

CHAPTER VI

OPTICAL, MAGNETIC AND ELECTRON SPIN RESONANCE STUDIES OF DIVALENT $3d^5$ ION DOPED IN $CsCdCl_3$

RESULTS AND DISCUSSION

I. Optical Studies

Divalent manganese of electronic structure $[A] 3d^5$ has sextet level 6S as its free ion ground term. In an weak-field octahedral lattice, Mn^{2+} ion gives rise to ${}^6A_{1g}$ as its lowest state. There are no other sextet levels for this ion. All the upper-lying states are spin-quartet, and hence transitions from the ground ${}^6A_{1g}$ to the excited quartet state are all spin-forbidden and of very low intensity and of narrow width. The energy levels of the various terms are given by²²

$${}^6A_{1g} ({}^6S) = -35B$$

$${}^4A_{1g} ({}^4G) = -25B + 5C$$

$${}^4A_{2g} ({}^4F) = -13B + 7C$$

$${}^4E_g ({}^4D, {}^4G)$$

$$(-22B + 5C - E)$$

$$-2\sqrt{3} B$$

$$-2\sqrt{3} B$$

$$(-21B + 5C - E)$$

= 0

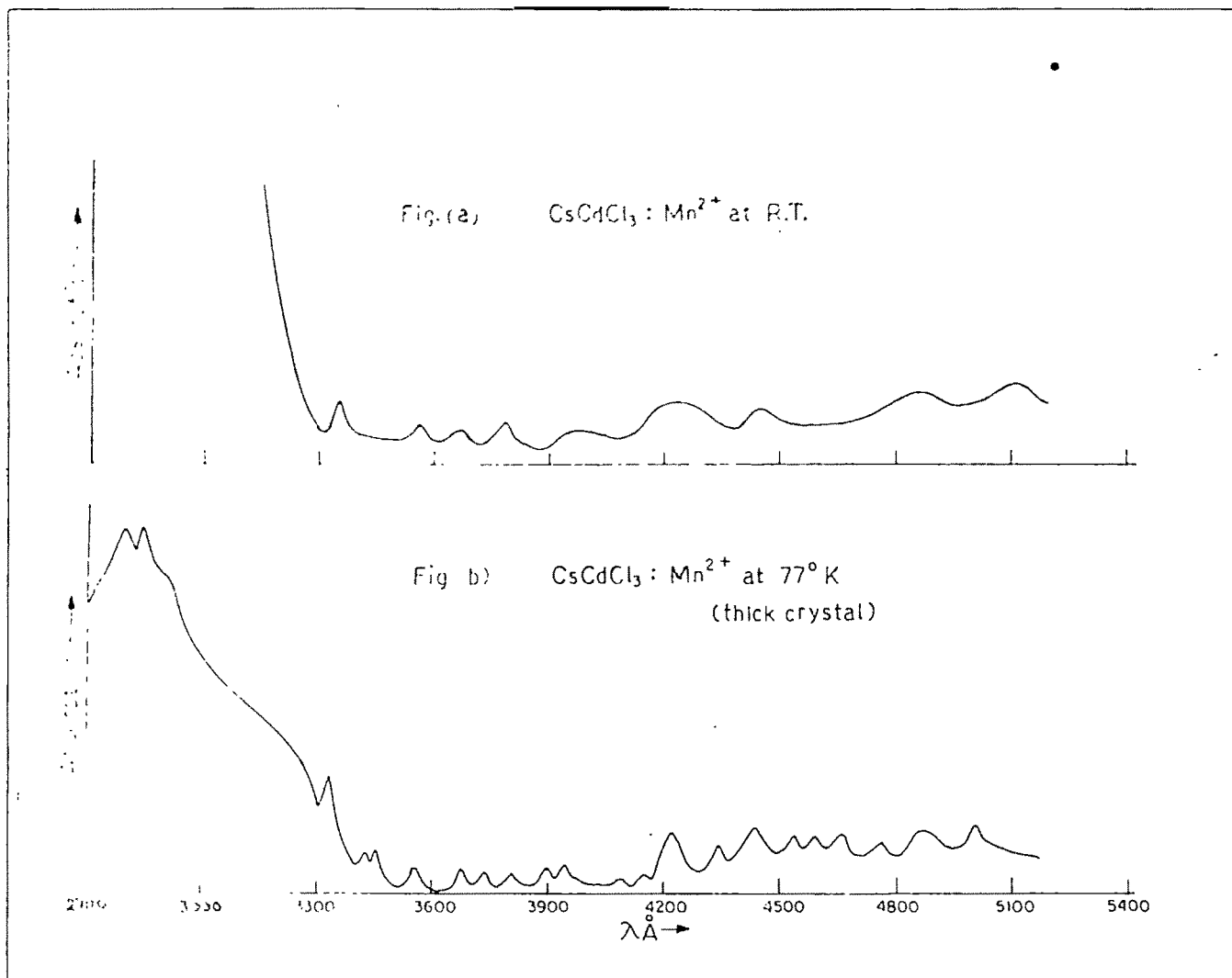


Fig.22. Absorption spectrum of Mn^{2+} in CsCdCl_3 .
 Fig.(a) shows the room temperature
 spectrum and that Fig.(b) taken at 77°K .

