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## A Theoretical Calculation of Zero-Field Splitting Parameter for Mn<sup>2+</sup> Ion in Cadmium Ammonium Phosphate Hexahydrate

Ram Kripal\* and Manju Singh

EPR Laboratory, Department of Physics, University of Allahabad, Allahabad 211002, India

### Research Article

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#### \*For Correspondence

Ram Kripal, EPR Laboratory, Department of Physics, University of Allahabad, Allahabad 211002, India, Tel: +91 532 2470532

E-mail: ram\_kripal2001@rediffmail.com

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#### ABSTRACT

The crystal field parameters (CFP) and zero-field splitting (ZFS) parameter D of Mn<sup>2+</sup> ion at axial symmetry site in cadmium ammonium phosphate hexahydrate (CAPH) single crystal are modeled. The calculation is carried out with the help of superposition model and the perturbation formulae. The theoretical ZFS parameter D is in good agreement with the experimental value. The theoretical modeling supports the conclusion drawn from experimental study that Mn<sup>2+</sup> ion occupies substitutional site in CAPH. Ignoring local distortion, the value of D comes out as  $306.1 \times 10^{-4} \text{ cm}^{-1}$ ; while considering small local distortion, the value of D is obtained as  $308.4 \times 10^{-4} \text{ cm}^{-1}$ . The experimental value of D is  $305.5 \times 10^{-4} \text{ cm}^{-1}$ .

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### INTRODUCTION

Electron paramagnetic resonance (EPR) studies yielding zero-field splitting (ZFS) parameters are important for the analysis of structural distortions and local site symmetry around the transition metal ions in crystals [1-7]. The microscopic spin-Hamiltonian (MSH) theory is widely used for the analysis of EPR spectra of transition metal ions. The spin Hamiltonian (SH) data from EPR spectra are correlated with optical spectroscopy and structural data with the help of MSH theory. Experimental and theoretical study indicated that the spin Hamiltonian parameters for transition metal (d<sup>5</sup> (6S)) ions in crystals are affected very sensitively by the local structure. Consequently the SH theory has been extensively used in various types of crystal lattices.

The crystal-field parameters are evaluated by means of superposition model [8,9]. The ZFS parameters are determined through the electrostatic, the spin-orbit coupling, and the crystal-field parameters of the d<sup>5</sup> ion in a crystal [10]. Out of iron group transition metal ions, Mn<sup>2+</sup> is important for the reason that its ground state is <sup>6</sup>S<sub>5/2</sub> [11-15]. The electron spin is affected by high order interaction of crystalline electric field, and in the presence of external magnetic field orientation of spins become free [16]. The spin-lattice relaxation time is large for S state ions, due to which Mn<sup>2+</sup> shows fine EPR spectra [2,15,17,18] at RT.

In this paper, the superposition model is used to obtain crystal field (CF) parameters and MSH theory together with CF parameters is used to predict the ZFS parameters for Mn<sup>2+</sup> ions at the substitutional sites in cadmium ammonium phosphate hexahydrate (CAPH) crystal at room temperature (RT).

#### Crystal Structure

The crystal structure of CAPH is analogous to the naturally occurring biomineral struvite [19]. This crystal belongs to orthorhombic system having space group Pmn2<sub>1</sub>. The unit cell dimensions are a = 6.941(2) Å, b = 6.137(2) Å and c = 11.199(4) Å [20], and there exist two molecules per unit cell (Z = 2). Six water molecules form a distorted octahedral environment around the cadmium atom. The bond length of Cd-O lies within the range from 2.046 to 2.1076 Å.

