

# ELECTRON PARAMAGNETIC RESONANCE OF $Mn^{2+}$ IN NaF SINGLE CRYSTALS\*

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## ABSTRACT

The electron paramagnetic resonance of  $Mn^{2+}$  in NaF single crystals is investigated at different temperatures from 573° K to 93° K. Four different spectra designated as I, II, III<sub>2</sub> and III<sub>4</sub> are observed. Spectrum I consists of a single broad resonance corresponding to precipitated  $Mn^{2+}$  ions. Spectrum II is isotropic and centred near  $g = 2.00$ . This spectrum corresponds to substitutional  $Mn^{2+}$  ions with remote charge compensating sites and therefore with local cubic symmetry. Spectrum III<sub>2</sub> with  $g = 2.014$  and spectrum III<sub>4</sub> with  $g = 1.995$  are also due to substitutional  $Mn^{2+}$  ions but subjected to tetragonal crystalline fields and are the same as those reported by earlier workers. Superhyperfine structure has been observed in spectra II, III<sub>2</sub> and III<sub>4</sub>. The analysis of that structure in spectra II and III<sub>2</sub> has been carried out for the first time and the constants  $A_s$  and  $A_\sigma$  are given. The spectra are analysed by the usual spin-Hamiltonian method.

## INTRODUCTION

It is known that when alkali halide crystals are doped with divalent impurities like  $Mn^{2+}$ , alkali vacancies are created to maintain charge neutrality. The divalent ions could individually go in substitutionally or interstitially in the crystal or could also go in clusters or precipitates. The vacancy could be a nearby neighbour to the divalent ion or it could be far away from it. The electron paramagnetic resonance (EPR) spectra<sup>1-7</sup> clearly indicate the different ways in which the impurity ions go into the crystals. Earlier work<sup>5, 6</sup> on  $Mn^{2+}$ :NaCl has shown that the following different types of EPR spectra could be obtained depending upon the way in which the crystal is grown: (I) a broad absorption due to clusters or precipitates of  $Mn^{2+}$ , (II) a spectrum showing only one hyperfine sextet which is due to  $Mn^{2+}$  in cubic symmetry

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the vacancies being far away, (III<sub>1</sub>) an orthorhombic spectrum due to Mn<sup>2+</sup> associated with a first neighbour alkali vacancy along the  $\langle 110 \rangle$  direction, (III<sub>2</sub>) a tetragonal spectrum due to Mn<sup>2+</sup> associated with a second neighbour alkali vacancy along  $\langle 100 \rangle$ , (IV) an orthorhombic spectrum due to Mn<sup>2+</sup> associated with a molecular oxygen ion in the first neighbour halogen site, and (V) a tetragonal spectrum due to Mn<sup>2+</sup> associated probably with a hydroxyl ion again in the first neighbour halogen site. Hayes and Jones<sup>3</sup> investigated the EPR of Mn<sup>2+</sup>:NaF and reported a strong tetragonal spectrum which is called here for convenience as III<sub>4</sub> and also a weak spectrum of the same kind which is designated here as III<sub>2</sub>. Both these spectra have also been analysed. They are reported to reveal super-hyperfine structure (SHFS) though the involved constants for only the strong spectrum III<sub>4</sub> had been obtained. In order to see whether the other types of the spectra reported for Mn<sup>2+</sup>:NaCl could also be found the EPR of Mn<sup>2+</sup>:NaF has been reinvestigated with larger samples at different temperatures in the range 573°–93° K. The present paper deals with the results obtained in such an investigation.

