

## OPTICAL ABSORPTION SPECTRUM OF $Mn^{2+}$ IN ZINC CESIUM SULPHATE HEXAHYDRATE

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The optical absorption spectrum of  $Mn^{2+}$  ions doped in a zinc cesium sulphate hexahydrate single crystal has been studied at room (300 K) and liquid nitrogen (77 K) temperatures. The observed bands are assigned as transitions from the ground state  ${}^6A_{1g}(S)$  to various excited quartet levels of a  $Mn^{2+}$  ion in a cubic crystalline field. At 77 K, the  ${}^4E_g(G)$  band exhibits splitting and this has been interpreted as due to the excitation-magnon interaction. The weak satellite bands are observed on the higher energy side of the  ${}^4A_{1g}(G)$  band and are ascribed to phonon progressions with  $\nu = 110 \text{ cm}^{-1}$ . The fine structure observed in the  ${}^4T_{2g}(D)$  band is explained as due to spin-orbit interaction.

### ОПТИЧЕСКИЙ СПЕКТР ПОГЛОЩЕНИЯ ИОНОВ $Mn^{2+}$ В ГЕКСАГИДРАТЕ СУЛЬФАТА ЦИНКО-ЦЕЗИЯ

В работе приведены результаты исследований оптического спектра поглощения ионов  $Mn^{2+}$ , добавленных в монокристалл гексагидрата сернокислой соли пин-коцезия при комнатной температуре (300 K) и при температуре жидкого азота (77 K). Наблюдаемые полосы тракуются как переходы из основного состояния  ${}^6A_{1g}(S)$  в различные возбужденные кватетные уровни ионов  $Mn^{2+}$  в кубическом интрукристаллическом поле. При температуре 77 K полоса  ${}^4E_g(G)$  обнаруживает расширение, что интерпретируется как результат взаимодействия между экситонами и спиновой волной. Слабые сопутствующие полосы соответствуют фоновой последовательности с  $\nu = 110 \text{ см}^{-1}$ . Тонкая структура, наблюдаемая в полосе  ${}^4T_{2g}(D)$ , объясняется как результат спин-орбитального взаимодействия.

### I. INTRODUCTION

Jain [1] studied the electron spin resonance spectrum of divalent manganese ions doped in a zinc cesium sulphate hexahydrate (ZCSH) single crystal and reported the spin-Hamiltonian parameters at 298 K. From the observed value of the average hyperfine splitting, Jain suggested that the manganese ion is surrounded by an octahedron of water molecules. He also reported that the  $Mn^{2+}$  ions are incorporated substitutionally into the divalent cation sites of ZCSH. The

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present paper reports the optical absorption spectrum of  $Mn^{2+}$  ions doped in a ZCSH single crystal.

The crystal structure of the Tutton salt, ZCSH is known to be monoclinic and contains two molecules in the unit cell, related by the space group  $P2_1/a$  [2, 3]. The divalent ion is situated at the positions (0,0,0) and (1/2, 1/2, 0) in the unit cell and is surrounded by a slightly distorted octahedron of six water molecules.

## II. EXPERIMENTAL

Doped single crystals of ZCSH were grown at room temperature by slow evaporation of the saturated aqueous solution of equimolar  $Cs_2SO_4$  and  $ZnSO_4 \cdot 7H_2O$  containing about one mole percent of manganese sulphate. The crystals obtained were pale pink in colour. A crystal of a thickness of about two millimeters was used in the present investigation.

The spectra were recorded both at room and liquid nitrogen temperatures with a Cary 17 spectrophotometer in the wavelength region 600 nm to 220 nm. The oscillator strengths of the bands were calculated by computing the area under the absorption curves.

## III. THEORY

The ground state electron configuration of  $Mn^{2+}$  is  $A 3d^5$ , where 'A' stands for the closed argon shell. In a cubic crystalline field of low to moderate strength, these five d electrons are distributed in the  $t_{2g}$  and  $e_g$  orbitals, with three in the former and two in the latter. Thus the ground state configuration is written as  $(t_{2g})^3(e_g)^2$ . This configuration gives rise to the electronic state  ${}^6A_{1g}$ ,  ${}^4T_{1g}$ ,  ${}^4T_{2g}$ ,  ${}^4E_g$ ,  ${}^4A_{1g}$ ,  ${}^4A_{2g}$  and to a number of doublet states of which  ${}^6A_{1g}$  lies lowest according to Hund's rule. Observed absorption bands from  ${}^6A_{1g}$  to all quarter states are both spin and parity forbidden. The weakness of these doubly forbidden transitions is reflected in the very pale colours of the manganese salts, frequently pink. No clear cut evidence for any transition to doublet states is known as these would be extremely weak.

