacuum of \(-10^{-5}\) torr for several hours. There was no change in the EPR spectrum of the as-grown samples up to 1400°C, the maximum attainable temperature. However a reduction of a sample previously oxidised at 1350°C eliminated the \( C_{1h} \) site.

### 7.4.2 Linebroadening of the \( C_{2v} \) and \( C_{1h} \) site \( \text{Fe}^{3+} \) EPR spectra

The linewidths for both sites of \( \text{Fe}^{3+} \) ions in SrO were measured as function of temperature, and are shown in Figure 7.17. There is a significant difference in the temperature range at which appreciable linebroadening starts for the two sites. It is unlikely that linebroadening is due to the same mechanism as for the divalent ions discussed in the preceding chapter since the first excited electronic state of \( \text{Fe}^{3+} \) is some 20,000 cm\(^{-1}\) higher than the \( ^6\text{S} \) ground state. Instead the broadening is assigned to an ionic relaxation which shortens the lifetime of the electronic states involved in the transition. Assuming a lorentzian line-shape of width \( \Delta H_0 \) at low temperatures, the broadened linewidth \( \Delta H(T) \) was fitted to

\[
\Delta H(T) = \Delta H_0 + \Delta H' \exp(-\Delta E/kT)
\]

where \( \Delta E \) represents an activation energy for the relaxation. The values of \( \Delta E \) determined by least-squares fitting\(^3\) are (0.14 ± 0.01) ev and (0.21 ± 0.01) for the \( C_{2v} \) and \( C_{1h} \) site respectively.
Fig. 7.17: Temperature dependence of the linewidth for EPR transitions of Fe$^{3+}$ ions at $C_{2v}$ and $C_{1h}$ sites in SrO. The solid lines represent best-fit curves based on equation 7.4.1.
7.5 Site Structures for Trivalent Ions in SrO

The EPR study of Fe\(^{3+}\) ions and Cr\(^{3+}\) ions in SrO suggests that the local site structures for these ions in SrO are quite different. The dominant cubic site spectrum for Cr\(^{3+}\) ions is interpreted as a simple substitutional site with remote charge compensation.

7.5.1 Site structure of Fe\(^{3+}\) ions at the site of orthorhombic symmetry.

There are two distinct types of model which can, in principle, explain the reduction of the local site symmetry of Fe\(^{3+}\) ions in SrO from cubic to orthorhombic. The first of these involves a neighbouring defect, such as a cation vacancy. Henderson et al.\(^6\) attributed Fe\(^{3+}\) sites of tetragonal symmetry in MgO to Fe\(^{3+}\) ions with next nearest neighbour cation vacancies at the (002) position, whilst Codling et al.\(^4\) explained the orthorhombic sites of Cr\(^{3+}\) and V\(^{2+}\) ions found in MgO by a nearest-neighbour cation vacancy at (110). In the case of MgO, the dominant trivalent ion spectrum arises from isolated octahedral sites and the spectra from ions coupled with nearby cation vacancies are much less intense. This pattern, of course, is not reproduced in the SrO:Fe\(^{3+}\) system, where a single, intense, orthorhombic spectrum is obtained in as-grown crystals. If the extra charge is (over) compensated by a cation vacancy, then only half of the Fe\(^{3+}\) ions in the crystal can have local charge compensation because of the requirements of charge neutrality; the other half must therefore be remotely charge compensated. The latter sites should give rise to a cubic Fe\(^{3+}\) spectrum, contrary to observation. Furthermore, if this model is correct, a finite population of sites where the Fe\(^{3+}\) ion is associated with a cation vacancy at \(<0,0,2>\) would be expected and an axial spectrum with tetragonal symmetry should have been observed, as in the case of MgO:Fe\(^{3+}\)\(^6\). No such spectrum was observed.
It is interesting to compare the spin-Hamiltonian parameters reported here for the orthorhombic SrO:Fe$^{3+}$ site with those reported by de Biasi et al.\textsuperscript{5} for an orthorhombic site in MgO:Fe$^{3+}$ which is probably due to a nearest neighbour cation vacancy. Transforming the coordinate system used in the present work to that used by de Biasi et al., the second-order parameters are,

\begin{align*}
(MgO:Fe^{3+})_{C_{2v}} & : B_0^0 = \pm 850 \times 10^{-4} \text{ cm}^{-1} \quad B_0^2 = \pm 230 \times 10^{-4} \text{ cm}^{-1} \\
(SrO:Fe^{3+})_{C_{2v}} & : B_0^0 = -653 \times 10^{-4} \text{ cm}^{-1} \quad B_0^2 = 1116 \times 10^{-4} \text{ cm}^{-1}.
\end{align*}

There is no clear relation between the two sets of parameters, which suggests that the site structures may be different.

It should, however, be pointed out that de Biasi et al.\textsuperscript{5} concluded that the orthorhombic site in MgO:Fe$^{3+}$ was not due to a single nearest neighbour cation vacancy. Their argument was based on a comparison of the components of the D tensor along the $<001>$-, $<110>$- and $<1\bar{1}0>$-type axes for the orthorhombic EPR spectra of Cr$^{3+}$ and V$^{2+}$ ions in MgO with those for Fe$^{3+}$ ions in MgO. Since the trends in the parameters did not follow those of some other host materials, de Biasi et al. proposed a model involving both a cation vacancy and a trapped hole on an oxygen ion. However, the arguments of de Biasi et al. for orthorhombic site do not appear convincing for the following reasons. Firstly, the comparison of Cr$^{3+}$, V$^{2+}$ and Fe$^{3+}$ spectra is not strictly valid since similar defects will not necessarily affect 3d$^3$ ions and 3d$^5$ ions in the same way. Quite different mechanisms are involved in the zero field splittings for these two types of ions. Second, the site structure proposed by de Biasi et al. for Fe$^{3+}$ ions in MgO has a symmetry ($C_{1h}$) lower than that observed. Finally, a trapped hole is itself paramagnetic, and should form an
exchange-coupled system with the Fe$^{3+}$ ion. In view of these arguments, the model proposed by de Biasi et al. appears to be inferior in many respects to the simple cation vacancy model. However, the arguments presented earlier show that there are difficulties in extending this simple model to the present case in SrO:Fe$^{3+}$.

An alternative model for the orthorhombic site of Fe$^{3+}$ ions in SrO does not involve any lattice defects, but assumes remote charge compensation. In this model an off-centre displacement of Fe$^{3+}$ ions along a $<110>$-type direction is assumed. This model can potentially explain the $C_{2v}$ site for Fe$^{3+}$ ions and the absence of any octahedral sites. In Section 7.4.2 an activation energy of 0.14 eV was estimated for the ionic relaxation of this site which is inconsistent with the motion of a cation vacancy, for which an activated energy of $\approx 2.76$ eV has been reported. A theoretical calculation of off-centre behaviour for Fe$^{3+}$ ions in SrO presented in the next chapter predicts relatively low values ($\leq 1$ eV) of activation energy for reorientation from one potential minima to another, and supports the off-centre assignment.

7.5.2 Site structure for Fe$^{3+}$ ions in the $C_{1h}$ site in SrO

From the angular variation study of the $C_{1h}$ site spectrum for Fe$^{3+}$ ions in SrO, it is evident that this site is predominantly trigonal in character, with a small perturbation of lower symmetry superimposed. The best-fit second-order S.H. parameters for this site were used to deduce the principal axis direction of the D tensor in the zx plane, and it was found that the z-axis of the D tensor is tilted by only 9° away from the $<111>$ direction towards the $<110>$ direction. The same tilt angle can be seen in the plots of the angular variation of the spectrum shown in Figure 7.13. The $C_{1h}$ site was found to be created only when the sample
was oxidised, and it is reasonable to assume that the $C_{1h}$ site results from a defect modification of the orthorhombic Fe$^{3+}$ site. Oxidation treatments are expected to produce mainly cation vacancies and/or an interstitial oxygen ion. Either of these defects, suitably situated relative to the Fe$^{3+}$ ion can, in principle, change the favoured direction of off-centre displacement of the Fe$^{3+}$ ion from $<110>$- to a $<111>$-type direction and result in a site of near-trigonal symmetry.

The most plausible models involving either a cation vacancy or an interstitial oxygen ion are shown in Figures 7.18 and 7.19.

The observed amount and direction of the tilt angle of the magnetic z-axis from the $<111>$ direction slightly favour the model involving an interstitial oxygen ion. However, the present state of experimental knowledge regarding the centre is not sufficient to choose between the models proposed here since both of them are equally capable of explaining the observed features of the spectrum.
Fig. 7.18: Possible site structure model for the $C_{1h}$ site of $Fe^{3+}$ ions in SrO involving a cation vacancy.
Fig. 7.19: Possible site structure model for the $C_{1h}$ site of $Fe^{3+}$ ions in SrO involving an interstitial oxygen ion. Other interstitial positions of the oxygen ion in the (110)-type plane are also possible.
References for Chapter VII

CHAPTER VIII

CALCULATION OF OFF-CENTRE DISPLACEMENTS AND LATTICE DISTORTIONS FOR $3d^n$ IONS IN ALKALINE EARTH OXIDES
8.1 Introduction

There is now a substantial body of experimental evidence which suggests that some transition metal ions in SrO undergo off-centre displacements. The EPR results presented in the preceding two chapters are compatible with this concept in the case of SrO:Fe\(^{2+}\), Ni\(^{2+}\) and Fe\(^{3+}\) whereas it appears that V\(^{2+}\), Mn\(^{2+}\) and Cr\(^{3+}\) remain on-centre. Manson and Edgar\(^1\) and Tolparov et al.\(^2\) have also suggested off-centre models to explain their results in SrO:Co\(^{2+}\) and SrO:Cu\(^{2+}\) respectively and this model has also been invoked in the case of BaO:Mn\(^{2+}\)\(^3\). In contrast, all of the transition metal ions appear to show on-centre behaviour in MgO and CaO.

It would obviously be useful to examine the possibility of off-centre displacements from a theoretical point of view, and such calculations are described in this chapter with an emphasis on the SrO system. In view of the inherent approximations in the model used, and in the uncertainties in the parameter values chosen to represent the various interactions, these calculations are not expected to give an accurate quantitative picture of lattice relaxation effects for each individual case. The major aim is to provide semi-quantitative information such as the preferred direction of off-centre displacement, if any, approximate distortion magnitudes and potential surfaces, and some idea of the relative magnitudes of the various mechanisms contributing to the effect.

8.2.1 Origin of Off-centre Displacement

In ionic crystals, the main source of cohesion is the electrostatic attraction between positively and negatively charged ions, but as two ions are brought close together their electronic charge distributions gradually overlap, giving rise to a repulsive interaction. The equilibrium separation between anions and cations is determined by the balance between these
electrostatic and repulsive forces.

An impurity ion substituting for a host cation will experience a different repulsive interaction with the ligands compared with the regular host cation. As a result, the anions surrounding the impurity ion are expected to be displaced from their regular lattice sites. If the impurity ion is located on the regular cation lattice site, the ligands will move radially towards or away from the impurity ion in a breathing mode contraction or expansion, without altering the local site symmetry. However, if the ionic radii of the impurity ion is considerably less than that of the host cation, the contraction of the ligands may be limited by their own overlap, and the impurity ion may move off-centre from the normal lattice site. Such off-centre displacements for small substitutional ions were first discussed by Mathew.

8.2.2 Lattice Models

In the simplest model of ionic crystals, commonly called the polarisable point ion (PPI) model, every ion is assumed to be a polarisable point-charge ion. In a perfect cubic lattice, the electric field acting on any ion sums to zero. However, a non-cubic distortion surrounding any ion results in a non-zero electric field which can polarize the ion. In the PPI model, effects due to the finite sizes of the ions are neglected except that the overlap repulsion between outer electron shells is generally taken to be of the Born-Mayer-Verway form, rather than the simple Born-Mayer potential. The PPI ion model has been used in the past for lattice distortion calculations in impurity doped alkali halides and alkaline earth oxides with reasonable success. However, the model may require some modifications in the latter application since the alkaline earth oxides are not as ionic as the alkali halides. Later it will be shown
that it is necessary to introduce an effective charge on the ions rather than the full ionic value of $2|e|$.

The other model which is more frequently used in lattice dynamics, rather than lattice statics is the shell model of ionic crystals, which will be discussed later in this chapter.

8.3 Application of the PPI Model to Off-Centre Lattice Distortion Calculations

In this application, the impurity ion is substituted for the divalent cation and the total energy relative to the perfect lattice is expressed as a function of the impurity displacement and the relaxation of the surrounding ions. The relaxation parameters which determine the static distortion are determined by minimizing the distorted lattice energy $\Delta E$ relative to the undistorted host lattice.

Following the alkali halide work, the three most plausible directions of displacement of an impurity ion were chosen for examination, namely, the $<111>$-, $<110>$- and $<100>$-type directions. An off-centre position along these directions will result in $C_{3v}$, $C_{2v}$ and $C_{4v}$ local site symmetries for the impurity ion respectively. A complete investigation of the potential surfaces for entirely arbitrary directions of the off-centre displacement was not considered to be feasible from the point of view of computer useage, but physical intuition suggests that potential minima along non-symmetry directions are improbable anyway.

The crystal lattice is divided into regions I and II. In region I all the ions, including the impurity ion, are allowed to relax and polarise. In the simplest case only the nearest neighbour ions are included in region I. This is because the nearest neighbour ions are by far the most important agents producing off-centre displacements of the magnetic ion. Region II
begins at the boundary of region I and includes the rest of the ions in the lattice which are not allowed to relax or to individually polarise. However, a collective polarisation is permitted by considering region II to be a polarisable continuum with polarisation induced by the relaxation of the ions in region I.

