ELECTRON PARAMAGNETIC RESONANCE AND SUPERPOSITION MODEL ANALYSIS

OF ZERO FIELD SPLITTING OF Mn IN Eu Mg (NO) \(2\)\(3\)\(3\)\(12\)\(2\) SINGLE CRYSTALS

ABSTRACT

EPR of Mn in Eu Mg (NO) \(2\)\(3\)\(3\)\(12\)\(2\) crystals has been studied at room temperature and at liquid nitrogen temperature. Angular variation studies of Mn spectra reveal the presence of two inequivalent Mn centers of unequal intensity. The Mn substitutes for Mg and shows the spectrum of two Mn complexes (site I and site II). The principal z-axes of two Mn complexes are along the trigonal axis and x-axes perpendicular to the trigonal axis. At liquid N\(2\) temperature, except an increase in the spread of the spectrum, no change in the g-values, or linewidths are observed. This indicates that Eu behaves like a diamagnetic ion down to 77 K. The spin-Hamiltonian analysis has been presented at room temperature and liquid nitrogen temperature.

Superposition model (SPM) analysis has also been carried out for ZFS of Mn in EMN. The SPM predicts the correct sign for both sites. The calculated value of ZFS parameter D for site I is

The contents of this chapter are published in

smaller than the experimental value and larger for site II. In these calculations, the assumption has been made that the crystalline structure in the vicinity of the magnetic ion is unchanged from those of host lattice. The experimental and theoretical values are in agreement if the local lattice relaxation is taken into account.

5.1 INTRODUCTION

The hydrated double nitrates of the rare earth elements form an interesting isomorphous series of salts for EPR studies. Their general formula is $\text{M}^3+ \text{M}^{2+} (\text{NO}_3)_2 \text{H}_2 \text{O}$, where $\text{M}^3+$ is a trivalent cation (Bi or an ion of the 4f group) and $\text{M}^{2+}$ is a divalent cation (Zn, Mg or an ion of the 3d group). Hence, it is easy to prepare solid solutions of paramagnetic double nitrates in diamagnetic ones over a wide range of relative concentrations, often from zero to 100%. These solid solutions have been the subject of numerous EPR investigations. The EPR study of Mn in double nitrates showed, in conformity with structure analysis data, that the unit cell contains two magnetically inequivalent $[\text{M} (\text{H}_2 \text{O})_6]$ complexes. The trivalent lanthanide ions in double nitrates are generally paramagnetic, their spin-lattice relaxation times at sufficiently high temperature are much shorter than those of the S-state ions. Because of this behaviour the magnetic interaction between paramagnetic ions and the S-state ions are averaged to zero with the consequence that magnetic resonance absorption by the S-state ion can be observed without extensive broadening. In this
chapter, we describe the EPR studies and superposition model (SPM) analysis of ZFS parameter D of Mn in Eu Mg (NO)·24 H O (EMN) single crystals.

5.2 CRYSTAL STRUCTURE

The crystal structure of EMN, which is isomorphous to Ce Mg (NO)·24 H O (CMN) and La Mg (NO)·24 H O (LMN) has been determined by Akimov et al. The primitive cell of EMN contains one formula unit and is rhombohedral with lattice constant \( a = 1.3116 \) nm and \( \beta = 49.34^\circ \). The space group is \( R\bar{3} \).

The lattice parameters in the hexagonal setting are \( a = 1.0949(3) \) nm, \( c = 3.448(2) \) nm. The coordinates of the atoms are listed in Table 5.1. The unit cell contains three Mg ions situated at two different lattice sites. One \((\text{Mg}^2+)\) occupies the \( C\) point symmetry site (site I) and the other two \((\text{Mg}^2+)\) occupy the \( C\) point symmetry site (site II). The Mg ions are surrounded by six water molecules forming a nearly regular octahedral complex. The polyhedra of atoms Mg and Mg are represented in Figures 5.1 and 5.2, respectively with the [111] directions in the rhombohedral unit cell perpendicular to the plane of the diagram.

