OPTICAL ABSORPTION STUDIES OF Mn^{2+} IONS IN D-GLUCONIC ACID MONOHYDRATE SINGLE CRYSTALS

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ABSTRACT

The optical absorption study of Mn^{2+} *doped D-Gluconic Acid Monohydrate single crystals is carried out at room temperature. Optical spectroscopy gives the electronic structure of transition ions in crystals, knowledge of the energy levels and crystal field parameters as well as better understanding of the physical interactions present in the system. The optical absorption study is a tool to investigate the site symmetry and different distortions present in the system. The observed optical bands are assigned as transitions from* $^6A_{1g}(S)$ *ground state to various excited quartet levels of* Mn^{2+} *ion in a cubic crystalline field. These bands are fitted with four parameters, inter-electronic parameters (B and C), crystal field parameter* (D_q) *and Tree's correction* (α)*.The values obtained for the parameters are* $B = 825\ cm^{-1}$, $C = 2275\ cm^{-1}$, $D_q = 760\ cm^{-1}$ *and* $\alpha = 76\ cm^{-1}$*, respectively. On the basis of data obtained the surrounding crystalline field and the nature of metal-ligand bonding are discussed.*

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Keywords: Single Crystal; Crystal field; Optical Absorption; Trees Correction; Racah Parameters

INTRODUCTION

Amongst paramagnetic ions of the iron group, divalent manganese is of interest because the shell of 3d-electrons responsible for the paramagnetism is just half-filled by the five electrons of these ions, and the resultant orbital angular momentum L is zero. The ground state is ^6S. When paramagnetic ions are introduced in such host lattices, local distortions will take place due to mismatch of paramagnetic ion size to that of the host ions **[1]**. The crystalline electric field can affect the electron spins only through high-order interactions **[2]**, so that the spins are almost completely free to orient themselves in an external magnetic field. Optical absorption studies of in various single crystals and glasses have been the subject of recent investigation for researchers **[3-6]**. In the present case for Mn^{2+} ions electron spin is only responsible for the optical properties **[7]**. 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 **[8-10]**.

Gluconic acid is a mild organic acid derived from glucose by a simple oxidation reaction. The reaction is facilitated by the enzyme glucose oxidase (fungi) and glucose dehydrogenase (bacteria such as Gluconobacter). Microbial production of gluconic acid is the preferred method and it dates back to several decades. The most studied and widely used fermentation process involves the fungus Aspergillus niger. Gluconic acid and its derivatives, the principal being sodium gluconate, have wide applications in food and pharmaceutical industry **[11]**. It is natural constituent in fruit juices and honey and is used in the pickling of foods. Its inner ester, glucono-d-lactone imparts an initially sweet taste which later becomes slightly acidic. It is used in meat and dairy products, particularly in baked goods as a component of leavening agent for preleavened products. It is used as a flavouring agent also. This developed our interest in gluconic compound, namely D-Gluconic Acid Monohydrate (DGAM).

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

CRYSTAL STRUCTURE

D-gluconic acid monohydrate ($C_6H_{12}O_7.H_2O$) single crystals are **monoclinic [12]**, belong to the space group $P2_1$ and contain two molecules in the unit cell. Cell parameters are a = 8.430, b = 5.403 and c = $10.406A^0$ and angle $\beta = 96.88^0$.

EXPERIMENTAL

Single crystals of Mn^{2+} doped D-gluconic acid monohydrate are grown by slow evaporation of an aqueous solution of D-gluconic acid to which 0.01mole % of manganese chloride is added. Light green transparent crystals are obtained in about 10 days. The optical absorption spectra are recorded at room temperature on a Unicam 5625 UV-Visible spectrophotometer in the wavelength range 195-925 nm.

OPTICAL ABSORPTION STUDIES

The optical spectra of Mn^{2+} doped crystals have been the subject of interest to a number of workers **[2-6]**. In a cubic crystalline field of moderate strength **[13]** $3d^5$ electrons of Mn^{2+} electrons are distributed in the t_{2g} and e_g orbitals with three in former and two in latter. Thus the ground state configuration is written as $(t_{2g})^3e_g^2$. The configuration gives rise to $^6A_{1g}$, $^4A_{1g}$, ^4E_g, $^4T_{1g}$, $^4T_{2g}$, $^4A_{2g}$, $^4A_{2g}$ (F) , $^4T_{1g}$(F) states and a number of doublet states. The $^6A_{1g}$ lies lowest and is the ground state. The other excited electronic configurations like $(t_{2g})^4e_g$, $(t_{2g})^2e_g^3$ and t_{2g} e_g^4 give rise to several doublet and quartet states. Thus all the absorption bands of high spin Mn^{2+} correspond to spin-forbidden transitions.