#### EXPERIMENTAL

Electron paramagnetic resonance (EPR) studies at room temperature are made with a large single crystal of NaF of an approximate volume of one cubic centimeter containing 0.1% of manganese. This crystal is cleaved from a melt-grown crystal supplied by OPTOVAC and is quite transparent. The crystal was grown in vacuum in a graphite crucible. Smaller crystals cut from the above large crystal are used for studying the spectra between 573° K and 93° K. A Varian X-band spectrometer V-4502-12 with 100 kc./sec. field modulation is used. Angular variation is studied with the sample in a V-4533 rotating cavity while the temperature studies are made with V-4547 variable temperature accessories. The magnetic field is measured with a model F-8 flux meter. The frequency of the proton resonance is measured with a Hewlett Packard frequency counter HP-524C. The field has been standardised using a polycrystalline sample of the free radical  $\alpha$ - $\alpha$ -diphenyl  $\beta$ -picryl hydrazyl (DPPH) as a field marker the g-value of which is taken as  $2.0036 \pm 0.0002$ .<sup>8</sup>

#### THEORY

The Mn<sup>2+</sup> spectrum has been discussed well by various authors.<sup>9-11</sup> Divalent manganese has a  $3d^5$  electron configuration for which the ground term is  ${}^6S_{5/2}$ . This state splits into three Kramers' doublets in the presence of an electric field having an axial or lower symmetry. This splitting gives

rise to five fine structure lines in the EPR spectrum of Mn<sup>2+</sup> which further split into sextets due to hyperfine interaction with the nucleus. An axial spectrum is described by a spin-Hamiltonian

$$\begin{aligned} H = g\beta\mathbf{H}\cdot\mathbf{S} + A^{55}\mathbf{S}\cdot\mathbf{I} + \frac{a}{6} [S_x^4 + S_y^4 + S_z^4 \\ - \left(\frac{1}{5}\right) S(S+1)(3S^2 + 3S - 1)] \\ + D \left[ S_z^2 - \left(\frac{1}{3}\right) S(S+1) \right]. \end{aligned} \quad (1)$$

The first term in Eqn. (1) describes the Zeeman interaction of the electron spin ( $S = 5/2$ ) with the applied static magnetic field  $H$ ,  $g$  is the spectroscopic splitting factor and  $\beta$  is the Bohr magneton. The second term is due to the nuclear hyperfine interaction,  $A^{55}$  being the hyperfine interaction constant due to the manganese nucleus. 'I' is the nuclear spin of manganese ( $I = 5/2$ ). The third and the fourth terms are related to the splittings of the electronic levels in the zero magnetic field due to the crystalline electric field. The crystal field parameters  $a$  and  $D$  correspond, respectively, to the cubic and tetragonal fields. In the present case a term of the type  $\sum \mathbf{S}\cdot\mathbf{A}^i\cdot\mathbf{I}_o^i$  is added to the spin-Hamiltonian since there exists a magnetic interaction between Mn<sup>2+</sup> ion and the surrounding F<sup>-</sup> ligand nuclei whose spin is  $I_o (= \frac{1}{2})$ . This interaction produces a shift  $\delta H$  in the field at which resonance occurs<sup>12, 8</sup>

$$\delta H = \sum_i \mathbf{I}_{oz}^i \{A_s^i + A_\sigma^i (3 \cos^2 \theta_{z, \sigma} - 1)\} \quad (2)$$

where the summation is over the six fluorine nuclei. It is assumed that the magnetic electrons are partly in  $p\sigma$  orbitals on fluorines and that the magnetic field is applied along the  $z$ -axis at an angle  $\theta_{z, \sigma}$  with the axis of each  $\sigma$  bond.  $A_s$  is the isotropic part and is determined by the  $s$  electron contact interaction.  $A_\sigma$  is the anisotropic part and it includes the dipole-dipole interaction and the coupling through the  $p\pi$  orbitals. As the six fluorines form an octahedron around Mn<sup>2+</sup>, the interaction parameters  $A_s$  and  $A_\sigma$  can be expected to be the same for all the fluorine nuclei. When the magnetic field is parallel to the crystallographic axis  $\langle 100 \rangle$ , two fluorines along the field direction will be equivalent while the four fluorines in the plane perpendicular to the field direction will be equivalent among themselves. In such a case Equation 2 takes the form

