

# ELECTRON PARAMAGNETIC RESONANCE OF $Mn^{2+}$ IN SINGLE CRYSTALS OF CESIUM SULPHATE

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## ABSTRACT

Electron paramagnetic resonance (EPR) of divalent manganese ion has been studied at 9.5 KMc/sec. These studies reveal that  $Mn^{2+}$  ion substitutes at a  $\beta$ - $Cs^+$  site and gets associated with a vacancy at a neighbouring  $\beta$ - $Cs^+$  site in the  $ab$ -plane. The  $z$ -axis of this  $\beta\beta$  complex makes an angle of  $25^\circ$  with the crystallographic  $b$ -axis. The spectra observed have been described by the spin-Hamiltonian for  $Mn^{2+}$  in rhombic crystalline field. The temperature dependence of the parameters  $D$  and  $E$  has been studied in the range  $293^\circ$ – $77^\circ$  K. The spectra for the observed complex along its three-principal axes have been analysed using second order perturbation equations. The spin-Hamiltonian parameters obtained from the spectra taken at room temperature are:

$$g_z = 2.000 \pm 0.003, \quad g_x = 2.015 \pm 0.003, \quad g_y = 2.000 \pm 0.003;$$

$$A_z = -93 \pm 1, \quad A_x = -91 \pm 1, \quad \text{and} \quad A_y = -91 \pm 1 \text{ G};$$

$$D = -941 \pm 3 \quad \text{and} \quad E = -14 \pm 4 \text{ G};$$

$$b_4^0 = (0.0), \quad b_4^2 = (13), \quad \text{and} \quad b_4^4 = -77 \pm 5 \text{ G}$$

## I. INTRODUCTION

DURING the past few years the technique of electron paramagnetic resonance (EPR) has been used for studying impurity ions in alkali sulphates.<sup>1-4</sup> The value of EPR methods to study the phase transition<sup>3-7</sup> is well known. Moreover, EPR has been an important structural tool in perovskites, spinels and garnets.<sup>8</sup> Chowdari and Venkateswarlu<sup>3</sup> found indications of a probable phase transition around  $-130^\circ$  C. in  $Mn^{2+}$  doped  $K_2SO_4$  single crystal. It was felt that it would be interesting to see whether such a transition occurs in the case of the isomorphous sulphates<sup>†</sup> which are not ferroelectric.

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†  $(NH_4)_2SO_4$  is known to become ferroelectric<sup>4</sup> below  $-50^\circ$  C.

Information about the lattice defects such as positive ion vacancies is valuable for the solid state studies in general. In the present studies  $Mn^{2+}$  which is an S-state ion belonging to the iron group transition elements is doped in single crystals of cesium sulphate. Analysis of the observed paramagnetic resonance spectra is made in the temperature range of 77° K. to 293° K and the spin-Hamiltonian parameters of the system  $Cs_2SO_4:Mn^{2+}$  for the observed complex in the *ab*-crystallographic plane have been obtained.

## II. CRYSTAL STRUCTURE

The crystal structures of isomorphous sulphates of potassium, ammonium, rubidium and cesium have been determined by Ogg.<sup>9</sup> They belong to the symmetry group  $V_h^{16}$  and contain two reflection planes, four glide planes; twelve dyad screw axes, and sets of four centres of symmetry. The orthorhombic unit cell dimensions are  $a = 6.218$ ,  $b = 10.884$  and  $c = 8.198$  Å. The structure of  $Cs_2SO_4$  consists of layers of atoms parallel to (100) planes the spacing between which is  $a/2$ . The reflection planes are  $(100)_+$  and  $(100)_-$  if we assume the origin of co-ordinates is at the centre of the unit cell. The unit cell contains four formula weights. Depending on the oxygen environment the cesium atoms are classified as  $\alpha$ - or  $\beta$ -type.<sup>9</sup> As a result there are four cesium ions of  $\alpha$ -type and four cesium ions of  $\beta$ -type in the unit cell (Fig. 1).

## III. EXPERIMENTAL

Cesium sulphate supplied by E. Merck and of analytical grade has been used. 0.3 mole per cent of  $MnSO_4$  has been added to a saturated aqueous solution of  $Cs_2SO_4$ . Slow evaporation yielded thin plates of transparent crystals, 1 cm  $\times$  1 cm  $\times$  0.2 cm size, with well-developed {001} faces. Spectrophotometric analysis<sup>‡</sup> of the experimental crystal showed that the manganese content is less than 1250 parts per million. The crystal has no detectable traces of water either to give infrared absorption bands on a Cary-14 spectrophotometer or proton resonance signal on a wide line nuclear magnetic resonance spectrometer. Desired orientation of the experimental crystal with respect to the magnetic field has been easy because of the known axes  $\langle 001 \rangle$  and  $\langle 100 \rangle$  the former being perpendicular to the well-developed face of the crystal while the latter is the

<sup>‡</sup> We are thankful to Dr. N. A. Narasimham, Spectroscopy Division, Bhabha Atomic Research Centre, Trombay, Bombay, for the analysis of the doped samples.

needle axis. X-ray rotation photographs taken along these directions confirmed the assignment of the axes. Measurements have been made at x-band with a Varian V-4502 EPR spectrometer having a 9-inch rotating magnet and 100 kc/sec field modulation. A Varian rotating cavity V-4533 has been used to determine the angular variation and the direction of the principal axes of the  $g$ -tensor. A speck of polycrystalline diphenylpicrylhydrazyl (DPPH) whose  $g$ -value is taken as  $2.0036^{10}$  has been used as a field marker. The magnetic field has been standardized using proton resonance in conjunction with a nuclear flux meter F-9 and a Beckman 10-110 Mc convertor 7571. Temperature variation experiments have been done using a Varian V-4530 temperature controller. The spectrometer has been operated at low power, the microwave power being one milliwatt.