## IV. RESULTS AND ANALYSIS

### 1. Spectrum in the visible region

The spectra recorded at 300 K and 77 K are shown in Figs. 1 and 2, respectively. In the visible region, six bands A, B, C, D, E and F have been observed in all, both at 300 K and 77 K. At 300 K, the bands A, B and F are broad, D and E are moderately sharp and C is sharp. The band E sharpens appreciably and positions of

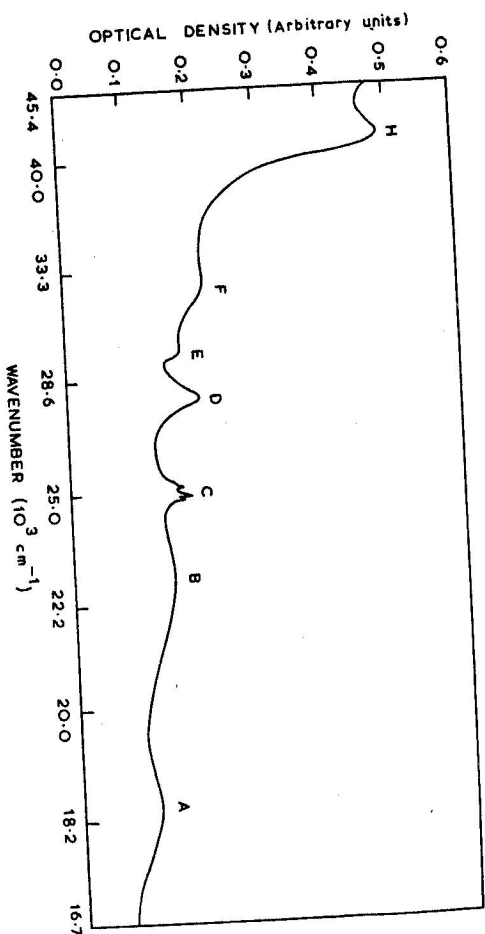


Fig. 1. Absorption spectrum of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate at room temperature (300 K).

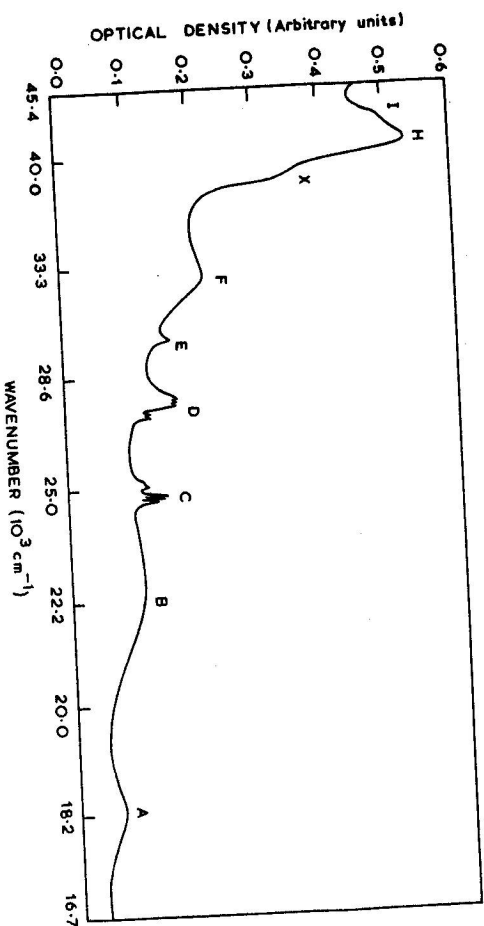


Fig. 2. Absorption spectrum of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate at liquid nitrogen temperature (77 K).

all the bands change when the temperature is lowered from 300 K to 77 K. On cooling the crystal, the bands A, B and D showed a red shift while the bands C, E and F showed a blue shift. The band D exhibited structure at 77 K while the C band exhibited structure both at 300 K and 77 K.