The octahedron shape of Mg polyhedron is more distorted than that of the Mg polyhedron. Each Eu ion is coordinated with 12 oxygens belonging to six nitrate ions located at the corners of a somewhat irregular icosahedron. The europium polyhedron has the symmetry \( C \). The mutual arrangement of the Eu and Mg atoms is shown in Figure 5.3.
Fig. 5.1 The polyhedron of atom Mg$_3$
Fig. 5.2 The polyhedron of atom Mg₂
Fig. 5.3 The (1 1 1) section of the rhombohedral unit cell. Only the Mg and Eu atoms are shown.
TABLE 5.1 - The Co-ordinates of atoms in BNH at room temperature.

<table>
<thead>
<tr>
<th>ATOM</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>0.24976(1)</td>
<td>0.24076</td>
<td>0.24976</td>
</tr>
<tr>
<td>Mg</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Mg</td>
<td>0.42805</td>
<td>0.42805</td>
<td>0.42805</td>
</tr>
<tr>
<td>ON</td>
<td>0.1932 (4)</td>
<td>0.4812(5)</td>
<td>0.2508(4)</td>
</tr>
<tr>
<td>ON</td>
<td>-0.0236(6)</td>
<td>0.6173(5)</td>
<td>0.3610(5)</td>
</tr>
<tr>
<td>ON</td>
<td>0.0140(4)</td>
<td>0.4180(4)</td>
<td>0.3801(5)</td>
</tr>
<tr>
<td>ON</td>
<td>0.3129(5)</td>
<td>0.0201 (5)</td>
<td>0.2477(5)</td>
</tr>
<tr>
<td>ON</td>
<td>0.5329(6)</td>
<td>-0.1175(6)</td>
<td>0.1408(8)</td>
</tr>
<tr>
<td>ON</td>
<td>0.4913(4)</td>
<td>0.0838(4)</td>
<td>0.1195(5)</td>
</tr>
<tr>
<td>OW</td>
<td>0.0484(6)</td>
<td>0.8755(5)</td>
<td>0.1797(5)</td>
</tr>
<tr>
<td>OW</td>
<td>0.2497(4)</td>
<td>0.5531 (4)</td>
<td>0.3773(4)</td>
</tr>
<tr>
<td>OW</td>
<td>0.6182(5)</td>
<td>0.3032(6)</td>
<td>0.4606(6)</td>
</tr>
<tr>
<td>OW</td>
<td>0.8347(4)</td>
<td>0.7277(5)</td>
<td>0.1234(5)</td>
</tr>
<tr>
<td>N</td>
<td>0.0584(5)</td>
<td>0.5099(5)</td>
<td>0.3306(5)</td>
</tr>
<tr>
<td>N</td>
<td>0.4485(5)</td>
<td>-0.0084(5)</td>
<td>0.1683(5)</td>
</tr>
</tbody>
</table>

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5.3 EXPERIMENTAL

Single crystals of EMN doped with Mn were grown at
\( \sim 300 \) K by slow evaporation of an aqueous solutions of EMN to which
0.5 wt % of manganese nitrate was added. The crystal grows in
flat hexagonal plates, the plane of which is perpendicular to the
c-axis. The crystals were very hygroscopic and takes about 3 to 4
months to grow. The EPR experiments were carried out using a
JEOL-JES FE 3X homodyne spectrometer operating at \( \sim 9.45 \) GHz and
equipped with a TE cylindrical cavity and 100 kHz field
011 modulation. The details are given in chapter 2.