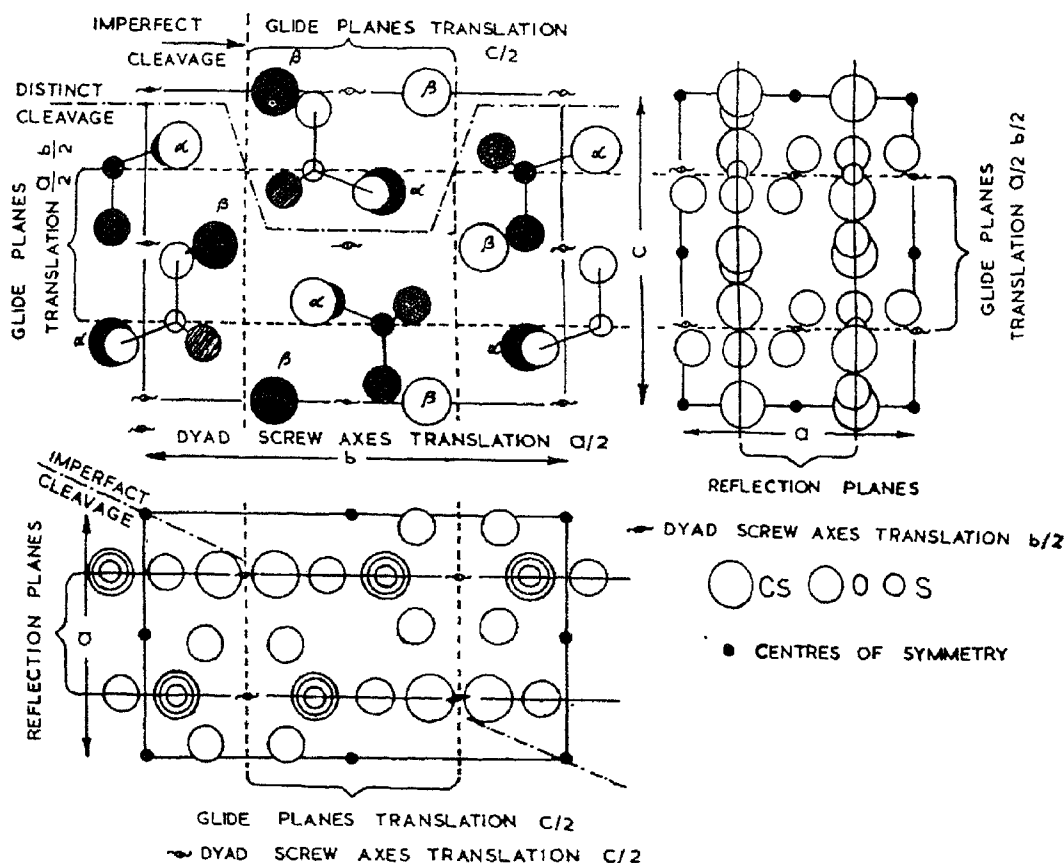


FIG. 1. Approximate positions of atoms and symmetries of  $\text{Cs}_2\text{SO}_4$  in the three principal planes (after Ogg<sup>9</sup>).

#### IV. THEORY

The ground state of  $\text{Mn}^{2+}$  with its  $3d^5$  configuration is  ${}^6S_{5/2}$ . In a crystal field of low symmetry such as  $\text{Cs}_2\text{SO}_4$  excited quartet levels get admixed

into the ground state<sup>11</sup> and the ground state is split into three Kramers' doublets. In a magnetic field the degeneracy is completely removed and five fine structure transitions are possible. Due to the interaction with the nucleus of spin 5/2 each electronic transition gives rise to six hyperfine transitions. Thus the electron paramagnetic resonance absorption of  $Mn^{2+}$  in cesium sulphate is expected to contain thirty lines. In general, the spectrum has more lines because of the presence of angular parts due to  $Mn^{2+}$  ions in equivalent positions or at different sites. Additional lines due to forbidden transitions are also possible.

The thirty line EPR spectra of  $Mn^{2+}$  obtained in the present case have been analysed using a general spin-Hamiltonian appropriate to the low symmetry:

$$\begin{aligned} \mathcal{H} = & g_z \beta H_z S_z + g_x \beta H_x S_x + g_y \beta H_y S_y + \frac{1}{3} b_2^0 O_2^0 + \frac{1}{3} b_2^2 O_2^2 \\ & + \frac{1}{60} b_4^0 O_4^0 + \frac{1}{60} b_4^2 O_4^2 + \frac{1}{60} b_4^4 O_4^4 \\ & + AS_z I_z + BS_x I_x + CS_y I_y. \end{aligned} \quad (1)$$

The operators  $O_n^m$  are given in an explicit form by Orbach<sup>12</sup> and  $g, b_i^k$  are parameters to be fixed by experiment. The following expressions<sup>3, 13, 14</sup> have been used to calculate the fine structure positions at resonance when  $H \parallel z$ . The usual parameters  $D, E$  and  $a$  replace the constants  $b_2^0, \frac{1}{3} b_2^2$  and  $2b_4^0$  respectively to give<sup>15</sup>

$$H_1 (M = 5/2 \leftrightarrow 3/2) = H_0 - 4D + 9E^2/(H_1 + D) - 5E^2/(H_1 + 3D) - 2a - 3Eb_4^2/H_0$$

$$H_2 (M = 3/2 \leftrightarrow 1/2) = H_0 - 2D - 9E^2/(H_2 + D) + 9E^2/(H_2 - D) - 5E^2/(H_2 + 3D) + 5/2 (a) - \left(\frac{3}{2}\right) Eb_4^2/H_0 - \frac{(b_4^4)^2}{20H_0}$$

$$H_3 (M = 1/2 \leftrightarrow -1/2) = H_0 - 9E^2/(H_3 - D) + 5E^2/(H_3 + 3D) + 5E^2/(H_3 - 3D) - 9E^2/(H_3 + D) + 6Eb_4^2/H_0$$

$$H_4 (M = -1/2 \leftrightarrow -3/2) = H_0 + 2D + 9E^2/(H_4 + D) - 9E^2/(H_4 - D) - 5E^2/(H_4 - 3D) - 5/2 (a) - \left(\frac{3}{2}\right) Eb_4^2/H_0 - \frac{(b_4^4)^2}{20H_0}$$

$$H_5 (M = -3/2 \leftrightarrow -5/2) = H_0 + 4D + 9E^2/(H_5 - D) - 5E^2/(H_5 - 3D) + 2a - 3Eb_4^2/H_0. \quad (2)$$

To take account of the hyperfine structure a term HFS has been added<sup>16</sup> to each of the above equations (2):

$$\begin{aligned} \text{HFS (for } H \parallel z) &= -Am - \frac{B^2 + C^2}{4H_0} \{I(I+1) - m^2\} \\ &\quad - \{(2M-1)m\} BC/H_0 \\ &= H(m \leftrightarrow m). \end{aligned} \quad (2a)$$

The same expression has been used cyclically when the static field  $H$  is parallel to  $x$  or  $y$ . The corresponding  $D^*$ ,  $E^*$ ,  $a^*$ ,  $b_4^{2*}$  and  $b_4^{4*}$  are related by standard transformation relations<sup>13, 17</sup> listed in Table I.  $A$ ,  $B$  and  $C$  are the  $z$ ,  $x$  and  $y$  components of hyperfine constant parameter. For manganese  $I = 5/2$  so that  $m$  takes the values  $-5/2$  to  $+5/2$ . Quadrupole effects<sup>16</sup> are found to be negligible in the present work.

## V. RESULTS AND DISCUSSION

The angular variation studies have revealed the existence of a complex in which  $Mn^{2+}$  substitutes a  $\beta$ - $Cs^+$  ion and gets associated with a neighbouring  $\beta$ - $Cs^+$  vacancy in the  $ab$ -plane the direction of association being the  $z$ -axis of the complex. It has been found that the  $z$ -axis of the complex makes an angle of  $25^\circ$  with the  $b$ -axis of the crystal. The  $y$ -axis of the complex is in the same  $ab$ -plane at an angle of  $90^\circ$  to the  $z$ -axis while its  $x$ -axis is along the  $c$ -axis of the crystal. Figures 2, 3 and 4 show the three spectra taken when the magnetic field is parallel to  $z$ -,  $y$ - and  $x$  axes respectively. Figure 5 gives the proposed model for the observed complex. The angle which the  $z$ -axis of the complex makes with the crystallographic  $b$ -axis as calculated from the structural parameters<sup>9</sup> is  $24^\circ 51'$  which agrees very well with the observed angle of  $25^\circ$ . The associated vacancy can occur in any one of the two directions  $Mn^{2+} - \beta$  (Fig. 5) and one expects two identical spectra when the static magnetic field is making equal angles of  $24^\circ 51'$  each on either side of  $b$ -axis. Experimental observations confirmed this to within  $1^\circ$ . Further, one also expects two sets of 30 lines for all the orientations of the crystal except when  $H$  is parallel to the crystallographic axes  $a$ ,  $b$  or  $c$ . For instance when  $H$  makes an angle of about  $25^\circ$  with the crystallographic  $b$ -axis, it is parallel to the  $z$ -axis of one  $Mn^{2+} - \beta$  ( $Cs^+$  vacancy) complex while at the same time it makes an angle of about  $50^\circ$  with the

other equivalent complex. Similarly when it is parallel to the  $y$ -axis of one complex it makes an angle of about  $40^\circ$  with the other equivalent complex. Thus in Figs. 2 and 3 where  $H$  is parallel to  $z$ - and  $y$ -axis respectively one sees a number of lines in addition to the identified set of 30 lines of one complex while in Figs. 4 and 6 where  $H$  is parallel to the  $x$ -axis (crystallographic  $c$ -axis) one sees mainly one set of 30 lines as in that orientation both the equivalent complexes make the same angle of  $90^\circ$  with  $H$ . It is of course possible that some of the unassigned lines in the spectra are due to a complex which is as yet unidentified.