## Theoretical Investigation

The Mn<sup>2+</sup> ion in CAPH crystal substitutes at Cd<sup>2+</sup> site [21]. The phenomenological SH of 3d<sup>5</sup> ion configuration for tetragonal symmetry crystal field can be written as [2,22,23]

$$\begin{aligned}
 H = & g \mu_B B.S + D\{S_Z^2 - S(S+1)\} \\
 & + \left(\frac{a}{6}\right) [S_X^4 + S_Y^4 + S_Z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)] \\
 & + \frac{F}{180} \{35S_Z^4 - 30S(S+1)S_Z^2 + 25S_Z^2 - 6S(S+1) + 3S^2(S+1)^2\} \\
 & + A(I.S)
 \end{aligned} \tag{1}$$

where the first term represents electronic Zeeman energy in which B is the external field, g is the spectroscopic splitting factor and  $\mu_B$  is Bohr magneton. The second, third, and fourth terms are the second order axial, fourth-rank cubic and fourth-rank axial ZFS terms [2]. The fifth term is the hyperfine interaction term. S, D, a, F represent the effective spin vector, second order axial, fourth-rank cubic and fourth-rank axial ZFS parameters, respectively. For the electronic Zeeman interaction isotropic approximation is used and usually it is valid for Mn<sup>2+</sup> ions [2,24]. From the EPR spectra the direction of the maximum overall splitting is taken as the z axis and the direction of minimum splitting as the x axis [25]. The laboratory axis system (x, y, z) corresponds to the crystallographic axis system (CAS). The Z- axis of the local site symmetry axis i.e. the symmetry adopted axis (SAA) is along the metal-oxygen bond and the rest two axes X, Y are perpendicular to this.

The Hamiltonian for a d<sup>5</sup> ion can be written as

$$H = H_0 + H_{cf} + H_{so}, \tag{2}$$

$$\text{in which, } H_{cf} = \sum_{kq} B_{kq} C_q^{(k)}$$

shows the crystal field Hamiltonian. H<sub>0</sub> and H<sub>so</sub> are free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Because of spin-spin coupling being very small [26-28], its contribution has not been considered in Eq. (2). The total crystal field of SO interaction is taken as perturbation term [29,30]. The calculation in the strong-field scheme is formulated by Macfarlane for F-state ions [31]. In CAPH crystal, oxygen atoms form a distorted octahedron around the Cd atom [20] and yield axial local symmetry. For axial symmetry, the SO contributions to the ZFS parameter D for 3d<sup>5</sup> ions can be written as [30]

$$D^{(4)}(SO) = \left(\frac{\xi^2}{63P^2G}\right) [14B_{44}^2 - 5B_{40}^2] - \left(\frac{3\xi^2}{70P^2D}\right) B_{20}[B_{20} - 14\xi] \tag{3}$$

where P = 7(B+C), G = 10B+5C and D = 17B+5C. P, G, and D are the energy separations between the excited quartets and the ground sextet. Racah parameters B and C describe the electron-electron repulsion. In Eq. (3) only fourth order term is considered as other perturbation terms are very small [32]. By considering the average covalency parameter N, the parameter B, C and  $\xi$  are specified in terms of N as, B = N<sup>4</sup>B<sub>0</sub>, C = N<sup>4</sup>C<sub>0</sub> and  $\xi = N^2 \xi_0$ , where B<sub>0</sub> and C<sub>0</sub> are the Racah parameters and  $\xi_0$  is the spin-orbit coupling parameter, for free ion [33,34]. B<sub>0</sub> = 960 cm<sup>-1</sup>, C<sub>0</sub> = 3325 cm<sup>-1</sup>,  $\xi_0 = 336 \text{ cm}^{-1}$  [2] are used here.

From optical study of Mn<sup>2+</sup> doped zinc ammonium phosphate (ZAPH) [35], B = 917 cm<sup>-1</sup> and C = 2254 cm<sup>-1</sup>. As CAPH is isomorphous to ZAPH [35]; B, C and Dq are taken from this paper. By using these data in Eq. (4) [36] below,

$$N = \left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}}\right) / 2 \tag{4}$$

N can be obtained.

By applying the superposition model the crystal-field parameters for Mn<sup>2+</sup> doped CAPH single crystal are calculated and using these parameters in Eq. (3) ZFS parameter D is determined. Similar approach has been used by several earlier workers [37] for estimating ZFS parameters.