From the nature and position of the bands observed, they have been attributed to a  $Mn^{2+}$  ion in octahedral symmetry [4]. Ligand field bands are sharp when the energy expressions for the transitions are independent of  $Dq$ , because the number of  $t_{2g}$  electrons is the same in both the excited and the ground states [4, 5]. The sharp bands C and E are therefore attributed to the  ${}^4A_{1g}(G)$ ,  ${}^4E_g(G)$  and the  ${}^4E_g(D)$ , states respectively. The shifts of these bands C and E are not in accordance with the slopes of the corresponding energy levels in the Tanabe-Sugano [6] energy level diagram for the  $d^5$  configuration. The energy of these two levels is independent of the crystal field parameter  $Dq$ , which increases as the temperature is lowered. The blue shift for these bands is less than  $50\text{ cm}^{-1}$ , which is smaller than the shifts shown by other bands. Therefore we feel that the blue shift of the bands C and E takes place mainly due to the thermal depopulation of the levels associated with the ground state. The broad bands A and B are assigned to  ${}^4T_{1g}(G)$  and  ${}^4T_{2g}(G)$ , respectively. These bands are generally observed to be broad, as their corresponding transitions involve a change of configuration from  $(t_{2g})^3(e_g)^2$  to  $(t_{2g})^4(e_g)$ . The remaining bands D and F are ascribed to  ${}^4T_{2g}(D)$  and  ${}^4T_{1g}(P)$  states, respectively.

In the analysis of the spectrum the Trees [7] correction parameter  $\alpha$  has been employed in addition to the crystal field parameter  $Dq$  and the Racah parameters B and C. The correction term introduced is relatively small and therefore it is

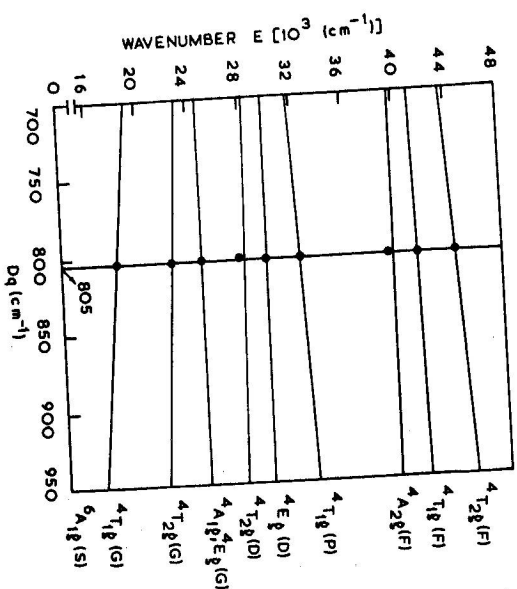


Fig. 3. Energy level diagram of  $Mn^{2+}$  in octahedral symmetry for  $B = 865\text{ cm}^{-1}$ ,  $C = 2950\text{ cm}^{-1}$  and  $\alpha = 76\text{ cm}^{-1}$ . The observed band energies in the spectrum of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate at 77 K are marked as solid circles at  $Dq = 805\text{ cm}^{-1}$ .

Table 1

Experimental data and analysis of the absorption spectrum of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate at room temperature  
( $B = 850\text{ cm}^{-1}$ ,  $C = 2970\text{ cm}^{-1}$ ,  $Dq = 790\text{ cm}^{-1}$  and  $\alpha = 76\text{ cm}^{-1}$ )

Absorption peak	Observed Wavelength (nm)	Observed Wavenumber ( $\text{cm}^{-1}$ )	Transition from ${}^6A_{1g}(S)$ to	Calculated Wavenumber ( $\text{cm}^{-1}$ )	Oscillator strengths
A	542.4	18436	${}^4T_{1g}(G)$	18414	$6.98 \times 10^{-6}$
B	438.3	22815	${}^4T_{2g}(G)$	22742	$1.55 \times 10^{-5}$
C	403.5	24783	${}^4E_g(G)$	24844	$7.53 \times 10^{-7}$
C	402.4	24850	${}^4A_{1g}(G)$	24844	$6.18 \times 10^{-7}$
C <sub>1</sub>	398.2	25113	—	—	—
C <sub>2</sub>	396.5	25220	${}^4T_{2g}(D)$	28041	$8.44 \times 10^{-6}$
D	357.1	28003	${}^4E_g(D)$	29882	—
E	335.9	29870	${}^4T_{1g}(P)$	32391	$1.60 \times 10^{-5}$
F	308.3	32435	${}^4T_{1g}(F)$	41359	$3.12 \times 10^{-5}$
H	241.2	41460	${}^4T_{1g}(F)$	—	—