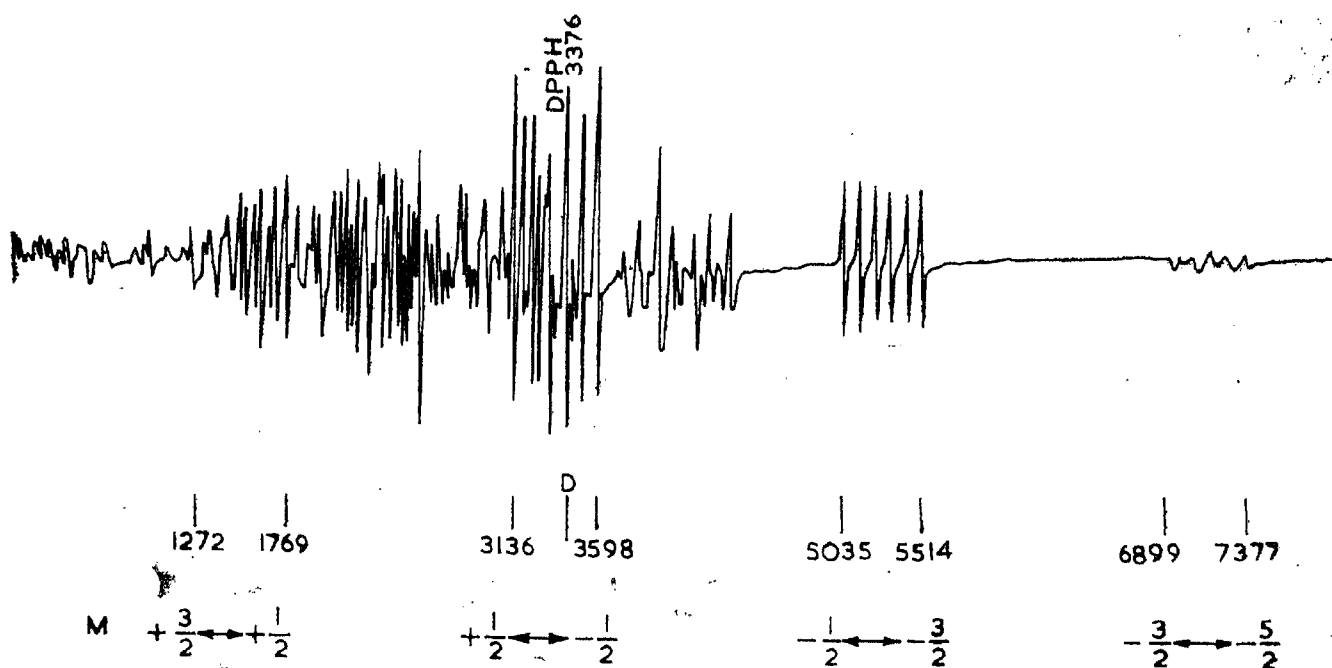


FIG. 2. EPR spectrum of  $Mn^{2+}$  in  $Cs_2SO_4$  single crystal at room temperature ( $293^\circ K$ ). The direction of the magnetic field is making  $25^\circ$  with the  $b$ -axis of the crystal in the  $ab$ -plane.  $H \parallel$  to  $z$ -axis. DPPH is the field marker. Numbers indicate field values in gauss.

Temperature variation studies from  $293^\circ K$  to  $77^\circ K$  show that there is no abrupt change in the spectral patterns. The spectrum recorded at  $77^\circ K$  with a small crystal in the low temperature tube is shown in Fig. 6. Within this temperature range of  $77^\circ K$  to  $293^\circ K$  the overall spread of the spectrum gradually increases as we go from low temperature to high temperature. Figure 7 shows the observed temperature variation of the parameters  $D^*$  and  $E^*$ . It is seen that the change in  $E^*$  is about 4% while that in  $D^*$  is 14%. This alters the ratio of  $D^*$  to  $E^*$  giving probably an indication of the overlap and covalency effects as suggested by Watkins.<sup>18</sup> The smooth

variation of the parameters D and E suggests that structural changes involving first or second order phase transitions have probably not occurred in this temperature range. Such changes are expected in  $\text{Cs}_2\text{SO}_4$  doped with  $\text{Mn}^{2+}$  as this crystal is isomorphous with  $\text{K}_2\text{SO}_4$  where a second order phase transition is indicated.<sup>3</sup>

The line widths at  $77^\circ\text{K}$  for  $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$  transition are found to be the same as those of  $\pm\frac{5}{2} \leftrightarrow \pm\frac{3}{2}$  transitions ( $\sim 9\text{G}$  indicating the crystals grown from slow evaporation of saturated solution do not develop strains which may tilt the paramagnetic axis as found by Bronstein and Maniv<sup>19</sup> in melt-grown crystals.

## VI. ANALYSIS OF THE SPECTRA

All the three spectra of the complex with  $H \parallel z$ ,  $H \parallel y$ - and  $H \parallel x$ -axes have been analysed at room temperature by the spin-Hamiltonian method. One of these with  $H \parallel x$ -axis has been further analysed at  $10^\circ$  intervals between  $77^\circ\text{K}$  and  $293^\circ\text{K}$  and the spin-Hamiltonian parameters have been determined at various temperatures within this range.