5.4 RESULTS AND DISCUSSION

For an arbitrary orientation of the crystal, the EPR
spectrum consists of a number of lines corresponding to allowed
and forbidden transitions (\( \Delta M = \pm 1, \Delta m = 0 \)). Angular variation
studies of Mn spectra reveal the presence of two inequivalent
Mn centers of unequal intensity. The Mn substitutes for Mg and
shows the spectrum of two Mn complexes. The spectrum having the
greater intensity is due to Mn substituting for Mg at site II
while spectrum having the lower intensity is due to Mn at site I.
The Mn center occupying the site II is more intense because
there are twice as many sites II as sites I. It was found that
the principal z-axes of two Mn complexes are along the trigonal
axis (Fig. 5.4) and x axes perpendicular to the c axis (Fig. 5.5).
For a field applied along the trigonal axis, each type of Mn
complexes produces an EPR spectrum consisting of five nearly
Fig. 5.4 EPR spectrum of $\text{Mn}^{2+}$ in $\text{Eu}_2\text{Mg}_3(\text{NO}_3)_7 \cdot 24\text{H}_2\text{O}$ single crystals at 800 K with magnetic field parallel to $z$-axis.
Fig. 5.5 EPR spectrum of Mn$^{2+}$ in Eu$_2$Mg$_3$(NC$_3$)$_{12}$·24H$_2$O single crystals at ~300 K with magnetic field parallel to x-axis.
equally spaced sets of six nearly equal spaced hyperfine components. The spectra of Mn showing large ZFS (site I) were measured for various angles of the magnetic field relative to c-axis. Fig. 5.6 shows the angular variation of the allowed fine structure transition ($\Delta M = \pm 1$) in zx plane for site I. It is seen from the angular variation plot in the zx plane that fine structure transition lines move in rapidly from z axis as $\theta$ changes. The lines collapse to a very small spread at an orientation $\theta = 55$ away from z axis. As $\theta$ increases further, the lines cross each other and spread out to a second maximum at $\theta = 90^\circ$ (x-axis). A $\pi/3$ rotational symmetry of the spectrum was observed when the crystal was rotated about the trigonal axis.

Experiments were also performed at 77 K to study the effect of paramagnetic Eu ions on the Mn spectra. However, at this temperature except an increase in the spread of the spectrum, no changes in the $g$ values or on the linewidths are observed and experiments at 4.2 K were not possible. This indicates that Eu behaves like a diamagnetic ion down to 77 K.

The EPR spectrum of Mn for both sites can be described by spin-Hamiltonian of the form.

\[
\mathcal{H} = \beta g_\parallel S \cdot B + \beta g_\perp (S \cdot B + S \cdot B) + D \left[ S - \frac{35}{12} \right] \frac{z}{2} - (7/36)(a-F) (S - 95/14 S + 81/16)
\]

\[
+ (a \mu B/36) \left[ S + \sum_{i=1}^{3} \exp(-3i\phi) + S \exp(3i\phi) \right]_{z}
\]

\[
+ \sum_{i=1}^{3} \exp(-3i\phi) + S \exp(3i\phi) \right]_{z}
\]

\[
+ A_\parallel S I + A_\perp (S I + S I)
\]

\[
\langle z z \rangle + \langle x x \rangle \quad \ldots \ldots \ldots \ldots (5.1)
\]
Fig. 5.6 Angular dependence of allowed fine structure $^2+_{\text{transitions}} (\Delta M = \pm 1)$ of Mn for site I in $zx$ plane at $\sim 300$ K. Theoretical (−) and experimental (0) results.
where the z-axis is parallel to the trigonal axis of the crystal. The symbols have their usual meaning and \( S = I = 5/2 \) for Mn. The field expressions for various fine structure transitions for B parallel to z axis are:

\[
\begin{align*}
B \ (M = 5/2 \rightarrow 3/2) &= B - 4 D + (4/3)(a-F) \\
B \ (M = 3/2 \rightarrow 1/2) &= B - 2 D - (5/2)(a-F) \\
B \ (M = 1/2 \rightarrow -1/2) &= B \\
B \ (M = -1/2 \rightarrow -3/2) &= B + 2 D + (5/2)(a-F) \\
B \ (M = -3/2 \rightarrow -5/2) &= B + 4 D - (4/3)(a-F)
\end{align*}
\]

\[\ldots \ldots \ldots (5.2)\]

The field expressions for various fine structure transitions for B parallel to x axis are:

\[
\begin{align*}
B \ (M = 5/2 \rightarrow 3/2) &= B + 2 D + (1/2)(a-F) + D/B \\
B \ (M = 3/2 \rightarrow 1/2) &= B + D - (5/8)(a-F) - 5D/4B \\
B \ (M = 1/2 \rightarrow -1/2) &= B - 2D/B \\
B \ (M = -1/2 \rightarrow -3/2) &= B - D + (5/8)(a-F) - 5D/4B \\
B \ (M = -3/2 \rightarrow -5/2) &= B - 2D - (1/2)(a-F) + D/B
\end{align*}
\]

\[\ldots \ldots \ldots (5.3)\]