$$\delta H = A_s \sum_1^6 I_{oz}^i + 2A_\sigma \sum_1^2 I_{oz}^i - A_\sigma \sum_1^4 I_{oz}^i \quad (2a)$$

where  $I_{Oz}$ , can take the values  $\frac{1}{2}$  or  $-\frac{1}{2}$ . The resulting number of lines in this case will be fifteen and the expressions for  $\delta H$  for the individual lines along with their relative intensities are given in columns 3 and 2 of Table I. In practice the number of lines observed will be smaller than fifteen. This is because of the considerable line width and the overlaps which will be dependent upon the relative magnitudes of  $A_s$  and  $A_\sigma$ . If  $A_\sigma$  is exactly equal to zero there will be seven lines all of which will be equally separated from one another.

The field values corresponding to the different transitions when the static magnetic field is parallel to the (100) direction are given by<sup>5, 6</sup>

$$H \left( M = +\frac{1}{2} \rightarrow -\frac{1}{2} \right) = H_0 \quad (3)$$

$$H \left( M = \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2} \right) = H_0 \mp 2D \pm \frac{5a}{2} \quad (4)$$

$$H \left( M = \pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2} \right) = H_0 \mp 4D \mp 2a \quad (5)$$

to which the following expression for hyperfine structure is to be added

$$H(m \leftrightarrow m) = -Am^{55} - \frac{A^{55^2}}{2H_0} [I(I+1) - m^2 + (2M-1)m] \quad (6)$$

Here  $H_0 = \frac{h\nu}{g\beta}$ ,  $\nu$  being the microwave frequency.

If the crystalline field has a higher symmetry, say cubic,  $D = 0$  and it splits  ${}^6S_{5/2}$  in  $o$  a doublet and a quartet. In moderate crystalline fields, the zero field splittings will be so small that the fine structure cannot be resolved, and the spectrum contains only an isotropic sextet at  $g = 2$ .

## RESULTS AND DISCUSSION

Four different kinds of spectra have been observed and are designated as spectra I, II, III<sub>2</sub> and III<sub>4</sub> for a convenient comparison with the corresponding spectra<sup>6</sup> in  $Mn^{2+} : NaCl$ . The spectrum I represents a broad overlapping absorption which is more prominent at low temperature. This is due to  $Mn^{2+}$  ions which occur in aggregates or clusters. Spectrum II shows a hyperfine sextet and is due to  $Mn^{2+}$  ions at the alkali sites having a cubic site symmetry with no nearby alkali vacancies. Spectra III<sub>2</sub> and III<sub>4</sub> are

TABLE I

*The observed and calculated superhyperfine structure in spectrum III<sub>2</sub> with  
A<sub>s</sub> = 14.3 G and A<sub>σ</sub> = 3.3 G*

(M = +5/2 → +3/2 and m = -5/2 → -5/2)

Line Nos.	Relative statistical weight	δH	δH in gauss	δH expected peaks in gauss	Calculated relative intensity	H = δH + 2128.0 in gauss	H observed in gauss	Observed relative intensity
1	1	-3A <sub>s</sub>	-42.9	-42.9	1	2085.1	2083.9	1
2	4	-(2A <sub>s</sub> + A <sub>σ</sub> )	-31.9	-31.9	4	2096.1	2097.2	5
3	2	-(2A <sub>s</sub> + A <sub>σ</sub> )	-22.0	-21.2	8	2106.8	2106.9	10
4	6	-(A <sub>s</sub> + 2A <sub>σ</sub> )	-20.9					
5	8	-(A <sub>s</sub> - A <sub>σ</sub> )	-11.0	-10.6	12	2117.4	2117.4	13
6	4	-3A <sub>σ</sub>	-9.9					
7	1	-(A <sub>s</sub> - 4A <sub>σ</sub> )	-1.1	0.0	14	2128.0	2128.8	14
8	12	0	0					
9	1	(A <sub>s</sub> - 4A <sub>σ</sub> )	1.1	10.6	12	2138.6	2138.9	14
10	4	3A <sub>σ</sub>	9.9					
11	8	(A <sub>s</sub> - A <sub>σ</sub> )	11.0	21.2	8	2149.2	2149.0	11
12	6	+(A <sub>s</sub> + 2A <sub>σ</sub> )	20.9					
13	2	2(A <sub>s</sub> - A <sub>σ</sub> )	22.0	31.9	4	2159.9	2159.4	6
14	4	(2A <sub>s</sub> + A <sub>σ</sub> )	31.9					
15	1	3A <sub>s</sub>	42.9	42.9	1	2170.9	2170.1	2

