

## An electron spin resonance study of $Mn^{2+}$ doped calcium hydrazine carboxylate monohydrate

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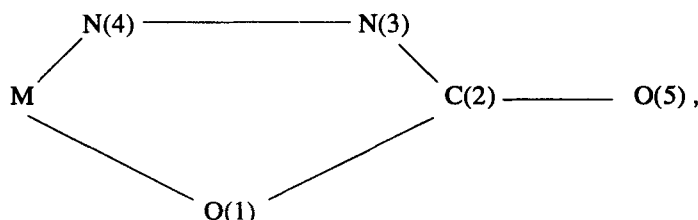
**Abstract.** Single crystals of calcium hydrazine carboxylate, monohydrate have been studied by ESR of  $Mn^{2+}$  doped in the calcium sites. X-band ESR indicated a large crystal field splitting necessitating experiments at Q band. The analysis shows two magnetically inequivalent (but chemically equivalent) sites with  $g_{xx} = 2.0042 \pm 0.0038$ ,  $g_{yy} = 2.0076 \pm 0.0029$ ,  $g_{zz} = 2.0314 \pm 0.001$ ,  $A_{zz} = 0.0099 \pm 0.0002 \text{ cm}^{-1}$ ,  $A_{xx} = 0.0092 \pm 0.0002 \text{ cm}^{-1}$ ,  $A_{yy} = 0.0082 \pm 0.0002 \text{ cm}^{-1}$ ,  $D = 3/2 D_{zz} = 0.0558 \pm 0.0006 \text{ cm}^{-1}$ , and  $E = 1/2 (D_{xx} - D_{yy}) = 0.0127 \pm 0.0002 \text{ cm}^{-1}$ .

One of the principal components of the crystal field, ( $D_{zz}$ ), is found to be along the  $Ca \leftrightarrow Ca$  direction in the structure and a second one, ( $D_{xx}$ ), along the perpendicular to the plane of the triangle formed by three neighbouring calciums. The A tensor is found to have an orientation different from that of the g and D tensors reflecting the low symmetry of the  $Ca^{2+}$  sites.

**Keywords.** Electron spin resonance;  $Mn^{2+}$  ESR; low symmetry effects in ESR;  $Ca(N_2H_3COO)_2 \cdot H_2O$ .

### 1. Introduction

The hydrazine carboxylate compounds consisting of the complexes of 3d-metals, calcium and magnesium with hydrazine carboxylic acid have attracted recent scientific attention (Ravindranathan and Patil 1985). While they present various types of octahedral coordination, all of them contain pentatomic chelate rings of the type



which are similar to rings formed by  $\alpha$ -amino acids with the same metals (Freeman 1967). Therefore, these complexes can serve as model compounds for non-crystallizable compounds of  $\alpha$ -amino acids. Braibanti *et al* (1971) determined the crystal structure of calcium hydrazine carboxylate monohydrate,  $Ca(N_2H_3COO)_2 \cdot H_2O$  and found that it belongs to the triclinic system with  $Z = 2$ . The two calcium ions were surrounded by six oxygens and two nitrogens forming what can be roughly

described as a pentagonal bipyramid, with a centred phase analogous to that observed in  $\text{CaCl}_2$  glycyglycylglycine  $\cdot 3\text{H}_2\text{O}$ . We are reporting here the results of our detailed single crystal ESR studies of the compound in X- and Q-bands, of  $\text{Mn}^{2+}$  doped dilutely in place of the  $\text{Ca}^{2+}$  ions. It was also interesting to characterize the ESR of  $\text{Mn}^{2+}$  in this not so common low symmetry surrounding.

## 2. Experimental

Single crystals of  $\text{Mn}^{2+}$  doped calcium hydrazine carboxylate monohydrate (CHCM) were prepared by the following procedure.

An aqueous solution containing  $\text{Ca}^{2+}$  ions was treated with hydrazine hydrate (99%) saturated with  $\text{CO}_2$  (g). The resulting mixture was allowed to stand exposed to the atmosphere. A colourless solid separated from the solution in about 8–10 days. The crystals were washed with alcohol and stored over  $\text{P}_2\text{O}_5$  in a vacuum desiccator. The composition of the crystals was checked by conventional chemical analysis to be  $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . Calcium content was fixed by EDTA titration and hydrazine was estimated by titration against standard  $\text{KIO}_3$  solution under Andrews conditions. The water content was determined by the weight loss.

