Abstract

The ESR study of $1\% \text{Mn}^{2+}$ doped in ZnMTH single crystal gives rise to the spin-Hamiltonian parameters $D = 385.6$, $E = 71.5$, $a = -9.5$ and $\Lambda = -93$ gauss from an analysis of the allowed hyperfine transitions corresponding to the orientation of the principal axis parallel to the magnetic field as shown by the absence of forbidden transitions. The large $g$ value viz., $2.035$ observed for this system has been attributed to a highly distorted cubic environment. An ionicity of $96.5\%$ is deduced for the metal-ligand bonding from a plot of $\Lambda$ vs the Pauling's covalency parameter. The analysis of forbidden hyperfine transitions is shown to lead to $Q' = 1.69$ and $Q'' = 0.304$ for the axial and rhombic components of the quadrupole coupling constants respectively of the $^{55}\text{Mn}$ nucleus.
9.1. Introduction

Electron spin resonance studies in organic acid complexes show that the dopant can go into substitutional or interstitial sites [1-5]. In addition, ESR studies throw light on the nature of the microsymmetry of the dopant [6]. A more interesting feature in such studies in the case of Mn$^{2+}$ systems is the observation of forbidden transitions which arise due to the admixture of the off diagonal terms of the type,

$$(S_z S_+) (S_- I_+), (S_z S_-) (S_+ I_-)$$

in the spin Hamiltonian [section 6.2.3]. However in most cases, where such forbidden transitions are observed, detailed analysis are precluded due to large line widths or presence of more than one inequivalent site. Consequently analyses of forbidden transitions have been reported only in few cases [7-9]. Wherever the analysis is possible one gets the Spin-Hamiltonian subjected to a more extensive analysis of the ESR spectra and additional hyperfine parameters relating to the quadrupole moment. In this chapter we present the results of a single crystal ESR study of Mn$^{2+}$ ions doped in zinc maleate tetrahydrate (hereafter ZnMTH). Rotation of the
single crystal along mutually perpendicular axes is shown to lead to variations in the intensities of allowed and forbidden transitions as predicted by theory including total absence of the forbidden transitions corresponding to $H || Z$. The line positions in the case of $H || Z$ have been analysed to give the spin Hamiltonian parameters. From the zero field splitting, information on the microsymmetry of Mn$^{2+}$ is obtained. From the value of $A$, the percentage ionicity in the metal-ligand bonding is estimated. Using the spin-Hamiltonian parameters, the line positions of the forbidden transitions also have been analysed as discussed in section 6.2.5, and the values of $Q'$ and $Q''$, the axial and rhombic components of the quadrupole coupling moment of $^{55}$Mn respectively, are derived.

9.2. Experimental section

Stoichiometric amount of Zn$^{2+}$ is taken in the form of sulphate (Analar. BDH) and precipitated as hydroxides using ammonium hydroxide. After eliminating excess ammonia by warming the solution, the resultant hydroxide is treated with 100% excess hot maleic acid (SD Chemical). Upon concentrating the solution colourless crystals separated out. The ZnMTH was doped with 1% Mn$^{2+}$ at the starting point. Zn$^{2+}$ in the
pure compound viz., ZnMTH was estimated as oxide. (Cald. for
$C_8H_{14}O_{12}Zn$, $Zn^{2+} = 17.79\%$, observed: $Zn^{2+} = 17.14\%$).

The detailed crystal structure of ZnMTH is not yet available. However, as per the preliminary reports, ZnMTH forms a triclinic system with space group $P\bar{1}$. There is slight difference in the unit-cell dimensions reported by the two groups. Antsyshkina et al. have reported $a = 7.30$, $b = 9.82$ and $c = 5.28$ Å and $\alpha = 110.2^\circ$, $\beta = 77.1^\circ$ and $\gamma = 117.0^\circ$ which may be compared with $a = 7.29$, $b = 9.73$, $c = 5.36$ Å and $\alpha = 110.48^\circ$, $\beta = 63.18^\circ$ and $\gamma = 63.18^\circ$ reported by Saroja and Raman [10,11]. There is one molecule of ZnMTH per unit cell. Experimentally the principal axis is located by observing the spectra at different orientations and achieving that orientation which gives rise to only allowed transitions with intensities free from forbidden transitions which corresponds to $H||Z$. Figure 9.1(inset) shows the morphology of the crystal and the plane (marked with crosses) which gives rise to 30 ESR transitions free from forbidden lines. The spectra were subsequently recorded by rotating in two other axes choosing these axes such that they form a mutually perpendicular system with respect to the principal axis. The spectra have been recorded at an interval of $10^\circ$. Other details of ESR measurements are already given in 2.1.
Fig. 9.1 Room temperature ESR spectrum of Mn$^{2+}$/ZnMTH in the X'Z plane at $\theta = 0^\circ$
9.3. Results and discussion