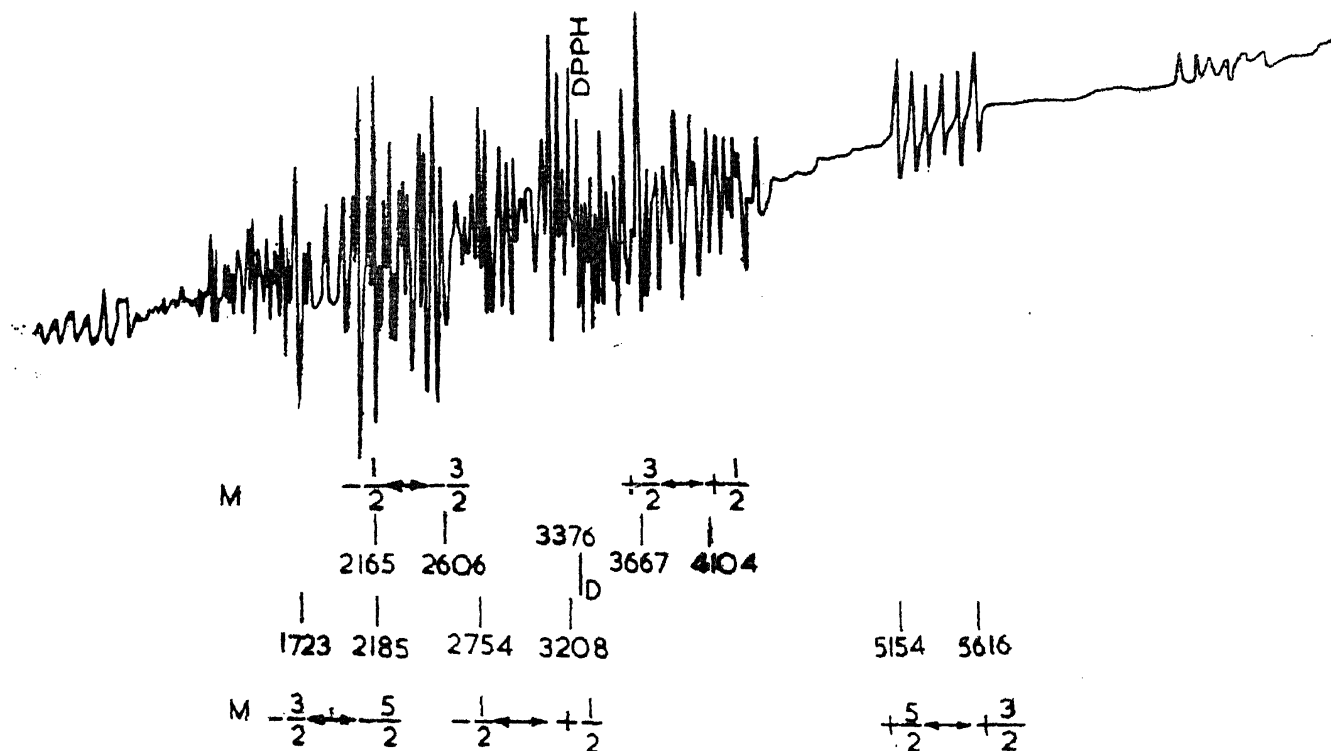


FIG. 3. EPR spectrum of  $\text{Mn}^{2+}:\text{Cs}_2\text{SO}_4$  single crystal at room temperature ( $293^\circ\text{K}$ ). The direction of magnetic field is  $65^\circ$  to the  $b$ -axis of the crystal in the  $ab$ -plane.  $H \parallel y$ -axis. DPPH is the field marker. Numbers indicate field values in gauss.

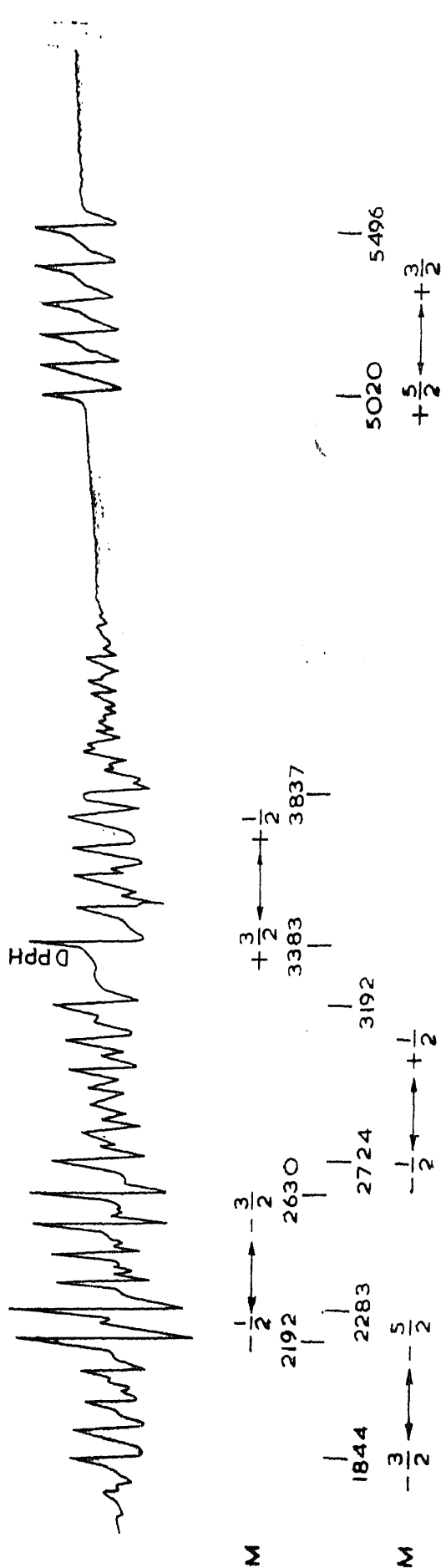


FIG. 4. EPR spectrum of  $Mn^{2+}$  in  $Cs_2SO_4$  single crystal at room temperature ( $293^\circ K$ ). The direction of magnetic field is parallel to the  $c$ -axis of the crystal in the  $ac$ -plane.  $H \parallel$  to  $x$ -axis. Numbers indicate field values in gauss.



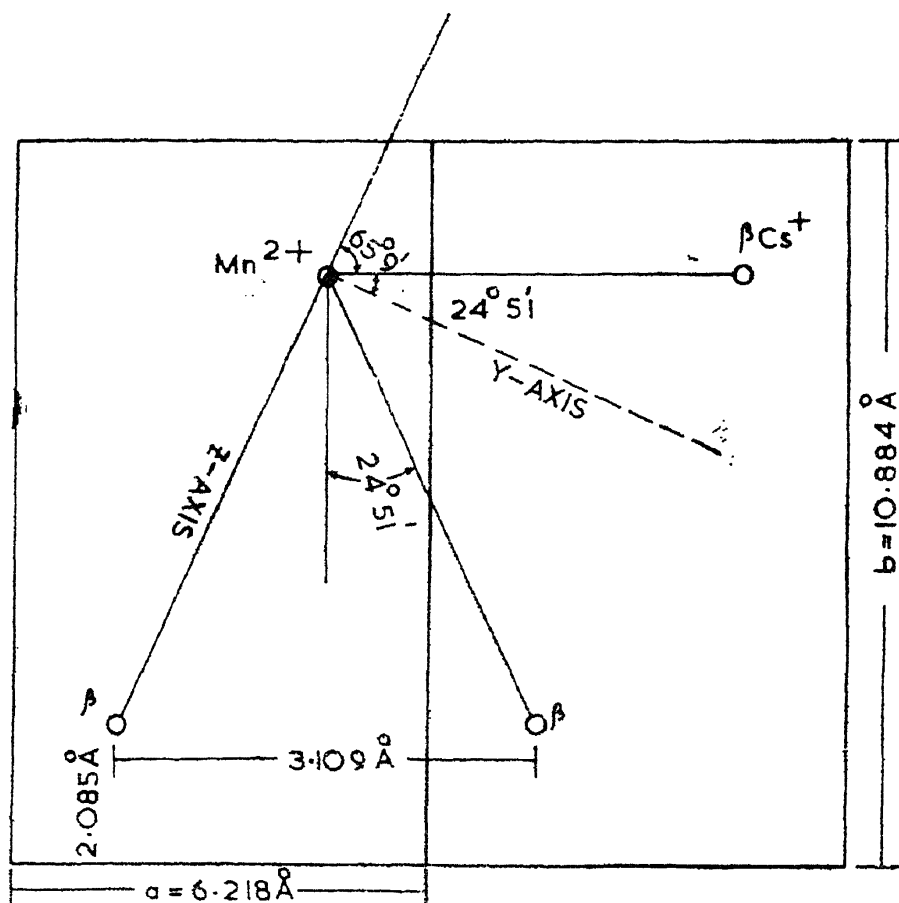


FIG. 5. Model of the  $\beta\beta$  complex in the  $ab$ -plane of  $\text{Cs}_2\text{SO}_4:\text{Mn}^{2+}$  crystal.  $\text{Mn}^{2+}$  substitutes in the  $\beta\text{-Cs}^+$  position and gets associated with a neighbouring vacancy.

