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## Research Article

### OPTICAL ABSORPTION STUDY OF $Mn^{2+}$ DOPED CADMIUM FORMATE DIHYDRATE SINGLE CRYSTALS

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#### ABSTRACT

The optical absorption study of  $Mn^{2+}$  doped Cadmium formate dihydrate single crystals is carried out at room temperature. The optical absorption study is a tool to investigate the site symmetry and different distortions present in the system. The electronic repulsion and crystal field parameters having good fit to the observed optical absorption spectra are evaluated. The band positions are fitted with the Racah parameters (B and C), the cubic crystal field splitting parameter ( $Dq$ ) and the Trees correction ( $\alpha$ ). The values obtained for the parameters are  $B = 875 \text{ cm}^{-1}$ ,  $C = 2933 \text{ cm}^{-1}$ ,  $Dq = 550 \text{ cm}^{-1}$  and  $\alpha = 76 \text{ cm}^{-1}$ , respectively. On the basis of data obtained the surrounding crystalline field and the nature of metal-ligand bonding are discussed.

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#### INTRODUCTION

Optical absorption studies of  $Mn^{2+}$  ions in various single crystals and glasses have been the subject of recent investigation [1-4]. As the resultant orbital angular momentum is zero because shell of 3d electrons of this ion is just half-filled by five electrons, electron spin is only responsible for the optical properties [5]. Optical studies provide information about energy level ordering of different orbital levels of the paramagnetic ion and crystalline field strength in the diamagnetic host lattice as well as associated distortions [6-8].

Cadmium has specific properties that make it suitable for a wide variety of industrial applications. These include: excellent corrosion resistance, low melting temperature, high ductility and high thermal and electrical conductivity. Cadmium compounds are used for electroplating other metals or alloys to protect them against corrosion and for manufacturing of stearate stabilizers [9-10]. Cadmium is also present as an impurity in non-ferrous metals (zinc, lead and copper), iron and steel, fossil fuels (coal, oil, gas, peat and wood), cement and phosphate fertilizers. In these products it is regarded as environmental concern. Because of high cycle lives, excellent low and high temperature performance cadmium is used as electrode for Ni-Cd batteries. Applications consuming lesser amounts of cadmium include the fungicides for golf courses, control rods and shields for nuclear reactors, television picture

tube phosphors, motor oils, and curing agents for rubber [11-12]. They are also used for light detection [13]. In molecular biology, they are used to block voltage dependent calcium channels from fluxing [14] calcium ions. Helium-cadmium lasers are used as common source of blue-ultraviolet light. They operate at either 325 or 422 nm and are used in fluorescence microscopes and other laboratory experiments [15]. This developed our interest in cadmium compound, namely cadmium formate dihydrate (CFD).

In the present investigation an optical absorption study of  $Mn^{2+}$  doped in CFD single crystals is done in order to find site symmetry, energy level ordering of various orbital levels of metal ion and nature of bonding present in the crystal. The study is further used to justify EPR results of  $Mn^{2+}$  in the same crystal [16].

##### Crystal Structure

The crystal structure of CFD,  $Cd(HCO_2)_2 \cdot 2H_2O$  [17] is monoclinic with the space group  $P2_1/c$ . The unit cell has the dimensions  $a = 8.984(4) \text{ \AA}$ ,  $b = 7.391(6) \text{ \AA}$ ,  $c = 9.760(3) \text{ \AA}$  and  $\beta = 97.32(3)^\circ$ ;  $Z = 2$ . The structure is isomorphous with the formates of manganese, zinc and copper and forms a three dimensional polymer. There are two formate ligands, exhibiting anti-anti and anti-syn configurations linking together cadmium atoms which are arranged in face centered

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position in the cell. Each of the cadmium atoms is crystallographically and chemically distinct.