arbitrarily fixed at the free ion value of  $76\text{ cm}^{-1}$ . Its inclusion is found necessary for a good fit of the observed and calculated values.

Reliable values for the crystal field parameter  $Dq$  are difficult to obtain for manganese (II) complexes since they depend mainly upon the evaluation of the Racah parameters B and C. The accurate method of calculating B and C from the energy matrices including the Trees correction has been reported by the authors [8].

The Racah parameters B and C are calculated from the following expressions

$$B = [94\alpha + \sqrt{49(E_2 - E_1)^2 - 768\alpha^2}]/49$$

$$C = [E_1 + E_2 - 27B - 26\alpha]/10.$$

In the above expressions  $E_1$  and  $E_2$  correspond to the energies of the transitions  ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$ ,  ${}^4E_g(G)$  and  ${}^6A_{1g}(S) \rightarrow {}^4E_g(D)$ , respectively.

The energy values for the quartet electronic states have been calculated for different values of  $Dq$  with  $B = 865\text{ cm}^{-1}$ ,  $C = 2950\text{ cm}^{-1}$  and  $\alpha = 76\text{ cm}^{-1}$  for the spectrum observed at 77 K. A good fit of the experimentally observed band positions is obtained as seen in Fig. 3 for  $Dq = 805\text{ cm}^{-1}$ .

The observed and calculated energies of the bands at 300 K and 77 K along with their assignments and oscillator strengths are given in Tables 1 and 2, respectively.

Table 2

Experimental data and analysis of the absorption spectrum of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate at liquid nitrogen temperature  
( $B = 865 \text{ cm}^{-1}$ ,  $C = 2950 \text{ cm}^{-1}$ ,  $Dq = 805 \text{ cm}^{-1}$  and  $\alpha = 76 \text{ cm}^{-1}$ )

Absorption peak	Observed Wavelength (nm)	Observed Wavenumber ( $\text{cm}^{-1}$ )	Transition from ${}^6A_{1g}(S)$ to	Calculated wavenumber ( $\text{cm}^{-1}$ )	Oscillator strengths
A	547.1	18278	${}^4T_{1g}(G)$	18288	$11.10 \times 10^{-6}$
B	440.0	22727	${}^4T_{2g}(G)$	22734	$3.07 \times 10^{-5}$
C <sub>1a</sub>	403.5	24780	${}^4E_g(G)$	24893	$1.08 \times 10^{-6}$
C <sub>1b</sub>	402.8	24826			$3.68 \times 10^{-7}$
C	401.6	24900	${}^4A_{1g}(G)$	24893	$5.11 \times 10^{-7}$
C <sub>2a</sub>	400.3	24980			
C <sub>2b</sub>	399.4	25037			
C <sub>3a</sub>	398.1	25120			
C <sub>3b</sub>	397.3	25170			
C <sub>4a</sub>	396.5	25220			
C <sub>4b</sub>	396.2	25240			
D <sub>2</sub>	366.8	27262			
D <sub>1</sub>	365.9	27329	${}^4T_{2g}(D)$	28150	$8.67 \times 10^{-6}$ *
D <sub>2</sub>	364.0	27472			
D <sub>1</sub>	360.9	27708			
D <sub>2</sub>	359.0	27855			
D <sub>3</sub>	359.0	29931	${}^4E_g(D)$	29937	—
E	334.1	32562	${}^4T_{1g}(P)$	32502	$4.96 \times 10^{-5}$
F	307.1	39275			
F	254.6	39275			
X	245.6	40715	${}^4A_{2g}(F)$	40592	—
G	245.6	40715	${}^4T_{1g}(F)$	41579	
H	240.7	41545			$7.49 \times 10^{-5}$ *
H	240.7	41545	${}^4T_{2g}(F)$	44539	
I	225.3	44385			

\* Integrated oscillator strength.