## Superposition Model

The superposition model is effectively used for explaining the crystal-field splitting. In recent times, this model is frequently applied for 3dn ions [8,32]. With the help of this model the crystal field parameters can be determined by the equations [38]

$$B_{20} = -2\overline{A_2} \left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_2} - 4\overline{A_2} \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_2}, \tag{5(i)}$$

$$B_{40} = 16\overline{A_4} \left(\frac{R_0}{R_{10} + \Delta R_1}\right)^{t_4} + 12\overline{A_4} \left(\frac{R_0}{R_{20} + \Delta R_2}\right)^{t_4}, \tag{5(ii)}$$

$$B_{44} = 2\sqrt{70} A_4 \left( \frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4}, \quad 5(\text{iii})$$

where  $R_0$  is the reference distance. In general, it is chosen as the mean value of all six bond lengths (for axial symmetry). The mean value of two out of six Cd-O bond lengths are indicated by  $R_{10}$  and the mean value of remaining four bond lengths are indicated by  $R_{20}$ , further  $\Delta R_1$  and  $\Delta R_2$  indicate the distortion parameters.  $\bar{A}_k$  and  $t_k$  are the intrinsic parameter and power law exponent, respectively [39,40].

For 6-fold cubic coordination  $\bar{A}_4(R_0) = (3/4)Dq$  [40]. For  $3d^5$  ions,  $\bar{A}_2(R_0)/\bar{A}_4(R_0)$  lies in the range 8-12 [32,40]. Using  $Dq = 756 \text{ cm}^{-1}$  [35],  $\bar{A}_4(R_0)$  and  $\bar{A}_2(R_0)$  can be determined taking the value of ratio  $\bar{A}_2(R_0)/\bar{A}_4(R_0)$ . The power law exponent in the case of  $\text{Mn}^{2+}$  ion is adopted as  $t_2 = 3$ ,  $t_4 = 7$  [41]. For the intrinsic parameter values for the superposition model semi-ab initio calculations are done for other transition metal ions [42].

## RESULTS AND DISCUSSION

In the present study the bond length of six ligands  $R_j$  (Figure 1) is calculated as given in Table 1. The value of B and C are taken from the optical study [35] as  $917$  and  $2254 \text{ cm}^{-1}$ , respectively. First of all ignoring the local distortion the value of D is calculated. For this, taking  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8$  and reference distance  $R_0 = 0.28 \text{ nm}$ , which is the mean value of six ligands distance, the value of D comes out to be  $D = 87342 \times 10^{-4} \text{ cm}^{-1}$ . From EPR study, the experimental value is given as  $D = 305.5 \times 10^{-4} \text{ cm}^{-1}$  [20]. Here it is seen that the theoretical value is very high. Now, if the ratio  $\bar{A}_2(R_0)/\bar{A}_4(R_0)$  is changed to 12, then  $D = 79282 \times 10^{-4} \text{ cm}^{-1}$ , which is again high. Further, using the same ratio and  $R_0 = 0.212 \text{ nm}$ , which is the sum of ionic radii of  $\text{Mn}^{2+} = 0.08 \text{ nm}$  and  $\text{O}^{2-} = 0.132 \text{ nm}$ , the result comes out as  $D = 1103 \times 10^{-4} \text{ cm}^{-1}$ , which is also very large. If  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8$  is taken, then D becomes  $467.4 \times 10^{-4} \text{ cm}^{-1}$ , which is again large. Now by taking  $R_0 = 0.210 \text{ nm}$ , the value comes out as  $D = 306.1 \times 10^{-4} \text{ cm}^{-1}$ , which is in reasonable agreement with the experimental value  $D = 305.5 \times 10^{-4} \text{ cm}^{-1}$ .

