

# EPR Studies of Mn<sup>2+</sup>-Doped Diammonium Hexaaqua Magnesium(II) Sulfate

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Electron paramagnetic resonance (EPR) studies of Mn<sup>2+</sup> impurity in single crystals of diammonium hexaaqua magnesium(II) sulfate have been carried out at 9.3 GHz (X-band) at room temperature. The EPR spectra exhibit a group of five fine structure transitions. The spin-Hamiltonian parameters were determined. Mn<sup>2+</sup> enters the lattice interstitially. The EPR spectrum of a powder sample supports the data obtained by single crystal studies. – PACS number: 76.30

*Key words:* Electron Paramagnetic Resonance; Spin-Hamiltonian; Fine Structure.

## 1. Introduction

Electron paramagnetic resonance (EPR) is an appropriate tool to determine exact site occupancy, since it is the most sensitive technique to local symmetry. EPR studies are generally carried out by doping paramagnetic impurities in diamagnetic hosts. EPR spectra of Mn<sup>2+</sup> at room temperature are well resolved due to long spin-lattice relaxation times in its ground state [1]. The zero field splitting of Mn<sup>2+</sup> is very sensitive to even small distortions [2]. In a previous EPR study [3] of Mn<sup>2+</sup>-doped diammonium hexaaqua magnesium(II) sulfate (DAHAMS) at 24 GHz, some spin-Hamiltonian parameters have been evaluated. In addition to this, the presence of a rhombic term in the spin-Hamiltonian has also been suggested. As nothing has been said about the *g*-values and the location of the impurity in the lattice, we have performed a detailed EPR study of the Mn<sup>2+</sup> impurity ion in single crystals of DAHAMS at 9.3 GHz at room temperature to find the *g* values and to ascertain the site symmetry and location of Mn<sup>2+</sup> in the lattice. The location of the ion in the lattice has been estimated by comparison of the direction cosines of the distortion axis with those of the Mg-O bonds, using refined crystal structure data [4, 5]. Powder EPR spectra have also been recorded and the parameters, thus determined, agree with those of single crystals. The magnitude of the hyperfine coupling constant has also been used to estimate the covalency of the bond between manganese and the ligands.

## 2. Experimental

Diammonium hexaaqua magnesium(II) sulfate is a member of the isomorphous series (NH<sub>4</sub>)<sub>2</sub>[M(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>, known as Tutton's salt. Its crystal structure is known to be monoclinic [4, 5] with space group *P*2<sub>1</sub>/*a*. The crystallographic axes are *a* = 9.316 Å, *b* = 12.596 Å and *c* = 6.198 Å, *Z* = 2 and the angle  $\beta$  = 107.79°.

Single crystals of diammonium hexaaqua magnesium(II) sulfate doped with Mn<sup>2+</sup> were grown by slow evaporation of aqueous solutions containing stoichiometric amounts of ammonium and magnesium sulfates. The Mn<sup>2+</sup> impurity was introduced by adding 0.01 mole-% of manganese sulfate. The EPR spectra were recorded at room temperature with a Varian EPR spectrometer operating at the X-band, and crystal rotations were carried out about the three mutually orthogonal axes at 10° intervals. The powder EPR spectrum has also been recorded at room temperature.

## 3. Results and Discussion

The ground state of Mn<sup>2+</sup>, having d<sup>5</sup> configuration, is unique among d<sup>*n*</sup> configurations. There is only one state with maximum spin multiplicity (<sup>6</sup>S<sub>5/2</sub>). This splits into three Kramer doublets ( $\pm 5/2$ ,  $\pm 3/2$ ,  $\pm 1/2$ ), which further split in an applied magnetic field, giving rise to five fine structure transitions. Each fine structure transition splits into six hyperfine components due