## V. DISCUSSION

When the crystal is cooled to 77 K, the bands  ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(G)$  and  ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(G)$  are shifted towards red by  $158 \text{ cm}^{-1}$  and  $88 \text{ cm}^{-1}$ , respectively. On the other hand the band  ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(P)$  showed a blue shift of  $127 \text{ cm}^{-1}$ . However, the exact value of the red shift of the band corresponding to the transition  ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(D)$  could not be determined as it is split up into several components at 77 K. These shifts are in accordance with the slopes of the above levels in the Tanabe-Sugano [6] energy level diagram for  $d^5$  configuration and in the energy level diagram of  $Mn^{2+}$  in ZCSH (see Fig. 3). The shifts of these bands are primarily due to the increase of  $Dq$  and secondarily due to the thermal depopulation of the ground state vibrational levels at 77 K.

The two states  ${}^4A_{1g}(G)$  and  ${}^4E_g(G)$  are normally degenerate, but their degeneracy is often lifted by covalency in the crystal. According to the covalency model presented by Stout [9], the removal of degeneracy can be explained on the differential expansion of the ( $t_{2g}$ ) and the ( $e_g$ ) orbitals. The relative order of the levels  ${}^4A_{1g}(G)$  and  ${}^4E_g(G)$  has long been debated. According to Ferguson [10] and Lohr [11], any of the two levels could be lower. Recent work of Ferguson et al. [12] confirms that the band  ${}^4E_g(G)$  lies lower than  ${}^4A_{1g}(G)$  by about  $90 \text{ cm}^{-1}$ .

### 1. Fine structure of the C band

At 300 K, the group of bands marked 'C' in Fig. 1, consists of four peaks C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub>, and C<sub>4</sub>, in the order of increasing energy. The weak peaks C<sub>3</sub> and C<sub>4</sub> appear as vibrational modes. The peaks C<sub>1</sub> and C<sub>2</sub> are to be assigned to the transitions  ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$  and  ${}^6A_{1g}(S) \rightarrow {}^4E_g(G)$ . Here it is to be noted that the  ${}^4A_{1g}(G)$  level is an orbital singlet and hence cannot split under the influence of either the low symmetry or the spin-orbit interaction, whereas the  ${}^4E_g(G)$  level may be split by any of the two perturbations. Hence the peak C<sub>1</sub> which got split into two components (C<sub>1a</sub> and C<sub>1b</sub>) at 77 K is attributed to the transition  ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$  and the peak which shows no splitting at 77 K is assigned to the  ${}^6A_{1g}(S) \rightarrow {}^4E_g(G)$  transition. These assignments are in accordance with the work of Ferguson et al. [12]. The fine structure of the 'C' band at 77 K is shown in Fig. 4.

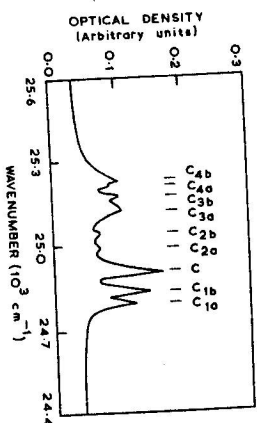


Fig. 4. Fine structure of the C band. ( ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G)$ ,  ${}^6A_{1g}(S) \rightarrow {}^4E_g(G)$ ) at 77 K.

The splitting of the  ${}^4E_g(G)$  band could be due to a variety of causes such as a spin-orbit coupling, a low symmetry field or an exciton-magnon interaction. The spin-orbit interaction must give three components. In the present investigation, it has split into two components separated by  $46 \text{ cm}^{-1}$ . The splitting of the C<sub>1</sub> band into two parts would have not been contrary to the spin-orbital splitting, where from theory one can suggest a degeneracy of nearly two levels [13]. However, against this interpretation there stands a significant splitting, because the spin-orbit splitting of the  ${}^4E_g(G)$  level is expected to be less than  $20 \text{ cm}^{-1}$  [13–15]. The lowering of symmetry is unlike to be responsible for the splitting, firstly



