

## Superposition Model Analysis of Zero-Field Splitting for $Mn^{2+}$ Doped in $Zn(ClO_4)_2 \cdot 6H_2O$ Single Crystals

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### Abstract

The crystal structure is orthorhombic zero-field splitting parameter  $b_2^0$  is evaluated as  $265.9 \times 10^{-4} \text{ cm}^{-1}$ . Though SPM predicts the correct sign but calculated value of  $b_2^0$  is greater than experimental value. It has been suggested by Barriuso et al. and Duan et al. that if  $R$  (metal-ligand bond distance) is greater than the normal Mn-ligand bond distance, the introduction of substitutional  $Mn^{2+}$  gives rise to an inward relaxation while the opposite occurs for  $R$  less than the normal Mn-ligands bond distance. Thus, it is a good approximation to take the value of  $R$  as the mean of the Mn-ligand bond distance and metal-ligand bond distance in the pure host to take into account the lattice relaxation. The ionic radii of  $Mn^{2+}$  and  $Zn^{2+}$  is comparable, So  $Mn^{2+}$  substituting the  $Zn^{2+}$  cation site perhaps does cause appreciable local distortion in  $Zn(ClO_4)_2 \cdot 6H_2O$  single crystal. Hence by using SPM theory suggested by Newman and Urban, it is possible to reproduce ZFS parameters  $b_2^0, b_2^2, b_4^0, b_4^2$  and  $b_4^4$  for  $Mn^{2+}$  doped in these single crystals at room temperature using the values of intrinsic parameters of  $\bar{b}_2$  and  $\bar{b}_4$  calculated in the present study. The superposition model analysis shows that for large values of ZFS parameters  $b_2^2, b_4^0, b_4^2, b_4^3$  and  $b_4^4$ . Intrinsic parameters  $\bar{b}_2$  and  $\bar{b}_4$  can be estimated with suitable errors but for small values of these spin-Hamiltonian parameters it is very difficult to predict the correct sign and magnitude. Hence we can conclude from the present study that superposition model is very useful to get information about the zero field splitting of parameters ions in host single crystals.

### Crystal Structure of $Zn(ClO_4)_2 \cdot 6H_2O$

The crystal structure of  $Zn(ClO_4)_2 \cdot 6H_2O$  has been recently worked out by Ghosh and Ray[1]. They find it to be isomorphous with  $Mg(ClO_4)_2 \cdot 6H_2O$ , of which the crystal structure was worked out in detail by West [2]. The unit cell is orthorhombic pseudo-hexagonal with space group  $Pmn2_1$ , and  $a_0 = 7.715 \text{ \AA}$ ,  $b_0 = 13.36 \text{ \AA}$  and  $c_0 = 5.22 \text{ \AA}$ . The crystal is pseudo-hexagonal exhibiting a three component orthorhombic twinning. Because of the pseudo-hexagonal nature of the unit cell. A refinement of  $Zn(ClO_4)_2 \cdot 6H_2O$  crystal verifies the continuous perchlorate water arrangement and three component twinning of the orthorhombic cell. There are two  $Zn^{2+}$  ions having monoclinic site symmetry in the orthorhombic unit cell. The octahedral of six water molecules which form the first coordination sphere around  $Zn^{2+}$  have a perfectly trigonal symmetry about the c-axis. The octahedral of six perchlorate ions form the second coordination about the c-axis. The zinc ion sublattice has orthorhombic arrangement and is responsible for lowering the site symmetry from trigonal to monoclinic ( $C_1$ ) at the  $Zn^{2+}$  site.

An ORTEPII view of the molecule with atom-numbering scheme is given in Fig. The Cl and O1 atoms of the  $ClO_4^-$  ions are located on a threefold axis and the two crystallographically different Cl-O bond lengths [1.450(5) and 1.432(5)  $\text{\AA}$ ] define the perchlorate ion distortion. Water molecules with OW atoms lying on mirror planes are hydrogen-bonded to O1 and O2 [OW-H...O1 3.065(8), OW-H...O2 3.050(4)  $\text{\AA}$ ].