The spectrum has been analysed using the expressions (5.2) and (5.3). The best fit parameters for the 77 and 300 K Mn EPR spectra at both sites are listed in Table 5.2. The signs of the parameters (given in Table 5.2) are relative and have been determined by assuming \( A_{1}\parallel \) to be negative. From Table 5.2, it is clear that the ZFS parameter D is very different for the two
sites and is temperature sensitive. The relative insensitivity of the parameter D of site I to temperature (Table 5.2) has also been noted for Ni in LMN and La Zn(NO$_3$)$_2$H$_2$O (LZN) as well. The value of D increases as the temperature decreases.

An increase in the value of D at low temperature can probably be explained as due to thermal contraction and vibrational mechanism of the lattice. The differing values of D for Mn at two sites indicate that the two sites differ greatly in the crystal field seen by the ions. The crystal field is presumed to be due to an octahedron of water molecules oriented with [111] axis along the trigonal axis of the crystal. The large difference in the D value is also observed for Ni doped LMN, LZN single crystals and for Mn in Mg$_2$SeO$_4$·6H$_2$O single crystals. In theoretical analysis of the ground state splitting of the S$^-$ state ion, it is generally recognised that more than one mechanism is required to account for the magnitude of the parameter D. Brandt et al. have determined the ZFS parameter D of Mn in LMN for both sites.

It is interesting to note that the values of D for site I and site II obtained in this experiment are nearly the same as the parameter D of Mn in LMN. A theoretical interpretation of the latter for site I was given by Chatterjee et al. They concluded that the relativistic second order effect of Wybourne yields the major contribution to the value of ZFS parameter D. Their calculated values are in agreement with the observed values for site I but not for site II.
TABLE 5.2 Spin-Hamiltonian parameters for Mn in Eu Mg (NO)\(_2\) 24 H\(_2\)O single crystals at 300 and 77 K. All crystal field and hyperfine parameters are in units of 10 cm.

<table>
<thead>
<tr>
<th>Spin-Hamiltonian parameters</th>
<th>Site I</th>
<th>Site II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>300 K</td>
<td>77 K</td>
</tr>
<tr>
<td>D</td>
<td>-192(1)</td>
<td>-224(1)</td>
</tr>
<tr>
<td>a-F</td>
<td>6.5(5)</td>
<td>5.5(5)</td>
</tr>
<tr>
<td>g(_|)</td>
<td>2.003(1)</td>
<td>2.004(1)</td>
</tr>
<tr>
<td>g(_\perp)</td>
<td>2.004(2)</td>
<td>2.004(2)</td>
</tr>
<tr>
<td>A(_|)</td>
<td>-90 (1)</td>
<td>-90 (1)</td>
</tr>
<tr>
<td>A(_\perp)</td>
<td>-90 (1)</td>
<td>-90 (1)</td>
</tr>
</tbody>
</table>

5.5 SUPERPOSITION MODEL ANALYSIS OF ZFS PARAMETER D

Assuming the ZFS to be solely due to the distortion of the first coordinate sphere of oxygens of water molecules, the experimental ZFS can be compared with those calculated from the crystal structure data for the pure host compound. The SPM of Newman and Urban which is discussed in detail in chapter 4,
allows such a comparison. We have determined the bond lengths and angle which the \( Mg - O \) makes with the \( c \) axis by using the Table 5.1. For this coordinates are transformed from rhombohedral to hexagonal axes by using the transformation.

\[
\begin{align*}
x &= (1/3) \ (2x-y-z) \\
y &= (1/3) \ (x +y -2z) \\
z &= (1/3) \ (x + y +z)
\end{align*}
\]

\[\ldots(5.4)\]

