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# $Mn^{2+}$ doped Single Crystals of Cd $K_2$ $(SO_4)_2 \cdot 6H_2O$: Spectroscopic and Local Structure Studies

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***Abstract***
*The splitting parameters of zero field of the $Mn^{2+}$ doped Cd $K_2$ $(SO_4)_2.6H_2O$ (CKS) single crystals are computed utilizing the superposition model. The estimated parameters agree well with those obtained from EPR. The conclusion of experiment that the $Cd^{2+}$ site is replaced by the $Mn^{2+}$ ion in CKS is confirmed by theoretical study. The crystal's optical spectra are obtained employing crystal field parameters obtained from the superposition model and crystal field analysis program. A fair correspondence is found with the experimental band positions. Thus, the experimental observations are verified by the theoretical calculations.*
***Keywords:*** *Inorganic compounds, Electron paramagnetic resonance, Zero field splitting, Single crystal, Crystal fields, Superposition model.*

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## I. Introduction

EPR studies yield information on the nature of the site into which the impurity ion enters and its symmetry [1-2]. EPR of $Mn^{2+}$ impurity has been widely studied in different single crystals due to sensitivity of its zero field splitting values to small structural distortions in the lattice [3-5].

The superposition model (SPM) is used generally to model the crystal field (CF) and zero field splitting (ZFS) parameters for uses in many other studies [6–10]. SPM and the point-charge model [11, 12, 13] are largely used to find the parameters of the crystal field (CF). SPM was proposed for CF under certain assumptions [14]. Finding a static spherical polar coordinate system ($R_L$, $\theta_L$, $\Phi_L$) for each ion or ligand from the host crystal's X-ray structural data is important for doing an SPM analysis on the CF. Mismatches of ionic charge, ionic size and inter-ionic bonding are likely to yield some local distortion when transition metal ions are doped. Critical analysis of experimental spin-Hamiltonian parameters for $Mn^{2+}$ and $Fe^{3+}$ in CaO and MgO crystals has been performed [15] providing the SPM parameters and showing that the CF for 3d ions satisfies the superposition principle. SPM intrinsic parameters based on reliable ligand distances have been estimated for the alkali earth oxides, [16].

The general formula $A_2^+ B^{2+} (XO_4)_2 . 6H_2 O$ crystals are known as Tutton single crystals where A is a monovalent cation, B is a divalent cation (usually a transition metal ion) and X is sulfur or selenium [17–18]. Tutton crystals are famous isostructural crystal family having the same monoclinic symmetry, the space group $P2_1/a$ and two formula units per unit cell Z = 2 [19]. Tutton crystals (salts) are valuable crystals because they are used widely in UV filters [20].

Cadmium potassium sulfate hexahydrate crystals (CKS) are crystallized in the monoclinic crystal system and belong to the Tutton crystalline salts family. Having suitable crystal sizes, high purity and small transparency in the UV region, they could be the potential candidates for optoelectronic devices [21]. Cadmium sulfate ($CdSO_4$) has various uses, including electroplating, pigment production, and as a component in batteries and solar cells [22]. Potassium sulfate is dominantly used as a fertilizer. It is preferred for the crops like tobacco and some fruits and vegetables. [23]. It is sometimes used as an alternative blast media similar to soda in soda blasting [24]. Cadmium potassium sulfate is likely related to the individual uses of its constituent compounds.

EPR study of $Mn^{2+}$ doped CKS has been done at 298 K and the spin-Hamiltonian parameters have been obtained [25]. From angular variation studies, it is concluded that magnetic $[Mn (H_2O)_6]^{2+}$ complexes are created when the $Mn^{2+}$ ion enters the divalent sites of the Tutton salt lattice. The a*bc axis system, where a* is perpendicular to b and c, (crystal axes) is used to discuss the orientations. The angular variation of the spectrum indicated that the crystal field symmetry is orthorhombic.