A thirty line spectra is typically observed for ESR of Mn$^{2+}$ in orthorhombic symmetry when no forbidden lines are present as shown in Figure 9.1. The ground state of Mn$^{2+}$ with d$^5$ configuration is unique among d$^n$ configurations in that there is only one state with maximum spin multiplicity ($^6S_{5/2}$). This state splits into three Kramers doublets ($\pm 5/2$, $\pm 3/2$ and $\pm 1/2$) in an orthorhombic crystalline field which are further split in the presence of applied magnetic field. These six levels will give rise to five fine structure transitions. Each fine structure transition will be further split into six hyperfine components due to nuclear spin of 5/2 of $^{55}$Mn isotope. Figure 9.2 shows the ESR spectra recorded in the X'Z-plane making an angle of 5° and 7° with Z-axis respectively. A neat thirty line spectrum indicates that there is only one type of site in the lattice. Even a small rotation of about 5° around the principal axis makes the presence of forbidden transitions conspicuous as shown in Figure 9.2 compared to Figure 9.1. When the principal axis is parallel to the magnetic field the separation in energy levels and hence the separation between the $M = 5/2 \rightarrow -3/2$ and $M = +3/2 \rightarrow +5/2$ will be maximum [12]. The ratio of the
Fig. 9.2 Room temperature ESR spectra of Mn$^{2+}$/ZnMTH in the X'Z plane at (a) $\theta = 5^\circ$ and (b) $\theta = 7^\circ$; longer vertical lines correspond to $\Delta m = 0$ transitions and small vertical lines corresponding to $\Delta m = \pm 1$ transitions.
relative intensities are proportional to \((J+M)(J-M+1)\). These therefore occur in the ratios \(5:8:9:8:5\) as observed.

The angular variation of the fine structure transitions corresponding to \(M \rightarrow M+1\), depends on the term \((3\cos^2\theta - 1)\), when the higher order terms are neglected [13]. The field for all the sextets will be same at the magic angle. However, if the higher order terms are also included, all the five curves corresponding to the five sextets may not meet at the same point. Figure 9.3 shows the angular variations of these transitions in the \(X'Z\) plane. The theoretical curves corresponding to each sextet is found to overlap closely with experimental points.

The line positions of the spectrum corresponding to \(H||Z\) are given by a set of five simultaneous equations in terms of spin Hamiltonian parameters, as discussed in section 6.2.5. The spin-Hamiltonian parameters \(D, E, 'a'\) whose significances have been discussed earlier (Section 6.2.3, p.162) are obtained using a computer programme based on these equations (appendix IV). The value of \(A\) is then calculated from the line positions in each sextet and the error given \(\text{viz.}, \pm 1\) G corresponds to the \(A\) value obtained from the different sextets. Expression 6.14 provides a check on the value of \(A\) obtained. The calculated field position of the sextets,
Fig. 9.3 Angular variation in $X'Z$ plane of the allowed transitions in the ESR spectrum of Mn$^{2+}$/ZnMTH at RT. Full curves: theoretical; circles: experimental.
$H_i$, and the experimental $H$ values are given in Table 9.1, along with the $D, E, 'a'$ and $A$ values. An indirect check on the relative sign of $D$ is as follows. If the separations of these sextets decreases on the high field side when the direction of the magnetic field is parallel to $Z$-axis, $D/A$ will be positive. In all the systems so far studied $A$ is negative [14]. In the present case the separation of the sextets increase towards the high field side and hence $D/A$ is negative which implies $D$ is positive if we take a negative sign for $A$ for the present system as well. The sign and magnitude of $D$ gives information regarding the microsymmetry of the metal ion. A positive $D$ is associated with a tetragonal compression or trigonal elongation [15]. In the present case the positive $D$ corresponds to tetragonal compression. Such a conclusion is in accordance with the known crystal structure of MnMTH if we assume that a similar symmetry is obtained when Mn$^{2+}$ goes substitutionally into ZnMTH. A comparison of the unit cell dimensions of MnMTH and ZnMTH suggests that these two systems are likely to be closely similar if not isomorphous, facilitating the above described situation [10,11,16]. However a definite conclusion regarding whether the microsymmetry is governed purely by the guest ion or dictated both by the guest ion as well as the parent diamagnetic zinc lattice can be drawn only when
Table 9.1. Observed and calculated $H_1$ values for $H||Z$ axis in Mn$^{2+}$/ZnMTTH along with D, E, a and A values.