due to Mn<sup>2+</sup> ions at the alkali sites with tetragonal site symmetries, the (100) axis being the tetragonal axis. These two spectra have been observed and analysed by the earlier workers though no models have been proposed. Spectrum III<sub>2</sub> has a large spread compared to spectrum III<sub>4</sub> showing that the Mn<sup>2+</sup> ions responsible for spectrum III<sub>2</sub> experience a larger crystalline field compared to those responsible for spectrum III<sub>4</sub>. These observations indicate that the complex responsible for the spectrum III<sub>2</sub> is a Mn<sup>2+</sup> ion at the alkali site associated with a second neighbour alkali vacancy while that responsible for the spectrum III<sub>4</sub> is again a similar Mn<sup>2+</sup> ion but associated probably with a fourth distant neighbour alkali vacancy. Both the complexes have their site symmetry axes along the (100) direction. It has been

observed that spectrum II is more intense than spectrum III<sub>4</sub> which is again more intense than spectrum III<sub>2</sub>. This observation indicates clearly that in Mn<sup>2+</sup>:NaF, remote charge compensation is preferred to the local charge compensation.

All the spectra II, III<sub>2</sub> and III<sub>4</sub> show superhyperfine structure. The spectra have been analysed using the expressions indicated earlier and the constants obtained are given in Table IV where the data available from the earlier work are also included. The spectrum II is overlapped by the transition  $M = \frac{1}{2} \leftrightarrow -\frac{1}{2}$  of the spectrum III<sub>4</sub> and also by that of the spectrum III<sub>2</sub>. Its separate existence has been confirmed by taking the spectrum of a powdered sample as has been done by Veigele and Tantilla<sup>15</sup> in the case of Mn<sup>2+</sup>:KF. Figure 1 shows the spectrum II as obtained from such a powdered or polycrystalline sample showing clearly the six hyperfine lines along with the superhyperfine structure.

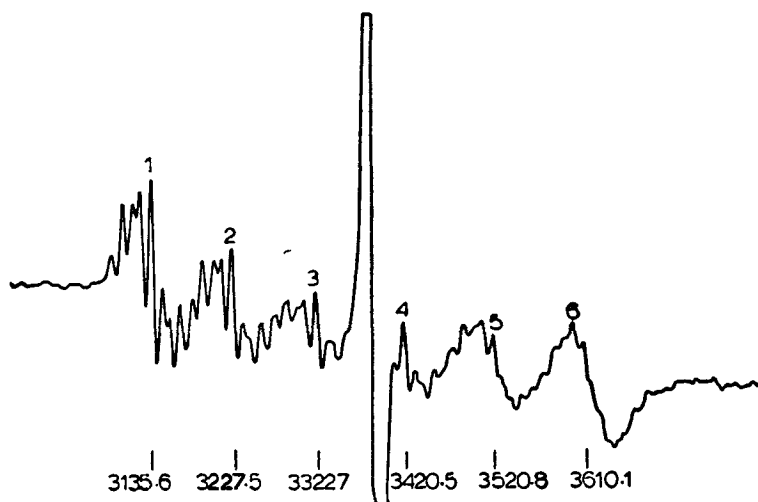


FIG. 1. The EPR spectrum II of Mn<sup>2+</sup>:NaF powdered (polycrystalline) sample at room temperature. Numbers indicate the field values in gauss. The central line is due to the field marker, DPPH.