In the present study, the ZFS parameters D and E are estimated for the $Mn^{2+}$ ion in CKS at 298 K (room temperature, RT) taking CF parameters from SPM and perturbation equations [26]. The objective is to locate the position of $Mn^{2+}$ ion and the distortion taking place in the CKS crystal. The results for the $Mn^{2+}$ ion at

the substitutional $Cd^{2+}$ site in CKS crystal with local distortion provide good agreement with the EPR experimental values. Further aim of the study is to find the extent to which CF theory and SPM technique can be applied to $Mn^{2+}$ ions in CKS crystals in order to produce an SPM parameter database. This will determine molecular nanomagnet (MNM) design and computer simulation of their magnetic and spectroscopic properties. The transition ion-based MNM class currently includes single-molecule magnets (SMM) [27], single-chain magnets (SCM) [28], and single ion magnets (SIM) [29]. Due to interesting magnetic properties of MNM, such as magnetization's macroscopic quantum tunneling and possible uses in high-density information storage and quantum computing, the above systems have attracted large attention from scientists and researchers [27, 28]. There are various synthesized SCM or SMM systems with $Mn^{2+}$and $Cr^{3+}$ ions [30]. Due to the fact that model calculations for simpler crystal systems can be used as a basis for more complex ones, the parameters of the model obtained in this case may be used for ZFS parameter calculations for $Mn^{2+}$ ions at appropriate sites in MNM. This work's modeling can be extended to get various crystals of scientific and industrial value in a number of other ion-host systems.

## II. Crystal Structure

The crystal structure of Tutton salt CKS is monoclinic with space group P $2_1$/ a [31], isomorphous with cadmium ammonium sulphate (CAS). The unit cell's parameters are: Z = 2, β = 106.86°, a = 9.433, b = 12.823 and c = 6.286 Å. All other divalent cations in the unit cell are in general positions, with the two inequivalent ones located at points (0, 0, 0) and (1/2, 1/2, 0). Water molecules form a slightly warped octahedron around each divalent cation. The other Tutton salts exhibit the same pattern of bond length, with the Cd-O(8) and Cd-O(7) bonds being larger than the Cd-O(9) bond. Figure 1 shows the symmetry adapted axis system (SAAS) and CKS crystal structure.

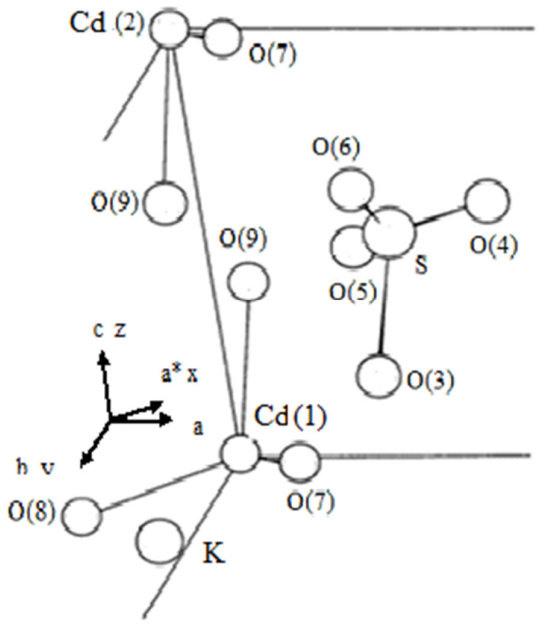


Fig. 1. The room-temperature CKS crystal structure and the symmetry-adapted axis system (SAAS).

## III. Crystal Field and Zero Field Splitting Parameter Calculations

The EPR spectra may be analyzed with the spin Hamiltonian [7]:

$$E(S_x^2 - S_y^2) + D\left\{S_Z^2 - \frac{1}{3}S(S+1)\right\} + \mu_B B.g.S = \mathcal{H} \qquad (1)$$

where B, $\mu_B$, g, D and E are the applied magnetic field, Bohr magneton, splitting factor, second rank axial, and second rank rhombic ZFS parameters [32–33]. Figure 1 shows the laboratory x, y, and z axes as well as

the a*, b, and c modified crystallographic axes (a* is normal to axes b and c). The directions of metal-ligand bonds being mutually perpendicular are referred to as the symmetry adapted axes (SAA) or the local symmetry axes of the site. As shown in Fig.1, the axis-Z of SAAS is along the crystal axis- c, and (X, Y) are perpendicular to the axis-Z. When $Mn^{2+}$ ions are doped in CKS crystal, they occupy $Cd^{2+}$ (1) sites with some local distortion in the lattice [34].