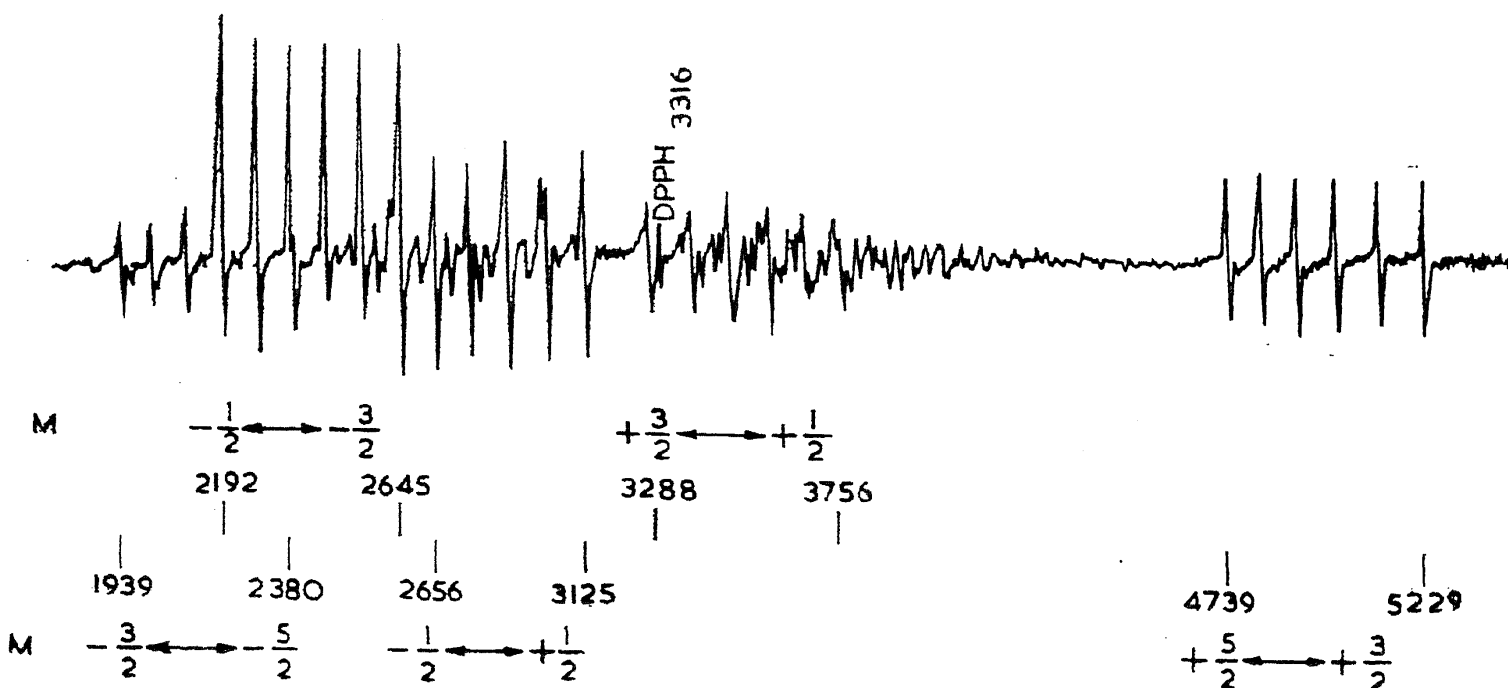


FIG. 6. EPR spectrum of  $\text{Mn}^{2+}$  in  $\text{Cs}_2\text{SO}_4$  single crystal at  $77^\circ\text{K}$ . The direction of magnetic field is parallel to the  $c$ -axis of the crystal in the  $bc$ -plane.  $H \parallel x$ -axis. Numbers indicate the field values in gauss.