It may be noted that one would be tempted to analyse the spectrum III<sub>4</sub> as a 90° part of the spectrum III<sub>2</sub>. Then one should see two components for III<sub>2</sub> when H is deviated from the  $\langle 100 \rangle$  direction and such components have not been observed. Further the spectrum III<sub>4</sub> is about ten times more intense than spectrum III<sub>2</sub> which will be difficult to understand unless these two are different spectra. A detailed analysis for these spectra confirmed that they are two different spectra. It appears that the  $\theta = 90^\circ$  spectrum

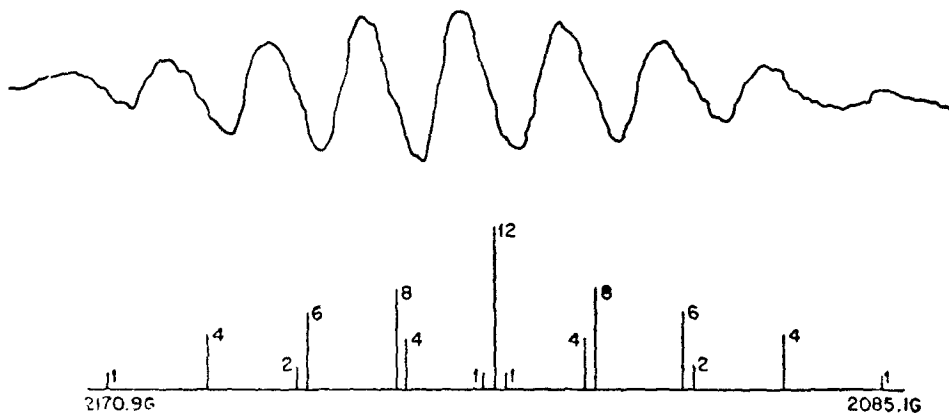


FIG. 2. The observed and calculated superhyperfine structure in the EPR spectrum III<sub>2</sub> of  $Mn^{2+}$ : NaF single crystal at room temperature with H parallel to the  $\langle 100 \rangle$  axis of the crystal for the transition  $M = +5/2 \rightarrow +3/2$  and  $m = -5/2 \rightarrow -5/2$ .

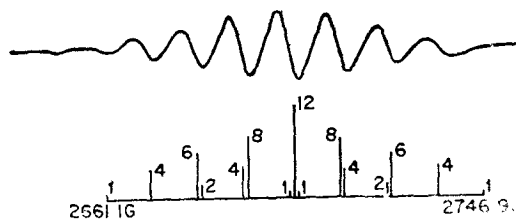


FIG. 3. The observed and calculated superhyperfine structure in the EPR spectrum III<sub>4</sub> of  $Mn^{2+}$ : NaF single crystal at room temperature with H parallel to the  $\langle 100 \rangle$  axis of the crystal for the transition  $M = +5/2 \rightarrow +3/2$  and  $m = -5/2 \rightarrow -5/2$ .

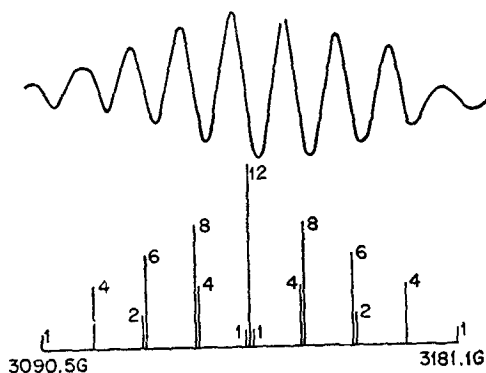


FIG. 4. The observed and calculated superhyperfine structure in the EPR spectrum I<sub>1</sub> of  $Mn^{2+}$ : NaF single crystal at room temperature with H parallel to the  $\langle 100 \rangle$  axis of crystal for the transition  $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$  and  $m = -5/2 \rightarrow -5/2$ .