The $Mn^{2+}$ ion spin Hamiltonian is given as [35],

$$\mathcal{H}_o + \mathcal{H}_{so} + \mathcal{H}_{ss} + \mathcal{H}_c = \mathcal{H} \qquad (2)$$

$$\mathcal{H}_c = \sum B_{kq} C_q^{(k)} \qquad (3)$$

where $B_{kq}$, in Wybourne notation, represent the CF parameters and $C_q^{(k)}$, the spherical tensor operators. $B_{kq} \neq 0$ in the orthorhombic symmetry crystal field only for k = 2, 4; q = 0, 2, 4. Using SPM, the CF parameters $B_{kq}$ in CKS are calculated [35].

The symmetry of the local field about $Mn^{2+}$ ions in CKS crystal is orthorhombic (OR-type I) [7], where the ZFS parameters D and E are evaluated as follows [36]:

$$D = \left(\frac{3\varsigma^2}{70P^2D'}\right)[-B_{20}^2 - 21\varsigma B_{20} + 2B_{22}^2] + \left(\frac{\varsigma^2}{63P^2G}\right)[-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2]$$

$$E = \left(\frac{\sqrt{6}\varsigma^2}{70P^2D'}\right)[2B_{20} - 21\varsigma]B_{22} + \left(\frac{\varsigma^2}{63P^2G}\right)[3\sqrt{10}B_{40} + 2\sqrt{7}B_{44}]B_{42} \qquad (4)$$

(5)

Here G = 10B+5C, D' = 17B+5C, P = 7B+7C. B and C provide Racah parameters and $\varsigma$, the spin-orbit coupling parameter. Utilizing average covalency parameter N, $B = N^4B_0$, $C = N^4 C_0$, $\varsigma = N^2 \varsigma_0$, where $\varsigma_0$ gives free ion spin-orbit coupling parameter and $B_0$ and $C_0$ are Racah parameters for free ion [35, 37]. $\varsigma_0 = 336$ $cm^{-1}$, $B_0 = 960$ $cm^{-1}$ and $C_0 = 3325$ $cm^{-1}$ for free $Mn^{2+}$ ion [7].

The covalency parameter N is found from $N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2$ using Racah parameters (B = 857 $cm^{-1}$, C = 2977 $cm^{-1}$) obtained from optical study of $Mn^{2+}$ ion in CKS [38].

The CF parameters using SPM are evaluated [14, 36], with co-ordination factor $K_{kq}(\theta_j, \varphi_j)$ and intrinsic parameter $\overline{A_k}(R_j)$, as

$$B_{kq} = \sum_j K_{kq}(\theta_j, \phi_j)\, \bar{A}_k(R_j) \qquad (6)$$

$\overline{A_k}(R_j)$ is obtained from

$$\overline{A_k}(R_0)\left(\frac{R_0}{R_j}\right)^{t_k} = \bar{A}_k(R_j) \qquad (7)$$

where the ligand's distance from the $d^n$ ion is denoted by $R_j$, $\overline{A_k}(R_0)$ is the intrinsic parameter, $R_0$ is the reference distance of the ligand from the metal ion and $t_k$ gives power law exponent. For $Mn^{2+}$doped crystals, $t_2 = 3$ and $t_4 = 7$ [36]. Since the co-ordination about $Mn^{2+}$ ion is octahedral, $\overline{A_4}$ is calculated from the relation [39]

$$\overline{A_4}(R_0) = \frac{3}{4}Dq \qquad (8)$$

From optical study [38], $Dq = 740$ $cm^{-1}$. Therefore, $\overline{A_4}(R_0) = 555$ $cm^{-1}$. For $3d^5$ ions the ratio $\frac{\overline{A_2}}{\overline{A_4}}$ falls in the range 8 - 12 [35, 40-41]. With $\overline{A_2} = 10\,\overline{A_4}$, $\overline{A_2} = 5550$ $cm^{-1}$.