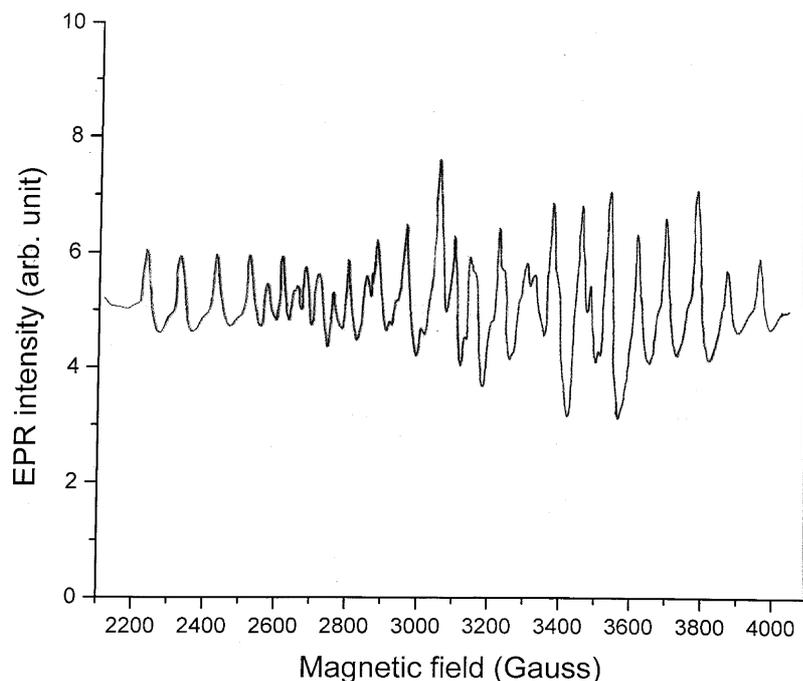


Fig. 1. Single crystal EPR spectrum of  $\text{Mn}^{2+}$  in DAHAMS for  $H||a$  axis at room temperature at 9.3 GHz.

to hyperfine coupling, giving rise to 30 allowed transitions.

The single crystal EPR spectrum of  $\text{Mn}^{2+}$ -doped DAHAMS at room temperature is shown in Fig. 1 for  $H||a$  axis. During crystal rotations in the three planes, a maximum of thirty resonance lines is obtained in the  $ab$  plane, indicating the presence of only one site in the lattice. The angular variations of fine structure lines follow a  $(3 \cos^2 \theta - 1)$  curve, and the spread of the spectrum is maximum at  $\theta = 0$  and  $90^\circ$ . The spectrum corresponding to  $\theta = 0^\circ$  offers a direct determination of the  $D$  and  $a$  parameters [6]. The separation of the outer groups amounts to  $(2D - 3a)$  while that of the inner group is  $[2D + (5/3)a]$ . It is to be noted that only the relative sign of the parameters can be determined from the consideration of the spectra.

The theoretical variations of the fine structure with the angle have been determined using equations given by Bleaney and Ingram [6]. These variations in the  $ab$  plane have been shown along with experimental points in Figure 2. In two other planes  $bc^*$  and  $c^*a$ , the lines got mixed up hence the angular variation could not be plotted for these planes. The experimental points represent the fine structure of the spectrum, i. e. the center of gravity of six respective hyperfine structure lines. Due to the isotropic nature of the spectrum of manganese salts it is sufficient to consider only

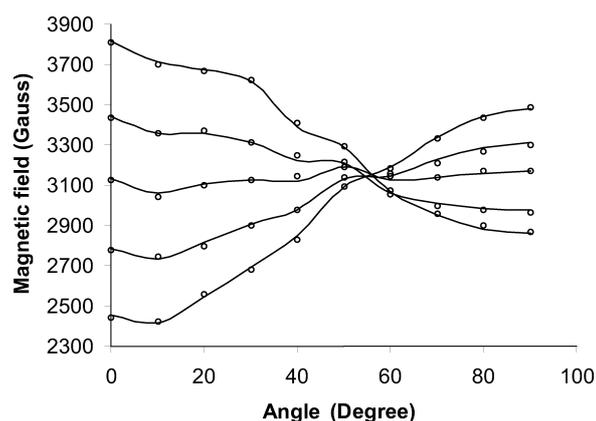


Fig. 2. Angular variation of EPR line positions of  $\text{Mn}^{2+}$  in DAHAMS in the  $ab$  plane. — Theoretical;  $\circ$  experimental.

the hyperfine structure observed parallel and perpendicular to the axis. The value of  $A$  has been obtained by taking the average of all separations of the hyperfine structure lines in the five groups, and  $B$  has similarly been obtained for the perpendicular case. For  $\text{Mn}^{2+}$ , the hyperfine splitting parameter  $A$  is taken to be negative [7,8]. Analysis of the EPR spectra shows that the separation of the sextets increases towards the high field side. This suggests that  $D$  and  $A$  have opposite signs. Therefore  $D$  is positive in this case [9].