TABLE II

The observed and calculated superhyperfine structure in spectrum III<sub>4</sub> with  
 $A_s = 14.3 \text{ G}$  and  $A_\sigma = 3.8 \text{ G}$

( $M = +5/2 \rightarrow +3/2$  and  $m = -5/2 \rightarrow -5/2$ )

Line Nos.	Relative statistical weight	$\delta H$	$\delta H$ in gauss	$\delta H$ expected peaks in gauss	Calculated relative intensity	H (calculated) = $\delta H + 2704.0$ in gauss	H observed in gauss	Observed relative intensity
1	1	$-A_s$	-42.9	-42.9	1	2661.1	2662.1	1
2	4	$-(2A_s + A_\sigma)$	-32.4	-32.4	4	2671.6	2672.0	3
3	6	$-(A_s + 2A_\sigma)$	-21.9	-21.7	8	2682.3	2682.0	8
4	2	$-2(A_s - A_\sigma)$	-21.0					
5	4	$-3A_\sigma$	-11.4	-10.8	12	2693.2	2693.8	12
6	8	$-(A_s - A_\sigma)$	-10.5					
7	1	$(A_s - 4A_\sigma)$	-0.9	0.0	14	2704.0	2703.1	14
8	12	0	0.0					
9	1	$-(A_s - 4A_\sigma)$	0.9	10.8	12	2714.8	2714.8	12
10	8	$(A_s - A_\sigma)$	10.5					
11	4	$3A_\sigma$	11.4	21.7	8	2725.7	2726.0	8
12	2	$2(A_s - A_\sigma)$	21.0					
13	6	$(A_s + 2A_\sigma)$	21.9	32.4	4	2736.4	2736.7	4
14	4	$(2A_s + A_\sigma)$	32.4					
15	1	$3A_s$	42.9	42.9	1	2746.9	2747.2	1

of III<sub>2</sub> is overlapped by the stronger spectrum III<sub>4</sub> and is not identifiable separately. Similarly the  $\theta = 90^\circ$  part of the spectrum III<sub>4</sub> is overlapped by the spectrum II and is not observable.

#### EFFECT OF TEMPERATURE

High temperature studies are made up to 573° K. One expects that the vacancies become mobile and get dissociated from Mn<sup>2+</sup> ions at higher temperatures.<sup>15 16</sup> In the present study the intensity of the axial and cubic spectra increased in the first instance with the increase of temperature indicating that the number of the corresponding magnetic centres has increased in the initial stages. This happens probably at the expense of the intensity



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TABLE III

*The observed and calculated superhyperfine structure in spectrum II with  
A<sub>s</sub> = 15.1 G and A<sub>σ</sub> = 3.7 G*

(M = + ½ ↔ - ½ and m = - 5/2 ↔ - 5/2)

Line Nos.	Relative statistical weight	δH	δH in gauss	δH expected peaks in gauss	Calculated relative intensity	H = δH + 3135.8 in gauss	H observed in gauss	Observed relative intensity
1	1	-3A <sub>s</sub>	-45.3	-45.3	1	3090.5	3091.4	1
2	4	-2(A <sub>s</sub> + A <sub>σ</sub> )	-33.9	-33.9	4	3101.19	3102.4	4
3	2	-2(A <sub>s</sub> - A <sub>σ</sub> )	-22.8	-22.6	8	3113.2	3112.6	8
4	6	-(A <sub>s</sub> + 2A <sub>σ</sub> )	-22.5					
5	8	-(A <sub>s</sub> - A <sub>σ</sub> )	-11.4	-11.3	12	3121.5	3123.7	13
6	4	-3A <sub>σ</sub>	-11.1					
7	1	-(A <sub>s</sub> - 4A <sub>σ</sub> )	-0.3	0	14	3135.8	3135.6	14
8	12	0	0					
9	1	(A <sub>s</sub> - 4A <sub>σ</sub> )	0.3	11.3	12	3147.1	3146.7	13.5
10	4	3A <sub>σ</sub>	11.1					
11	8	(A <sub>s</sub> - A <sub>σ</sub> )	11.4	22.6	8	3158.4	3157.7	10
12	6	(A <sub>s</sub> + 2A <sub>σ</sub> )	22.5					
13	2	2(A <sub>s</sub> - A <sub>σ</sub> )	22.5	33.9	4	3169.7	3169.6	6
14	4	(2A <sub>s</sub> + A <sub>σ</sub> )	33.9					
15	1	3A <sub>s</sub>	45.3	45.3	1	3181.1	3182.4	2