The observed absorption spectrum of Mn^{2+} ions in DGAM single crystal is shown in **Figs. 1** and **2.** The spectrum consists of seven main bands located at 19185, 24335, 25305, 26196, 26970, 28642 and 34445 cm^{-1}. In addition to the above, some weak bands at 38999 and 40737 cm^{-1} are also observed. Similar weak bands were also reported at room temperature by several authors **[14-17]**. Among the bands observed in the present studies, the band at 24335, 26970 and 34445 cm^{-1} are found to be sharp. Ligand field bands are sharp when the energy expressions for the transitions are independent of D_q, because the number of t_{2g} electrons is the same in both the excited and ground states [**13**]. The sharp bands are therefore assigned to ${}^6A_{1g}(S)\rightarrow{}^4A_{1g}(G)$, ${}^6A_{1g}(S)\rightarrow{}^4E_g(G)$ and ${}^6A_{1g}(S)\rightarrow{}^4T_{1g}(P)$ states, respectively, as energy expressions for these are independent of D_q. The two states ${}^4A_{1g}(G)$ and ${}^4E_g(G)$ are normally degenerate **[18]**, but their degeneracy is often lifted by covalency in the crystal **[18]**. Therefore the bands at 26970 cm^{-1} and 24335 cm^{-1}, are attributed to ${}^4E_g(G)$ and ${}^4A_{1g}(G)$ respectively. The relative ordering of the levels are discussed by Fergusan **[18]** and Lohr **[19].** Third sharp band at 34445 cm^{-1} is assigned to ${}^6A_{1g}(S)\rightarrow{}^4T_{1g}(P)$. Using the Tanabe-Sugano diagram **[20]** the other bands at 19185, *25305*, 26196, 28642, 38999 and 40737 cm^{-1}, are assigned to ${}^4T_{1g}(G)$, ${}^4T_{2g}(D)$, ${}^4T_{2g}(G)$, ${}^4E_g(D)$, ${}^4A_{2g}(F)$ and ${}^4T_{2g}(F)$ states respectively. The wavelengths and the wave numbers of the bands are given in **Table 1**, together with the assignments.

The energy levels are calculated using the Racah parameters (B and C), the crystal field splitting parameter (D_q) and the Trees correction (α). The correction term is relatively small, and so it is arbitrarily fixed at the free ion value of 76 cm^{-1}. The energy matrices including Trees correction have been given **[21]** by Mehra.

The electrostatic parameters B and C are evaluated from the energy states ${}^4E_g(G)$ and ${}^4E_g(D)$ which are independent of D_q .

The energy matrix for ${}^4E_g$ (*G, D*) is:

$$\begin{vmatrix} -22B+5C+12\alpha & -2\sqrt{3}B+4\sqrt{3}\alpha \\ -2\sqrt{3}B+4\sqrt{3}\alpha & -21B+5C+14\alpha-E \end{vmatrix}=0 \qquad (1)$$

The energy for the ground state ${}^6A_{1g}(S)$ is $-35B$.