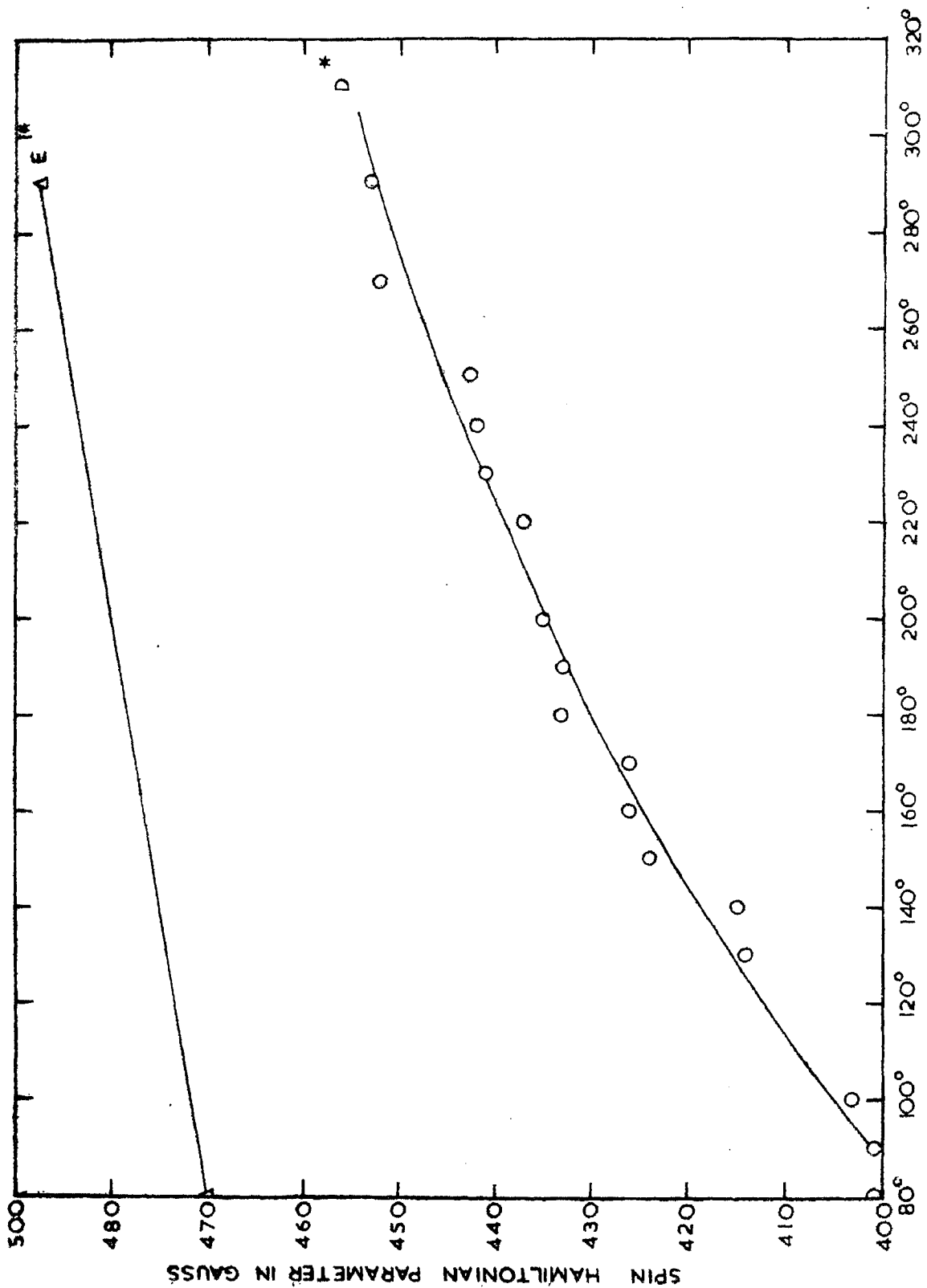


FIG. 7. Temperature variation of spin Hamiltonian parameters  $D_{\beta}^*$  and  $E_{\beta}^*$  in the range 293° K to 77° K for the observed  $\beta\beta$ -complex in the  $ab$ -plane.

The procedure which has been adopted for analysis is as follows: The three spectra relevant to the complex are examined and  $M$ -values are assigned to each of the well-defined sextets. Assuming  $A$ 's to be negative,<sup>20</sup> the relative sign of  $D$  and the sequence of  $M$  and  $m$  are determined by comparing the separation between the extreme hyperfine components of fine structure groups in high and low fields.<sup>16</sup> In the present case  $D$  is found to be negative, that is, it has the same sign as  $A$ . Approximate values for the components of hyperfine tensor  $A_z (= A)$ ,  $A_x (= B)$  and  $A_y (= C)$  are obtained from the high field sextet specially taken with a low sweep rate of the magnetic field of about 0.4 kilogauss per minute. The first and the sixth lines of each transition fixed the position of the fine structure line. Using these fields the parameters have been found by a least square analysis with the help of equations (2). Then the field values corresponding to the thirty lines have been utilized and the terms (2  $a$ ) are added to equations (2) and the process is repeated to get the parameters. For the spectrum which has a large effective value of  $D$  (that is, for the spectrum with  $H \parallel z$ -axis), the very low field transitions cannot be obtained with an  $x$ -band spectrometer. For this case a computer program is written for an IBM computer to diagonalise the relevant  $36 \times 36$  energy matrix.<sup>21</sup> The approximate parameters obtained have been used in the usual transformation relations (Table I) to get the values of  $D^*$  and  $E^*$  which served as input parameters. They are varied until the calculated values compared favourably with the experimental values for a least-square fit. Thus to avoid inaccuracies inherent in second order perturbation formulae and to get the probable low-field values at  $x$ -band frequencies the  $D$  parameter obtained by diagonalising the energy matrix corresponding to the largest spread spectrum has been taken to be correct. For the value of  $E$  the effective values of  $D^*$  as obtained by the  $x$ - and  $y$ -axes spectra are taken as guide lines. The effective  $E^*$  values along the  $x$ - and  $y$ -axes together with  $D^*$  values serve to fix the parameters  $D$  and  $E$  ultimately. This is particularly necessary as small variations in  $E$  have great influence on the parameters obtained in  $x$  and  $y$  directions. In principle it is possible to minimize the parameters to get the agreement between the observed and the calculated values by utilizing the relations (2) to within 10 G which is the order of line width in the present case. The minimized value of  $H_0$  is utilized for calculating the corresponding  $g$ -value of the spectrum. However, to obtain the correlation among the spectra taken along the three axes  $z$ ,  $x$ , and  $y$  as determined by the transformation relations<sup>13, 20</sup> given in Table I, the values of the parameters which are slightly different from the minimized values are taken (at the risk of increasing the standard deviation between the

TABLE I

Relationships† among the constants of the spin-Hamiltonian for three mutually perpendicular orientations of the magnetic field H

| Effective value of the constants | H    z    | H    x                                  | H    y                                  |
|----------------------------------|-----------|---|---|
| $D^*$                            | D         | $\frac{1}{2}(-D + 3E)$                  | $-\frac{1}{2}(D + 3E)$                  |
| $b_2^{0*}$                       | $b_2^0$   | $-\frac{1}{2}(b_2^0 - b_2^2)$           | $-\frac{1}{2}(b_2^0 + b_2^2)$           |
| $E^*$                            | E         | $-\frac{1}{2}(D + E)$                   | $\frac{1}{2}(D - E)$                    |
| $b_2^{2*}$                       | $b_2^2/3$ | $-(3b_2^0 + b_2^2)/6$                   | $(3b_2^0 - b_2^2)/6$                    |
| $b_4^{0*}$                       | $b_4^0$   | $\frac{1}{8}(3b_4^0 - b_4^2 + b_4^4)$   | $\frac{1}{8}(3b_4^0 + b_4^2 + b_4^4)$   |
| $a^*/2$                          | $a/2$     |   |   |
| $b_4^{2*}$                       | $b_4^2$   | $-\frac{1}{2}(5b_4^0 - b_4^2 - b_4^4)$  | $-\frac{1}{2}(5b_4^0 + b_4^2 - b_4^4)$  |
| $b_4^{4*}$                       | $b_4^4$   | $\frac{1}{8}(35b_4^0 + 7b_4^2 + b_4^4)$ | $\frac{1}{8}(35b_4^0 - 7b_4^2 + b_4^4)$ |
| $A^*$                            | A         | B                                       | C                                       |
| $B^*$                            | B         | C                                       | A                                       |
| $C^*$                            | C         | A                                       | B                                       |
| $g^*$                            | $g_z$     | $g_x$                                   | $g_y$                                   |

† We are thankful to Dr. Daniel Schechter of Solid State Physics Laboratory, TRW Systems, for kindly sending a memo which discussed in detail the effects of interchanging site axes.

experimental and calculated values). This procedure served as an additional check on the preliminary assignments made and was useful to sort out the lines in question from the angular parts. This method is a sophisticated version of that followed by Bronstein and Maniv<sup>19</sup> who tried different assignments of the transitions to obtain the expected relation between the parameters  $D^*$  and  $E^*$  in the spin-Hamiltonian. Table II gives the observed and calculated fields at resonance for the fine structure positions only while Tables III, IV, and V give the observed and calculated fields at resonance for the entire spectrum of thirty lines for the three spectra with the input parameters as indicated in each case. The main analysis of the observed

complex is contained in these Tables. Table VI gives the values of the parameters obtained at 77° K for the spectrum with  $H \parallel x$ -axis of the complex.