Manganese ( $\text{Mn}^{2+}$ ) doped  $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  was prepared by treating an aqueous solution containing  $\text{Ca}^{2+}$  and  $\text{Mn}^{2+}$  ions in required concentrations with the ligand  $\text{N}_2\text{H}_3\text{COO}^-$  as above. The product,  $\text{Ca}_{1-x}\text{Mn}_x(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  crystallized from the mixture. The crystals were pale pink in colour indicating the presence of  $\text{Mn}^{2+}$  in  $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . Doping of  $\text{Mn}^{2+}$  in  $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  is possible due to the isomorphic crystal structures of  $\text{Ca}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and  $\text{Mn}(\text{N}_2\text{H}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  and comparable ionic sizes of  $\text{Ca}^{2+}$  (0.99 Å) and  $\text{Mn}^{2+}$  (0.8 Å).

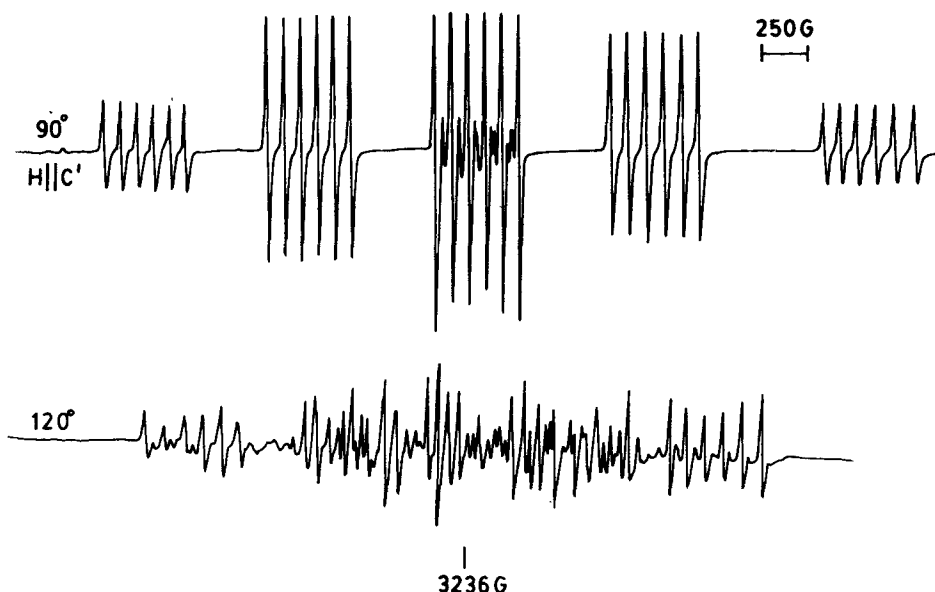
The ESR studies of the single crystals of the compound were carried out at X-band using a Varian E-109 spectrometer and at Q-band using a E-112 X/Q-band spectrometer. A 100 kHz magnetic field modulation was used. Spectra were recorded for different orientations of the magnetic field in three mutually orthogonal planes. A small amount of DPPH was used as the *g*-marker.

## 3. Results and analysis

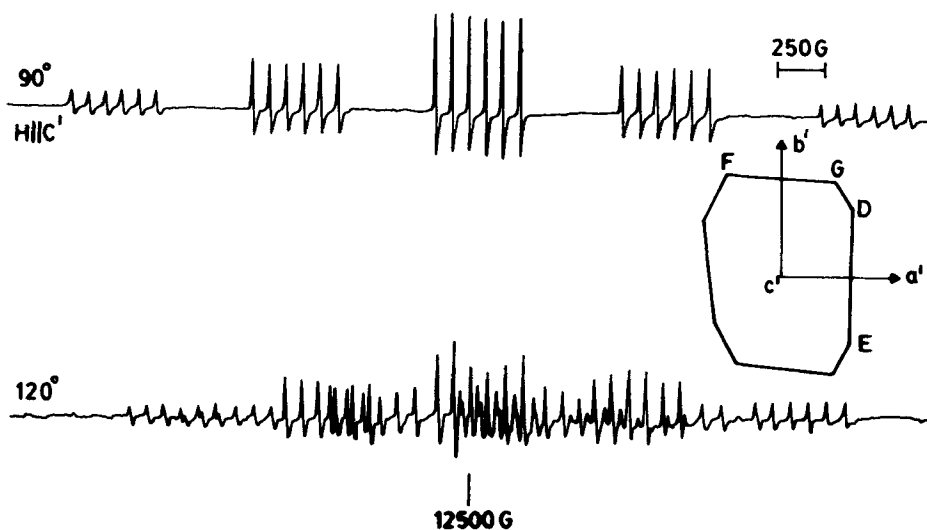
Some typical spectra at X-band ( $\nu = 9.15$  GHz) are shown in figure 1. In general, the ESR spectra of  $\text{Mn}^{2+}$  ( $S = 5/2$ ,  $I = 5/2$ ) consist of five fine-structure multiplets, each consisting of a six-line hyperfine structure. It is apparent from the figure that the  $\text{Mn}^{2+}$  is experiencing a large crystal field splitting. Therefore, a treatment involving the zero field splitting as a perturbation on the Zeeman interaction is not valid at X-band. So experiments were repeated at Q-band ( $\nu = 35.45$  GHz). Figure 2 shows some spectra at Q-band for CHCM at room temperature along with the assignment of the rotation axes with respect to the crystal morphology. Since the crystal belongs to the triclinic system, the crystallographic axes are not orthogonal to each other. Since  $Z = 2$  (Braibanti *et al* 1971), the observed spectrum is a superposition of two 30-line spectra. The unit cell of CHCM is triclinic and no apparent symmetry operation relates the two  $\text{Ca}^{2+}$  sites. Therefore the two  $\text{Mn}^{2+}$  sites can, in principle, be chemically as well as magnetically inequivalent.