The relaxations of different ions in region I are symmetry related, and the number of relaxation parameters are restricted by the symmetry elements of the different point groups. Taking the cubic axes as the basis set, the different symmetry operations for $C_{4v}$, $C_{3v}$ and $C_{2v}$ point groups are given in Table 8.1. The coordinates of an arbitrary ion in the distorted lattice, located at

$$r' = (x, y, z) + (dx, dy, dz),$$

are related to those of other ions in the distorted lattice by the transformation matrices $R$, where $R$ is an operator of the appropriate point group. This group theoretical method is particularly useful when the relaxing ions extend beyond the nearest neighbour shell. Figures 8.1a - 8.1c show the nearest neighbour relaxation parameters for different directions of displacement of the impurity ion.

8.4 Interactions Involved in the Lattice Distortion

The total change in energy $\Delta E$ relative to the perfect lattice is divided into four parts. The monopolar electrostatic energy $\Delta E_c$ arises from the coulomb interaction between all point charges. The polarisation energy $\Delta E_p$ is the sum of contributions from dipole-dipole interaction, dipole-monopole interactions, and self-energy of the dipoles in region I, and from the polarisation of the continuum in region II. The repulsive energy $\Delta E_r$ is given by the sum of the nearest-neighbour repulsive inter-
Fig. 8.1: The relaxation modes for the impurity ion and the nearest neighbour oxygen ions, shown in figures 8.1 (a), (b) and (c) for the \(<100\>\), \(<110\>\) and \(<111\>\)-type off-centre displacements of the impurity ion respectively.
Form of the symmetry operations for the $C_{4v}$, $C_{3v}$ and $C_{2v}$ sub-groups of $O_h$ using the crystal cubic axes as the basis set. Matrices of all operators except the identity operator are given.

<table>
<thead>
<tr>
<th>$\langle 110 \rangle$ is the 2-fold axis of symmetry</th>
<th>$\langle 111 \rangle$ is the 3-fold axis of symmetry</th>
<th>$\langle 001 \rangle$ is the 4-fold axis of symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$</td>
<td>$C_{3v}$</td>
<td>$C_{4v}$</td>
</tr>
</tbody>
</table>
|\[
\begin{bmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
-1 & 0 & 0 \\
\end{bmatrix}
\] |\[
\begin{bmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1 \\
\end{bmatrix}
\] |\[
\begin{bmatrix}
0 & 0 & 1 \\
0 & 1 & 0 \\
1 & 0 & 0 \\
\end{bmatrix}
\] |
| $c_2$ | $c_3$ | $c_4$ |
| $\sigma_v$ | $\sigma_{11}$ | $\sigma_{11}$ |
| $\sigma_d$ | $\sigma_{12}$ | $\sigma_{12}$ |
| $\sigma_d^1$ | $\sigma_{13}$ | $\sigma_{13}$ |
| $\sigma_d^2$ | $\sigma_{14}$ | $\sigma_{14}$ |
actions. Finally, the crystal field stabilization energy of the impurity ion is included.

8.5 Change in the Monopolar Electrostatic Energy

The change in monopolar electrostatic energy relative to the perfect lattice may be calculated following the method developed by Quigley and Das. A short description of the derivation of the final expression is given below.

Quigley and Das superimposed upon the distorted lattice virtual charge pairs ±Q, located at the normal lattice sites left vacant by the relaxing ions. Half of the superimposed charges have the right sign to restore the perfect lattice, thus simplifying the calculations. The distorted lattice will now comprise of the following charges:

(A) Virtual charges Q located at regular lattice sites r, left vacant by the relaxing ion.

(B) Virtual charges -Q located at regular lattice sites r.

(C) Charges Q located at the distorted lattice sites r'.

All of these charges interact with each other, both within and between the groups A, B & C. The change in the electrostatic energy \( \Delta E_c \) relative to the perfect lattice is given by

\[
\Delta E_c = E_B + E_C + E_{AC} + E_{BC} + E_{AC}.
\]

\[
= \frac{1}{2} \sum_{J \neq K} \sum_{K} Q J Q K \left( \frac{1}{r_{JK}} + \frac{1}{r_{J'K'}} - \frac{1}{r_{J'K}} - \frac{1}{r_{JK'}} \right) + \sum_{J \neq K} Q J V_L(\xi_J, \theta_J, \phi_J), \quad (8.5.1)
\]
where \( r = |r - r'| \), and primes refer to distorted lattice positions. Here \( V_L \) represents the electrostatic potential at \( \Delta r = (\xi, \theta, \phi) \) in the vicinity of a regular lattice site due to a surrounding perfect lattice. This term can be expanded in spherical harmonics as,

\[
V_L(\xi J, \theta J, \phi J) = \sum_{\ell=1}^{\infty} \sum_{m=-\ell}^{\ell} a^m_{\ell} Y^m_{\ell}(\theta J, \phi J),
\]

(8.5.2)

where \( a^m_{\ell} = \frac{4\pi}{2\ell+1} \sum_{i} \frac{Q_i}{r_i^{\ell+1}} Y^m_{\ell}(\theta_i, \phi_i) \),

(8.5.3)

and the summation "i" is over the surrounding perfect lattice of charges \( Q_i \). In the final expression for \( V_L \), the \( \ell=0 \) term is omitted because it just gives the Madelung potential. The octahedral symmetry restricts the summation over \( \ell \) to \( \ell = 4 \& 6 \) and to higher even-order terms. \( V_L \) ordinarily constitutes less than 10% of the total electrostatic energy, and the \( \ell=6 \) term is in turn only 10% of the \( \ell=4 \) term. Higher order terms are therefore neglected, and the final expression in cartesian coordinates is given by,

\[
V_L(x, y, z) = \frac{35 \times 2e}{4 \times a_0^5} (-1.0275) \left[ x^4 + y^4 + z^4 - \frac{3}{5} x^6 \right] - \frac{21 \times 2e}{2 \times a_0^7} (-1.3339) \times \left\{ x^6 + y^6 + z^6 + \frac{15}{4} \left[ x^4 y^2 + x^2 y^4 + x^4 z^2 + x^2 z^4 + y^4 z^2 + y^2 z^4 \right] - \frac{15}{14} x^6 \right\}
\]

(8.5.4)

where \( a_0 \) is the normal inter-ionic distance, \( e \) is the proton charge, and for an anion site an overall negative sign has to be introduced on the right-hand side of equation (8.5.4).

8.6 The Change in the Polarisation Energy

8.6.1 Dipole-Monopole and Dipole-Dipole Interactions

The calculation of these interactions is also simplified by Quigley and Das's method of the superposition of virtual charge pairs at
vacant lattice sites.

The monopole-dipole polarisation energy, including dipole self-energy is given by,

$$ (\Delta E_p)_{\text{m.d}} = -\frac{1}{2} \sum_{J \in D} \mu_J \cdot E_J = -\frac{1}{2} \sum_{J \in D} \alpha_J |E_J|^2 , \quad (8.6.1) $$

where $E_J$, the electric field acting on $J$th ion with electronic polarisibility $\alpha_J$, is given by,

$$ E_J = \sum_{K \neq J} \frac{Q_K \cdot \mathcal{P}_{J'K'}}{|r_{J'K'}|^3} - \frac{Q_K \cdot \mathcal{P}_{J'K}}{|r_{J'K'}|^3} + \nabla_L(J') . \quad (8.6.2) $$

Once the electric field at the $J$th ion is determined, it is straightforward to calculate the dipole-dipole interaction energy as,

$$ (\Delta E_p)_{\text{d.d}} = \frac{1}{2} \sum_{J \neq K} \alpha_J \alpha_K \left\{ \frac{E_J \cdot E_K}{|r_{J'K'}|^3} - \frac{3(r_{J'K'} \cdot E_J)(r_{J'K'} \cdot E_K)}{|r_{J'K'}|^5} \right\} . \quad (8.6.3) $$

8.6.2 The polarisation energy of the continuum

When the ions are relaxed in region I the electric field generated by them will produce a polarisation of the continuum in region II. The principle of calculating this energy is that the polarised continuum in region II will produce an effective electric field at region I where the ions are displaced. This field will interact with the displaced ions giving rise to the interaction energy, called here the polarisation energy of the continuum. This contribution has not been considered in previous treatments. The crystal is considered as a dielectric medium with a hollow sphere of radius $'a'$ within which the ions are allowed to relax. Spherical polar coordinates are used with the origin at the centre of the sphere.

If the surrounding dielectric of relative permittivity $\varepsilon$ were
replaced by a vacuum, the potential due to the system of charges, within
the sphere would be given, for values of \( r \) larger than the distance of
any charge from the origin, by:

\[
\phi_0 = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} b^{(m)}_{\ell} \frac{1}{r^{\ell+1}} P^{(m)}(\cos \theta)e^{im\phi}
\]  

(8.6.4)

where the coefficients \( b^{(m)}_{\ell} \) can be calculated from the coordinates of the
charges.

In the actual case of a surrounding dielectric, let \( \phi_1 \) be the
potential in the dielectric and \( \phi_2 \) the potential inside the spherical
cavity for values of \( r \) larger than the distance of any charge from the
origin. In both regions there are no true or apparent charges and thus
Laplace's equation \( \nabla^2 \phi = 0 \) holds for \( \phi_1 \) and \( \phi_2 \). Therefore \( \phi_2 \) and \( \phi_1 \)
can be written as,

\[
\phi_2 = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left( A^{(m)}_{\ell} r^{\ell} + B^{(m)}_{\ell} \frac{1}{r^{\ell+1}} \right) P^{(m)}(\cos \theta)e^{im\phi}
\]  

(8.6.5)

and,

\[
\phi_1 = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left( C^{(m)}_{\ell} r^{\ell} + D^{(m)}_{\ell} \frac{1}{r^{\ell+1}} \right) P^{(m)}(\cos \theta)e^{im\phi}
\]  

(8.6.6)

the constants \( A^{(m)}_{\ell} \), \( B^{(m)}_{\ell} \) etc. can be evaluated by applying the following
boundary conditions,

(1) \( (\phi_1)_{r \to \infty} = 0 \) 

(8.6.7)

\[ \therefore C^{(m)}_{\ell} = 0 \text{ for all } \ell \text{ and } m. \]

(2) The potential must be continuous at the boundary. Hence,

\( (\phi_1)_{r=a} = (\phi_2)_{r=a}. \)

(3) The radial component of the electric displacement must be continuous
across the boundary. Hence,

\[
\varepsilon \left( \frac{\partial \phi_1}{\partial r} \right)_{r=a} = \left( \frac{\partial \phi_2}{\partial r} \right)_{r=a}
\]
The associated Legendre functions are mutually independent, and so from boundary conditions (2) and (3),

\[ D^{(m)}_\ell = A^{(m)}_\ell a^{2\ell+1} + B^{(m)}_\ell \]  

(8.6.8)

and

\[ -(\ell+1)e D^{(m)}_\ell = \ell A^{(m)}_\ell a^{2\ell+1} - (\ell+1)B^{(m)}_\ell . \]  

(8.6.9)

From equations (8.6.8) and (8.6.9),

\[ A^{(m)}_\ell = -\frac{(\varepsilon - 1)(\ell + 1)}{\ell + (\ell + 1)e} a^{-2\ell - 1} B^{(m)}_\ell \]  

(8.6.10)

\[ D^{(m)}_\ell = \frac{2\ell + 1}{\ell + (\ell + 1)e} B^{(m)}_\ell \]  

(8.6.11)

\[ \therefore \phi_2 = \sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \left[ -\frac{(\varepsilon - 1)(\ell + 1)}{\ell + (\ell + 1)e} a^{-2\ell - 1} B^{(m)}_\ell \right] \frac{r^\ell}{r^{\ell+1}} P_n^m(\cos \theta) e^{im\phi} . \]  

(8.6.12)

Finally, in the special case of \(\varepsilon = 1\), we have,

(4) \( (\phi_2)_{\varepsilon = 1} = \phi_0 \)

(5) \( (\phi_1)_{\varepsilon = 1} = \phi_0 \)

\[ \therefore B^{(m)}_\ell = b^{(m)}_\ell . \]  

(8.6.13)

Now introduce the potential \(\phi_2'\) as

\[ \phi_2' = \phi_2 - \phi_0 . \]  

(8.6.14)

Using equations (8.6.13), (8.6.12), (8.6.6) and noting that \(\varepsilon = 1\) for the region of \(\phi_0\),

\[ \phi_2' = -\sum_{\ell=0}^{\infty} \sum_{m=-\ell}^{\ell} \frac{(\varepsilon - 1)(\ell + 1)}{\ell + (\ell + 1)e} \frac{1}{a^{2\ell + 1}} b^{(m)}_\ell \frac{P_n^m(\cos \theta)}{r^\ell} e^{im\phi} . \]  

(8.6.15)

This is the potential of the "reaction field" inside the sphere, due to the polarisation of the dielectric continuum.

If there is a single charge \(Q_j\) on the z-axis at a distance \(S_j\) from the origin, then the potential will have axial symmetry about the
z-axis and the associated Legendre polynomials are reduced to Legendre polynomials. Also, \( \phi_0 \) can be expressed as,

\[
\phi_0 = \sum_{\ell=0}^{\infty} \frac{Q_\ell}{r^{\ell+1}} S_\ell^J P_\ell^J(\cos \theta),
\]

(8.6.16)

comparing the above equation with equation (8.6.4)

\[
b_\ell = Q_\ell S_\ell^J
\]

(8.6.17)

and therefore

\[
\phi_2' = - \sum_{\ell=0}^{\infty} \frac{(\ell-1)(\ell+1) + 1}{\ell+1} \frac{1}{2^{\ell+1}} Q_\ell S_\ell^J r^\ell P_\ell^J(\cos \theta).
\]

(8.6.18)

The principle of superposition can be applied to consider the effect of all the charges in region I. The potential \( \phi_2' \) at a point \( r \) along the z axis due to different charges in the cavity is,

\[
\phi_2' = \sum_{J=1}^{\text{all ions in region I}} \sum_{\ell=0}^{\infty} \frac{(1-\epsilon)(\ell+1)}{\ell+1} \frac{1}{2^{\ell+1}} Q_\ell S_\ell^J P_\ell^J(\cos \theta_J),
\]

(8.6.19)

where \( \theta_J \) is the angle between the z axis and the \( J \)th ion.