TABLE II

*Influence of the parameters  $b_4^0$  and  $b_4^2$  on resonant field values (fine structure)\**

| Spectrum  | With $b_4^0$ and $b_4^2$             |                                      |                  |                  |                                | Without $b_4^0$ and $b_4^2$          |                                      |                                |
|---|--------------------------------------|--------------------------------------|------------------|------------------|--------------------------------|--------------------------------------|--------------------------------------|--------------------------------|
|   | Experi-<br>mental<br>gauss†          | Calculated<br>gauss†                 | $b_4^0$<br>gauss | $b_4^2$<br>gauss | Standard<br>deviation<br>gauss | Experi-<br>mental<br>gauss†          | Calculated<br>gauss†                 | Standard<br>deviation<br>gauss |
| Spectrum $z$<br>Using $D = -941$<br>$E = -14$<br>$H_0 =$<br>3383 G<br>$g_z =$<br>1.9995       | 7138<br>5275<br>3367<br>1521<br>-383 | 7147<br>5264<br>3334<br>1503<br>-383 | 0                | 13               | 13                             | 7138<br>5275<br>3367<br>1521<br>-383 | 7147<br>5264<br>3384<br>1503<br>-383 | 13                             |
| Spectrum $y$<br>Using $D^* = 496$<br>$E^* = -461$<br>$H_0^* =$<br>3366 G<br>$g_y =$<br>2.0096 | 1954<br>2386<br>2982<br>3886<br>5385 | 1923<br>2357<br>3001<br>3876<br>5394 | -18              | 7                | 22                             | 1954<br>2386<br>2982<br>3886<br>5385 | 1854<br>2448<br>2996<br>3787<br>5469 | 78                             |
| Spectrum $x$<br>Using $D^* = 452$<br>$E^* = 475$<br>$H_0^* =$<br>3357 G<br>$g_x =$<br>2.0149  | 2064<br>2411<br>2958<br>3610<br>5258 | 2039<br>2431<br>2955<br>3648<br>5247 | -8               | -45              | 23                             | 2064<br>2411<br>2958<br>3610<br>5258 | 2026<br>2481<br>2917<br>3617<br>5298 | 44                             |

\* Least-square fit using equations 2 (a).

† The values listed in these columns correspond to the five fine structure resonant field values.

The spin-Hamiltonian parameters with deviations as suggested by correlating those obtained from transformed site axes are summarised in Table VII. The spectrum is broadly insensitive to the parameter  $b_4^4$  and as such its value is chosen to have consistency in the transformed parameters  $b_4^{2*}$  and  $b_4^{0*}$ .

TABLE III

The lines of  $Cs_2SO_4: Mn^{2+}$  at room temperature (293° K)  $H \parallel z$ -axis of the complex\*

(All values in gauss)

DPPH<sup>a</sup> 3376 G

| Line $+5/2 \leftrightarrow +3/2$ |            | $+3/2 \leftrightarrow +1/2$ |            | $+1/2 \leftrightarrow -1/2$ |            | $-1/2 \leftrightarrow -3/2$ |            | $-3/2 \leftrightarrow -5/2$ |            |
|----------------------------------|------------|-----------------------------|------------|-----------------------------|------------|-----------------------------|------------|-----------------------------|------------|
| Observed <sup>†</sup>            | Calculated | Observed                    | Calculated | Observed                    | Calculated | Observed                    | Calculated | Observed                    | Calculated |
| X                                | -612       | 1272                        | 1271       | 3136                        | 3150       | 3035                        | 5032       | 6899                        | 6914       |
| X                                | -520       | 1384                        | 1384       | 3230                        | 3243       | 5137                        | 5125       | 7019                        | 7007       |
| X                                | -427       | 1478                        | 1456       | 3325                        | 3336       | 5231                        | 5218       | 7104                        | 7100       |
| X                                | -334       | 1563                        | 1549       | 3410                        | 3429       | 5317                        | 5311       | 7189                        | 7193       |
| X                                | -241       | 1666                        | 1642       | 3496                        | 3523       | 5419                        | 5404       | 7292                        | 7286       |
| X                                | -148       | 1769                        | 1735       | 3598                        | 3616       | 5514                        | 5497       | 7377                        | 7379       |

\* Input parameters (for  $36 \times 36$  Energy Matrix):

$A_x (= A) = -93$ ,  $A_y (= B) = -91$  and  $A_z (= C) = -91$  G.

$H_{0z} = 3383$  G;  $g_x = 1.9995$ ;  $D = -941$ ,  $E = -14$ ,  $b_4^0 = 0$ ,  $b_4^2 = 13$  and  $b_4^4 = -77$  G-Standard deviation 16 G.

<sup>a</sup> Diphenylpicrylhydrazyl.

<sup>†</sup> X not observed at x-band.

## VII. GENERAL COMMENTS ON THE CONSISTENCY OF THE SPIN-HAMILTONIAN PARAMETERS OBTAINED FROM THE $H \parallel z$ , $H \parallel y$ AND $H \parallel x$ SPECTRA

The parameters  $D$ ,  $E$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  given in Table VII are those obtained from the analysis of the spectrum taken with  $H \parallel z$ -axis of the complex. The effective values of these parameters in the  $y$  and  $x$  directions have been obtained from the analysis of the spectra with  $H \parallel y$ - and  $H \parallel x$ -axes and are listed in Tables IV and V. The second column in Table VIII shows the effective values of the parameters along the  $z$  direction which are the same as those given in Table III and also in Table VII and designated  $D$ ,  $E$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$ . Column 3 in Table VIII shows these parameters calculated using the effective values obtained from the analysis of the spectrum with  $H \parallel x$  using the necessary relations given in Table I. Similarly

TABLE IV. *The lines of Cs<sub>2</sub>SO<sub>4</sub>:Mn<sup>2+</sup> at room temperature (293° K)  
H || y-axis of the complex\**

(All values in gauss)

DPPH<sup>a</sup> 3376G

| Line -3/2 ↔ -5/2 |            | -1/2 ↔ -3/2 |            | -1/2 ↔ +1/2 |            | +1/2 ↔ +3/2 |            | +3/2 ↔ +5/2 |            |
|------------------|------------|-------------|------------|-------------|------------|-------------|------------|-------------|------------|
| Observed         | Calculated | Observed    | Calculated | Observed    | Calculated | Observed    | Calculated | Observed    | Calculated |
| 1723             | 1703       | 2165        | 2129       | 2754        | 2771       | 3667        | 3639       | 5154        | 5152       |
| 1819             | 1784       | 2258        | 2213       | 2846        | 2857       | 3752        | 3728       | 5246        | 5243       |
| 1920             | 1867       | 2350        | 2299       | 2932        | 2946       | 3834        | 3819       | 5338        | 5337       |
| 2025             | 1953       | 2446        | 2387       | 3024        | 3037       | 3922        | 3912       | 5430        | 5433       |
| 2093             | 2042       | 2555        | 2478       | 3116        | 3130       | 4012        | 4008       | 5512        | 5531       |
| 2185             | 2133       | 2606        | 2572       | 3208        | 3226       | 4104        | 4107       | 5616        | 5633       |

\* Input parameters [for second order perturbation equations 2 (a)]:

$A_y (= C) = -91$ ,  $A_x (= 1) = -93$  and  $A_z (= B) = -91$  G.

$H_{0y} = 3366$  G,  $g_y = 2.0096$ ;  $D_y = 496.5$ ,  $E_y = -461$ ,  $(b_4^0)_y = -18$  and  $(b_4^2)_y = 7$  G,  
Standard deviation 34 G.

<sup>a</sup> Diphenylpicrylhydrazyl.