In the hexagonal setting the position of atoms are at \((0,0,0;1/3,2/3,2/3;2/3,1/3,1/3) + (i)\) \( Mg \) at \((0,0,0)\). (ii) \( Mg \) at \\
\((0,0,z); \ 0,0,z)\) and oxygen of \( H O \) are at \( x,y,z; y,x-y,z; y-x,x,z; y, y-x,z; x-y, x,z. \) By using equation \((5.4)\)

and above mentioned positions of atom for the hexagonal axes setting, we obtained the atomic positions of \( Mg \), \( Mg \), \( H O (1) \), \( H O (2) \) and \( H O (3) \) are given in Table 5.3:

<table>
<thead>
<tr>
<th>TABLE 5.3 -- Atomic coordinates for ( Mg ) and ( H O )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Atom</strong></td>
</tr>
<tr>
<td>-----------------------------------</td>
</tr>
<tr>
<td>( Mg )</td>
</tr>
<tr>
<td>( 1 )</td>
</tr>
<tr>
<td>( Mg )</td>
</tr>
<tr>
<td>( 2 )</td>
</tr>
<tr>
<td>( H O (1) )</td>
</tr>
<tr>
<td>( 2 )</td>
</tr>
<tr>
<td>( H O (2) )</td>
</tr>
<tr>
<td>( 2 )</td>
</tr>
<tr>
<td>( H O (3) )</td>
</tr>
<tr>
<td>( 2 )</td>
</tr>
</tbody>
</table>
Mg$^{2+}$ in EMN at site I is surrounded by six water molecules at a distance $R = 0.2051$ nm and at site II is surrounded by two sets of three oxygen ligands each as nearest neighbours at distance 0.2051 and 0.2059 nm. The angle $\theta$ which $Mg-O$ makes with c axis at site I is 54.52° and for site II are 54.36° and 123.12°. The ZFS parameter $D$ calculated by using equations (4.1) and (4.2), with $b = -0.05$ cm, $t = 7$ and $R = 0.22$ nm (the reference distance for $Mn^{2+}$ surrounded by six oxygens), are $-26 (2) \times 10^{-10}$ cm and $102 (2) \times 10^{-10}$ cm for sites I and II, respectively. The SPM predicts the correct sign for both sites. The calculated value of $D$ for site I is smaller than the experimental value and larger for site II.

In these calculations, the assumption has been made that the crystalline structure in the vicinity of the magnetic ion is unchanged from those of the host lattice. The difference in calculated and experimental values of $D$ may be principle results from the local relaxation. It has been shown that if $R$ (metal - ligand bond distance) > normal $Mn^{2+}$ ligand bond distance, the introduction of substitutional $Mn^{2+}$ gives rise to an inward relaxation while the opposite occurs for $R < Mn$ ligand bond distance. The ionic radii of $Mn^{2+}$ and $Mg^{2+}$ are 0.080 and 0.066 nm, respectively. Therefore, $Mn^{2+}$ substitution for $Mg^{2+}$ would allow some expansion of $O^-$ octahedron around $Mn^{2+}$. A movement of oxygen along the c axis is assumed such that $Mn^{2+}$ - oxygen bond length increases from that of the $Mg^{2+}$ - oxygen. This causes a change in the value of $\theta$. It is found that an increase of about 2% in bond lengths (from 0.2051 to 0.2094 nm) cause the angle $\theta$ to
change to 52.92° for site I. An increase of about 0.78% in bond length of \( \text{Mg (2)} - \text{O (2)} \) (from 0.2051 to 0.2067 nm) and \( \text{Mg (2)} - \text{O(3)} \) (from 0.2059 to 0.2075 nm) causes \( \Theta \) to change to 53.77° and 123.84°, respectively. These values of \( R \) and \( \Theta \) lead to \( D \) values - 192x10 and 25x10 cm for sites I and II, respectively. A change of bond lengths of about 3% - 4% are observed from extended X-ray absorption fine structure (EXAFS) measurements in \( \text{KZnF}^{2+} \) and \( \text{KCDF}^{2+} \) doped with Mn.
REFERENCES

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23. CRC Handbook of Chemistry and Physics, edited by D. R. Lide (1990-91) p. 12-1.