Keeping terms up to \( \ell=2 \) only,

\[
\phi_2' = \sum_{J=1}^{\text{all ions in region I}} \left\{ \frac{(1-\epsilon) Q_\ell}{\epsilon} + \frac{2(1-\epsilon)}{1+2\epsilon} \frac{r}{a^3} Q_\ell S_\ell^J P_1^J(\cos \theta_J) + \frac{3(1-\epsilon) r^2}{2+3\epsilon} a^5 Q_\ell S_\ell^J P_2^J(\cos \theta_J) \right\}.
\]

(8.6.20)

The first term is a constant and does not change as the ions relax inside the cavity. The 2nd and 3rd terms represent dipole and quadrupole moment contributions to the potential. Including only the dipole moment term, the change in energy due to the polarisation of the continuum is thus given by,

\[
(\Delta E_p)_{\text{cont.}} = \frac{1}{2} \sum_{J \neq D} \frac{2(1-\epsilon)}{1+2\epsilon} \frac{S_{J^K}}{a^3} Q_J Q_K P_1^J(\cos \theta_J^K).
\]

(8.6.21)
It can be easily shown that for a perfect cubic lattice, this contribution is zero as is expected.

8.7 The Change in the Repulsive Interaction Energy

The repulsive interaction potential between a pair of ions is taken to be of the Born-Mayer-Verway form. It is known from the work of Dienes et al. that a "polarisation catastrophe" occurs for the simple Born-Mayer potential, when the ions are much closer than the sum of their ionic radii. This is because the Born-Mayer potential is finite at zero separation of the ions, whilst the polarisation and coulomb energies become infinitely negative. The Born-Mayer-Verway potential has the following form,

\[
R_{BMV}(r) = \begin{cases} 
Ae^{-r/P} & \text{for } r \geq \Sigma r_0 \\
B + \frac{C}{r^2} & \text{for } r < \Sigma r_0 
\end{cases}
\] (8.7.1)

where A, P, B & C are constants and \( \Sigma r_0 \) is the sum of the ionic radii of the ions involved. The constants A, B, C and P are not independent but are related through the requirements of continuity at \( r = \Sigma r_0 \).

The change in repulsive energy is obtained by taking the difference between the pairwise sum of nearest-neighbour repulsive energies in the distorted lattice with an impurity ion, and the perfect host lattice. The summation involves the relaxed ions D and their nearest neighbours N.

The change in repulsive energy is given by,

\[
\Delta E_R = \sum_{J'eD} \sum_{K'eN} R_{BMV}(r_{J'K'}) - \sum_{JeD} \sum_{KeN} R_{BMV}(r_{JK}) .
\] (8.7.2)
8.8 Crystal Field Stabilization Energy of the Impurity Ion

Apart from the above interaction, there is an additional important contribution to the distortion energy for open shell impurity ions which has not been previously considered, the crystal field stabilization energy. The ground state electronic energy of a $3d^n$ ion is sensitive to the local environment through the electron-lattice coupling, or equivalently the crystal field. The exception to this is the $^6S$ ground term of Mn$^{2+}$ which has zero orbital angular momentum and consequently shows only very small splittings, typically less than 0.5 cm$^{-1}$, due to higher order mixing effects. On the other hand, the crystal field splitting of other $3d^n$ ions which do not have an S-state ground term can make substantial contributions to the total energy of the system. For example, for Fe$^{2+}$ ions in MgO, the $^5D$ ground term shows a large splitting of about 1 eV. In order to calculate this contribution, the following Hamiltonian was diagonalised,

$$ V_{CF} = \sum_{\ell m} B_{\ell m} O^{m}_{\ell} + \lambda L.S, \quad (8.8.1) $$

where $O^{m}_{\ell}$ are operator equivalents defined, for example, by Abragam & Bleaney$^{10}$. The $B_{\ell m}$ are crystal field parameters and $\lambda$ is the spin-orbit coupling parameter which is taken to be equal to the free ion value. The basis set is restricted to the ground term of the impurity ion, which permits the use of the operator equivalent form $L.S$ for the spin-orbit interaction. It should be noted that the parameters $B_{\ell m}$ are not identical to those used earlier in this thesis.

8.9 Estimation of the Interaction Parameters

The polarisibilities of the alkaline-earth ions and the oxygen ion were taken from the work of Tessman, Kahn & Schockley$^{11}$. Fraga et al.$^{12}$ calculated the free ion polarisibilities of the transition metal ions, and these values were used in the present calculation.
The repulsive interaction parameters can be determined from the compressibility and lattice constants of appropriate rocksalt hosts. The total energy per unit cell is given by,

$$U(r) = \frac{\alpha_p (Ze)^2}{r} + D e^{-r/\rho}$$  \hspace{1cm} (8.9.1)

where \(D = 6A\) and \(\alpha_p\) is the Madelung constant for a crystal with rocksalt structure. Hush and Pryce\(^\text{13}\) have shown that crystal field energies provide an additional important contribution to the cohesion of a crystal containing ions with unfilled d shells. This contribution is of the form \(-\frac{C_{\text{eff}}}{r^5}\) .

Clendenen and Drickamer\(^\text{14}\) have estimated the values of \(C_{\text{eff}}\) for transition metal oxides. This crystal field energy is quadratic in charge (see equation 1 of Hush & Pryce's paper\(^\text{13}\) ) so when reduced ionicity is considered a term of the form \(-\frac{C_{\text{eff}}}{r^5}\) (ionicity\(^2\)) has to be added to the total energy of the crystal per unit cell. The pressure \(p\) and compressibility \(\beta\) are related to the total energy per unit cell by:

$$p = -\frac{dU(r)}{dv}; \hspace{0.5cm} \frac{1}{\beta} = -\frac{dp}{dv}$$  \hspace{1cm} (8.9.2)

where \(v\) is the volume of the unit cell. For static equilibrium \(p=0\) and \(r=r_{eq}\), the equilibrium separation between nearest neighbour anions and cations. The compressibilities and lattice constants for transition metal oxides are given in Table 8.2. The parameters \(B\) and \(C\) in equation (8.7.1) can be determined from \(A\) and \(\rho\) by the requirement of continuity of the function (equation 8.7.1) and its derivative at \(r=r_0\), the sum of the ionic radii of the cation and the anions. The ionic radii of different ions involved in the calculation were taken from the tabulation by Shannon & Prewitt\(^\text{15}\).

The parameters \(B^m_L\) in equation (8.8.1) for the crystal field stabilization energy were calculated using the empirical superposition model of crystal fields developed by Newman (see Chapter III). The
### Table B.2

Parameters used in the off-centre/on-centre lattice distortion calculation for $3d^n$ ions in the alkaline earth oxides. No entry means that the relevant parameter was not necessary in the calculation or does not apply.

<table>
<thead>
<tr>
<th>Crystals</th>
<th>Compressibility $\beta$ in $10^{-3}$ (kbar)$^{-1}$</th>
<th>Lattice constant $A$ in $\bar{\AA}$</th>
<th>Repulsive force parameter $\rho$ in $10^{-10}$ erg $\bar{\AA}$</th>
<th>Polarisability of positive ion $a^+$ in $\bar{\AA}$</th>
<th>Polarisability of negative ion $a^-$ in $\bar{\AA}$</th>
<th>$\epsilon_0$</th>
<th>$C_{\text{eff.}}$ in $10^{-52}$ erg cm$^5$</th>
<th>$E_2(2.13\bar{\AA})$ in cm$^{-1}$</th>
<th>$E_4(2.13\bar{\AA})$ in cm$^{-1}$</th>
<th>Spin-orbit coupling constant $\lambda$ in cm$^{-1}$</th>
<th>Ionic radii of positive ion $X^+$ in $\bar{\AA}$</th>
<th>Ionic radii of negative ion $X^-$ in $\bar{\AA}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.75</td>
<td>4.2</td>
<td>3.504</td>
<td>.429</td>
<td>0.103</td>
<td>2.00</td>
<td>9.86</td>
<td>-740</td>
<td>26.55</td>
<td>-103</td>
<td>.720</td>
<td>1.4</td>
</tr>
<tr>
<td>CaO</td>
<td>0.87</td>
<td>4.81</td>
<td>9.645</td>
<td>.382</td>
<td>0.552</td>
<td>2.00</td>
<td>11.1</td>
<td>-132</td>
<td>-4.60</td>
<td>-178</td>
<td>1.000</td>
<td>1.4</td>
</tr>
<tr>
<td>SrO</td>
<td>1.73</td>
<td>5.12</td>
<td>2.761</td>
<td>.531</td>
<td>1.60</td>
<td>2.00</td>
<td>13.1</td>
<td>120</td>
<td>3.56</td>
<td>-324</td>
<td>1.160</td>
<td>1.4</td>
</tr>
<tr>
<td>BaO</td>
<td>2.283</td>
<td>5.5</td>
<td>2.471</td>
<td>.573</td>
<td>1.86</td>
<td>2.00</td>
<td>-43.2</td>
<td>154</td>
<td>5.42</td>
<td>91</td>
<td>1.360</td>
<td>1.4</td>
</tr>
<tr>
<td>MnO</td>
<td>0.70</td>
<td>4.446</td>
<td>8.117</td>
<td>.370</td>
<td>.46</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>0.65</td>
<td>4.304</td>
<td>9.483</td>
<td>.362</td>
<td>.44</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CoO</td>
<td>0.52</td>
<td>4.258</td>
<td>16.70</td>
<td>.324</td>
<td>.42</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NiO</td>
<td>0.50</td>
<td>4.177</td>
<td>9.61</td>
<td>.324</td>
<td>.39</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>.24</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>.26</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
intrinsic parameter $\tilde{B}_4$ for 3d$^n$ ions can be determined from their Dq values in cubic crystals. For example, for Fe$^{2+}$ ions, $\tilde{B}_4(2.13 \AA) = 26.55 \text{ cm}^{-1}$, based on the Dq value determined by Low and Weger$^{16}$ for MgO:Fe$^{2+}$. The power law exponent $t_4$ for the fourth order parameters was taken to be equal to 8 following Stedman$^{17}$. It is more difficult to estimate $\tilde{B}_2$ since crystal field fittings for divalent 3d$^n$ ions in oxide hosts in sites with symmetry lower than cubic have seldom been attempted, and there is little experimental or theoretical evidence pertaining to the variation of this parameter with distance. However, from a superposition model analysis of Fe$^{2+}$ ions in pyrope-almandine garnets, Newman et al.$^{18}$ have determined the second-order parameter $\tilde{A}_2 = 7060 \text{ cm}^{-1}$, assuming a cubic radial variation, and following these workers the value of $\tilde{B}_2$ was taken to be $-672 \text{ cm}^{-1}$ (2.20 $\AA$) and $t_2 = 3$. For other 3d$^n$ ions $t_2$ was also assumed to be 3 and the $\tilde{B}_2$ intrinsic parameters were estimated from the Fe$^{2+}$ ion value using scaling factors of $<r^2>$ for different 3d$^n$ ions introduced by Bleaney & Stevens$^{19}$.

8.10 Comments on the Parameters

The major problem in the use of any type of repulsive potential is that the fitting of the parameters is necessarily made at an equilibrium interionic distance $r_0$, and so a particular form is expected to be an accurate representation of these repulsive potentials only for a limited variation of $r$ about $r_0$. There is no experimentally verified expression for the repulsive potential over a wide range of values of the interionic distances. Some work has been done on these potentials for alkali halides, but very little on alkaline earth oxides. Tharmalingam and Lidiard$^{20}$ have used Born-Mayer-Verway potentials in their calculations on migration of vacancy pairs. The increased hardness at small separations introduced by this potential proved to agree better with experimental activation energies
for divacancy migration. Another problem, first pointed out by Wilson et al., is in the choice of interactions involving the defect. When a 3d ion, for example an Fe$^{2+}$ ion, substitutes for a Sr$^{2+}$ ion in SrO, the repulsive interaction parameter between Fe$^{2+}$ in the substituted site and the oxygen ligand is assumed to be the same as between Fe$^{2+}$ and O$^{2-}$ ions in FeO. This neglects the effects caused by the different environment of Fe$^{2+}$ ions in SrO, that is the Fe$^{2+}$ - O$^{2-}$ interaction is changed by the fact that the second nearest neighbours are Sr$^{2+}$ ions which are at a greater distance from the defect than the separation of Fe$^{2+}$ - Fe$^{2+}$ second nearest neighbour pairs in FeO.

A further problem is that in the PPI model, the polarisation energy is overestimated, particularly when the ions move very close together. The main contribution to the polarisibility of an ion is from the outer shell. However, when another ion penetrates into this outer shell, its polarising effects will be reduced, not enhanced as in the PPI model.

8.11 Modifications to the Calculations for Trivalent Impurity Ions

The extra positive charge for the central impurity ion will affect the changes in electrostatic and polarisation energies. However, the same formal expressions for $\Delta E_c$ and $\Delta E_p$ can be used provided the values of $Q_j$ etc. are changed appropriately.