Since the system is of low symmetry and therefore, in general no principal axis

of any tensor is expected to be along any of the crystallographic axes it was necessary to carry out angular variation experiments in three orthogonal planes. Moreover, in such a situation it is possible that the principal axes systems of the



**Figure 1.** Some typical spectra at X-band ( $\nu = 9.15$  GHz) of  $Mn^{2+}$  doped calcium hydrazine carboxylate monohydrate



**Figure 2.** Some typical spectra at Q-band ( $\nu = 35.45$  GHz) of  $Mn^{2+}$  doped calcium hydrazine carboxylate monohydrate. (The orientation of the axes of rotation with respect to the crystal morphology is also indicated).

three tensors  $\mathbf{g}$ ,  $\mathbf{A}$  and  $\mathbf{D}$  in the spin Hamiltonian are not coincident with each other (Pilbrow and Lowrey 1971). For the analysis of such a case the method due to Lund and Vanngard (1965) which is a generalization to hyperfine and crystal field interactions, of the Schonland (1959) method of the analysis of Zeeman interaction seems to be most suitable. It enables the determination of the magnitudes and orientations of the three tensors through experiments involving the rotation of the magnetic field in three orthogonal planes of the crystal. Therefore, we have used this method for the analysis and a brief description of the same follows.

We start with the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathcal{H}_a, \quad (1)$$

where

$$\mathcal{H}_a = \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}, \quad (2)$$

with the conventional meanings for the symbols. The first term on the right hand side of (1) represents the Zeeman interaction and  $\mathcal{H}_a$  stands for the crystal field and the hyperfine interactions. For the Q-band spectra, since the Zeeman interaction is of much larger strength, one can safely treat the crystal field and the hyperfine interactions as perturbations. Then, the energy of the system, correct up to the second order terms in perturbation can be written as

$$W(M_z) = \beta g H M_z + \langle M_z | H_a | M_z \rangle + \sum_{M_z' \neq M_z} \frac{|\langle M_z | H_a | M_z' \rangle|^2}{\beta g H (M_z - M_z')}. \quad (3)$$

In order to extract  $\langle M_z | \mathcal{H}_a | M_z \rangle$  from the experimental data one must first eliminate the contribution from the off-diagonal terms. If one reverses the signs of  $M_z$  and  $M_z'$  in (3) it is found that

$$W(-M_z) = -\beta g H M_z + \langle M_z | H_a | M_z \rangle - \sum_{M_z' \neq M_z} \frac{|\langle M_z | H_a | M_z' \rangle|^2}{\beta g H (M_z - M_z')}, \quad (4)$$

and hence the sum  $W(M_z) + W(-M_z)$  is independent of the off-diagonal terms. In practice, since  $H$  is varied while  $\nu$  is kept constant, this elimination of the off-diagonal terms is accomplished by subtracting from each other, equations corresponding to transitions with electronic and nuclear magnetic quantum numbers of opposite signs, such as  $(M_z, M_I \leftrightarrow M_z - 1, M_I)$  and  $(-M_z + 1, -M_I \leftrightarrow -M_z, -M_I)$ . To facilitate the evaluation of the eigenvalues of the spin Hamiltonian (1) a new coordinate system with  $\mathbf{H} \cdot \mathbf{g}$  as the axis of quantization (Z axis) is chosen. In this coordinate system one can explicitly write the perturbing Hamiltonian  $\mathcal{H}_a$  in the form

$$\mathcal{H}_z = \frac{\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g} \cdot \mathbf{H}}{|\mathbf{H} \cdot \mathbf{g}|^2} (3S_z^2 - S^2) + \frac{\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{A}}{|\mathbf{H} \cdot \mathbf{g}|} S_z I_z. \quad (5)$$