${}^4T_{1g} ({}^4F, {}^4P, {}^4G)$

$$\begin{array}{rcl}
 -10 Dq - 25B + 6C - E & - 3\sqrt{2} B & - C \\
 & -16B + 7C - E & - 3\sqrt{2} B & = 0 \\
 & & 10 Dq - 25B + 6C - E &
 \end{array}$$

${}^4T_{2g} ({}^4F, {}^4G, {}^4D)$

$$\begin{array}{rcl}
 -10 Dq - 17B + 6C - E & \sqrt{6} B & - 4B + C \\
 & - 22B + 5C - E & - \sqrt{6} B & = 0 \\
 & & 10 Dq - 17B + 6C - E & \\
 & & & (115)
 \end{array}$$

From our room temperature absorption spectrum (Fig. 22a), we assign the absorption band at 22470 cm^{-1} to ${}^6A_{1g} ({}^6S) \rightarrow {}^4A_{1g} ({}^4G)$ transition and the bands at 28090 cm^{-1} and 23560 cm^{-1} to ${}^6A_{1g} ({}^6S) \rightarrow {}^4E_g ({}^4D)$ and ${}^6A_{1g} ({}^6D) \rightarrow {}^4E_g ({}^4G)$ transitions respectively. From these we have calculated the values of the Racah parameters B and C to be $\sim 650 \text{ cm}^{-1}$ and $\sim 3200 \text{ cm}^{-1}$ respectively; reduced appreciably from the free ion values of $B = 960 \text{ cm}^{-1}$, $C = 3325 \text{ cm}^{-1}$. In order to identify the triplet terms which involve cubic field strength parameter Dq, besides B and C, we have solved the energy matrices of ${}^4T_{1g}$ and ${}^4T_{2g}$

term, with above values of B and C and varying Dq by 20 cm^{-1} from 760 cm^{-1} to 960 cm^{-1} , with the help of 1130 IBM data processing machine. It is found that with Dq = 860 cm^{-1} , B = 650 cm^{-1} and C = 3200 cm^{-1} , the ${}^6A_{1g} (S) \rightarrow {}^4T_{2g} ({}^4G)$ transition occurs at 19690 cm^{-1} , close to the observed value. At 77°K (Fig. 22b) the several bands found at room temperature is seen to be split into two or more components. This is presumably due to the spin-orbit interaction and the presence of small trigonal field in CsCdCl_3 . Our observed and predicted values are given in Table 22. The problem of complete assignment and identification of the entire spectrum is complicated and is being further pursued.

Table 21 : Observed and calculated energy levels of CsCdCl_3
: Mn^{2+} with parameters $Dq = 860 \text{ cm}^{-1}$, $B = 650 \text{ cm}^{-1}$
and $C = 3200 \text{ cm}^{-1}$

Transitions	Observed (in cm^{-1})		Calculated (in cm^{-1})
	Room Temp.	77°K	
${}^6\text{A}_{1g} (\text{S}) \longrightarrow$			
${}^4\text{T}_{1g} ({}^4\text{G})$	-	-	16250
${}^4\text{T}_{2g} ({}^4\text{G})$	{ 19610 20530	{ 19960 20510 20980 21430	19690
${}^4\text{A}_{1g} ({}^4\text{G})$	22470	{ 21760 22020 22490	22470
${}^4\text{E}_g ({}^4\text{G})$	23560	{ 23010 23670 24090 24390	23560
${}^4\text{T}_{2g} ({}^4\text{D})$	25250 26410 27240	{ 25310 25640 26310 26740 27200	25220
${}^4\text{E}_g ({}^4\text{D})$	28090	{ 28100 28900	28090
${}^4\text{T}_{1g} ({}^4\text{P})$	29850	{ 29200 30030	31770
${}^4\text{A}_{2g} ({}^4\text{F})$	-	{ 35200 35770	35700

II. Magnetic Studies

The ground state for half filled 3d shell ($3d^5$) is an orbital singlet and the asymmetric crystalline electric field even in combination with spin-orbit coupling leaves the six-fold degenerate 6S states unsplit upto the second order of perturbation. The anisotropy for this state should have been then normally zero and the magnetic moment should correspond exactly to spin only value of 5.916 BM and obey the Curie law. The orbital non-degenerate 6S state however may split slightly due to higher order perturbation (insipient j-j coupling, configurational interaction⁵¹ of the form $3s3d^54s$ with $3s^23d^5$) involving simultaneously the crystal field and the spin-orbit coupling⁵⁰, and it was found to agree with anisotropy measurements of Krishnan and Banerjee¹⁵⁴ and adiabatic diamagnetization measurement of Kurti and Simon¹⁵⁵.