Substituting $E=-35B+T$ in above we have

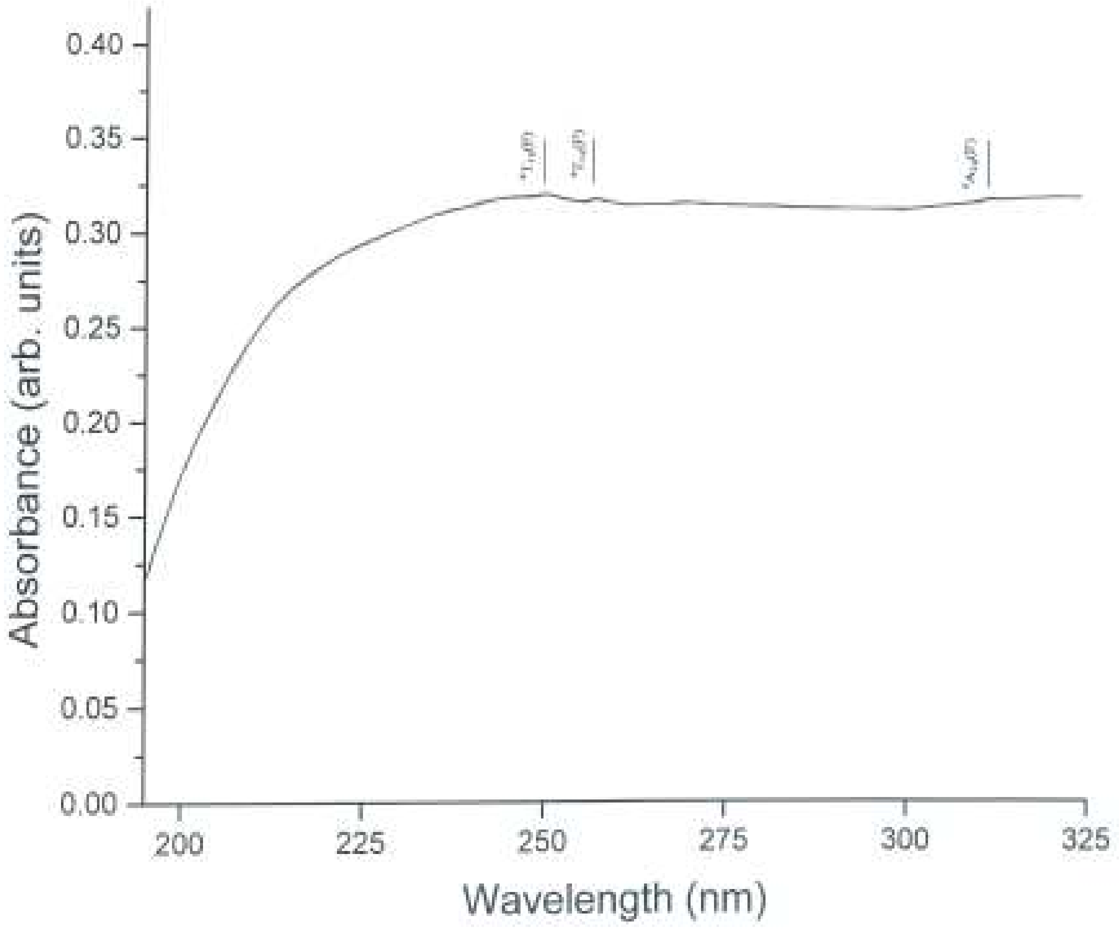

Fig. 1. Optical absorption spectrum in D-gluconic acid monohydrate (DGAM) in the wavelength range 195-325 nm.