**Experimental**

Single crystals of CFD were grown at room temperature by slow evaporation of dilute aqueous solution of CdSO<sub>4</sub> in slight excess of formic acid. For Mn<sup>2+</sup> doped crystals, 0.01 wt % of MnCl<sub>2</sub>·4H<sub>2</sub>O was added as paramagnetic impurity. After few days, good pink colored single crystals of Mn<sup>2+</sup> doped CFD with well-defined faces were obtained. The optical absorption spectra are recorded on a Unicam 5625-UV/Visible spectrophotometer at room temperature in the wavelength range 300-625 nm.

**RESULTS AND DISCUSSION**

In a cubic crystalline field of moderate strength [18] Mn<sup>2+</sup> electrons are distributed in the t<sub>2g</sub> and e<sub>g</sub> orbitals with three in former and two in latter. Thus the ground state configuration is written as (t<sub>2g</sub>)<sup>3</sup>e<sub>g</sub><sup>2</sup>. The configuration gives rise to <sup>6</sup>A<sub>1g</sub>, <sup>4</sup>A<sub>1g</sub>, <sup>4</sup>E<sub>g</sub>, <sup>4</sup>T<sub>1g</sub>, <sup>4</sup>T<sub>2g</sub> and <sup>4</sup>A<sub>2g</sub> states and a number of doublets. The <sup>6</sup>A<sub>1g</sub> lies lowest and is the ground state. The other excited electronic configurations like (t<sub>2g</sub>)<sup>4</sup>e<sub>g</sub>, (t<sub>2g</sub>)<sup>2</sup>e<sub>g</sub><sup>3</sup> and (t<sub>2g</sub>)<sup>3</sup>e<sub>g</sub><sup>2</sup> give rise to several doublet and quartet states. Thus all the absorption bands of high spin Mn<sup>2+</sup> correspond to spin-forbidden transitions.

The observed absorption spectrum of Mn<sup>2+</sup> ions in CFD single crystal is shown in Fig. 1. The nature and position of bands show that Mn<sup>2+</sup> ions are in a site of octahedral symmetry [19-20]. The EPR study by same author in same system [16] (for Mn<sup>2+</sup>) indicates that the site symmetry around transition ion is nearly cubic (O<sub>h</sub>-Octahedral). Thus present optical study justifies the earlier EPR study.

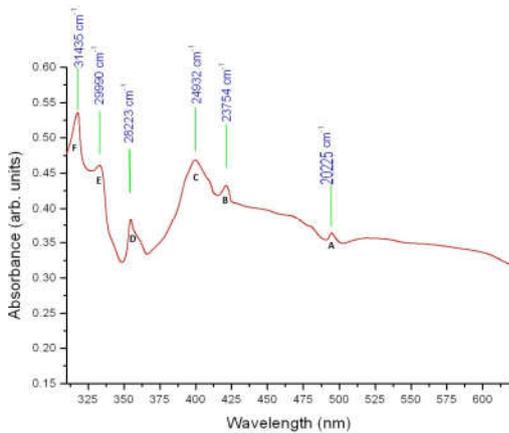


Fig 1

The optical absorption spectrum consists of six bands centered at 494.44 nm (20225 cm<sup>-1</sup>), 420.98 nm (23754 cm<sup>-1</sup>), 401.10 nm (24932 cm<sup>-1</sup>), 354.23 nm (28223 cm<sup>-1</sup>), 333.45 nm (29990 cm<sup>-1</sup>) and 318.2 nm (31435 cm<sup>-1</sup>) which are denoted by A, B, C, D, E and F respectively. Among the observed bands A and B have small widths than C, D, E and F bands. Ligand bands are sharp when the energy expressions for the transitions are independent of Dq because the number of t<sub>2g</sub> electrons is the same in both the ground and excited states [18]. The sharp bands are therefore assigned to <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>A<sub>1g</sub>(G), <sup>4</sup>E<sub>g</sub>(G) and <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>E<sub>g</sub>(D), respectively because their energies are