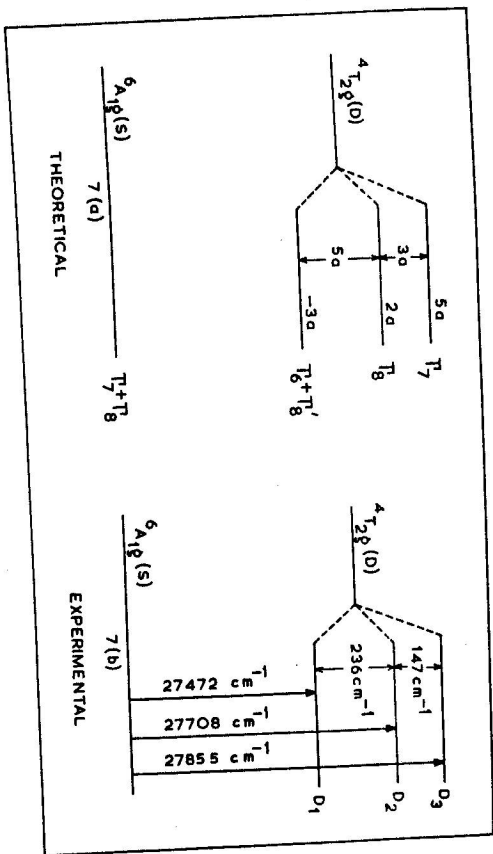


Fig. 7. Spin-orbit splitting of the  ${}^4T_{2g}(D)$  band.

therefore the low temperature spectrum is expected to reveal the fine structure of the level. Several authors have reported the spin-orbit splitting for the  ${}^4T_{2g}(D)$  level [14, 18–20].

The  ${}^4T_{2g}(D)$  level splits under spin-orbit coupling as

$$T_8 \times T_{2g} = T_6 + T_7 + 2T_8.$$

First order splittings calculated from Lande's formula using fictitious  $L^1 = 1$  are (Goode [13])

$$E = 5a(T_7), 2a(T_8) \text{ and } -3a(T_6 + T_8).$$

$T_6$  and  $T_8$  are very close together and hence we can have three spin-orbit components with their spacings in the ratio of 3:5 as shown in Fig. 7a. Therefore, only three out of the five observed lines should be spin-orbit in origin. In the present investigation, the peaks  $D_1$ ,  $D_2$  and  $D_3$  seem to be the spin-orbit components of the  ${}^4T_{2g}(D)$  level. The separation  $D_3 - D_2$  and  $D_2 - D_1$  as shown in Fig. 7b are in the ratio 147:236  $\approx$  3:5 which agrees well with the first order splitting ratio.

In the absorption spectrum of  $\text{RbMnF}_3$ , Mehra et al. [14] have diagonalised the energy matrices inclusive of the spin-orbit interaction with  $B = 840 \text{ cm}^{-1}$ ,  $C = 3080 \text{ cm}^{-1}$ ,  $Dq = 780 \text{ cm}^{-1}$  and  $\alpha = 76 \text{ cm}^{-1}$  and obtained the value of the spin-orbit splitting  $\zeta$  as  $320 \text{ cm}^{-1}$  for the observed separations of  $129 \text{ cm}^{-1}$  and  $212 \text{ cm}^{-1}$  for the  ${}^4T_{2g}(D)$  components. As the spacing of the spin-orbit components observed in the present work are also in the same order as those of Mehra et al., the  $\zeta$  value in the present case also might be around  $350 \text{ cm}^{-1}$ .

In the light of the above discussion, the remaining peaks  $D_x$  and  $D_y$  do not form part of the spin-orbit components of the  ${}^4T_{2g}(D)$  band. It is also not probable that these peaks constitute the vibrational progression, as they are located on the lower energy side of the spin-orbit components. However, Janardhanam [20] observed four peaks (located at  $27280 \text{ cm}^{-1}$ ,  $27330 \text{ cm}^{-1}$ ,  $27495 \text{ cm}^{-1}$  and  $27610 \text{ cm}^{-1}$ ) on the lower energy side of the three spin-orbit components (located at  $27705 \text{ cm}^{-1}$ ,  $27910 \text{ cm}^{-1}$  and  $28035 \text{ cm}^{-1}$ ) of the  ${}^4T_{2g}(D)$  band in the absorption spectrum of a  $\text{Mn}^{2+}$  doped zinc ammonium sulphate hexahydrate and attributed them successively to the superposition of the vibrational mode of the  $\text{SO}_4^{2-}$  radical on the spin-orbit components of the  ${}^4T_{2g}(D)$  band. We are, therefore, of the opinion that the peaks  $D_x$  and  $D_y$  in the present work may also be assigned to similar lines.