<table>
<thead>
<tr>
<th>Cald.</th>
<th>Obs</th>
<th>D</th>
<th>E</th>
<th>a</th>
<th>A</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(+3 gauss)</td>
<td>(+1 gauss)</td>
<td>(+1 gauss)</td>
<td>(+1 gauss)</td>
<td>(+1 gauss)</td>
</tr>
<tr>
<td>$H_1$</td>
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<td>1780</td>
<td>385.6</td>
<td>71.5</td>
<td>-9.5</td>
</tr>
<tr>
<td>$H_2$</td>
<td>2493</td>
<td>2495</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_3$</td>
<td>3290</td>
<td>3275</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_4$</td>
<td>4070</td>
<td>4075</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H_5$</td>
<td>4815</td>
<td>4818</td>
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</table>
a knowledge of a detailed crystal structure for the ZnMTH becomes available.

The g value (viz., 2.035) shows large anisotropy. Most of the Mn$^{2+}$ systems reported in literature show g values close to free spin value of 2.0023. However deviation from this value has been observed in highly distorted systems such as Mn$^{2+}$ doped tris ethylene diamine Zinc(II), Mn$^{2+}$ doped lithium ammonium tartrate monohydrate [17,18]. Two mechanisms have been suggested for the enhancement of g-value. The spin-orbit coupling produces a slight breakdown of LS coupling introducing an admixture of the excited state $^{4}P_{1/2}$ but the expected deviation in this case is small. A more dominant contribution comes due to covalent bonding excited states of symmetry $^{6}T_{lg}$ whose single electron states will tend to be full or empty depending upon the nature of the metal-ligand bondings [19,20]. The D value of 0.0358 cm$^{-1}$ does indicate a significantly large distortion from cubic symmetry for Mn$^{2+}$/ZnMTH [15]. An estimate of the covalency in the present case may be obtained from the hyperfine splitting constant A. The relation between A and the local bonding of the Mn$^{2+}$ and the nearest neighbour ligands has been derived phenomenologically on a more quantitative basis by plotting A versus the Pauling covalency parameter [21,22].
From this curve we obtain, for $A = -93$ gauss, an ionicity of 96.5% for Mn$^{2+}$/ZnMTH. Similar values have been found for Mn$^{2+}$ doped (NH$_4$)$_2$(COO)$_2$H$_2$O[23], K$_2$(COO)$_2$·H$_2$O[24] and Cd(COO)$_2$·3H$_2$O[9] single crystals.

Figure 9.2 shows the appearance of forbidden transitions when the crystal is rotated by 5 and 7° respectively, the intensities becoming larger with increasing rotation. The increase in intensity with angular variation is illustrated for the first sextet in Figure 9.4. Theoretically intensities for forbidden transitions vary as $\sin 2\theta$ (eq. 6.19) and the observed spectral behaviour is in agreement with the expected trend. These forbidden transitions occur in pairs corresponding to $\Delta m_I = \pm 1$ (see section 6.2.5). The relationship for the positions of the different forbidden transitions and the hyperfine parameters are presented in section 6.2.5 and the computer programmes based on these expressions are given in appendices Va and Vb. Using these programmes the line positions for the forbidden transitions have been analysed. For all the sextets the doublet separations have been calculated and are given in Table 9.2 along with the experimental doublet separations. A good fit is obtained for $Q' = 1.69$ and $Q'' = 0.304$, which are the axial and rhombic components of the quadrupole coupling constant of the $^{55}$Mn nucleus.
Fig. 9.4 Angular variation of ESR spectra of Mn$^{2+}$/ZnMTH in X'Z plane. The first sextet is given to illustrate the variation of intensities of forbidden transitions.
Table 9.2. Observed and calculated doublet separations $\Delta H$(in G) of the forbidden hyperfine transitions ($\Delta m = \pm 1$) for various transitions ($\Delta M = \pm 1$) in the $X'Z$-plane ($\phi = 0^\circ$, $\theta = $ Variable) of the complex Mn$^{2+}$/zinc maleate tetrahydrate single crystals at 298 K.