Then, the energy for the transition  $(M_z, M_I \leftrightarrow M_z - 1, M_I)$  is given, to the first order in perturbation, by

$$E = W(M_z, M_I) - W(M_z - 1, M_I) = \beta gH + F(M_z - 1/2) + KM_I, \quad (6)$$

where 
$$F = \frac{\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g} \cdot \mathbf{H} \times 3}{|\mathbf{H} \cdot \mathbf{g}|^2}$$

and 
$$K = \frac{|\mathbf{H} \cdot \mathbf{g} \cdot \mathbf{A}|}{|\mathbf{H} \cdot \mathbf{g}|}. \quad (7)$$

Taking the magnetic field  $H$  along the unit vector  $\mathbf{l}$  we get

$$F g^2/3 = \mathbf{l} \cdot \mathbf{T}^{(f)} \cdot \mathbf{l},$$

where  $\mathbf{T}^{(f)} = \mathbf{g} \cdot \mathbf{D} \cdot \mathbf{g},$

and  $K^2 g^2 = \mathbf{l} \cdot \mathbf{T}^{(h)} \cdot \mathbf{l},$

and  $g^2 = \mathbf{l} \cdot \mathbf{T}^{(g)} \cdot \mathbf{l},$

where  $\mathbf{T}^{(g)} = \mathbf{g}^2. \quad (8)$

Thus effecting the elimination of the contributions from second order terms one can calculate  $g^2$ ,  $Fg^2/3$ , and  $K^2g^2$ . These quantities can be fitted to the Schonland form

$$\alpha' + \beta' \cos 2\theta + \gamma' \sin 2\theta, \quad (9)$$

where  $\alpha'$ ,  $\beta'$  and  $\gamma'$  are constants. From these constants the components of the tensors  $T^{(g)}$ ,  $T^{(f)}$  and  $T^{(h)}$  can be calculated. Figure 3 shows the experimental points of four transitions  $M_z, M_I \leftrightarrow M_z - 1, M_I$  where  $M_z = 5/2, 3/2, M_I = 5/2$  and  $M_z = -5/2, -3/2, M_I = -5/2$ , at Q-band, fitted to the spin Hamiltonian in (1) in the three orthogonal planes. Figure 4 shows the fit at X-band in a 'c' plane for the same transitions. It can be seen that the fit between the experimental points and the calculated points at X-band is poor, while for Q-band the fit is very good. The matrix  $T^{(g)}$  formed from the constants  $\alpha'$ ,  $\beta'$  and  $\gamma'$  (9) in the three planes at Q-band were diagonalized to yield the principal components of the  $g$  tensor and the direction cosines with respect to the rotation axes 1, 2 and 3. The crystal field and the hyperfine coupling tensors were calculated from the matrices formed from the fits corresponding to  $Fg^2/3$  and  $K^2g^2$  respectively, to be

$$\mathbf{D} = \mathbf{g}^{-1} \cdot \mathbf{T}^{(f)} \cdot \mathbf{g}^{-1},$$

and

$$\mathbf{A}^2 = \mathbf{g}^{-1} \cdot \mathbf{T}^{(h)} \cdot \mathbf{g}^{-1}. \quad (10)$$

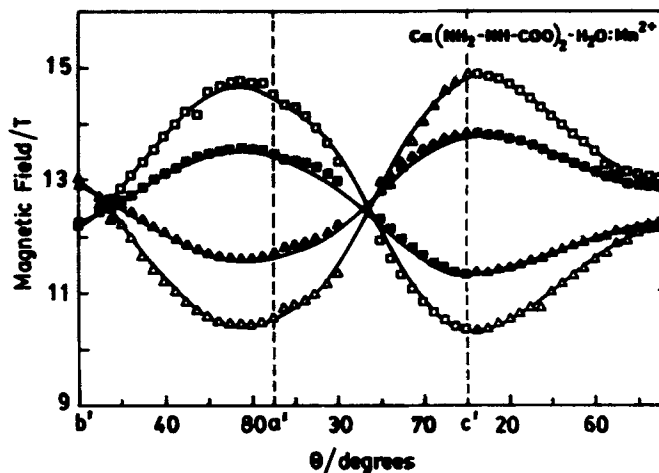


Figure 3. Fitting curves of the experimental points corresponding to the four transitions  $M_z, M_I \leftrightarrow M_z - 1, M_I$  [ $M_z = 5/2, 3/2; M_I = 5/2$  and  $M_z = -1/2, -3/2; M_I = -5/2$ ] at Q-band to the spin Hamiltonian in (1).