of the spectrum I which is found to be more prominent at the 93° K. On further increase of temperature, at about 533° K the 'SHFS' gets smeared up and the intensity of the axial spectra start diminishing with a corresponding increase in the intensity of the cubic spectrum. One can infer from these observations that the charge compensation is occurring by the production of alkali vacancies and the vacancies become mobile above 533° K and get dissociated at higher temperature thus making the local symmetry of Mn<sup>2+</sup> cubic. This is reflected in the exchange of intensities between axial and cubic spectra, the intensity of the latter being enhanced at the cost of the intensity of the former.

The superhyperfine structure has been analysed following the procedure of Tinkham.<sup>12</sup> A comparison of the observed and calculated SHFS pattern for the transition  $M = +5/2 \rightarrow +3/2$ ,  $m = -5/2 \rightarrow -5/2$  in the spectra III<sub>2</sub> and III<sub>4</sub> is shown in Tables I and II respectively while that for the transition  $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$ ,  $m = -5/2 \rightarrow -5/2$  in the spectrum II is shown in Table III. The corresponding spectra are shown in Figs. 2, 3 and 4 respectively in which the calculated SHFS patterns are also drawn to scale. The values obtained for the constants  $A_s$  and  $A_\sigma$  for all the three spectra are given in Table IV where the data available from the earlier work on spectrum III<sub>4</sub> are also included.

TABLE IV  
Spin-hamiltonian parameters\* of  $Mn^{2+}$  in NaF at 300° K

Parameter	Spectrum I	Spectrum II	Spectrum III <sub>2</sub>	Spectrum III <sub>4</sub>
$g$ ..	2.0	$2.003 \pm 0.002$	$2.014 \pm 0.004$ ( $2.00 \pm 0.01$ )†	$1.995 \pm 0.003$ ( $1.996 \pm 0.006$ )†
$A^{55}$ ( $\times 10^{-4}$ cm. <sup>-1</sup> )	...	$-90.4 \pm 1.6$	$-92.8 \pm 0.5$ ( $92 \pm 4$ )†	$-93.8 \pm 1.0$ ( $91 \pm 4$ )†
$D$ ( $\times 10^{-4}$ cm. <sup>-1</sup> ) ..	...	...	$221.0 \pm 0.2$ ( $220 \pm 8$ )†	$89.0 \pm 0.5$ ( $89 \pm 5$ )†
$a$ ( $\times 10^{-4}$ cm. <sup>-1</sup> ) ..	...	...	0.2	-1.3
$A_s^{10}$ ( $\times 10^{-4}$ cm. <sup>-1</sup> )	...	$14.2 \pm 0.4$	$13.4 \pm 0.2$	$13.3 \pm 0.3$ ( $14.4 \pm 0.3$ )†
$A_\sigma^{19}$ ( $\times 10^{-4}$ cm. <sup>-1</sup> )	...	$3.5 \pm 0.6$	$3.1 \pm 0.3$	$3.5 \pm 0.5$ ( $2.8 \pm 0.7$ )†

\* It is to be noted that the constants  $A_s$  and  $A_\sigma$  are given here in units of  $10^{-4}$  cm.<sup>-1</sup> while they are given in gauss in Tables I, II and III.

† These values are those obtained by Hayes and Jones<sup>8</sup> at 90° K.

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