For the repulsive interactions, there is a problem in the choice of repulsive parameters since the oxides of Fe$^{3+}$ or Cr$^{3+}$ do not have the rocksalt structure. For trivalent ions, in divalent hosts Das, Borg & Ray used the Mayer relation given by

$$A_2 = A_1 e^{(r_2-r_1)/\rho_1}$$

$$\rho_2 = \rho_1$$

(8.11.1)
where $A_2$ and $\rho_2$ are the Born-Mayer parameters for $\text{Cr}^{3+} - \text{O}^{2-}$ or $\text{Fe}^{3+} - \text{O}^{2-}$ and $A_1$ and $\rho_1$ denote the corresponding parameters for a divalent ion - $\text{O}^{2-}$ pair in which the divalent ion resembles the trivalent ion in such respects as ionic radius etc. The parameters $r_1$ and $r_2$ denote the equilibrium cation-anion distance in the reference pair and in the pair to be investigated. For trivalent ions, $r_2$ was taken to be equal to the sum of the ionic radii of the impurity ion and the $\text{O}^{2-}$ ion. For $\text{Cr}^{3+} - \text{O}^{2-}$ and $\text{Fe}^{3+} - \text{O}^{2-}$ the reference pair was taken to be $\text{Co}^{2+} - \text{O}^{2-}$.

A computer program was written to calculate the lattice distortion energy considering all the interactions described earlier. The lattice energy, relative to the perfect lattice, as a function of the relaxation parameters of the ions was minimized using a standard ANU Library subroutine "PRAXIS".

8.12 Results of the PPI Model Calculations

8.12.1 Divalent $3d^n$ ions in alkaline earth oxides

The methods of calculation described above were applied to $\text{Mn}^{2+}$, $\text{Fe}^{2+}$, $\text{Ni}^{2+}$ and $\text{Co}^{2+}$ ions in all the alkaline earth oxide series of hosts $\text{MgO}$, $\text{CaO}$, $\text{SrO}$ and $\text{BaO}$. A total of seven ions, the impurity ion and the six ligands were permitted to relax. In the following discussion the difference in energy between an off-centre distorted lattice configuration and that of an (octahedrally distorted) lattice with an $\text{Me}^{2+}$ ion at the regular lattice site will be referred to as the off-centre stabilization energy.

The first group of calculations were performed neglecting the crystal field stabilization energy and the polarisation energy of the continuum. Table 8.3 gives the displacements in Å and corresponding off-centre stabilization energies in eV for different directions of off-
Off-centre displacements and corresponding stabilization energies of divalent $3d^n$ ion alkaline earth oxides using a PPI model of 7 relaxing ions and 100% ionicity. The calculation does not include the crystal field stabilization energy or the polarization energy of the continuum. The off-centre displacements are in Å and energies in eV. A positive value of stabilization energy implies that off-centre displacement is favoured over an on-centre position. All ions were found to be on-centre in MgO.

<table>
<thead>
<tr>
<th>Hosts</th>
<th>Direction of off-centre displacement</th>
<th>Mn$^{2+}$</th>
<th>Fe$^{2+}$</th>
<th>Co$^{2+}$</th>
<th>Ni$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Displacement</td>
<td>Stabilization</td>
<td>Displacement</td>
<td>Stabilization</td>
</tr>
<tr>
<td></td>
<td></td>
<td>in Å</td>
<td>in eV</td>
<td>in Å</td>
<td>in eV</td>
</tr>
<tr>
<td>CaO</td>
<td>&lt;111&gt;</td>
<td>0.20</td>
<td>0.03</td>
<td>0.21</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>&lt;110&gt;</td>
<td>0.17</td>
<td>0.02</td>
<td>0.20</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>&lt;100&gt;</td>
<td>0.11</td>
<td>0.01</td>
<td>0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>SrO</td>
<td>&lt;111&gt;</td>
<td>0.40</td>
<td>0.24</td>
<td>0.44</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>&lt;110&gt;</td>
<td>0.32</td>
<td>0.17</td>
<td>0.36</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>&lt;100&gt;</td>
<td>0.23</td>
<td>0.09</td>
<td>0.25</td>
<td>0.16</td>
</tr>
<tr>
<td>BaO</td>
<td>&lt;111&gt;</td>
<td>0.67</td>
<td>0.91</td>
<td>0.69</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>&lt;110&gt;</td>
<td>0.54</td>
<td>0.65</td>
<td>0.55</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>&lt;100&gt;</td>
<td>0.38</td>
<td>0.34</td>
<td>0.39</td>
<td>0.53</td>
</tr>
</tbody>
</table>
centre displacements. In Figures 8.2a to 8.2d the different off-centre potential energies for Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ in SrO as a function of impurity displacements are shown.

Two general trends are evident from the Table 8.3. First, there is a correlation between off-centre instabilities and the difference in ionic radii of impurity and host cation as expected. Second the energetically favoured direction of off-centre displacement is generally along a \( <111> \) direction with \( <110> \) and \( <100> \) displacements having higher off-centre stabilization energies in that order.

The calculations were next refined by adding the crystal field stabilization energy, with the general result that the off-centre stabilization energies were all significantly increased, except of course for Mn$^{2+}$, illustrating the importance of this term. For MgO all the ions were predicted to be stable on-centre, but for CaO, SrO and BaO all ions were found to be susceptible to off-centre displacements, with the minimum energy configuration again corresponding to a \( <111> \)-type lattice distortion. For example, the values of \( <111> \) off-centre stabilization energies for Fe$^{2+}$ were 0.30, 0.95 and 1.36 eV in CaO, SrO and BaO respectively, compared with the values of 0.04, 0.24 and 0.91 eV for Mn$^{2+}$ ions. These two ions have approximately the same ionic radii, and so the crystal field term can qualitatively explain the greater susceptibility of Fe$^{2+}$ ions to off-centre displacements. It would be interesting to examine the effects of the crystal field stabilization energies in the case of SrO:$V^{2+}$ since $V^{2+}$ is on-centre in SrO, but unfortunately repulsive interaction data for this ion is not available. Whilst the calculations at this stage give a good indication of the relative trends in off-centre behaviour in the alkaline earth oxides, they suffer from the qualitative prediction of weak off-centre behaviour for some cases such as SrO:Mn$^{2+}$ and CaO:Mn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$, Co$^{2+}$ which have been experimentally observed to be on-centre.
Fig. 8.2: The $<111>$, $<110>$ and $<100>$ off-centre potential energy labelled A, B and C respectively. For SrO:Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$ and Ni$^{2+}$ the potential energy curves were obtained using a 7-ion relaxation model and 100% ionicity, but neglecting the crystal field stabilization energy and the polarization energy of the continuum.
The model was therefore further refined by adding the contribution of the polarised continuum in region II and a measure of reduced ionicity. The alkaline earth oxides are not as ionic in character as the alkali halides, and so the values of the point charges were reduced from $\pm 2|e|$ to $\pm 2K|e|$ where $K$ ranges from 0.8 to 1. A 7-ion relaxation model was again used, but the calculations were restricted to the present case of interest, SrO.

In Figures 8.3a to 8.3d the variations of the off-centre stabilization energies for different ions for different types of displacements are shown. The figures illustrate two general trends. First, the contribution of the polarised continuum acts to increase the off-centre stabilization energy. This is in accord with expectations since the continuum polarisation energy increases monotonically as the impurity ion is displaced away from the regular cation site towards the dielectric. Second, a reduced ionicity decreases the $<100>$ and $<111>$ off-centre stabilization energies, but some increase is evident in the $<110>$ energy. A reduction in the ionicity scales down all the electrostatic contribution by the same factor, but the repulsive interaction, although reduced, is not simply scaled in this way due to its exponential character. The general effect is to make it a shorter range potential, but it is difficult to make simple predictions about the consequences of this change since the relative energies of the on-centre and several off-centre configurations depend strongly on the numerous different interionic separations for each case.

The prediction of $<111>$ off-centre behaviour for SrO:Fe$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ evident in Figures 8.3b to 8.3d is in satisfactory agreement with experiment. The stabilization energies at 90% ionicity are in the range of 0.8 to 1.4 eV and the energy barriers to reorientation are ~0.5 to 0.8 eV. These figures also illustrate the importance of including the crystal field
Fig. 8.3: The <111>, <110> and <100> off-centre stabilization energies, labelled A, B, C respectively, for SrO:Mn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ as functions of ionicity using a 7-ion relaxation model. The calculation includes the crystal field stabilization energy and the polarization energy of the continuum. The results for Mn$^{2+}$, Fe$^{2+}$, Ni$^{2+}$ & Co$^{2+}$ are shown in figs. 8.3 (a), (b), (c) and (d) respectively.
Fig 8.3c

Off-centre stabilization energy in eV

SrO:Ni$^{2+}$

A

B

C

100%  96%  92%  88%  84%  80%

Ionicity

Fig 8.3d

Off-centre stabilization energy in eV

SrO:Co$^{2+}$

A

B

C

100%  96%  92%  88%  84%  80%

Ionicity
stabilization energy and the anisotropic effects it can produce, depending upon the ground term of the particular ion. The former effect can be clearly seen by contrasting the case of SrO:Mn$^{2+}$ with the others, particularly Fe$^{2+}$ which it closely matches in ionic radii, and the second effect is best seen by the curves for SrO:Ni$^{2+}$ for which a $<100>$ distortion is preferred over a $<110>$ distortion for reduced ionicities less than ~97%. However, despite the general success of the calculation, SrO:Mn$^{2+}$ is still quantitatively predicted to be an off-centre system, contrary to observation.

8.12.2 Trivalent ions in alkaline earth oxides

In the first calculation, which excluded crystal field and continuum polarisation effects, both Cr$^{3+}$ and Fe$^{3+}$ ions were predicted to be strongly on-centre in MgO and CaO. This is expected, since the stronger coulomb attraction due to the extra positive charge on the trivalent ions which will pull the oxygen ligands towards the impurity ion and form a strongly bound on-centre system.

In the case of SrO, and including the crystal field stabilization energy for Cr$^{3+}$, Cr$^{3+}$ ions were still predicted to be strongly on-centre but Fe$^{3+}$ ions were off-centre along a $<110>$-type direction with a stabilization energy of 0.07 eV. However with reduced ionicity (98%) both Fe$^{3+}$ and Co$^{3+}$ ions were predicted to be on-centre. But, with the introduction of the polarization energy from the continuum, both of the trivalent ions were predicted to be off-centre along a $<111>$-type direction, contrary to observation.

Table 8.4 gives the result of the calculation for the two trivalent ions for the $<110>$ and $<111>$ directions of displacement using 100% ionicity and a 7-ion relaxation model, both with and without the
Table 8.4

<111> and <110> off-centre stabilization energies for Fe\(^{3+}\) and Cr\(^{3+}\) ions in SrO, using a PPI model of seven relaxing ions and 100% ionicity. The energies are in eV.

<table>
<thead>
<tr>
<th>Ion</th>
<th>&lt;111&gt; Without crystal field stab. energy</th>
<th>&lt;111&gt; With crystal field stab. energy</th>
<th>&lt;110&gt; Without crystal field stab. energy</th>
<th>&lt;110&gt; With crystal field stab. energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe(^{3+})</td>
<td>6.84</td>
<td>-</td>
<td>4.33</td>
<td>-</td>
</tr>
<tr>
<td>Cr(^{3+})</td>
<td>9.63</td>
<td>6.79</td>
<td>4.07</td>
<td>3.64</td>
</tr>
</tbody>
</table>

Table 8.5

Simple shell model parameters for the Strontium Oxide host\(^ {22} \). \(e\) is the electronic charge and \(v_0\) is the volume of the primitive unit cell.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C_{11}) in (10^{12}) dyne/cm(^2)</td>
<td>2.05</td>
</tr>
<tr>
<td>(C_{12}) in (10^{12}) dyne/cm(^2)</td>
<td>0.64</td>
</tr>
<tr>
<td>(C_{44}) in (10^{12}) dyne/cm(^2)</td>
<td>0.50</td>
</tr>
<tr>
<td>Core-shell spring constant (K_{Sr}) for Sr(^{2+}) ion in units of (e^2/v_0)</td>
<td>325.10</td>
</tr>
<tr>
<td>Core-shell spring constant (K_0) for O(^{2-}) ion in units of (e^2/v_0)</td>
<td>71.78</td>
</tr>
<tr>
<td>Shell charge on Sr(^{2+}) ion in units of (e)</td>
<td>-1.417</td>
</tr>
<tr>
<td>Shell charge on O(^{2-}) ion in units of (e)</td>
<td>-2.117</td>
</tr>
<tr>
<td>Ionic charge (Z) in (e)</td>
<td>1.78</td>
</tr>
</tbody>
</table>
crystal field contribution for Cr$^{3+}$ ion. The very large predicted stabilization energies are physically unrealistic and are probably due to the combined effects of the necessarily indirect estimation of the repulsive parameters and to an overestimate of the polarisation energy induced by the extra charge on the trivalent ion. However, whilst the results cannot be regarded with any confidence, it is interesting to note that the crystal field energy for Cr$^{3+}$ reduces the off-centre stabilization energy. This may in part account for V$^{2+}$, which is isomorphic with Cr$^{3+}$, being on-centre in SrO.

8.13 Shell Model Calculation of Lattice Distortion

The PPI model calculations described earlier gave a reasonable understanding of the basic mechanisms contributing to off-centre instabilities in transition metal doped alkaline earth oxides. However, the PPI model has been supplanted in recent years by more sophisticated models of ionic interactions, such as the various shell models, which give a better description of the lattice dynamics and associated phenomena for ionic crystals$^8,22$. It is therefore of interest to see if the predictions of the PPI model are still valid when a simple shell model of the interaction is used.