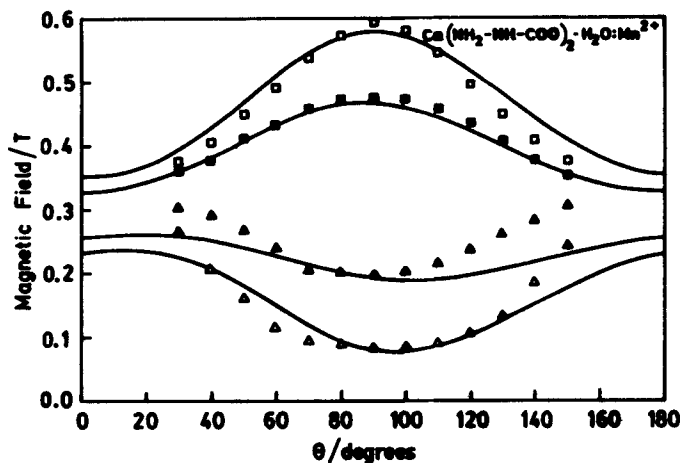


Figure 4. Fitting curves of the experimental points corresponding to the four transitions  $M_z, M_I \leftrightarrow M_z - 1, M_I$  [ $M_z = 5/2, 3/2; M_I = 5/2$  and  $M_z = -(1/2), -(3/2); M_I = -(5/2)$ ] in the  $a'b'$  plane at X-band to the spin Hamiltonian in (1).

The matrices  $D$  and  $A^2$  were diagonalized to yield the principal components along with the direction cosines. Table 1 summarizes these results for one of the sites and table 2 for the other site.

As a check on the spin Hamiltonian parameters obtained in this way, we have also attempted to calculate the line positions using the parameters and compare them with the corresponding experimental values. Now we describe briefly, the procedure adopted to do the same using the values of tables 1 and 2 for the spin Hamiltonian parameters of (1). The field values for the centres of the hyperfine

**Table 1.** Principal components of  $g$ ,  $D$  and  $A$  tensors along with the direction cosines for site 1, with respect to the laboratory frame  $a'$ ,  $b'$ ,  $c'$  for  $Mn^{2+}$  in CHCM.

Principal components	Direction cosines			
	$a'$	$b'$	$c'$	
$g_{zz}$	$2.0274 \pm 8.79 \times 10^{-4}$	$0.9671 \pm 1.94 \times 10^{-4}$	$0.17443 \pm 5.23 \times 10^{-4}$	$0.1851 \pm 5.55 \times 10^{-4}$
$g_{yy}$	$2.0090 \pm 8.34 \times 10^{-4}$	$-0.2002 \pm 5.79 \times 10^{-4}$	$0.9709 \pm 4.73 \times 10^{-4}$	$-0.1310 \pm 3.106 \times 10^{-3}$
$g_{xx}$	$2.0004 \pm 8.36 \times 10^{-4}$	$0.1568 \pm 1.052 \times 10^{-3}$	$0.1638 \pm 2.976 \times 10^{-3}$	$0.9740 \pm 3.385 \times 10^{-4}$
$D_{zz}/G$	$390.2 \pm 4.3$	$0.9656 \pm 0.3 \times 10^{-4}$	$-0.2585 \pm 1.1 \times 10^{-4}$	$0.0264 \pm 0.46 \times 10^{-4}$
$D_{yy}/G$	$-55.9 \pm 4.7$	$0.2565 \pm 1.03 \times 10^{-4}$	$0.9645 \pm 0.32 \times 10^{-4}$	$-0.0621 \pm 1.72 \times 10^{-4}$
$D_{xx}/G$	$-341.9 \pm 5.7$	$0.0416 \pm 0.67 \times 10^{-4}$	$0.0532 \pm 1.65 \times 10^{-4}$	$-0.9977 \pm 0.1 \times 10^{-4}$
$A_{zz}/G$	$106.8 \pm 1.6$	$0.7343 \pm 0.0108$	$-0.4709 \pm 0.0557$	$0.4856 \pm 0.0381$
$A_{yy}/G$	$80.2 \pm 3.1$	$0.6670 \pm 0.16 \times 10^{-4}$	$0.3814 \pm 0.0109$	$0.6399 \pm 0.48 \times 10^{-4}$
$A_{xx}/G$	$102.2 \pm 2.1$	$0.1161 \pm 0.0577$	$0.7937 \pm 0.0279$	$-0.5789 \pm 0.0507$

**Table 2.** Principal components of  $g$ ,  $D$  and  $A$  tensors along with the direction cosines for site 2, with respect to the laboratory frame  $a'$ ,  $b'$ ,  $c'$  for  $Mn^{2+}$  in CHCM.