## IV. Results and Discussion

Using the ligand configuration around $Mn^{2+}$ ion shown in Fig. 1 and SPM, the CF parameters of the $Mn^{2+}$ ion at the $Cd^{2+}(1)$ sites are estimated. Table 1 gives atoms' coordinates in CKS single crystal with bond length R (with and without distortion) and angles θ, φ for site I. The ZFS and CF parameters as well as $R_0$, reference distance is given in Table 2. Table 2 shows that $R_0$ = 0.200 nm being slightly less than the sum of radii of ions (0.223 nm) of $Mn^{2+}$ = 0.083 nm and $O^{2-}$ = 0.140 nm with no distortion give ZFS parameter values at octahedral substitutional site I to be different from the EPR experimental ones [25]. Experimental parameters of ZFS |D| and |E| ($10^{-4}$ $cm^{-1}$) for site I from EPR are 309.4, 75.0, respectively. |E|/|D| is obtained as 0.242 being smaller than the standard value 0.33 [33]. |D| and |E| found theoretically without distortion are larger than the EPR experimental values. The value of |E|/|D| is also larger than the standard value 0.33 [33]. Hence, local distortion is introduced into calculation. Using above value of $R_0$ and local distortion, the ZFS parameter values for substitutional octahedral sites I are in good match with the EPR experimental ones [25]. The parameters $t_2$ = 3 and $t_4$ = 7 with transformation S2 for standardization [33] are used to obtain |E|/|D| ratio near to 0.33 and calculated ZFS parameters very close to experimental values from EPR.

Table 1. Atoms' coordinates, bond length R (with and without distortion) and angles θ, φ in CKS single crystal (site I).

| $Mn^{2+}$ Position | Ligands | Ligands' spherical polar co-ordinates | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | x | y | z | R(nm) | | $\theta^0$ | | $\varphi^o$ | |
| | | (Å) | | | | | | | | |
| | | Without distortion | | | | | | | | |
| Site : Substitutional | O7 | 0.1839 | 0.1149 | 0.1745 | 0.22977 | $R_1$ | 85.64 | $\theta_1$ | 85.40 | $\varphi_1$ |
| Cd(1) | O8 | -0.1730 | 0.1200 | 0.0336 | 0.22968 | $R_2$ | 89.16 | $\theta_2$ | 94.32 | $\varphi_2$ |
| (0.0000, 0.0000, | O9 | 0.0001 | -0.0760 | 0.3210 | 0.22405 | $R_3$ | 81.76 | $\theta_3$ | 90.00 | $\varphi_3$ |
| 0.0000) | O7' | -0.1839 | -0.1149 | -0.1745 | 0.22977 | $R_4$ | 94.35 | $\theta_4$ | 94.60 | $\varphi_4$ |
| | O8' | -0 .1839 | 0.3851 | 0.6745 | 0.70454 | $R_5$ | 84.51 | $\theta_5$ | 91.50 | $\varphi_5$ |
| | O9' | 0.1839 | 0.6149 | 0.3255 | 0.82041 | $R_6$ | 87.73 | $\theta_6$ | 88.71 | $\varphi_6$ |
| | | With distortion | | | | | | | | |
| I | O1 | | | | 0.28492 | | 66.64 | | 86.90 | |
| | O2 | | | | 0.29348 | | 71.16 | | 92.32 | |
| | O3 | | | | 0.28406 | | 62.76 | | 88.00 | |
| | O4 | | | | 0.29327 | | 85.35 | | 90.60 | |
| | O5 | | | | 0.78954 | | 82.51 | | 91.50 | |
| | O6 | | | | 0.90541 | | 89.73 | | 90.71 | |