8.14 The Simple Shell Model of Ionic Crystals

In the simple shell model, it is assumed that an ion consists of a massless rigid spherical shell representing the outer electrons and a heavy core consisting of the nucleus and tightly bound inner electrons. In an electric field the shell moves bodily with respect to the core, creating a net ionic polarisation. The polarisibility is made finite by a harmonic restoring force of spring constant k which acts between the core and the shell centres. In a crystal, the overlap dependent repulsive
forces between ions are assumed to act mainly between the shells.

The simple shell model is restricted to nearest-neighbour shell-shell interactions, and contains only six parameters: the shell-shell force constants between nearest neighbour A and ρ, the shell and core charges Y and X = Z-Y, the core-shell force constant k, and the total core mass M. These parameters can be determined from macroscopic properties of the crystal, viz. the elastic coefficients $C_{11}$, $C_{12}$, $C_{44}$, the dielectric constants $\varepsilon_0$, $\varepsilon_\infty$, the phonon frequencies $\omega_L$, $\omega_T$ and the lattice constant $a_0$. However in practice these model parameters are usually obtained by fitting the phonon-dispersion curves of crystal.

In the presence of an electric field, the shell and core centres will be displaced relative to each other as shown in the following figure.

![Diagram](image)

In the polarised state, the force between the shell and the core is described by the potential,

$$ V = \frac{1}{2} k (\xi - \xi_c)^2 $$

(8.14.1)

and the force between the ions which is assumed to act between shells
only is given by

\[ V_{ij} = f(|\vec{r}_{si} - \vec{r}_{sj}|) \]  

(8.14.2)

where \( \vec{r}_{si} \) and \( \vec{r}_{sj} \) are the position of the shell centres for ions i and j. The electrostatic potential generated by the core shell system is equivalent to that of a point charge \( Z \) and a dipole moment \( \mu \) whose magnitude depends upon the choice of origin. The shell-centred dipole moment is given by

\[ \mu_s = X(\vec{r}_c - \vec{r}_s) \]  

(8.14.3)

and the core-centred dipole moment is,

\[ \mu_c = Y(\vec{r}_s - \vec{r}_c) \]  

(8.14.4)

In a static electric field the forces on the core are given by

\[ XE_c + k(\vec{r}_s - \vec{r}_c) = 0, \]  

(8.14.5)

where \( E_c \) is the electric field at the core. From equations (8.14.5), (8.14.3) and (8.14.4) it follows that

\[ (a_{core})_{Stat} = -\frac{XY}{k} \quad \text{and} \quad (a_{shell})_{Stat} = \frac{X^2}{k}, \]  

(8.14.6)

provided \( E_s = E_c \).

In the presence of an electrostatic potential \( V \), the electrostatic energy of the shell model ion (excluding the dipole self energy) is given by,

\[ E = XV(\vec{r}_c) + YV(\vec{r}_s + \Delta \vec{r}) \]

where \( \Delta \vec{r} = \vec{r}_s - \vec{r}_c \) and \( \vec{r}_s, \vec{r}_c \) are the position vectors of shell centre and
the core. Expanding $V(\xi - \Delta \xi)$ in a Taylor's series, and retaining terms up to second order, it can be shown that,

$$E = ZV(\xi_s) + \nabla V \mu_s + \frac{1}{2X} \nabla(\nabla V \mu_s) \mu_s.$$  

(8.14.7)

The shell model energy is thus equivalent in first order to that obtained on the PPI model with a charge $Z$ at $\xi_s$ and a point dipole $\mu_s$ at $\xi_s$.

The dipole self energy is given by,

$$\langle E_{\text{dip}} \rangle_{\text{Self}} = \frac{1}{2} k (\xi_c - \xi_s)^2,$$

$$= \frac{1}{2} \frac{X^2}{k} E_c^2,$$

$$= \frac{1}{2} \frac{X^2}{k} E_s^2 = \frac{1}{2} \alpha_s E_s^2.$$  

(8.14.8)

The polarisation energy of the continuum remains unchanged if one assumes that the charges $Z$ are located at the centre of the shell.

Finally the repulsive energy, which is assumed to act between shells, remains unchanged for a shell-centred calculation. Thus the same formal expressions for different interactions derived for the PPI model can be used for the simple shell model provided that the various interactions are taken between shell centres and shell model polarisabilities are used.

8.15 Results of Shell Model Calculations

8.15.1 Divalent ions in SrO

The experience gained with the PPI model showed that the details of off-centre instabilities are relatively sensitive to the details of the model, in particular the choice of parameter values, and in this situation,
the calculations cannot hope to give accurate quantitative results for each individual system, but should be capable of demonstrating the trends from one system to another. In this spirit, the shell model calculations described here were performed for a hypothetical ion with the characteristics of the transition metal ion series, varying such parameters as the ionic radius and the number of lattice ions permitted to relax. These calculations cannot incorporate crystal field effects, since these depend upon the particular electronic configuration considered. The hypothetical ion will hereafter be referred to as the test ion.

The shell model parameters describing the Sr$^{2+}$, O$^{2-}$ ions and their interactions were the values deduced by Reider et al. from their least squares fitting to phonon dispersion data for SrO. The repulsive interaction parameters for the impurity ion - O$^{2-}$ pair were determined from the bulk modulus and the lattice parameter of the crystal. The bulk modulus B is given by

$$B = \frac{n g^2}{18 r_0^4} \left( \frac{r_n}{\rho} - 2 \right)$$  \hspace{1cm} (8.15.1)$$

where $r_0$ is the nearest neighbour distance. The variation of B with $r_0$ for transition metal oxides has the approximate form

$$B = \frac{n g^2}{18 r_0^4} \exp \left( \frac{r_n}{k_1} - k_2 \right)$$  \hspace{1cm} (8.15.2)$$

where $k_1$ and $k_2$ are empirical constants. The above function was fitted to the experimental values for the bulk moduli of MnO, NiO, CaO and FeO$^{14}$ in the least squares sense. The values of $k_1$ and $k_2$ thus obtained were then used to generate the bulk modulus of the test ion oxide as a function of the cation. The lattice constant was taken as twice the sum of the ionic radii of the test ion and the O$^{2-}$ ion. Equations (8.15.1) and (8.15.2) may then be used to determine the repulsive interaction parameters from the bulk modulus and equilibrium lattice spacings.
A series of calculations were performed by varying the polarisability, ionic charge and the ionic radii of this test ion. In order to economise on computer usage, the calculations here were restricted to \(<111>\)-type off-centre distortions. In the first set of calculations the off-centre stabilization energy was determined as a function of test ion radius for 100% ionicity and a test ion polarisability appropriate to Mn\(^{2+}\). The results, plotted in Figure 8.4, show the expected trend with ionic radius. The off-centre stabilization energy falls below about \(\approx 0.05\) eV for ionic radii greater than \(\approx 0.97\) Å. Static off-centre effects may not be observed for stabilization energies less than \(\approx 0.05\) eV because of motional averaging effects, and so this figure represents a somewhat arbitrary boundary between on-centre and off-centre behaviour. In the next stage, the effect of reducing the ionicities by up to 10% of the nominal values was investigated and these results are also plotted in Figure 8.4. In the case of 90% ionicity, the transition point for off-centre behaviour is predicted to be at \(\approx 0.83\) Å, in better agreement with experiment.

In a final set of numerical experiments, the model was extended to include 26 neighbouring ions, and the off-centre stabilization energies were determined as a function of ionic radius for 100%, 94% and 90% ionicities as shown in Figure 8.5. The general effect is to lower the off-centre stabilization energy and to reduce the limiting ionic radius at which off-centre effects are expected. For example, for 100% and 90% ionicities, the ionic radius at which the stabilization energy falls to 0.05 eV are 0.91 Å and 0.79 Å respectively. The latter value is consistent with Mn\(^{2+}\) ion remaining on-centre in SrO, whilst the smaller ions Fe\(^{2+}\), Co\(^{2+}\) and Ni\(^{2+}\) would be expected to move off-centre, in accordance with experiment.
Fig. 8.4: Stabilization energy for $<111>$ -type off-centre displacements as a function of ionic radii for a divalent impurity ion using a 7-ion relaxation model. Simple shell model polarisabilities are assumed for host cation and anion, whilst the polarisability of the test ion was taken to be equal to that of a Mn$^{2+}$ ion.
Fig. 8.5: Similar plots as in figure 8.4, but using a 27-ion relaxation model.
In summary, the studies using a simple shell model have shown that the transition between off-centre/on-centre behaviour for $3d^n$ ions in SrO occurs for an ionic radius which is less than that of some of the larger ions of the group, providing a sufficient number of relaxing ions and the effects of reduced ionicity are taken into account. This prediction is a quantitative improvement over the PPI model described earlier which predicted the relatively large Mn$^{2+}$ ion to move off-centre.

8.15.2 Trivalent ions in SrO

In view of the failure of the PPI model to account for the observed on-centre and $<110>$ off-centre behaviour for Cr$^{3+}$ and Fe$^{3+}$ ions respectively, it was decided to attempt a calculation for these systems using the simple shell model, but including the crystal field contribution for Cr$^{3+}$ ions. The major difference relative to the PPI model is that induced dipole on the oxygen ligands are reduced through the use of the shell model polarizabilities. The results of the calculation for a 7-ion relaxation model, shown in Table 8.6, are in surprisingly good agreement with experiment. Again it was found by numerical experiment that the difference between the cases of Cr$^{3+}$ and Fe$^{3+}$ ions lay in the crystal field contribution, forcing the Cr$^{3+}$ ion back on-centre.
Off-centre displacements and corresponding stabilization energies for Fe$^{3+}$ and Cr$^{3+}$ ions in SrO, using a simple shell model. Displacements are in ångström units and energies are in eV. A positive value of off-centre stabilization energy means the off-centre configuration is favoured over an on-centre position.

<table>
<thead>
<tr>
<th></th>
<th>Fe$^{3+}$</th>
<th>Cr$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;111&gt;</td>
<td>&lt;110&gt;</td>
</tr>
<tr>
<td>Off-centre stabilization energy</td>
<td>.08 eV</td>
<td>.68 eV</td>
</tr>
<tr>
<td>Off-centre displacement</td>
<td>.18 Å</td>
<td>.22 Å</td>
</tr>
<tr>
<td>Off-centre stabilization energy</td>
<td>&lt; .01 eV</td>
<td>.01 eV</td>
</tr>
<tr>
<td>Off-centre displacement</td>
<td>&lt; .01 Å</td>
<td>~ .01 Å</td>
</tr>
</tbody>
</table>
References on Chapter VIII

CHAPTER IX

CONCLUSIONS
9.1 Transition Metal Ions in MgTiO$_3$

EPR spectra for Co$^{2+}$, Ni$^{2+}$, Mn$^{2+}$, Mn$^{4+}$, Fe$^{3+}$ and Cr$^{3+}$ ions in MgTiO$_3$ host crystals have been investigated and analysed. Spectra characteristics of a single site were observed for all of the divalent impurity ions and for Mn$^{4+}$ ions, whilst for trivalent ions EPR spectra from two sites were observed. All of the observed spectra exhibited trigonal symmetry which is consistent with the ions occupying host cation sites, that is Mg$^{2+}$ or Ti$^{4+}$ ion sites, or interstitial spaces. There is no reason to suppose that the latter occupation scheme is anomalously favoured in MgTiO$_3$, and in general the Madelung energy favours substitution for host cations. Hence the simple substitutional model is adopted here. The trigonal symmetry observed for all sites requires that neighbouring lattice defects, if any, must lie along the three-fold axis.

Since only single site EPR spectra were observed for Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ ions, and because CoTiO$_3$, NiTiO$_3$ and MnTiO$_3$ lattices exist in nature and are iso-structural with MgTiO$_3$, it is concluded that Co$^{2+}$, Ni$^{2+}$ and Mn$^{2+}$ ions substitute for Mg$^{2+}$ ions in MgTiO$_3$.

The angular variation of the two Fe$^{3+}$ ion spectra in MgTiO$_3$ clearly demonstrates that they result from the two distinct cation sites in MgTiO$_3$, rather than from different perturbations on Fe$^{3+}$ ions occupying either the Ti$^{4+}$ or the Mg$^{2+}$ site. The comparison of the polar plot of the angular variation of the Fe$^{3+}$ ion spectra with that for Mn$^{2+}$ ions at the Mg$^{2+}$ ion site, shows that Fe$^{3+}$ ions at site #1 occupy the Mg$^{2+}$ site, and those at site #2 occupy the Ti$^{4+}$ site. It is more difficult to arrive at definite conclusions regarding the possible presence of neighbouring lattice defects. However, on the basis of oxidation and reduction treatments, the concentration dependence of the relative intensities of the two spectra, and the close similarity between the two sites as evident from both EPR
and Mössbauer studies, the following site structure models are proposed for Fe\(^{3+}\) ions in MgTiO\(_3\):

Site #1 \([\text{Fe}^{3+}]_{\text{Mg}^{2+}} - [\text{Mg}^{2+}]_{\text{Ti}^{4+}}\),

Site #2 \([\text{Mg}^{2+}]_{\text{Mg}^{2+}} - [\text{Fe}^{3+}]_{\text{Ti}^{4+}}\).

However further work is required to substantiate or refute these models. For example, a detailed Mössbauer study of oxidation and reduction effects on the two sites would be useful since this technique is sensitive to all oxidation states of iron, unlike EPR. ENDOR measurements might also be useful if the weak dipolar coupling from adjacent Mg\(^{2+}\) or Ti\(^{4+}\) nuclei could be resolved.