Principal components	Direction cosines			
	$a'$	$b'$	$c'$	
$g_{zz}$	$2.0314 \pm 1.01 \times 10^{-3}$	$0.20408 \pm 0.0103 \times 10^{-4}$	$0.97778 \pm 2.24 \times 10^{-3}$	$-0.04634 \pm 1.4 \times 10^{-3}$
$g_{yy}$	$2.0077 \pm 2.93 \times 10^{-3}$	$0.9697 \pm 2.17 \times 10^{-3}$	$0.19543 \pm 1.01 \times 10^{-3}$	$0.14646 \pm 7.18 \times 10^{-3}$
$g_{xx}$	$2.0043 \pm 0.38 \times 10^{-4}$	$-0.1341 \pm 7.16 \times 10^{-3}$	$0.07482 \pm 3.12 \times 10^{-3}$	$0.98811 \pm 1.09 \times 10^{-3}$
$D_{zz}/G$	$-393.6 \pm 4.6$	$0.1794 \pm 8.8 \times 10^{-4}$	$0.9837 \pm 1.62 \times 10^{-4}$	$0.0139 \pm 5.97 \times 10^{-4}$
$D_{yy}/G$	$76.7 \pm 2.0$	$0.9834 \pm 1.54 \times 10^{-4}$	$0.1789 \pm 8.93 \times 10^{-4}$	$-0.0315 \pm 2.45 \times 10^{-4}$
$D_{xx}/G$	$345.0 \pm 4.3$	$0.02845 \pm 2.57 \times 10^{-4}$	$0.0194 \pm 0.24 \times 10^{-4}$	$0.9994 \pm 0.01 \times 10^{-4}$
$A_{zz}/G$	$105.4 \pm 2.2$	$0.7775 \pm 5.815 \times 10^{-3}$	$0.4105 \pm 8.61 \times 10^{-4}$	$-0.4763 \pm 8.74 \times 10^{-3}$
$A_{yy}/G$	$87.2 \pm 2.8$	$-0.2891 \pm 2.02 \times 10^{-3}$	$0.9061 \pm 5.2 \times 10^{-4}$	$0.3080 \pm 3.37 \times 10^{-3}$
$A_{xx}/G$	$97.8 \pm 2.5$	$0.5584 \pm 7.04 \times 10^{-3}$	$-0.1025 \pm 7.91 \times 10^{-3}$	$0.8232 \pm 3.8 \times 10^{-3}$

sextets are calculated for the Q-band spectra corrected to the third order in perturbation. To accomplish this it is necessary to calculate the spectrum for a given orientation of the magnetic field in the laboratory frame from spin Hamiltonian parameters in the principal axes frame given in the tables. We have followed the procedure adopted by Okumura (1962) and Balasivasubramanian *et al* (1983) for this purpose.

The spin Hamiltonian expressed in terms of the polar coordinates of the crystal field system is given by (Okumara 1962),

$$\begin{aligned}
 \mathcal{H} = & \beta gHS_z + a [(S_z^2 - 1)/3S(S + 1)] + b (2S_z S_+ - S_+) \\
 & + b^* (2S_z S_- + S_-) + CS_+^2 + C^* S_-^2 + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I},
 \end{aligned}
 \tag{11}$$

where  $a$ ,  $b$  and  $c$  are functions in the polar and azimuthal coordinates  $\theta$  and  $\varphi$  of the magnetic field  $H$  with respect to the crystal field system. Table 1 provides the relation between the laboratory frame  $a'$ ,  $b'$ ,  $c'$  system of coordinates and the crystal field system of coordinates. Therefore to evaluate the polar and azimuthal angles  $\theta$  and  $\varphi$ , it is necessary to transform the system of coordinates of the laboratory frame to the system of coordinates of the crystal field. From table 1, it can be seen that the principal component  $D_{xx}$  is parallel to the laboratory axis  $c'$ . Therefore by applying the Euler method of the rotation of the laboratory frame around the  $c'$ -axis by an angle  $\alpha$ , say, (it is the same as the angle between  $D_{yy}$  and  $b'$ -axis), the system of coordinates  $a'$ ,  $b'$ ,  $c'$  will transform to the principal system of coordinates  $D_{xx}$ ,  $D_{yy}$ ,  $D_{zz}$ . The matrix of transformation is

$$R(\alpha) = \begin{vmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{vmatrix}. \quad (12)$$