Carefully grinding the crystal for removing shape anisotropy, our measurements show no appreciable magnetic anisotropy of the crystal which is not surprising in view of the very low expected anisotropy and low concentration of Mn^{2+} in the crystal. Measurement of magnetic susceptibility ranging from $300^{\circ}K$ to $80^{\circ}K$ shows that Mn^{2+} in $CsCdCl_3$ obeys Curie law with slight deviations at low temperature. In Table 22, we have given magnetic susceptibility at intervals of $20^{\circ}K$. Graphs of \bar{K} vs T and P_{eff}^2 vs T (P_{eff} = magnetic moment) is given in Fig. 23. The value of the magnetic moment at $300^{\circ}K$ and $80^{\circ}K$ is found to be 5.932 BM and 5.90 BM respectively.

Table 23 : Magnetic susceptibility of $\text{CsCd}_{1-x}\text{Mn}_x\text{Cl}_3$
(x = 5.2 mol %)

Temperature $^{\circ}\text{K}$	$\chi_1 = \chi_{11}$	$= \bar{K} \times 10^6$
300		14670
280		15720
260		16920
240		18340
220		20000
200		21990
180		24440
160		27490
140		31400
120		36640
100		43690
80		53330

As there is a slight deviation from Curie law at low temperature we have used the relation $KT = AT + B + \frac{C}{T}$ to find out A, B and C which are found to be 0.3×10^{-4} , 4.36 and -3.3 respectively. The coefficient A corresponds to the high frequency term in susceptibility, and is very small compared to others as is to be expected for very high term separation. From the relation $\frac{C}{B} = \theta$ where θ is Weiss temperature in Curie-Weiss law, the value of θ is found to be $(0.75)^{\circ}\text{K}$ i.e. Δ , the spin-separation of 0.52 cm^{-1} . This is somewhat larger than the value found by