**Table : Fractional atomic Coordinates**

	x	y	z
Zn	0.000	0.000	0.2500
Cl	0.3333	0.6666	0.0062(12)
O1	0.3333	0.6666	0.2796(26)
O2	0.4320(4)	0.5680(4)	0.0860(16)
OW	0.1242(4)	0.8758(4)	0.5044(21)

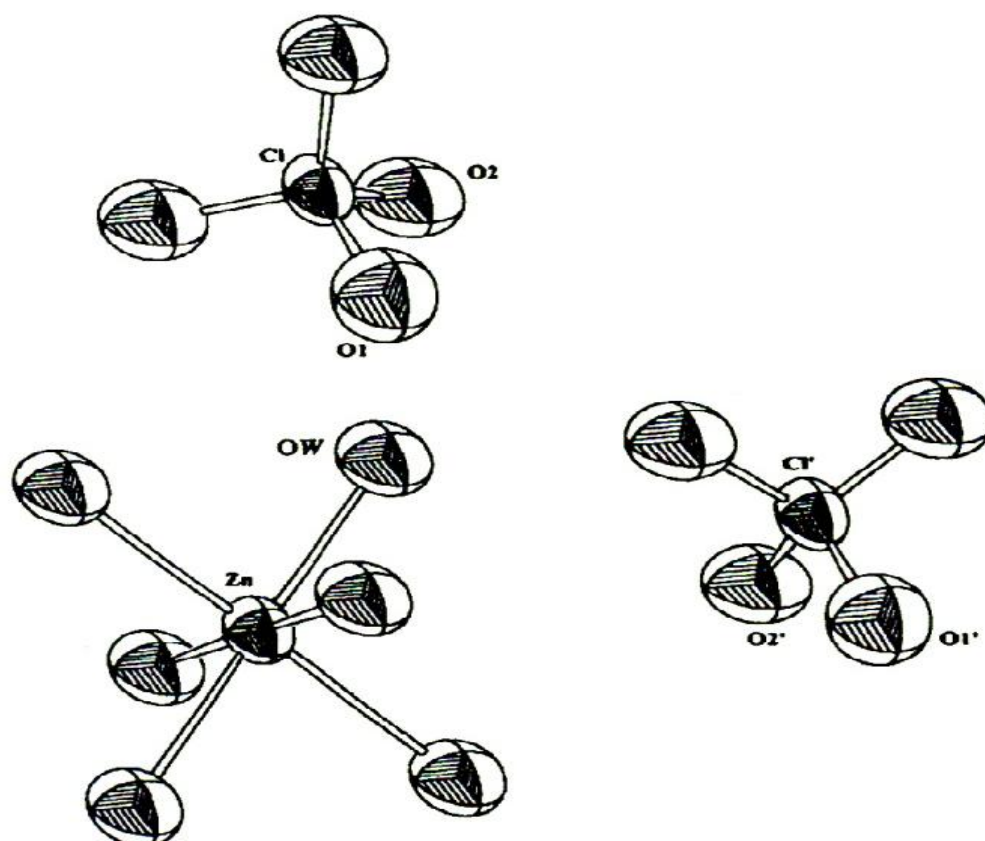


Fig. An ORTEP (Johnson, 1976) view (50% probability level) of the molecule.