The direction cosines of the magnetic field  $H$  in  $c'a'$  plane with respect to the principal system of coordinates are given by

$$\begin{vmatrix} \cos \theta & \sin \varphi \\ -\sin \theta & \cos \varphi \\ \sin \theta & \cos \varphi \end{vmatrix} = \begin{vmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} \sin \theta' \\ 0 \\ \cos \theta' \end{vmatrix}, \quad (13)$$

where  $\theta'$  is the angle between the magnetic field  $H$  and the  $c'$  axis in  $c'a'$  plane. From (13), the values of the polar and the azimuthal angles  $\theta$  and  $\varphi$  can be calculated. Using the angles  $\theta$  and  $\varphi$  evaluated in this way, the positions of the centres of the fine structure multiplets corrected to third order in perturbation have been calculated (Balasivasubramanian *et al* 1983) as follows:

$$|\pm \frac{5}{2}\rangle \longleftrightarrow |\pm \frac{3}{2}\rangle:$$

$$h\nu = G + 4a + \frac{1}{G} [128 bb^* - 16 cc^*] \\ + \frac{1}{G^2} [\mp 576 abb^* \mp 24 acc^* \pm 480 (bbc^* + b^*b^*c)],$$

$$|\pm \frac{3}{2}\rangle \longleftrightarrow |\pm \frac{1}{2}\rangle:$$

$$h\nu = G \pm \frac{1}{2} a + \frac{1}{g} [-16 bb^* + 20 cc^*] \\ + \frac{1}{G^2} [\pm 192 abb^* \mp 132 acc^* \mp 480 (bbc^* + b^*b^*c)],$$

and  $|+\frac{1}{2}\rangle \longleftrightarrow |-\frac{1}{2}\rangle:$

$$h\nu = G + \frac{1}{G} [-64 bb^* + 32 cc^*].$$

Where



$$G = g \beta H,$$

$$a = [D(3 \cos^2 \theta - 1) + \frac{3}{2} \sin^2 \theta \cos 2\varphi],$$

$$b = [-D \sin \theta \cos \theta + \frac{1}{4} E \sin \theta (1 + \cos \theta) \exp(2i\varphi) - (1 - \cos \theta) \exp(2i\varphi)] \exp(-i\varphi),$$

$$c = [\frac{1}{4} D \sin^2 \theta + \frac{1}{8} E (1 + \cos \theta)^2 \exp(2i\varphi) + (1 - \cos \theta)^2 \exp(-2i\varphi)] \exp(-2i\varphi).$$

Figure 5 shows the plots of the calculated positions of the centres of the fine structure multiplets corrected to third order in perturbation and the experimental points in the  $c'a'$  plane. From this figure it can be seen that the calculated line positions of the spectrum at high field side are quite satisfactory. However, at low field side there is a departure of the calculated points from the experimental ones. At this stage it must be noted that in these calculations we neglect the effect of the higher order correction in the hyperfine interaction. Also from tables 1 and 2 it is seen that the hyperfine tensor  $\mathbf{A}$  is not coincident with  $\mathbf{g}$  and  $\mathbf{D}$  tensors. These facts, along with the anisotropy of the hyperfine interaction (tables 1 and 2) result in the departure in the calculation of the centres of the fine structure multiplets and thus cause a slight difference in the calculated and the experimental line positions.

#### 4. Discussion

X-ray structure of calcium hydrazine carboxylate monohydrate shows that the

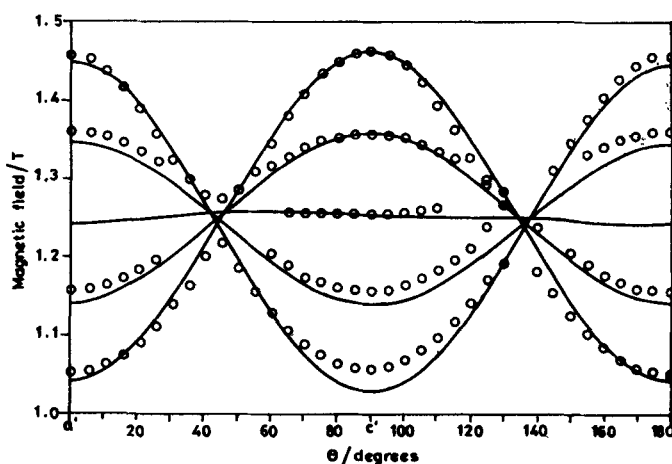


Figure 5. Calculated curves and experimental points of the centres of the fine structure multiplets for Q-band spectra in the  $a'c'$  plane.