independent of Dq. Generally two bands <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>A<sub>1g</sub>(G), <sup>4</sup>E<sub>1g</sub>(G) and <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>E<sub>1g</sub>(D) are sharp as they arise from intraconfigurational transitions. The two states <sup>4</sup>A<sub>1g</sub>(G) and <sup>4</sup>E<sub>g</sub>(G) are normally degenerate [21]. Lifting of degeneracy of <sup>4</sup>A<sub>1g</sub>(G) and <sup>4</sup>E<sub>g</sub>(G) levels depends on various perturbing factors [22]. In case of non-degenerate states relative ordering of levels <sup>4</sup>A<sub>1g</sub>(G) and <sup>4</sup>E<sub>g</sub>(G) have been discussed by Ferguson [23] and Lohr [24]. In fact the position of <sup>4</sup>E<sub>g</sub>(G) state is influenced by the interaction with <sup>4</sup>E<sub>g</sub>(D) state while the position of <sup>4</sup>A<sub>1g</sub>(G) is not affected. Thus <sup>4</sup>E<sub>g</sub>(G) level should be affected more by slight changes in the environment in different crystals as compared with <sup>4</sup>A<sub>1g</sub>(G) level. In the present study these two states, namely <sup>4</sup>A<sub>1g</sub>(G) and <sup>4</sup>E<sub>g</sub>(G) are degenerate due to ionic nature of bonding. The bands located at 24932 cm<sup>-1</sup> and 29990 cm<sup>-1</sup> are attributed as <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>A<sub>1g</sub>(G), <sup>4</sup>E<sub>g</sub>(G) and <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>E<sub>g</sub>(D), respectively. The transitions <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>T<sub>1g</sub>(G) and <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>T<sub>2g</sub>(G) are observed to be slightly less sharp since they involve a change of configuration from (t<sub>2g</sub>)<sup>3</sup>(e<sub>g</sub>)<sup>2</sup> to (t<sub>2g</sub>)<sup>4</sup>(e<sub>g</sub>)<sup>1</sup> [18]. Thus the bands observed at 20225 cm<sup>-1</sup> and 23754 cm<sup>-1</sup> are attributed to states <sup>4</sup>T<sub>1g</sub>(G) and <sup>4</sup>T<sub>2g</sub>(G). Following energy level diagram for d<sup>5</sup> configuration by Tanabe and Sugano [25], the moderately weak bands D and F are assigned to the transitions <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>T<sub>2g</sub>(D) and <sup>6</sup>A<sub>1g</sub>(S) → <sup>4</sup>T<sub>1g</sub>(P), respectively. Therefore the bands located at 28223cm<sup>-1</sup> and 31435 cm<sup>-1</sup> are attributed to levels <sup>4</sup>T<sub>2g</sub>(D) and <sup>4</sup>T<sub>1g</sub>(P). The wavelengths and wave numbers of the absorption bands together with the assignments are given in Table 1.

Table 1

Absorption Peaks	Transition from	Observed		Calculated
		wavelength (nm)	wave number(cm-1)	wave number (cm-1)
A	<sup>4</sup> T <sub>1g</sub> (G)	494.44	20225(5)	20260
B	<sup>4</sup> T <sub>2g</sub> (G)	420.98	23754(6)	23697
C	<sup>4</sup> A <sub>1g</sub> (G)	401.1	24932(7)	24935
D	<sup>4</sup> E <sub>g</sub> (G)			
	<sup>4</sup> T <sub>2g</sub> (D)	354.23	28223(9)	28606
E	<sup>4</sup> E <sub>g</sub> (D)	333.45	29990(10)	29979
F	<sup>4</sup> T <sub>1g</sub> (P)	318.12	31435(12)	31760

**Optical Analysis**

We studied the optical absorption spectra of Mn<sup>2+</sup> ions in CFD single crystal to gather support for our EPR results. The optical spectra show six bands, characteristic of Mn<sup>2+</sup> ions in octahedral symmetry.