	$g_x$	$g_y$	$g_z$	$A$	$B$	$D$	$E$	$a$
(NH <sub>4</sub> ) <sub>2</sub> [Mg(H <sub>2</sub> O) <sub>6</sub> ](SO <sub>4</sub> ) <sub>2</sub>	2.1179	2.1663	2.1409	-53.7	-64.9	208.5	54	-14.5
single crystal	±0.0002	±0.0002	±0.0002	±2	±2	±2	±2	±1
Powder	$g = 2.0953$			$A = 61.17$				

Table 1. Spin-Hamiltonian parameters for Mn<sup>2+</sup> in DAHAMS single crystal;  $A$ ,  $B$ ,  $D$  and  $a$  are all in units of  $10^{-4} \text{ cm}^{-1}$ .

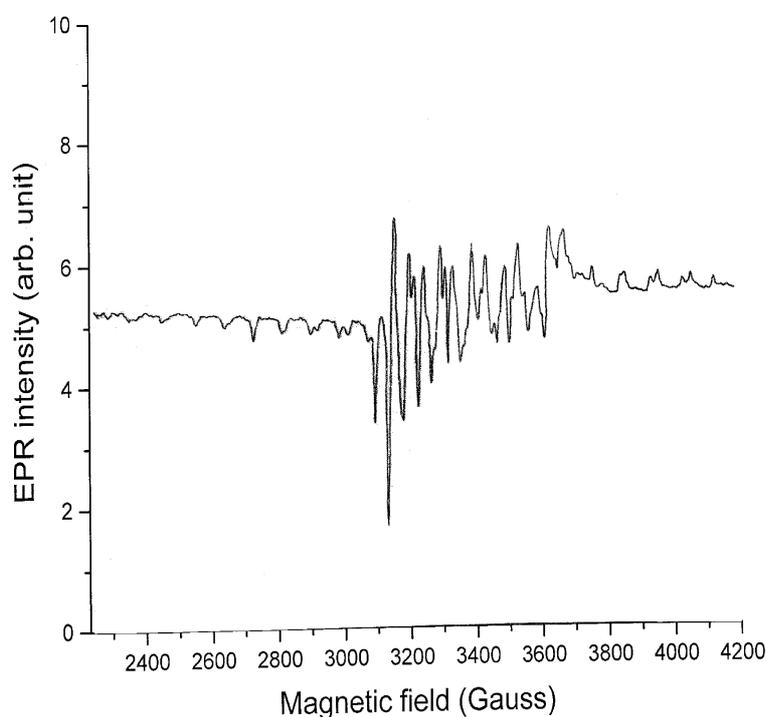


Fig. 3. Powder EPR spectrum of Mn<sup>2+</sup> in DAHAMS at room temperature at 9.3 GHz.

The observed EPR spectrum can be described by a spin-Hamiltonian of the form

$$\begin{aligned} \mathcal{H} = & \beta(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) \\ & + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) \\ & + \frac{a}{6}[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S + 1)] \\ & + A_z S_z I_z, \end{aligned}$$

where the first term is the electronic Zeeman term, the second and third terms are axial and rhombic contributions of the zero field splitting, and the fourth and fifth terms represent the cubic field and the hyperfine interaction term.

The EPR spectra have been analyzed using the above spin-Hamiltonian. The best fit parameters, obtained using a computer program, are listed in Table 1. The EPR study of Mn<sup>2+</sup>-doped DAHAMS was also carried out by Ingram [3], but the parameters reported at 24 GHz (in units of  $10^{-4} \text{ cm}^{-1}$ :  $A = B = 90$ ,  $D = 231$ ,  $E = 54$ ,  $a = 3$ ) are different from that of

Table 2. Direction cosines of Mg-O bonds in DAHAMS and that of the distortion axis.

	$\ell$	$m$	$n$
Mg-O(3)	0.7137	0.5483	0.6934
Mg-O(4)	0.8459	0.1727	0.8110
Mg-O(5)	0.6392	0.2075	0.9517
Mg-O(6)	0.5603	0.3539	0.9313
Mg-O(7)	0.7580	0.6322	0.4969
Mg-O(8)	0.7179	0.6620	0.0900
Mg-O(9)	0.0090	0.4249	0.9024
Distortion axis	0.5878	0.5852	0.5862

the present study at 9.3 GHz (in units of  $10^{-4} \text{ cm}^{-1}$ :  $A = 53.7$ ,  $B = 64.9$ ,  $D = 208.5$ ,  $E = 54$ ,  $a = -14.5$ ).