The results of oxidation and reduction treatments, and also the concentration dependence of the two Cr\(^{3+}\) ion spectra did not show any clear trends which could be used as the basis for proposing site models for Cr\(^{3+}\) ions in MgTiO\(_3\). However, the two spectra do show zero-field splittings in the \(^4A_2\) ground state of opposite sign and quite different magnitudes, and so a crystal field calculation, based on the models of Stedman\(^1\) and Newman\(^2\) was performed in order to estimate the theoretical splittings for Cr\(^{3+}\) ions at both cation sites in MgTiO\(_3\). The calculated values are in close agreement with the observed values when spectrum #1 is associated with Cr\(^{3+}\) ions at the Mg\(^{2+}\) site and spectrum #2 is associated with Cr\(^{3+}\) ions at the Ti\(^{4+}\) site. In contrast with the case of the #1 Fe\(^{3+}\) site, no local defect is required, and indeed the inclusion of such a defect destroys the agreement between theory and experiment.

From the similarity of the Mn\(^{4+}\) ion spectra with that for the Cr\(^{3+}\) ions at site #1 (the Mg\(^{2+}\) site), it is concluded that the former spectra
is due to Mn$^{4+}$ ions at the Mg$^{2+}$ ion site. A parallel calculation of the zero-field splitting for the $^4A_2$ ground state of Mn$^{4+}$ ions at the Mg$^{2+}$ ion site was performed and the result was in good agreement with experiment. This assignment of Mn$^{4+}$ ions to the Mg$^{2+}$ site is at first surprising, since Mn$^{4+}$ ions would, by the simplest arguments, be expected to occupy the Ti$^{4+}$ site. It is possible that a small concentration of such ions does exist. However, in the associated EPR spectrum, the resonance lines would have approximately the same width as those in the site #2 Cr$^{3+}$ spectrum, and this, together with the low concentration, could prevent the recognition of the spectrum in a region where there are many other resonance lines.

Finally, the observation of only single sites for Cr$^{3+}$ and Mn$^{4+}$ ions in MgTiO$_3$ in the fluorescence studies of Louat et al. $^3$ can be potentially explained by the relative strengths of the cubic components of the crystal fields at the Mg$^{2+}$ and Ti$^{4+}$ ion sites. Optical double resonance experiments, which can correlate EPR and optical spectra would be one interesting method of testing the association predicted here between the site #2 Cr$^{3+}$ EPR spectra and the optical fluorescence spectra in MgTiO$_3$:Cr$^{3+}$.

9.2 Transition Metal Ions in SrO

Trigonally symmetric sites were observed in this work for Fe$^{2+}$ and Ni$^{2+}$ ions in SrO, in contrast to the octahedral sites for Mn$^{2+}$ $^4$ and V$^{2+}$ $^5$ ions in the same host which were reported previously and confirmed in the present work. The trigonal sites observed for Fe$^{2+}$ and Ni$^{2+}$ ions, and the absence of any octahedral sites for these ions in SrO, are difficult to explain by any model other than a $<111>$-type off-centre displacement for the impurity ion, similar to that used to explain the trigonal spectrum for Mn$^{2+}$ ions in BaO$^6$.

This interpretation is to some extent in conflict with the work
of Sochava et al.\textsuperscript{7} who claim to have identified a \textless 110 \textgreater  off-centre site in SrO:Co\textsuperscript{2+}. The co-existence of this spectrum of \textit{C}\textsubscript{2\textnu} symmetry with the \textit{C}\textsubscript{3\textnu} spectrum in both SrO:Co\textsuperscript{2+} and SrO:Ni\textsuperscript{2+} has been confirmed by an optical investigation in this laboratory\textsuperscript{8}. However, it was found that the intensity ratio of the \textit{C}\textsubscript{2\textnu} sites to the \textit{C}\textsubscript{3\textnu} sites for both Ni\textsuperscript{2+} and Co\textsuperscript{2+} ions was considerably higher in oxidised samples, which suggests that the sites are due to the association of a defect, possibly a cation vacancy or an oxygen interstitial, with the transition metal ion.

For SrO:Cr\textsuperscript{3+}, previous observations of octahedral sites\textsuperscript{9} were confirmed in the present work. But for Fe\textsuperscript{3+} ions in the same host, a single intense orthorhombic site spectrum was observed in the as-grown single crystals. This \textit{C}\textsubscript{2\textnu} site for Fe\textsuperscript{3+} ions could further be reduced to a new \textit{C}_{1\text{h}} site by oxidation treatments. Thus the pattern of a dominant octahedral and weaker tetragonal and rhombic site, as observed in the MgO:Fe\textsuperscript{3+} system\textsuperscript{10}, was not reproduced for Fe\textsuperscript{3+} ions in SrO. In addition, there is no relation between the spin-Hamiltonian parameters for Fe\textsuperscript{3+} ions in \textit{C}\textsubscript{2\textnu} sites in MgO\textsuperscript{11} and SrO. It is concluded that the site structure for Fe\textsuperscript{3+} ions in SrO is different to that in MgO and that the present results are best explained by a \textless 110 \textgreater-type off-centre displacement model. The \textit{C}_{1\text{h}} site is thought to be a modification of the \textit{C}\textsubscript{2\textnu} site due to the association of a defect, for example, a cation vacancy or an oxygen interstitial suitably situated to create the pseudo-trigonal \textit{C}_{1\text{h}} site. The different off-centre models for the divalent and trivalent transition metal ions in SrO proposed here have been tested by static lattice distortion calculations using polarisable point ion (PPI) and simple shell models of the ionic crystals. For divalent ions in SrO, the calculations predicted \textless 111 \textgreater-type off-centre displacements for the smaller ions. The differential effect with regard to the on-centre/off-
centre behaviour of Mn$^{2+}$ ions versus Ni$^{2+}$, Co$^{2+}$ and Fe$^{2+}$ ions is attributed partially to the difference in ionic radii of these ions, but mainly to the contribution from the crystal field stabilization energy for the latter ions. The calculation also illustrated the need to take into account a reduction in the ionicity of the alkaline earth oxides and to permit a sufficiently large number of ions to relax. In the absence of these latter considerations, Mn$^{2+}$ ions are predicted to be off-centre, contrary to experimental observation.

For trivalent ions the simple shell model calculations gave a more plausible result than the PPI model. The latter model appears to grossly overestimate the polarisation energies due to the extra charge of the trivalent ion. In contrast, the simple shell model predicted a $<110>$-type off-centre motion for Fe$^{3+}$ ions, and an on-centre position for Cr$^{3+}$ ions in SrO. The prediction of an on-centre position for Cr$^{3+}$ ions is mainly due to the crystal field stabilization energy acting in opposition to any off-centre displacement.

This thesis has presented strong evidence for off-centre displacements in strontium oxide doped with transition metal ions, but further experiments would be useful to probe the potential surfaces involved in the effect. In principle, dielectric loss, ionic thermo-current, electric field or stress induced dipole re-orientation experiments could provide useful information of this nature. An AC electric field modulation EPR experiment was in fact attempted in the latter stage of the present research for both Ni$^{2+}$ and Fe$^{2+}$ ions in SrO. However, the experiment was unsuccessful due to a very poor signal-to-noise ratio which is attributed to the particular electrode structure and geometry used. Significant improvements could be obtained by using evaporated silver electrodes thinner than or close to the skin depth for microwave radiation, so that the rf field can penetrate through the electrode into the sample.
References for Chapter IX

8. I.H. Brunskill, personal communication.
Electron paramagnetic resonance spectra of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions in $\text{SrO}$: Evidence for off-centre displacement of $\text{Fe}^{2+}$ ions

A Edgar and Y Haider
Department of Solid State Physics, Research School of Physical Sciences, Australian National University, Canberra ACT 2600, Australia

Received 23 January 1978

Abstract. The electron paramagnetic resonance (epr) spectra of $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions in single crystals of $\text{SrO}$ are reported. $\text{Fe}^{3+}$ ions occupy sites of orthorhombic symmetry and their epr spectra have been fitted with an $S = \frac{1}{2}$ spin-Hamiltonian in which the dominant second-order terms have coefficient values of $B_0^2 = (884.7 \pm 0.3) \times 10^{-4} \text{ cm}^{-1}$ and $B_2^2 = (-422.0 \pm 0.5) \times 10^{-4} \text{ cm}^{-1}$. $\text{Fe}^{2+}$ ions occur at sites of trigonal symmetry, and the single observed resonance line may be described by a spin-Hamiltonian with $S' = \frac{1}{2}$, $g = 0$, $g || = 3.992 \pm 0.005$ and $A_{\text{Fe}^{57}} = 30.2 \pm 0.6 \times 10^{-4} \text{ cm}^{-1}$. Variable temperature experiments indicate that the $\text{Fe}^{2+}$ resonance occurs between the two levels of a doublet lying $12 \pm 1 \text{ cm}^{-1}$ above a ground state singlet. A lattice distortion calculation, based on a model of polarisable point ions, and which incorporates the crystal field stabilisation energy, is applied to the cases of $\text{Fe}^{2+}$ and $\text{Mn}^{2+}$ ions substituted into alkaline earth oxide host lattices. The calculation is used to support an interpretation of the spectroscopic data for $\text{SrO}:\text{Fe}$ in which the trigonal $\text{Fe}^{2+}$ site arises from an off-centre displacement of the $\text{Fe}^{2+}$ ion along a $\langle 111 \rangle$ axis.

1. Introduction

The incorporation of impurity cations into the crystal lattices of insulating solids usually occurs by direct substitution of the impurity for a host cation. When the host cation lattice site has cubic point group symmetry, the equilibrium position of the substituted ion is expected to coincide with that of the ion it replaces, and, in the absence of Jahn–Teller effects, the only change in the local crystal structure is a breathing-mode expansion or contraction centred on the substituted ion. However in cases where the ionic radius of the impurity cation is much less than that of the host cation, it is possible for the equilibrium position of the impurity ion to be shifted away from the regular lattice site. The effect arises because overlap forces between a small impurity ion at a regular lattice site and its nearest neighbour lattice ions are relatively weak since the ionic separation is greater than the sum of the ionic radii, and this repulsive interaction, which usually stabilises the impurity ion at the regular site, may be overcome by attractive electrostatic forces. The best documented example of such an off-centre displacement is that of $\text{Li}^+$ ions in lithium-doped $\text{KCl}$, although other examples such as $\text{KCl}:\text{Cu}^+$, $\text{RbCl}:\text{Ag}^+$ and fluorine anions in $\text{NaBr}:\text{F}^-$ have been found (for example, see the reviews by Barker and Sievers 1975, and Narayanamurti and Pohl 1970).

Alkaline earth oxide host lattices are isostructural with the alkali halides, and so similar off-centre displacements might be expected to occur in suitably doped crystals. However,
an important difference is that the alkaline earth oxides generally accommodate divalent rather than monovalent impurities, with the advantage for studies of off-centre effects that many divalent ions can be studied by spectroscopic techniques. The earliest identification of an off-centre displacement in the alkaline earth oxides is for the case of BaO: Mn$^{2+}$, for which Sochava et al (1971) found an EPR spectrum of trigonal symmetry about a ⟨111⟩ axis below ≈140 K, but a motionally averaged, isotropic spectrum above 250 K. The authors explained these results by postulating off-centre potential minima along ⟨111⟩ directions, with adjacent minima being separated by a potential barrier of ≈0.04 eV. However, Weightman et al (1971) have observed a quite different Mn$^{2+}$ spectrum, also of trigonal symmetry, in BaO: Mn$^{2+}$, and one of the models which they propose to explain their results is identical to that used by Sochava et al (1971), i.e. a ⟨111⟩ off-centre motion of a substitutional Mn$^{2+}$ ion. Motional averaging effects were not observed in this case.

In the case of SrO: Cu$^{2+}$, Tolparov et al (1974) observed a Cu$^{2+}$ EPR spectrum of orthorhombic symmetry below ≈6 K, but one of tetragonal symmetry above that temperature, and interpreted their results as being due to the combined effects of a ⟨111⟩ off-centre motion and a Jahn–Teller interaction in the $^2$E ground state. More recently Sochava et al (1976) have reported that the EPR spectrum of SrO: Co$^{2+}$ shows the presence of two distinct Co$^{2+}$ centres, of C$_2$v and C$_5$ symmetry. The first of these centres was tentatively identified as arising from an off-centre motion of Co$^{2+}$ along a ⟨110⟩ direction, whilst the second centre was thought to be a perturbation by a neighbouring defect on the first. However, in a preliminary study (Manson and Edgar 1977) of the optical absorption, EPR and magnetic circular dichroism of SrO: Co$^{2+}$, it was found that the dominant EPR spectrum in our samples displayed trigonal symmetry about a ⟨111⟩ axis. In contrast to the non-octahedral sites observed in SrO: Cu$^{2+}$ and SrO: Co$^{2+}$, Holroyd and Kolopus (1963) and Kolopus et al (1965) found that V$^{2+}$ and Mn$^{2+}$, which have larger ionic radii than Cu$^{2+}$ and Co$^{2+}$, occupy octahedral sites in SrO.

These experimental observations are in general accord with the intuitive notion that the instability of a substitutional transition metal ion in the alkaline earth oxides with respect to off-centre motion depends upon the difference of host and impurity cation radii. Thus the larger ions, V$^{2+}$ and Mn$^{2+}$, are stable at on-centre positions in SrO, whereas the smaller ions, Co$^{2+}$ and Cu$^{2+}$, undergo off-centre displacements. However, the experimental evidence for off-centre displacements of 3d$^n$ ions in alkaline earth oxides is not clear-cut as for the alkali halide systems: of the three systems thus far investigated, different sites have been reported for BaO: Mn$^{2+}$ and SrO: Co$^{2+}$, and the case of SrO: Cu$^{2+}$ is complicated by Jahn–Teller effects. Experimental investigations of other possible off-centre 3d$^n$ ions in the alkaline earth oxides are evidently desirable.