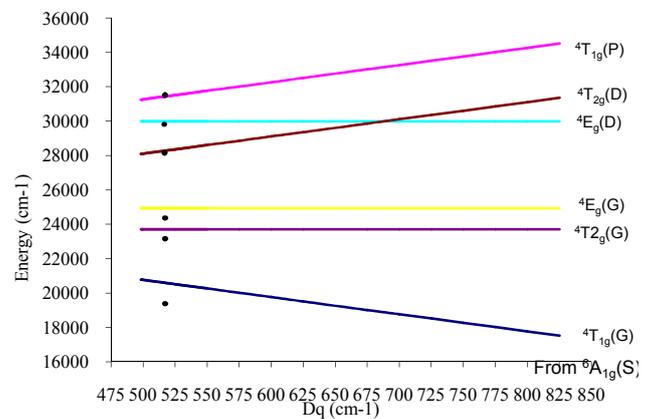


Fig 2

The octahedral symmetry is also obtained by EPR study [16]. The energy levels are evaluated using inter-electronic repulsion parameters B and C, the crystal field splitting parameter Dq and the trees correction  $\alpha$  [25]. The correction term is relatively small, and therefore it is arbitrarily fixed at free ion value of  $76 \text{ cm}^{-1}$ . The energy matrices including Trees correction have been given by Mehra [26]. The electrostatic parameters B and C are calculated from the energy states  ${}^4E_g(G)$  and  ${}^4E_g(D)$  which are independent of crystal field splitting parameter Dq. The value of crystal field splitting parameter Dq depends on the Racah parameters B and C [27].

Once the assignments of bands of optical spectrum have been made, the values of B and C are then used to solve secular equations of Mehra [26] to evaluate single value of Dq. The energy values for quartet electronic state are calculated for different values of Dq with  $B = 875 \text{ cm}^{-1}$ ,  $C = 2933 \text{ cm}^{-1}$  and  $\alpha = 76 \text{ cm}^{-1}$ . A good fit of the experimentally observed band positions is obtained for  $Dq = 550 \text{ cm}^{-1}$  as seen from the graph in Fig.2. It is seen from Table 1 that the observed and calculated values of band positions are in good agreement which justifies our assignments. The free ion value of Racah inter-electronic repulsion parameters  $B_0$  and  $C_0$  are  $960 \text{ cm}^{-1}$  and  $3325 \text{ cm}^{-1}$  respectively [28]. Evaluated values of B and C in the present work are consistent with the values reported for  $\text{Mn}^{2+}$  in other systems [29-30, 20]. The present values of B ( $875 \text{ cm}^{-1}$ ) and C ( $2933 \text{ cm}^{-1}$ ) are near to free ion values ( $960 \text{ cm}^{-1}$ ,  $3325 \text{ cm}^{-1}$ ) showing ionic nature of bonding in the crystal. From EPR study [16] the value of hyperfine parameter ( $A = 98 \times 10^{-4} \text{ T}$ ) is also consistent with ionic character [20]. Experimental evidence for reduction of the electrostatic parameters B and C in octahedral complexes is given by Owen and Thornley [31]. From the nature of optical bands in present work, we may propose octahedral symmetry for  $\text{Mn}^{2+}$  in CFD single crystal.

## CONCLUSIONS

Optical absorption study of  $\text{Mn}^{2+}$  doped CFD has been done at room temperature. The observed optical bands have been assigned to transitions from  ${}^6A_{1g}(S)$  ground state to different excited quartet levels of  $\text{Mn}^{2+}$  ions. The Racah parameters B and C as well as crystal field splitting parameter Dq have been evaluated. A good fit of observed band positions to calculated values have been obtained for  $Dq = 550 \text{ cm}^{-1}$ . The site symmetry around the transition ion is predominantly octahedral. The results allow us to conclude that ionic nature of bonding is present between transition ion and ligands.

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