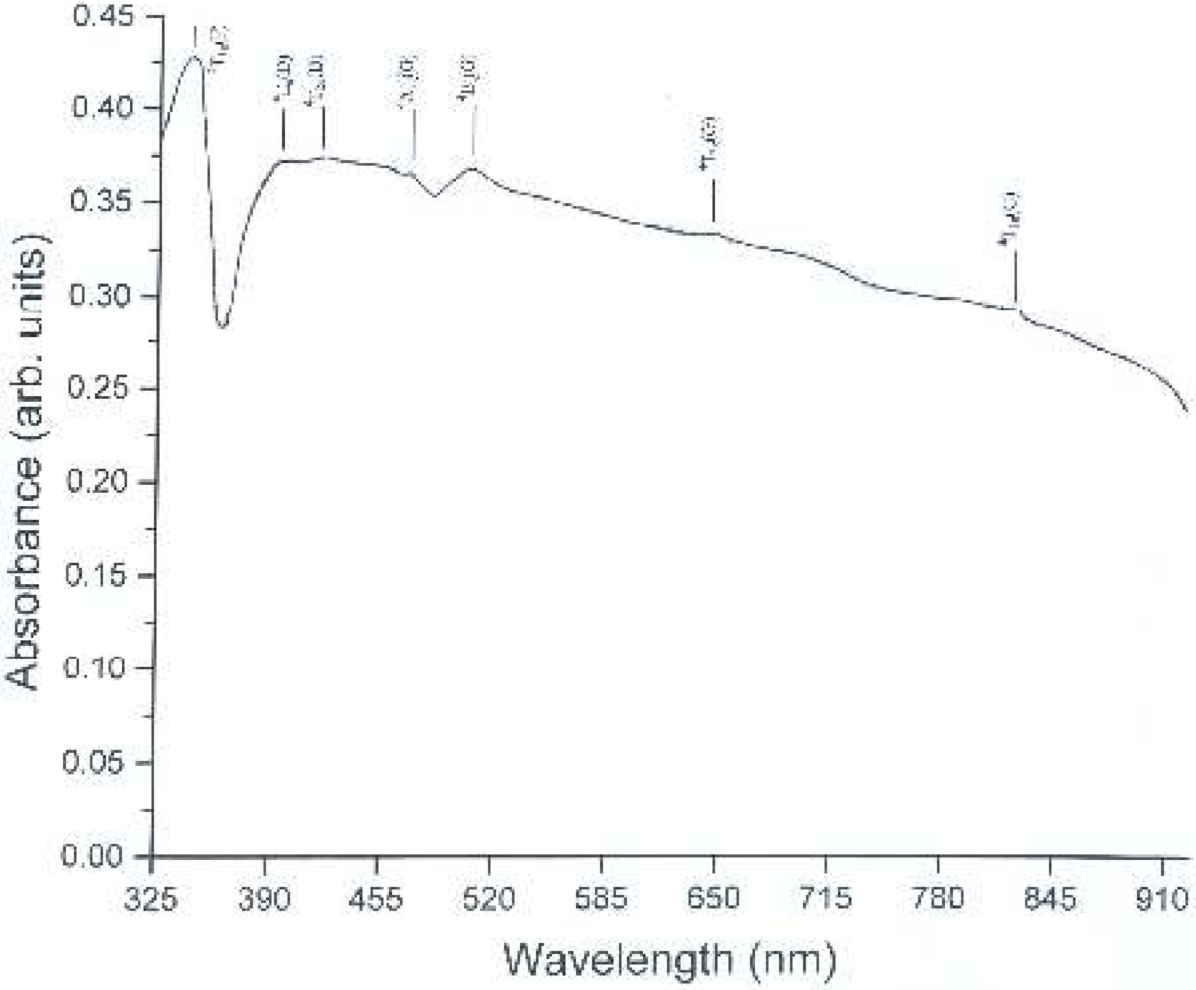

Fig. 2. Optical absorption spectrum in D-gluconic acid monohydrate (DGAM) in the wavelength range 325-925 nm.

Table 1: The Experimental data and the analysis of the absorption spectrum of Mn^{2+} ions in DGAM.

(B=825 cm^{-1} C= 2275 cm^{-1}, Dq= 760 cm^{-1} and α= 76cm^{-1})

The uncertainties are given in brackets.

Transition from $^6A_{1g}(S)$	Wavelength Observed (cm^{-1})	Wavelength Calculated (cm^{-1})
$^4T_{1g}(G)$	19185(9)	19196
$^4A_{1g}(G)$	24335(5)	24345
$^4T_{2g}(D)$	25305(6)	25335
$^4T_{2g}(G)$	26196(9)	26210
$^4E_g(G)$	26970(8)	26995
$^4E_g(D)$	28642(7)	28654
$^4T_{1g}(P)$	34445(9)	34465
$^4A_{2g}(F)$	38999(6)	39010
$^4T_{2g}(F)$	40735(5)	41005

$$\begin{vmatrix} 13B+5C+12\alpha-T & (-2B+4\alpha)\sqrt{3} \\ (-2B+4\alpha)\sqrt{3} & 14B+5C+14\alpha-T \end{vmatrix}=0 \qquad (2)$$

Solving the above matrix, we get

$$T=1/2[\,(27B+10C+26\alpha) \pm \sqrt{49B^2-188B\alpha+196\alpha^2}\,]$$

The solution for the above equation is

$$T_1 = ½\ [(27B+10C+26\alpha) - \sqrt{49B^2-188B\alpha+196\alpha^2}\,] \qquad (3)$$

$$T_2 = ½\ [(27B+10C+26\alpha) + \sqrt{49B^2-188B\alpha+196\alpha^2}\,] \qquad (4)$$

$$(T_2-T_1)^2 = [49B^2-188B\alpha+196\alpha^2]$$

$$B=(94\,\alpha \pm \sqrt{49(T_2-T_1)^2-768\alpha^2}\,)\Big/ 49$$

In the above expression we always take the positive value.