In this paper, we report the EPR spectra of Fe$^{2+}$ and Fe$^{3+}$ ions in single crystals of SrO, and describe calculations of the instability of Fe$^{2+}$ and Mn$^{2+}$ ions with regard to off-centre displacements in SrO using a polarisable point ion model which incorporates the crystal field stabilisation energy.

### 2. Experimental methods

EPR spectra were recorded with a Varian E–12 35 GHz spectrometer using cylindrical cavities resonating in the $^{10}_2$ mode, and 100 kHz or 10 kHz magnetic field modulation. The magnetic field strength produced by the electromagnet over its range of 0–2 T was determined to within $2 \times 10^{-4}$ T using the Varian Fieldial hall-probe system, which was
calibrated against the nuclear magnetic resonance of protons and \(^7\text{Li}\) nuclei in a saturated solution of lithium chloride. Microwave frequency measurements were made indirectly by attaching a small speck of the g-marker compound diphenylpicrylhydrazyl (dpph) to the samples.

Various resonant cavities were employed depending upon the temperature range to be covered. Between 4.2 K and 2 K a Varian E–265 cavity and glass dewar system was used, and the standard E–266 silver helix cavity was operated between 90 K and 295 K by immersing the aluminium tail-piece in liquid nitrogen. Both of these systems provide for rotation about the vertical axis only, and so samples were mounted on precision-cut perspex wedges in order to study angular variation of the spectrum in the (001), (110) and (112) planes. A more versatile cavity system (Edgar 1976) incorporating sample rotation about a horizontal axis was used over the 10 K to 295 K temperature range.

All of the strontium oxide samples used in this work were grown by W C Spicer Ltd from 99.9 % pure strontium carbonate using the arc-melted technique. The concentration of iron oxide dopant in the melt was 1 % by weight, but analysis of the resultant single crystals showed dopant concentrations of typically 500 ppm. In addition to the EPR spectra of the deliberate dopant, all of the samples also displayed spectra characteristic of Mn\(^{2+}\), and in some cases, Gd\(^{3+}\) ions at sites of octahedral symmetry.

3. Experimental results

At room temperature, only the cubic Mn\(^{2+}\) EPR spectrum common to all of our samples of SrO was observed, but below \(\approx 150\) K a complex spectrum comprising many resonance lines appeared. By studying the degeneracies of lines along the high symmetry directions \(\langle 001\rangle, \langle 111\rangle\) and \(\langle 110\rangle\), and by measuring the angular variation of the spectrum in the (110) plane, it was determined that the spectrum was due to Fe\(^{3+}\) ions at six magnetically inequivalent sites of orthorhombic symmetry. The EPR spectrum with the field aligned along a \(\langle 111\rangle\) direction is shown in figure 1. The positions of the resonance lines were fitted with the \(S = \frac{5}{2}\) spin–Hamiltonian:

\[
\mathcal{H} = \beta (g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + B_2^0 O_2^0 + B_2^2 O_2^2 + B_4^0 O_4^0 + B_4^2 O_4^2 + B_4^4 O_4^4,
\]

where the equivalent operators \(O_m^m\) are defined in Abragam and Bleaney (1970), and the axes \(x, y, z\) are chosen to be parallel to \(\langle 001\rangle, \langle 110\rangle\) and \(\langle 110\rangle\) respectively. A programme was written to perform a least squares fitting of the parameters \(g_x, g_y, g_z, B_1^m\) to the 40 measured field strengths; the resonant line positions predicted using the best-fit parameters given in Table 1 closely match the experimental values with a standard deviation of less than 3 G. The overall sign of the parameters was determined in a depopulation experiment at 2 K. Some additional weak lines in the spectrum could not be assigned to this orthorhombic site, but were not examined in detail; however their angular variation indicated that they do not arise from an Fe\(^{3+}\) site of cubic symmetry, and no evidence for such a site could be found.

Below \(\approx 120\) K a second spectrum appeared, comprising of single resonance lines from four magnetically inequivalent sites of trigonal symmetry. Each line reached a minimum field strength of \(\approx 0.6\) T, corresponding to an effective \(g\) value of \(\approx 4\), along a \(\langle 111\rangle\) axis. In this orientation the lineshape was asymmetric, being broader on the low field side, and below \(\approx 20\) K the main resonance line was sufficiently narrow that two hyperfine satellite lines could be resolved with total intensity \(\approx 2\%\) that of the parent line. When the magnetic field was rotated away from the threefold axis, the resonance line
Figure 1. Q-band (35.0 GHz) EPR spectrum for SrO: Fe recorded at \( \approx 104 \) K with the magnetic field applied along a \( \langle 111 \rangle \) axis. Resonance lines arising from both the Fe\(^{3+} \) site (A) of orthorhombic symmetry and from the Fe\(^{2+} \) site (B) of trigonal symmetry are indicated. C are lines from Mn\(^{2+} \), and D from dpph.

shifted to higher field strengths with an effective \( g \) value given by \( g_\parallel \cos \theta \) until the line moved above the maximum field of the electromagnet.

These features of the spectrum support an interpretation in which the observed resonance lines are due to an even-electron valence state of iron. The weak hyperfine pattern arises from the isotope Fe\(^{57} \), which has a nuclear spin of \( \frac{1}{2} \) and is 2.2% naturally abundant; the other naturally occurring isotopes of iron all have zero nuclear spin.

Table 1. Spin-Hamiltonian parameters for Fe\(^{3+} \) ions at a site of orthorhombic symmetry in strontium oxide. Forty field strengths were used in fitting the spin-Hamiltonian to spectra recorded at 90 K, and the standard deviation of observed and predicted field strengths was 2.7 Gauss. The parameters \( B_{i}^{\pi} \) are given in units of \( 10^{-4} \text{ cm}^{-1} \).

<table>
<thead>
<tr>
<th>( g_x )</th>
<th>( g_y )</th>
<th>( g_z )</th>
<th>( B_{0}^{0} )</th>
<th>( B_{2}^{0} )</th>
<th>( B_{0}^{2} )</th>
<th>( B_{2}^{2} )</th>
<th>( B_{4}^{4} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0060</td>
<td>2.0058</td>
<td>2.0062</td>
<td>884.7</td>
<td>-422.0</td>
<td>0.31</td>
<td>-1.00</td>
<td>0.98</td>
</tr>
<tr>
<td>( \pm 0.0005 )</td>
<td>( \pm 0.0005 )</td>
<td>( \pm 0.0005 )</td>
<td>( \pm 0.3 )</td>
<td>( \pm 0.5 )</td>
<td>( \pm 0.02 )</td>
<td>( \pm 0.09 )</td>
<td>( \pm 0.09 )</td>
</tr>
</tbody>
</table>

Asymmetric lineshapes of the type observed here are typical of transitions between eigenstates of the form \( | \pm M_s \rangle \) with \( M_s \) integral, which occur only for even-electron systems. Such transitions are strictly forbidden in axial symmetry, but become weakly allowed in the presence of non-axial perturbations such as random strain (Abragam and Bleaney 1970). These perturbations split the otherwise degenerate states in zero magnetic field, and give rise to an asymmetric lineshape which is broadened on the low field side. The most plausible even-electron valence state is Fe\(^{2+} \), and we have interpreted our results with the conventional spin-Hamiltonian,

\[ \mathcal{H} = g_\parallel \beta H_z S_z + A_\parallel I_z S_z, \]
where the effective spin $S' = \frac{1}{2}$ and the terms have their usual meaning. The measured parameters have the values $g_\parallel = 3.992 \pm 0.005$ and $A_\parallel (Fe^{57}) = (30.2 \pm 0.6) \times 10^{-4} \text{ cm}^{-1}$ at 8 K. By measuring the intensity of the Fe$^{2+}$ resonance line relative to that of a standard powder sample of dphe between 2 K and 30 K it was determined that the doublet between which resonance occurs lies $12 \pm 1 \text{ cm}^{-1}$ above a non-magnetic ground state.

The observation of Fe$^{57}$ hyperfine structure reported here is quite unusual for divalent iron. Generally, the large linewidth prevents such structure being resolved. In the present case the narrow linewidth for $H || <111>$ may be attributed in part to the low concentration of electronic and nuclear spins in the sample. However, the major factor is that a large trigonal component of the trigonal crystal field leaves an isolated orbital singlet state lowest, as shown later. This has the effect of reducing the sensitivity of the line position to small variations in the crystal field since such shifts involve admixtures of other orbital states.

4. Site structure for Fe$^{2+}$ ions in SrO

4.1. Experimental evidence

There are several possible models which, in principle, could explain the occurrence of trigonally symmetric sites of Fe$^{2+}$ ions in SrO, which is in such marked contrast to the substitutional sites of octahedral symmetry found for Fe$^{2+}$ ions in the isostructural MgO and CaO host lattices. We first consider whether Fe$^{2+}$ ions substitute for Sr$^{2+}$ ions, or whether they are located at interstitial sites in the SrO lattice. On a hard sphere argument, the interstitial site can accommodate ions of radius $\leq 0.82$ Å, and so Fe$^{2+}$ ions of radius $0.77$ Å can fit into this space. A feasible model of the site structure therefore comprises an interstitial Fe$^{2+}$ ion, charge compensated by a local defect or defects whose net effective charge is $-2|e|$ and whose distribution is trigonally symmetric about a $<111>$ axis. However, the Madelung constant for an interstitial site in a perfect rocksalt lattice is zero, and even in the case of charge compensation by a nearest neighbour cation vacancy the stabilising electrostatic energy for such a site is less than that of the regular cation site. Furthermore, it would be expected that some remotely-compensated sites with effective $T_d$ symmetry would be observed experimentally, particularly in samples which have been heated to disassociate the centres and subsequently quenched. We have not observed EPR spectra with cubic symmetry other than those of Mn$^{2+}$ and Gd$^{3+}$ in any of our samples, either before or after heating to 1200°C and subsequent quenching to room temperature. Finally, the cubic component of the crystal field for an interstitial site is expected to have a sign appropriate to tetrahedral coordination of oxygen ligands, whereas it is shown later in this work that the EPR spectra of Fe$^{2+}$ in SrO can be satisfactorily predicted with a crystal field whose cubic component has a sign corresponding to octahedral coordination. These arguments lead us to reject the possibility of interstitial site locations, and we now consider models involving substitutted sites.

The octahedral site symmetry of a substitutional divalent 3$d^n$ ion can be effectively lowered by neighbouring defects, a static Jahn–Teller interaction, or an off-centre displacement. No charge compensation is required for a substitutional divalent ion which, taken together with the absence of sites of $O_6$ symmetry, argues against a local defect model. Regarding a possible Jahn–Teller effect, we have also observed trigonally symmetric sites for the ions Co$^{2+}$ and Ni$^{2+}$ in SrO (Manson and Edgar 1977, Brunskill, Manson and Edgar 1978, unpublished). A static even-mode Jahn–Teller effect would not provide a consistent explanation for all three ions in either substitutional or interstitial
sites, since Ni$^{2+}$ and Co$^{2+}$ have orbital singlet states lowest in octahedral and tetrahedral environments respectively. Furthermore, we have observed that the trigonal Co$^{2+}$ site lacks inversion symmetry (Manson and Edgar 1977), which is contrary to the even-mode $T_{2g}$ coupling expected for a static Jahn–Teller effect. We therefore consider that the site structure model which is most consistent with all the experimental evidence is that of a substitutional Fe$^{2+}$ ion, displaced from the regular lattice cation site along a $<111>$ axis.

4.2. Theoretical calculation of off-centre potentials

Wilson et al (1967) and Quigley and Das (1967) have explored the potential surface of off-centre Li$^+$ ions in alkali halide crystals using a model comprising polarisable point ions with repulsion between nearest neighbours given by the Born–Mayer or related forms. We have adapted their methods of calculation to the case of divalent 3d$^n$ ions substituted into the alkaline earth oxide lattices, and SrO in particular, in order to test the theoretical support for an interpretation of the spectra of these systems which involves off-centre motion. In this paper we present the results for Fe$^{2+}$ and Mn$^{2+}$, these ions representing the two types of substitutional site observed in SrO. Results for other ions will be given elsewhere.

In our calculation, the substitutional 3d$^n$ ion Me$^{2+}$ and its six oxygen ligands are permitted to relax subject to the constraint that the total lattice distortion has $C_{3v}$, $C_{4v}$ or $C_{2v}$ symmetry, depending upon whether the Me$^{2+}$ ion is displaced along the $<111>$, $<100>$ or $<110>$ axes respectively. The relaxation parameters which determine the (static) distortion of the lattice are determined by minimising the difference in energy $\Delta E$ between the distorted lattice configuration and that of the undistorted SrO lattice.

The methods used to calculate the point charge (Quigley and Das 1967) and point dipole (Wilson et al 1967) contributions to $\Delta E$ have been adequately described in the references and will not be reiterated here. Ionic polarisability data for this part of the calculation was taken from the work of Tessman et al (1963) and the book of Fraga et al (1976). The contribution from interionic repulsion of nearest neighbours was calculated using the Born–Mayer–Verwey potential with parameters taken from Clendenen and Drickamer (1966) and Das (1965). This form of the repulsive potential is harder than the simple Born–Mayer form at short distances and eliminates the 'polarisation catastrophe' (Quigley and Das 1967) which can occur with the softer potential.