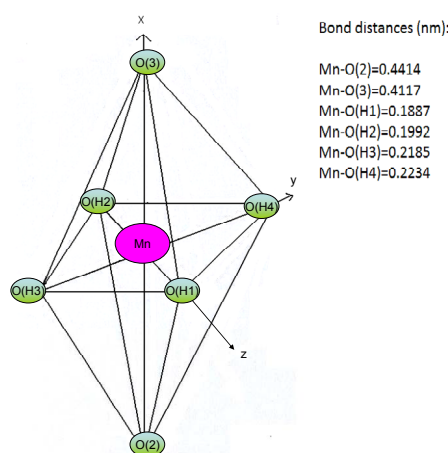


Figure 1: Coordination about  $\text{Mn}^{2+}$  ion in CAPH.

Table 1. Metal-oxygen bond distances  $R_j$  for  $\text{Mn}^{2+}$  ion in cadmium ammonium phosphate hexahydrate single crystal.

Metal-Oxygen	Metal-Oxygen bond distance $R_j$ (nm)
Mn-O(2)	0.4414
Mn-O(3)	0.4117
Mn-O(H1)	0.1887
Mn-O(H2)	0.1992
Mn-O(H3)	0.2185
Mn-O(H4)	0.2234

O (H1), O (H2), O (H3), O (H4) are the oxygen atoms of water molecules.

Further, considering local distortions as  $\Delta R_1 = -0.0008 \text{ nm}$  and  $\Delta R_2 = -0.0009 \text{ nm}$ , reference distance  $R_0 = 0.28 \text{ nm}$  (the mean value of six ligands distance) and ratio  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8$ , the value of D comes out to be  $62759.9 \times 10^{-4} \text{ cm}^{-1}$ . It is noticed that the theoretical value is very high. Again taking the same value of  $R_0$  (0.28 nm) but changed value of the ratio,  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 12$ , the value of D comes out as  $55681.7 \times 10^{-4} \text{ cm}^{-1}$ , which is also larger than the experimental value. Further, using the same ratio but  $R_0 = 0.212 \text{ nm}$ , which is the sum of ionic radii of  $\text{Mn}^{2+} = 0.08 \text{ nm}$  and  $\text{O}^{2-} = 0.132 \text{ nm}$ , the result comes out as  $D = 1289.8 \times 10^{-4}$ , which is again very high and if  $\bar{A}_2(R_0)/\bar{A}_4(R_0) = 8$  is taken with the same  $R_0 = 0.212 \text{ nm}$ , the result comes out as  $D = 37.0 \times 10^{-4} \text{ cm}^{-1}$ , which is very low as compared to experimental value. At  $R_0 = 0.166 \text{ nm}$ , the value of D comes out as  $308.4 \times 10^{-4} \text{ cm}^{-1}$ , which is in reasonable agreement with the experimental result  $D = 305.5 \times 10^{-4} \text{ cm}^{-1}$ .

By using Eq. 5(i) - 5(iii), crystal-field parameters  $B_{kq}$  are obtained as:  $B_{20} = -19896 \text{ cm}^{-1}$ ,  $B_{40} = 7468.1 \text{ cm}^{-1}$ ,  $B_{44} = 10325.1$

$\text{cm}^{-1}$  when distortion parameters  $\Delta R_1$  and  $\Delta R_2$  are not considered in the calculation. Considering  $\Delta R_1 = -0.008 \text{ \AA}$  and  $\Delta R_2 = -0.009 \text{ \AA}$ , the  $B_{kq}$  parameters are:  $B_{20} = -9484 \text{ cm}^{-1}$ ,  $B_{40} = 1329.8 \text{ cm}^{-1}$ ,  $B_{44} = 1839.6 \text{ cm}^{-1}$ . The above theoretical investigation suggests that  $\text{Mn}^{2+}$  ion enters the host lattice substitutionally in CAPH. This supports the conclusion drawn by EPR study.

## CONCLUSION

Zero-field splitting parameter  $D$  for  $\text{Mn}^{2+}$  doped CAPH in axial symmetry has been calculated with the help of superposition model and perturbation formulae. The theoretical value of  $D$  is in reasonable agreement with the experimental value. This analysis indicates that  $\text{Mn}^{2+}$  ion enters the host lattice substitutionally, which supports the experimental result obtained by EPR.

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