complex crystallizes in the triclinic space group *P1* with two formula units per unit cell. The structure consists of chains parallel to [001] formed by a sequence of cations and anions (figure 6). The resulting coordination number around the  $\text{Ca}^{2+}$  ions is 8 with six O atoms and two N atoms. Two O atoms are shared between two  $\text{Ca}^{2+}$  ions and form bridges along the *c*-direction with an angle of  $145.03^\circ$  inclined to each other while the three neighbouring  $\text{Ca}^{2+}$  ions form a triangle with an angle of about  $115^\circ$  between the  $\text{Ca(I)} \rightarrow \text{Ca(II)}$  and the  $\text{Ca(I)}-\text{Ca(III)}$  directions. The direction of the normal to the plane of the triangle is common to all the Ca-triangles in the structure and leads to the coincidence of the spectra for the two sites of the paramagnetic centres for the magnetic field along that direction. From tables 1 and 2, it can be seen that (i) the two sites show very similar magnitudes of the principal components of the three tensors *g*, *D* and *A*, thus showing that the two sites are only magnetically inequivalent, and (ii) the  $D_{xx}$  components of the two sites are very nearly coincident with each other and are

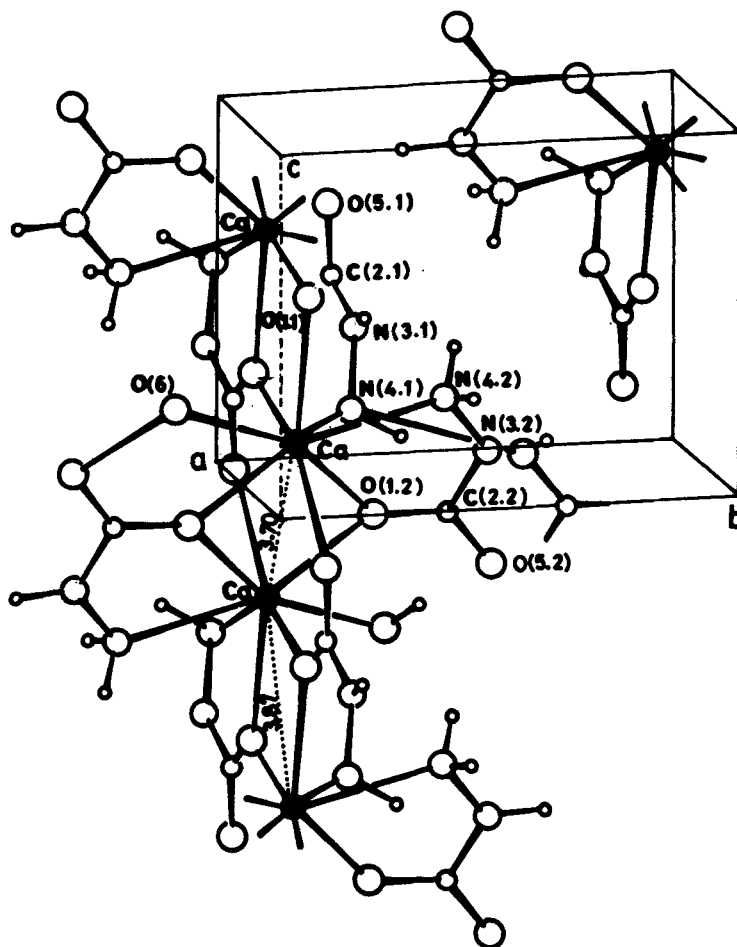


Figure 6. Structure of CHCM showing  $\text{Ca} \leftrightarrow \text{O}$  bridges along the [001] direction.

parallel to the  $c'$  direction, which is consistent with the fact that parallel to the  $c'$  direction one observes only one set of  $Mn^{2+}$  signals. Also from the tables it can be seen that the  $D_{zz}$  components of the two sites are inclined to each other at an angle of about  $115^\circ$ . Therefore, it can be concluded that the  $D_{zz}$  component of the crystal field tensor is parallel to the  $Ca \longleftrightarrow Ca$  direction and the  $D_{xx}$  component [ $D_{xx}(1)/D_{xx}(2)$ ] is along the normal to the plane of the triangles formed by the three neighbouring  $Ca^{2+}$  ions.

## 5. Conclusion

The ESR spectra of  $Mn^{2+}$  substituting dilutely for  $Ca^{2+}$  in calcium hydrazine carboxylate monohydrate single crystals show interesting low symmetry effects. The  $Mn^{2+}$  ions experience large crystal field interactions. The hyperfine tensor has a different orientation from that of the Zeeman and the crystal field tensors. The orientation of the zero-field tensor is correlated with some special directions in the crystal structure; the  $D_{zz}$  principal component is along the  $Ca \longleftrightarrow Ca$  direction and the  $D_{xx}$  component is oriented along the perpendicular to the plane formed by three neighbouring  $Ca^{2+}$  ions.

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