TABLE V. *The lines of Cs<sub>2</sub>SO<sub>4</sub>:Mn<sup>2+</sup> at room temperature (293° K)  
H || x-axis of the complex\**

(All values in gauss)

DPPH<sup>a</sup> 3316G

| Line -3/2 ↔ -5/2 |            | -1/2 ↔ -3/2 |            | -1/2 ↔ +1/2 |            | +1/2 ↔ +3/2 |            | +5/2 ↔ +3/2 |            |
|------------------|------------|-------------|------------|-------------|------------|-------------|------------|-------------|------------|
| Observed         | Calculated | Observed    | Calculated | Observed    | Calculated | Observed    | Calculated | Observed    | Calculated |
| 1844             | 1821       | 2192        | 2207       | 2724        | 2724       | 3383        | 3411       | 5020        | 5004       |
| 1927             | 1902       | 2283        | 2290       | 2814        | 2810       | 3486        | 3499       | 5098        | 5095       |
| 2009             | 1985       | 2361        | 2376       | 2903        | 2899       | 3571        | 3590       | 5184        | 5189       |
| 2098             | 2071       | 2449        | 2465       | 3002        | 2990       | 3667        | 3684       | 5284        | 5285       |
| 2192             | 2160       | 2537        | 2556       | 3096        | 3083       | 3758        | 3780       | 5389        | 5383       |
| 2283             | 2251       | 2630        | 2649       | 3192        | 3179       | 3837        | 3879       | 5496        | 5484       |

\* Input parameters [for second order perturbation equations 2 (a)]:

$A_x (= B) = -91$ ,  $A_z (= A) = -93$  and  $A_y (= C) = -91$  G.

$H_{0x} = 3357$  G,  $g_x = 2.0149$ ;  $D_x = 452$ ,  $E_x = 475$ ,  $(b_4^0)_x = -8$  and  $(b_4^2)_x = -45$  G,  
Standard deviation 19 G.

<sup>a</sup> Diphenylpicrylhydrazyl.

TABLE VI. The lines of  $Cs_2SO_4: Mn^{2+}$  at  $77^\circ K$   $H \parallel x$ -axis of the complex\*  
(All values in gauss)DPPH<sup>a</sup> 3316 G

| Line $-3/2 \leftrightarrow -5/2$ |            | $-\frac{1}{2} \leftrightarrow -3/2$ |            | $-\frac{1}{2} \leftrightarrow +\frac{1}{2}$ |            | $+3/2 \leftrightarrow +\frac{1}{2}$ |            | $+5/2 \leftrightarrow +3/2$ |            |
|----------------------------------|------------|-------------------------------------|------------|---|------------|-------------------------------------|------------|-----------------------------|------------|
| Observed                         | Calculated | Observed                            | Calculated | Observed                                    | Calculated | Observed                            | Calculated | Observed                    | Calculated |
| 1939                             | 1928       | 2192                                | 2181       | 2656  | 2645       | 3288                                | 3296       | 4739                        | 4745       |
| 2024                             | 2011       | 2274                                | 2267       | 2745  | 2733       | 3387                                | 3387       | 4822                        | 4838       |
| 2107                             | 2096       | 2368                                | 2355       | 2838  | 2823       | 3487                                | 3480       | 4913                        | 4934       |
| 2192                             | 2184       | 2459                                | 2445       | 2932  | 2916       | 3585                                | 3575       | 5012                        | 5032       |
| 2283                             | 2275       | 2552                                | 2538       | 3027  | 3012       | 3672                                | 3673       | 5116                        | 5138       |
| 2380                             | 2368       | 2645                                | 2634       | 3125  | 3110       | 3756                                | 3774       | 5229                        | 5236       |

\* Input data [for second order perturbation equations 2 (a)]:

 $A_x (= B) = -93$ ,  $A_y (= A) = -93$ ,  $A_z (= C) = -93$  and  $H_{00} = 3304$  G,  $g_x = 2.0109$   
 $D_0 = 401$ ,  $E_0 = 470$ . $(b_4^0)_0 = -20$  and  $(b_4^2)_0 = 56$  G.

Standard deviation 13 G.

<sup>a</sup> Diphenylpicrylhydrazyl.TABLE VII. Spin-Hamiltonian Parameters for  $Mn^{2+}$  in  $Cs_2SO_4$  at Room Temperature  $293^\circ K$ 

| Parameter           | Value <sup>a</sup>     |
|---------------------|------------------------|
| $g_z$               | $2.000 \pm 0.003$      |
| $g_x$               | $2.015 \pm 0.003$      |
| $g_y$               | $2.000 \pm 0.003$      |
| $A_x (= A)^a$       | $-93 \pm 1$ G          |
| $A_y (= B)$         | $-91 \pm 1$ G          |
| $A_z (= C)$         | $-91 \pm 1$ G          |
| $D^b$               | $-941 \pm 3$ G         |
| $E$                 | $-14 \pm 4$ G          |
| $b_4^0$ (or $a/2$ ) | (0) G                  |
| $b_4^2$             | (13) G                 |
| $b_4^4$             | $-77 \pm 5$ G          |
| $\phi^c$            | $25^\circ \pm 1^\circ$ |

(a) A's are assumed to be negative.

(b) The sign of D is relative to A.

(c) The angle between the direction of the complex taken as z-axis and the longest crystallographic axis.

(d) The values given in parenthesis are to be taken as either approximate or uncertain.



TABLE VIII

*Comparison of some of the parameters\* obtained from the H || z spectrum (Table VII) with those derived from the effective parameters from the H || x and H || y spectra using the relations in Table I*

| Parameter | As observed from H    z spectrum (Table VII) (gauss) | Derived from the effective parameters of the H    x spectrum using relations in Table I (gauss) | Derived from the effective parameters of the H    y spectrum using relations in Table I (gauss) |
|-----------|--|---|---|
| D         | - 941  | - 938.5   | - 940   |
| E         | - 14   | - 11.5  | - 18  |
| $b_4^0$   | 0  | + 2.6   | - 7.6   |
| $b_4^2$   | 13   | - 2.5   | - 48.5  |
| $b_4^4$   | - 77   | - 74.4  | - 72.6  |

\* Other parameters A's and g's are not listed again here (see Tables III, IV, V and VII). The values of  $A_x$ ,  $A_y$ , and  $A_z$  obtained from the H || z spectrum are just the same as those obtained from the H || x and H || y spectra.

Column 4 of Table VIII shows the parameters derived using the constants obtained from the analysis of the spectrum with H || y along with the necessary relations given in Table I. The values of the parameters D are consistent within  $\pm 2.5$  G while those of E are consistent within  $\pm 4$  G. The magnitude of these deviations can probably be taken as the error in the determination of the values of the parameters D and E. It is satisfactory to see that these deviations are not large. However, the inconsistencies or deviations can probably be reduced by using expressions involving higher orders of perturbation than used here as the term D in general and the effective values of the term E in the y and x directions have large magnitudes. As pointed out earlier the parameters obtained from the analysis of the spectrum with H || z are taken to be more accurate than those obtained from the other two spectra as the higher order terms in E are least effective when H is parallel to the z-axis of the complex.

It is interesting to note, though alarming in a way, that the deviations in the values of the parameters  $b_4^0$  and  $b_4^2$  in the Columns 2, 3 and 4 of Table VIII are as large as the magnitude of their values. This raises a question about the usefulness of keeping these parameters in the present analysis. Table II shows the magnetic resonance field values (fine structure) calculated with and without the parameters  $b_4^0$  and  $b_4^2$ . The observed values are also included in the table for comparison and it can be seen that the standard deviation decreases to some extent when the parameters  $b_4^0$  and  $b_4^2$  are included in the analysis.

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