Table 2. The $Mn^{2+}$ doped CKS crystal's CF and ZFS parameters.

| | | CF parameters ($cm^{-1}$) | | | | | ZFS parameters ($10^{-4}cm^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| Site | $R_0$(nm) | $B_{20}$ | $B_{22}$ | $B_{40}$ | $B_{42}$ | $B_{44}$ | \|D\| | \|E\| | \|E\|/\|D\| |
| | | Without distortion | | | | | | | |
| Site I $\frac{A_2}{A_4}$ =10 | 0.200 | -14763.7 | -18221.8 | 2420.828 | 2574.151 | 4824.854 | 2262.4 | 1164.2 | 0.514 |
| | | With distortion | | | | | | | |
| Site I $\frac{A_2}{A_4}$ =10 | 0.200 | -6449.77 | 3179.051 | -6.06927 | 75.69374 | 2669.833 | 309.4 | 102.9 | 0.332 |
| | | | | | | Exp. | 309.4 | 75.0 | 0.242 |

The CFA computer program [42] and $B_{kq}$ parameters (with distortion) are used to calculate the optical spectra of $Mn^{2+}$ doped CKS single crystals. By diagonalizing the full Hamiltonian, the $Mn^{2+}$ ion's energy band positions are computed.
Table 3 gives the energy band positions (experimental and calculated) for substitutional site I [38].

Table 3. Both calculated and experimental Energy bands of single crystal of CKS doped $Mn^{2+}$.

| Transition from $^6A_{1g}(S)$ state | Band experimental ($cm^{-1}$) | Band calculated ($cm^{-1}$) I |
|---|---|---|
| $^4T_{1g}(G)$ | 18868 | 23612, 23628, 23776, 23845, 24041, 24110 |
| $^4T_{2g}(G)$ | 23042 | 24241, 24256, 24502, 24541, 24582, 24625 |
| $^4A_{1g}(G)$ | 24875 | 24937, 24966 |
| $^4E_g(G)$ | 24950 | 24970, 24978, 24988, 25000 |
| $^4T_{2g}(D)$ | 28163 | 26769, 26824, 27205, 27268, 28834, 28843 |
| $^4E_g(D)$ | 29940 | 29332, 29374, 29885, 29969 |
| $^4T_{1g}(P)$ | 31746 | 30406, 30478, 31484, 31512, 35234, 35345 |
| $^4A_{2g}(F)$ | | 38648, 38759 |
| $^4T_{1g}(F)$ | | 40610, 40707, 40751, 40896, 40969, 40985 |

It is observed from Table 3 that the calculated and experimental energy band positions agree reasonably well. Therefore, the theoretical results verify the EPR experimental one [25, 38] that $Mn^{2+}$ ions enter the CKS crystal at substitutional $Cd^{2+}(1)$ octahedral site. The model parameters found may be utilized in ZFS parameter calculations for $Mn^{2+}$ ions at similar molecular nano magnet sites.

## V. Conclusions

To find the splitting parameters of zero field, the superposition model and perturbation theory are applied for CKS single crystals doped with $Mn^{2+}$ ions. The obtained ZFS parameters match well with the experimental values from EPR. The calculated positions of the optical energy bands correspond reasonably well with those from the experiment. Therefore, the experimental finding that $Mn^{2+}$ ions replace $Cd^{2+}$ (1) sites in CKS is confirmed by the theoretical investigation. The model parameters estimated in this study may be utilized for ZFS parameter determinations for $Mn^{2+}$ ions at appropriate sites in MNM. The above modeling technique may be useful in finding different crystals of various scientific and industrial applications.

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**Declarations**

**Ethical Approval:**

There were no human or animal subjects in this study, and it wasn't conducted in any protected or private locations. Corresponding locations did not require any special permissions.

**Competing interests:**

The author affirms that no known conflicting financial interests or personal relationships could have influenced any of the work presented in this paper.

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**Availability of data and materials:**

Upon request, the data will be made available.

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