<table>
<thead>
<tr>
<th>$m$</th>
<th>$M = \frac{1}{2}$</th>
<th>$M = \frac{3}{2}$</th>
<th>$M = -\frac{1}{2}$</th>
<th>$M = -\frac{3}{2}$</th>
<th>$M = -\frac{1}{2}$</th>
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<tr>
<td></td>
<td>$m = \pm 1$</td>
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<td>$m = \pm 1$</td>
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<tr>
<td></td>
<td>$\theta = 5^\circ$</td>
<td>$\theta = 10^\circ$</td>
<td>$\theta = 5^\circ$</td>
<td>$\theta = 15^\circ$</td>
<td>$\theta = 25^\circ$</td>
<td></td>
</tr>
<tr>
<td>obs</td>
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<td>------------------</td>
</tr>
<tr>
<td>- 5/2</td>
<td>23.8 24.7</td>
<td>201.6 202.8</td>
<td>149.2 152.5</td>
<td>369.2 377.0</td>
<td>330.1 339.4</td>
<td></td>
</tr>
<tr>
<td>- 3/2</td>
<td>24.5 25.0</td>
<td>205.8 207.1</td>
<td>155.8 158.5</td>
<td>372.3 383.2</td>
<td>341.3 350.2</td>
<td></td>
</tr>
<tr>
<td>- 1/2</td>
<td>24.9 25.3</td>
<td>210.8 211.5</td>
<td>163.1 164.8</td>
<td>379.2 389.7</td>
<td>350.9 362.4</td>
<td></td>
</tr>
<tr>
<td>+ 1/2</td>
<td>25.0 25.5</td>
<td>215.8 216.0</td>
<td>168.3 171.2</td>
<td>388.3 396.4</td>
<td>362.3 374.4</td>
<td></td>
</tr>
<tr>
<td>+ 3/2</td>
<td>25.1 25.8</td>
<td>217.5 220.8</td>
<td>174.2 177.7</td>
<td>395.5 403.5</td>
<td>377.0 386.7</td>
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</tr>
</tbody>
</table>
respectively. The relatively large deviation between the observed and calculated doublet separations in $M = +5/2 \rightarrow +3/2$ and $M = -5/2 \rightarrow -3/2$ sextets may be attributed to the large angle ($\Theta = 15$ and $25$) at which the comparison is made. The perturbation theory gives quantitatively unsatisfactory results at large angles and a considerable deviation of the direction of the nuclear magnetic moment from that of H has to be taken into account [25]. For these sextets the forbidden transitions were observable only at large angles i.e., away from the principal axis and hence a comparison at smaller angles was not possible.

9.4. Conclusions.

$\text{Mn}^{2+}$ when doped in zinc maleate tetrahydrate is found to occupy a compressed octahedral site, substitutionally replacing the $\text{Zn}^{2+}$ ion. The spin-Hamiltonian parameters have been determined to be $D = 385.6$, $E = 71.5$, $a = -9.5$ and $A = -93$ gauss, where $D$, $E$, $a$ and $A$ are the axial component of zero field splitting, the rhombic component of zero field splitting, the cubic field term and the hyperfine coupling constant respectively. The unusually large anisotropy in the $g$ value viz., $2.035$ has been ascribed to a highly distorted cubic environment. An ionicity of $96.5\%$ is deduced for the
metal-ligand bonding from a plot of $A$ vs the Pauling's covalency parameter [22]. The analysis of forbidden ESR transitions which give good agreement between calculated and observed $\Delta H$, the splitting of the lines leading to $Q = 1.69$ and $Q'' = 0.304$ which are the axial and rhombic components of the quadrupole coupling constants of the $^{55}$Mn nucleus respectively.
References:


13. Ref 12, p.437.