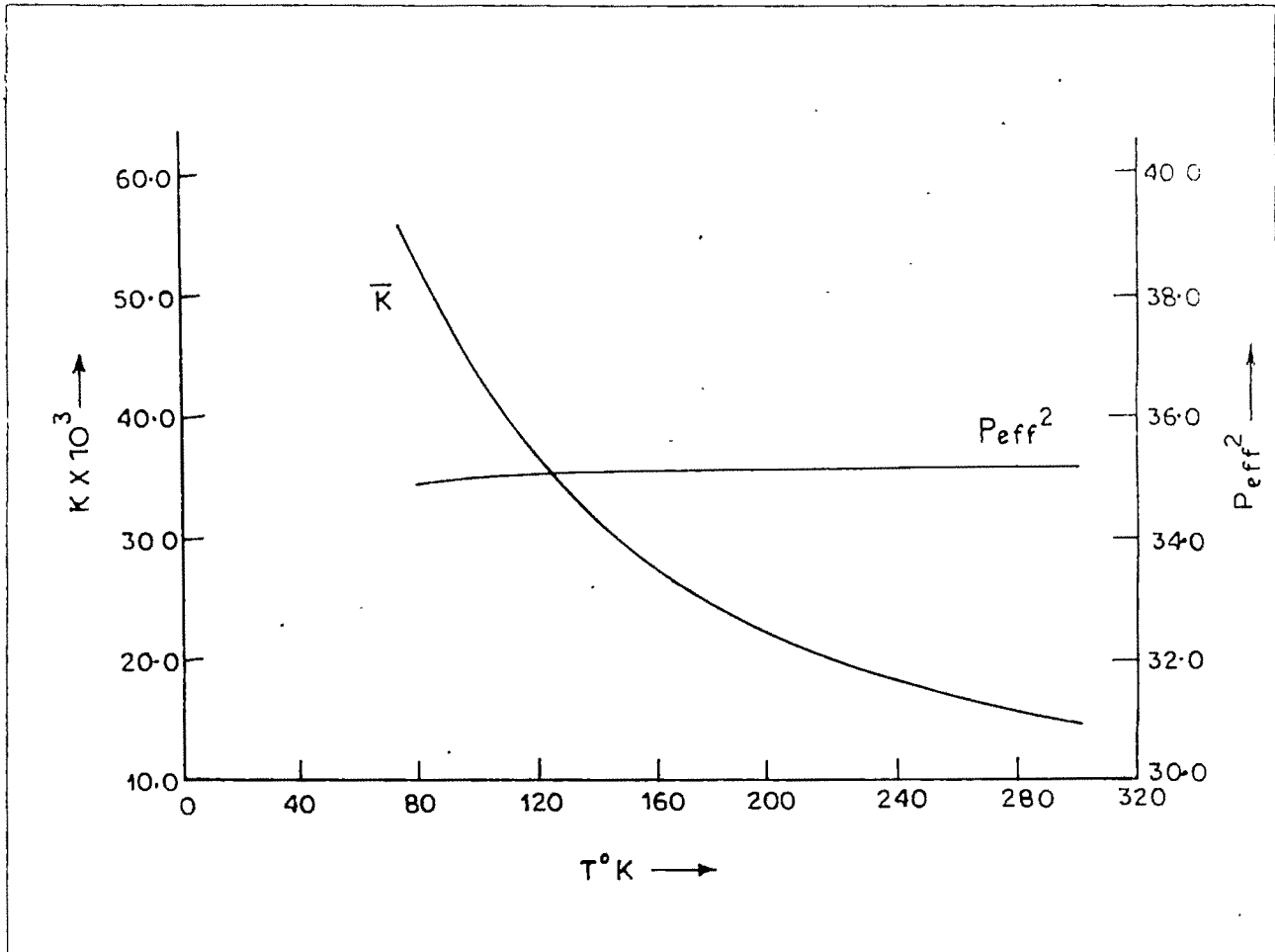


Fig.23. Variation of mean susceptibility (\bar{K}) and mean moment square (P_{eff}^2) with temperature ($CsCdCl_3 : Mn^{2+}$).

154
Krishnan and Banerjee in Mn^{2+} Tutton salts. The effective magnetic moment is found to be 34.96 showing little deviation from the free ion value (spin only value).

III. Electron Spin-Resonance

For Mn^{2+} , the 3d-shell is exactly half-filled and the orbital momentum of the resulting ground state remains unquenched. So a long spin-lattice relaxation time and g-values very close to the free-spin value can be expected. The six-fold spin-degeneracy will be resolved into three Kramer's doublet $\pm 1/2$, $\pm 3/2$ and $\pm 5/2$, leading to five-line fine structure. The characteristic six-line hyperfine structure will arise due to nuclear spin of $5/2$. In our room temperature e.p.r. spectrum of $CsCdCl_3 : Mn^{2+}$ (Fig. 24) which we have taken in Fertilizer Corporation of India, Sindri in X-band, we have observed only one set of six-line hyperfine structure. The spectrum is same for c-axis normal ^{and} along ~~the field~~ the field. From the observed spectra we have calculated the isotropic g to be 2.001 and the hyperfine constant A and B to be also of isotropic value 85.7 G. We could not obtain the zero field splitting from the e.p.r. spectrum and hence could not correlate this with θ , observed from susceptibility measurement. But the g value from e.p.r. agrees well with the value obtained from susceptibility (2.0058).

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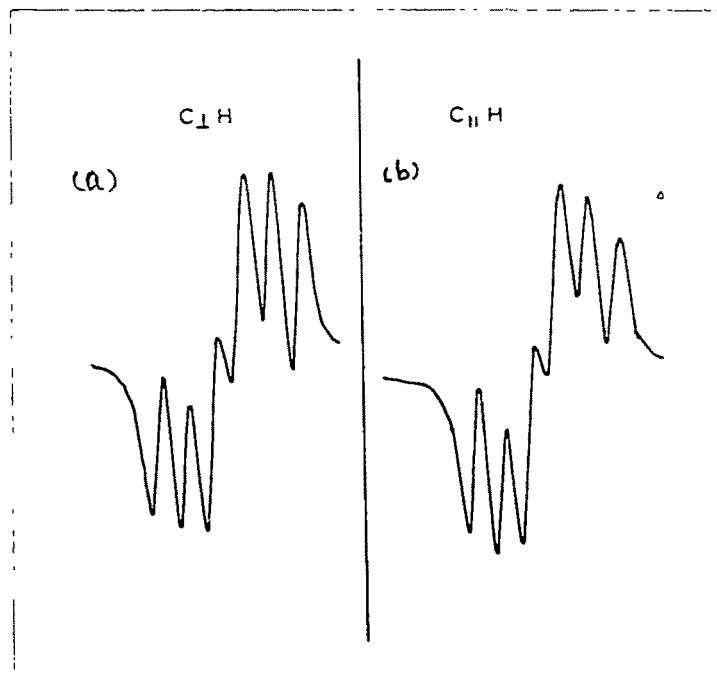


Fig.24. E.S.R. spectrum of Mn^{2+} in $CsCdCl_3$
* at room temperature.

- (a) C-axis \perp to the magnetic field
- (b) C-axis \parallel to the magnetic field