$$B=(94\,\alpha + \sqrt{49(T_2-T_1)^2-768\alpha^2}\,)\Big/ 49 \qquad (5)$$

Assuming 188=196, we have

$$T = ½\,[\,(27B+10C+26\alpha) \pm (7B-14\alpha)\,] \qquad (6)$$

$T_1 = 10B + 5C + 20\alpha \quad = {}^4E_g(G)$

$T_2 = 17B + 5C + 6\alpha \quad = {}^4E_g(D) \qquad (7)$

Thus,

$$C = (T_1 + T_2 - 27B - 26\alpha)\Big/ 10 \qquad (8)$$

We have taken T_1 as ${}^6A_{1g}(S) \rightarrow {}^4A_{1g}(G), {}^4E_g(G)$

and T_2 as ${}^6A_{1g}(S) \rightarrow {}^4E_g(D)$ since the energy states ${}^4A_{1g}(G), {}^4E_g(G)$ are normally degenerate.

Once the assignments of the bands of the spectrum have been made, the values of B and C are then used in solving the secular equations of Mehra **[21]** to evaluate a single value of D_q.

The energy values for quartet electronic states are determined for different values of D_q with are B = 825 cm^{-1}, C = 2275 cm^{-1} and α = 76 cm^{-1}. A good fit of experimentally observed band positions is obtained for D_q = 760 cm^{-1} as it can be seen from the graph in **Fig.3**. It is interesting to note that the observed and calculated values are in good agreement, justifying the assignments.

The free ion value of the Racah parameter B is 960 cm^{-1} **[22]** In the present study, we obtained the value of B=825 cm^{-1} .The considerable decrease in the value of the Racah electron repulsion parameter B (from 960 to 825 cm^{-1}) indicates that there exists a strong covalent bonding between the central metal ion and the ligand. The parameters B and C are reduced considerably

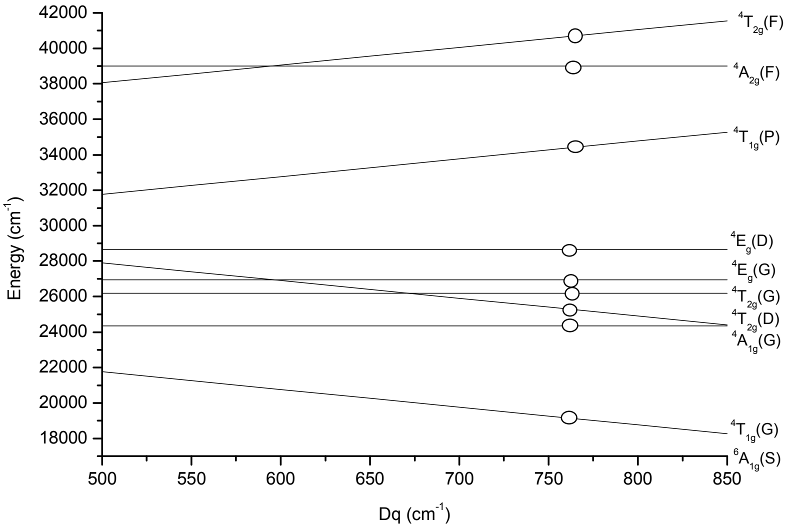

Fig.3. The energy level diagram of Mn^{2+} in DGAM showing the variation of the levels and Dq with B = 825 cm^{-1}, C = 2275 cm^{-1} and α = 76 cm^{-1} (the circles show the experimental energy values).

from those of the free ion value because of covalent bonding **[23-24]**. Experimental evidence for a reduction in inter-electronic parameters (B and C) is given by Owen and Thornley **[25]**.

CONCLUSIONS

In this paper we report the absorption spectrum of Mn^{2+} in D-Gluconic Acid Monohydrate single crystals recorded at room temperature in the wavelength range from 195-925 nm. The bands observed have been assigned to transitions from the $^6A_{1g}(S)$ ground state to various excited levels of Mn^{2+} ion in cubic crystalline field. The observed band positions have been fitted with four parameters B, C, D_q and α and covalency of the metal ligand bond has been discussed. A good fit of the observed band positions to the calculated values has been obtained for $D_q = 760\ cm^{-1}$. The covalency of metal ligand band has also been discussed. The strong covalent bonding between central metal ion and ligands has been predicted.

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