We have also included a new contribution to $\Delta E$ arising from the crystal-field splitting of the free-ion ground state term, a contribution which is very different for Fe$^{2+}$ as compared with Mn$^{2+}$. The $^6S$ ground term of Mn$^{2+}$ has zero orbital angular momentum and consequently shows only very small splittings, typically less than 0.5 cm$^{-1}$, due to high order mixing effects. In contrast the $^5D$ ground term of Fe$^{2+}$ shows large splittings; for example in MgO the electronic energy is lowered $\approx$0.5 eV by the crystal field. In order to calculate this contribution we have diagonalised the Hamiltonian,

$$V_{CF} = \sum_{l,m} B_l^m O_l^m + \lambda L \cdot S,$$

where $O_l^m$ are operator equivalents defined in Abragam and Bleaney (1970) p 863, and the basis set is restricted to the $^5D$ ground term, thus neglecting spin–orbit admixtures of higher free-ion terms induced by the spin–orbit interaction. This restriction permits the use of the operator equivalent form $L \cdot S$ for the spin–orbit coupling, and we have taken the free ion value of $\lambda = -103$ cm$^{-1}$ from Abragam and Bleaney (1970). The parameters
For non-octahedral sites may be calculated using the empirical superposition model of
crystal fields described by Newman (1971), and previously applied to 3d" ions by Stedman
(1969) and Edgar (1976). Briefly, the parameters $B_i$ are determined by adding the individual contributions of nearest neighbour ions located at $(r_i, \theta_i, \phi_i)$ according to

$$B_i = \sum_i K_i \theta_i \phi_i B(r_i)$$

where the $K_i$ are coordination factors determined by the ligand cage geometry, and the $B(r_i)$ are ‘intrinsic parameters’ giving the single ligand contributions when the ligand is located on the axis of quantisation. We have taken $B_4 = 26.55 (2.13/r_i) cm^{-1}$, based on the value of $Dq$ determined by Low and Weger (1960) for MgO:Fe$^{2+}$ and the power law variation expected for both electrostatic and contact crystal field mechanisms (e.g. see Stedman 1969). It is more difficult to estimate $B_2$ since crystal field fittings for Fe$^{2+}$ ions in sites with symmetry lower than cubic have seldom been attempted, and there is little experimental or theoretical evidence pertaining to the variation of this parameter with distance. However, from a superposition model analysis of Fe$^{2+}$ in pyrope-
almandine garnets, Newman et al (1978) have determined the second order parameter $A_2 = 7060 cm^{-1}$ assuming a cubic radial variation, and we follow these workers by taking $B_2 = -672 (2.20/r_i) cm^{-1}$.

We have applied this method of calculation to the cases of Fe$^{2+}$ and Mn$^{2+}$ ions in all of the alkaline-earth oxide series of host lattices. In the following discussion we shall refer to the difference in energy between an off-centre distorted lattice configuration, and that of a (distorted) lattice with the Fe$^{2+}$ or Mn$^{2+}$ ion at the regular lattice site, as the stabilisation energy. For MgO, both ions are stable on-centre, but for CaO, SrO and BaO both are susceptible to off-centre displacements, with the minimum energy configuration corresponding to a $<111>$-type lattice distortion of trigonal symmetry. The magnitude of the distortion may be judged from Mn$^{2+}$ ion displacements of 0.2, 0.5 and 0.8 Å and stabilisation energies of 0.04, 0.24 and 0.91 eV for CaO, SrO and BaO respectively. Similar values are obtained for Fe$^{2+}$ ions. The prediction of off-centre displacements for SrO:Mn$^{2+}$, CaO:Mn$^{2+}$ and CaO:Fe$^{2+}$ is contrary to experimental findings, although for CaO the stabilisation energies are quite small and dynamic averaging effects may be important. However, we have checked that the EPR spectrum of SrO:Mn$^{2+}$ maintains octahedral symmetry down to 2 K, and so theory and experiment are irreconcilable in this case.

To overcome this problem we have introduced a measure of covalency into the model by reducing the effective point charges of all ions in the lattice to 93% of their nominal values $2|e|$. This reduction factor was chosen so as to force Mn$^{2+}$ ions in SrO into an almost on-centre position with a stabilisation energy of only 0.06 eV, which is not inconsistent with experiment. With this adjustment, both ions are on-centre in MgO and CaO, both are off-centre along a $<111>$ direction in BaO, and Fe$^{2+}$ is off-centre along a $<111>$ direction in SrO with a stabilisation energy of 0.20 eV. Table 2 gives a summary of the lattice distortion for Fe$^{2+}$ and Mn$^{2+}$ in SrO using the reduced charge model. The important difference between the cases of SrO:Mn$^{2+}$ and SrO:Fe$^{2+}$ is that the crystal field contribution significantly increases the stabilisation energy for Fe$^{2+}$, making the observation of a static off-centre displacement more probable for Fe$^{2+}$ than Mn$^{2+}$. At the same time, the crystal field contribution partially corrects the strong tendency for the lattice distortion energy to favour a $<111>$ type distortion as the minimum energy configuration, and for SrO:Fe$^{2+}$ the $<110>$-type distortion has only a slightly higher energy than the $<111>$ type.
Table 2. Lattice distortions and energies calculated for Fe\(^{2+}\) and Mn\(^{2+}\) ions in SrO using the polarisable point ion model described in the text and an effective charge on each ion of 93% of the nominal charge. The distortion parameters \(p_1 - p_7\) represent the displacements of the Me\(^{2+}\) ion and its six nearest neighbour oxygen anions expressed in terms of the nearest neighbour separation. The various distortions are illustrated in figure 2 of the paper by Wilson et al (1967).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Lattice distortion type</th>
<th>Displacement of central ion (Å)</th>
<th>Stabilisation energy (eV)</th>
<th>(p_1)</th>
<th>(p_2)</th>
<th>(p_3)</th>
<th>(p_4)</th>
<th>(p_5)</th>
<th>(p_6)</th>
<th>(p_7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(^{2+})&lt;br&gt;(\langle111\rangle)</td>
<td></td>
<td>0.33</td>
<td>0.06</td>
<td>0.075</td>
<td>0.067</td>
<td>0.011</td>
<td>-0.005</td>
<td>0.007</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn(^{2+})&lt;br&gt;(\langle110\rangle)</td>
<td></td>
<td>0.27</td>
<td>0.04</td>
<td>0.074</td>
<td>0.067</td>
<td>0.011</td>
<td>-0.008</td>
<td>0.007</td>
<td>-0.038</td>
<td>0.008</td>
</tr>
<tr>
<td>Mn(^{2+})&lt;br&gt;(\langle100\rangle)</td>
<td></td>
<td>0.19</td>
<td>0.02</td>
<td>0.074</td>
<td>0.066</td>
<td>-0.008</td>
<td>0.008</td>
<td>0.041</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{2+})&lt;br&gt;(\langle111\rangle)</td>
<td></td>
<td>0.40</td>
<td>0.20</td>
<td>0.090</td>
<td>0.078</td>
<td>0.014</td>
<td>0.007</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{2+})&lt;br&gt;(\langle110\rangle)</td>
<td></td>
<td>0.33</td>
<td>0.19</td>
<td>0.090</td>
<td>0.084</td>
<td>0.012</td>
<td>0.001</td>
<td>0.011</td>
<td>-0.015</td>
<td>0.012</td>
</tr>
<tr>
<td>Fe(^{2+})&lt;br&gt;(\langle100\rangle)</td>
<td></td>
<td>0.20</td>
<td>0.08</td>
<td>0.083</td>
<td>0.086</td>
<td>0.000</td>
<td>0.011</td>
<td>0.037</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
It is possible to check that the predicted off-centre motion is consistent with our spectroscopic measurements for SrO:Fe$^{2+}$. From the lattice distortion summarised in table 2 we obtain $B_2^0 = 227 \text{ cm}^{-1}$, $B_4^0 = -27.5 \text{ cm}^{-1}$ and $B_2^1 = 1095 \text{ cm}^{-1}$, which taken together with the free-ion value of spin–orbit coupling, predict that the ground electronic state is an orbital singlet, split by spin–orbit coupling into two doublets and a ground state singlet. The first excited doublet, corresponding to $M_s = \pm 1$, lies 17 cm$^{-1}$ above the ground state and has a $g$-value of $g_\| = 3.96$. By diagonalising the magnetic hyperfine interaction within a basis set comprising the direct product of the $T_{2g}$ orbital triplet states and electronic and nuclear spins of 2 and $\frac{1}{2}$ respectively, we deduce the hyperfine parameter for the $M_s = \pm 1$ state to be $A_\| = 0.0030 \text{ cm}^{-1}$, based on a core polarisation field of 250 kG per unit spin and a radial expectation value $\langle r^{-3} \rangle = 5.08 \text{ a.u.}$ (Abragam and Bleaney 1970). The $g$-value and hyperfine parameter are evidently in excellent agreement with the experimental values of $g_\| = 3.992 \pm 0.005$ and $A_\| = 30.2 \pm 0.6 \times 10^{-4} \text{ cm}^{-1}$, but it should be pointed out that the theoretical values are characteristic of an orbital singlet ground state for Fe$^{2+}$ in a trigonal crystal field and are relatively insensitive to variations of the order of 10% in the parameters. In contrast, the zero field splitting is much more sensitive to the magnitudes of the trigonal component of the crystal field and the spin–orbit coupling. For example, if the latter parameter is reduced by covalency effects to 80% of its free ion value, a factor which is not unreasonable for MgO:Fe$^{2+}$ (Low and Weger 1960, Ham 1967), we find that the $M_s = \pm 1$ doublet lies 12 cm$^{-1}$ above the ground state, in agreement with experiment. Whilst this splitting is evidently quite sensitive to the operator equivalent parameters, we conclude that the orbital singlet ground state predicted by the lattice distortion calculation is fully consistent with our spectroscopic measurements.

5. Site structure for Fe$^{3+}$ ions in SrO

One possible site structure, suggested by previous investigations of Fe$^{3+}$ and Cr$^{3+}$ ions in MgO (Codling and Henderson 1971; de Basi and Caldas 1977; Henderson et al 1971), involves a substitutional Fe$^{3+}$ ion and nearest neighbour cation vacancy along a $\langle 110 \rangle$ direction. However, for MgO the dominant trivalent ion spectrum arises from isolated octahedral sites, and the spectra from ions coupled with nearby cation vacancies are much less intense. This pattern is not reproduced in SrO:Fe$^{3+}$, where a single, intense, non-octahedral spectrum is observed. Furthermore, cation vacancies are not expected to be highly mobile below room temperature, and so the broadening of the SrO:Fe$^{3+}$ spectrum above 150 K, which is unusual for an S-state ion, is difficult to explain on this model. Finally, the spin-Hamiltonian parameters reported here bear no systematic relation to those determined for the orthorhombic site in MgO:Fe$^{3+}$ (de Basi and Caldas 1971).

An alternative interpretation is that Fe$^{3+}$ ions undergo off-centre displacements along a $\langle 110 \rangle$ direction, but we have been unable to check this possibility theoretically because the extra charge of the trivalent ion induces divergencies in the calculation. A shell-model approach would be better in this respect, but we note that it has been argued (Kleppman 1976) that $\langle 110 \rangle$ off-centre displacements of impurity ions in rock-salt lattices can only be produced by including additional terms such as quadrupolar deformability in the Hamiltonian. (There is no evidence that quadrupolar deformability is significant for Fe$^{2+}$ or Fe$^{3+}$ ions, and we have not included it in the calculation reported here.) An off-centre model can potentially explain the spectral broadening.
through thermally-induced motion between equivalent off-centre potential minima. However, there is at present insufficient evidence available to distinguish this model from one involving some local defect other than a cation vacancy.

6. Conclusions

All of the experimental and theoretical evidence that we have presented is consistent with an interpretation of the site structure for Fe\(^{2+}\) ions in SrO involving an off-centre motion of the Fe\(^{2+}\) ion along a \langle111\rangle direction. We have not been able to make a firm identification of the structure of the orthorhombic site for Fe\(^{3+}\) ion in SrO, but the site appears to be of a different character to that observed in MgO:Fe (de Biasi and Caldas 1976).

The major value of the lattice distortion calculation described here for SrO:Fe\(^{2+}\) and SrO:Mn\(^{2+}\) lies not so much in the quantitative results, which are relatively sensitive to the parameters used in the polarisabla point-ion model, but in the qualitative picture which emerges regarding the stability of 3d\(^n\) ions in the alkaline earth oxides. The lattice energy strongly favours an on-centre Me\(^{2+}\) ion in MgO, and an off-centre Me\(^{2+}\) ion in BaO, with the most energetically favourable lattice distortion being consistently of the \langle111\rangle type. For CaO, Me\(^{2+}\) ions are on-centre, but the forces binding them to the on-centre site are quite weak, a feature which is consistent with the experimental observation of a low-frequency localised mode for CaO:Ni\(^{2+}\) (Manson and Wong 1975). For SrO, the balance between repulsive and attractive forces is quite delicate, and the crystal field contribution to the lattice energy is crucial in determining the magnitude, and possibly the direction, of any off-centre motion. This near-balance may offer an explanation of the different site symmetries reported for SrO:Co\(^{2+}\) (Sochava \textit{et al} 1976, Manson and Edgar 1977) through the agency of frozen-in lattice strain.

Acknowledgments

The authors wish to thank Dr N B Manson for helpful discussion, and Dr D C Price for the loan of a programme for calculating hyperfine interactions.

References

Barker A S Jr and Sievers A J 1975 \textit{Rev. Mod. Phys.} \textbf{47} Suppl. 2
Clendenen R L and Drickamer H G 1966 \textit{J. Chem. Phys.} \textbf{44} 4223–8
EPR spectra of Fe$^{2+}$ and Fe$^{3+}$ ions in SrO

Manson N B and Edgar A 1977 3rd Specialised Colloque Ampere (Dublin)
Newman D J, Price D C and Runciman W A 1978 American Mineralogist to be published
Quigley R J and Das T P 1967 Phys. Rev. 164 1185