The powder spectrum of Mn<sup>2+</sup> in DAHAMS is shown in Figure 3. The unsymmetrical nature of the powder spectrum indicates the presence of the  $E$  term in the spin-Hamiltonian [10]. The values of the parameters evaluated from this spectrum are also given in Table 1, along with the single crystal data. These values agree.

The presence of only one site in the lattice, makes it easy to calculate the direction of the distortion axis.

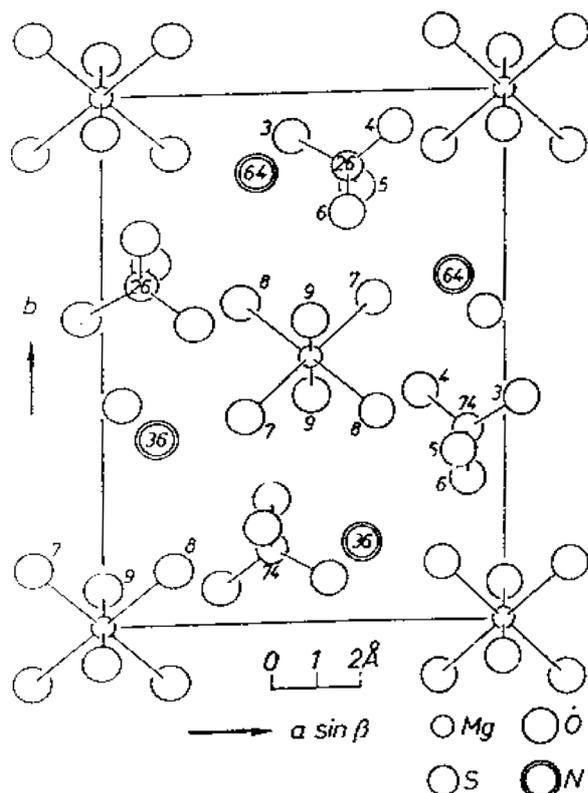


Fig. 4. Crystal structure of (NH<sub>4</sub>)<sub>2</sub>[Mg(H<sub>2</sub>O)<sub>6</sub>](SO<sub>4</sub>)<sub>2</sub>. The numbers at the sulfur and nitrogen atoms indicate their *z* coordinates.

A simple way to identify the distortion axis in such a case has been discussed by Rao and Subramanian [2]. In this method, the maximum value for fine structure splitting is calculated for rotations about three mutually orthogonal axes. The maximum splitting in each plane for the extreme lines is  $4D'(3\cos^2\theta' - 1)$ , where the value of  $D'$  can be found from the powder pattern by measuring the separation between the extreme set of sextets. The direction cosines of the distortion axis are given in Table 2 along with the direction cosines of some Mg-O bonds (Fig. 4). It is clear from the table that direction cosines of the distortion axis do not match with any Mg-O direction. This clearly indicates

that Mn<sup>2+</sup> does not substitute Mg<sup>2+</sup> but enters the lattice interstitially.

The nature of bonds between the manganese ion and its immediate surrounding may be estimated by the determination of the hyperfine splitting constant. The covalency of the bond between Mn<sup>2+</sup> and ligands affects the magnitude of the hyperfine coupling constant [11, 12]. The covalency  $C$  of a bond between the atoms P and Q is approximately related to their electronegativities  $\chi_P$  and  $\chi_Q$  by [13]

$$C = [1 - 0.16(\chi_P - \chi_Q) - 0.035(\chi_P - \chi_Q)^2]/n,$$

where  $n$  is the number of neighbour atoms.

Using the values  $\chi_{Mn} = 1.4$  and  $\chi_O = 3.5$  [14], we have found 20% covalency, indicating that the bonds present in the Mn<sup>2+</sup>:DAHAMS crystal are more ionic. The value of the hyperfine splitting constant 62, predicted from Matumura's plot [11], also agrees reasonably with the observed value 61,  $(A + 2B)/3$ .

We have also reported the optical absorption of manganese-doped DAHAMS [15], and the proposed distortion in the lattice on the basis of this study is consistent with the present EPR study.

#### 4. Conclusion

The EPR study of Mn<sup>2+</sup>-doped diammonium hexa-aqua magnesium(II) sulfate has been carried out at room temperature. The spin-Hamiltonian parameters  $g$ ,  $A$ ,  $B$ ,  $D$ ,  $E$  and  $a$  have been determined. Mn<sup>2+</sup> is expected to enter the lattice interstitially. The covalency of the metal ligand bond has also been estimated.

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