## 2. Spectrum in the ultraviolet region

Transitions to the three highest levels  ${}^4A_{2g}(F)$ ,  ${}^4T_{1g}(F)$  and  ${}^4T_{2g}(F)$  arising from the  ${}^4F$  level of the free ion are expected to lie in the ultraviolet region. From the slopes of these levels in the energy level diagram, one expects a sharp  ${}^4A_{2g}(F)$  band followed by two broad bands  ${}^4T_{1g}(F)$  and  ${}^4T_{2g}(F)$  on the higher energy side. Reliable experimental results available on the observed  $\text{Mn}^{2+}$  bands in this region, that is, below  $300 \text{ nm}$  are very few as the high background absorption which is predominant in this region obscures the true nature of these bands.

In the present investigation only one broad band is observed in the ultraviolet region at  $300 \text{ K}$  as shown in Fig. 1, centred at  $41460 \text{ cm}^{-1}$ . This band marked H is assigned to the transition  ${}^6A_{1g}(S) \rightarrow {}^4T_{1g}(F)$  and the calculated value is in good agreement with the observed value as shown in Table 1.

When the crystal is cooled to  $77 \text{ K}$ , three more bands in addition to the band H at  $300 \text{ K}$  are observed. The three new bands are marked as X, G and I. The ultraviolet spectrum recorded at  $77 \text{ K}$  is shown in Fig. 8. The band marked X is located around  $39000 \text{ cm}^{-1}$ . The band marked G appears as a weak band on the lower energy side of the H band at  $40175 \text{ cm}^{-1}$  and is assigned to the transition  ${}^6A_{1g}(S) \rightarrow {}^4A_{2g}(F)$ . The band H showed a blue shift of  $85 \text{ cm}^{-1}$  ( $41545 - 41460$ ), which is in accordance with the slope of this level. The last band marked I is assigned to the transition  ${}^6A_{1g}(S) \rightarrow {}^4T_{2g}(F)$ . The position of this band at  $77 \text{ K}$  is  $44385 \text{ cm}^{-1}$ .

The assignment of the X band is not straightforward, since no quartet level is expected to lie around the position of the X band. The transitions to doublet states and charge transfer states are ruled out on the basis of intensity and energy considerations. This band may in all probability be due to the simultaneous electronic excitation of a pair of manganese ions as explored by Ferguson et al. [25], Ferguson [10], Srivastava et al. [16] and Srivastava [17] in the case of transition metal ions. A characteristic feature of such an absorption is that the



intensity of the band increases abnormally when the temperature is lowered. The behaviour of the X band is in agreement with this fact. Regarding the shift of this band, it is not possible to say anything as it could not be observed at 300 K.

The observed and calculated energies, assignments and their oscillator strengths for the ultraviolet bands at room and liquid nitrogen temperatures with the visible absorption bands are given in Table 1 and 2, respectively.

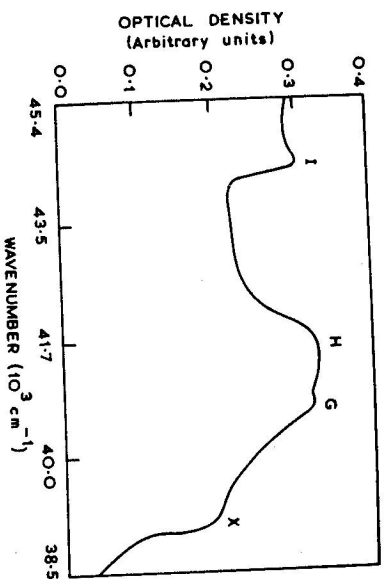


Fig. 8. Absorption spectrum of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate in the ultraviolet region at 77 K.

## VI. CONCLUSION

The appearance of magnon side bands in the visible region spectrum, seen in centrosymmetric complexes of manganese, justify our assumption of the octahedral site symmetry for the ion of  $Mn^{2+}$  in zinc cesium sulphate hexahydrate.

## ACKNOWLEDGEMENTS

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