### Superposition Model

The SPM of the crystal field is based on two assumptions:

- i) The total ZFS experienced at an ion in a crystal is due to its nearest neighboring ions.
- ii) The electric field at an ion caused by another ion depends upon exactly what ions are present, and the distance between them, irrespective of the other surroundings. Therefore in calculations, the total electric field at central ion M is given by the axially symmetric contributions of the ligands and the contribution of the far distant neighbors as well as interaction between ligands are ignored. The ZFS parameters are given by

$$b_n^m = \sum K_n^m(n_i, w_i) \bar{b}_n(R_i) \dots\dots\dots(1)$$

where the summation is taken over all ligands.  $R_i$ ,  $\theta_i$  and  $\phi_i$  are the spherical coordinates of the  $i^{\text{th}}$  ligand when the paramagnetic ion is at the origin. The angular functions  $K_n^m(\theta_i, \phi_i)$  are tabulated by Newman et al [3] and Rudowicz [4]. The  $\bar{b}_n$  is the intrinsic parameter, which depends upon the nature of the ligand and the co-valency of the bonding, and obeys the single potential law

$$\bar{b}_n(R_i) = (R_o / R_i)^{t_n} \bar{b}_n(R_o) \dots\dots\dots (2)$$

where  $R_o$  is the normal distance of the metal ion-ligand and  $R_i$  of the  $i^{\text{th}}$  ligand from the origin. The power law exponent  $t_n$  depends on the particular system being brought into use. According to the SPM, from equations (1) and (2), the ZFS parameters  $b_2^0$ ,  $b_2^2$ ,  $b_4^0$ ,  $b_4^2$  and  $b_4^4$  are given by

$$b_2^0 = \sum_i [(3 \cos^2 \theta_i - 1) / 2] [R_o / R_i]^{t_2} \bar{b}_2[M.X] \quad (3)$$

$$b_2^2 = \sum_i [(3 \sin^2 \theta_i \cos 2\phi_i) / 2] [R_o / R_i]^{t_2} \bar{b}_2[M.X] \quad (4)$$

$$b_4^0 = \sum_i [(35 \cos^4 \theta_i - 30 \cos^2 \theta_i + 3) / 8] [R_o / R_i]^{t_4} \bar{b}_4[M.X] \quad (5)$$

$$b_4^2 = \sum_i [5 / 2 (7 \cos^2 \theta_i - 1) \sin 2\theta_i \cos 2\phi_i] [R_o / R_i]^{t_4} \bar{b}_4[M.X] \quad (6)$$

$$b_4^4 = \sum_i [(35 \sin^4 \theta_i \cos 4\phi_i) / 8] [R_o / R_i]^{t_4} \bar{b}_4[M.X] \quad (7)$$

Where  $M \rightarrow$  metal  
 $X \rightarrow$  ligand

**Table: The value of  $R$  and  $\theta$  of Metal – O(w) bond distances.**

M-O bond	$R_i$ (nm)	$\theta$ (deg)	$\phi$ (deg)
Zn-O(w)	0.2149	50.84	-30.02

**Table: Intrinsic parameter  $\bar{b}_2$  and  $\bar{b}_4$  obtained for  $Mn^{2+}$  in  $Zn(ClO_4)_2 \cdot 6H_2O$  single crystals**

Host	Spin Hamiltonian Parameters in $cm^{-1}$	Intrinsic Parameters in $cm^{-1}$
<b><math>Zn(ClO_4)_2 \cdot 6H_2O</math></b>	$b_2^0 = -0.01267$	$\bar{b}_2 = -0.0219$
	$b_2^1 = -0.3597$	$\bar{b}_2 = -0.0219$
	$b_2^2 = 0.02093$	$\bar{b}_2 = -0.0219$
	$b_4^0 = -0.1554$	$\bar{b}_4 = -0.0055$
	$b_4^2 = -0.04885$	$\bar{b}_4 = -0.0055$
	$b_4^3 = 0.0000$	$\bar{b}_4 = -0.0055$
	$b_4^4 = +0.0296$	$\bar{b}_4 = -0.0055$

### Result and Discussion

EPR of  $Zn(ClO_4)_2 \cdot 6H_2O$  has been reported by A.K. Jain et. Al. Here  $Zn^{2+}$  in  $Zn(ClO_4)_2 \cdot 6H_2O$  is surrounded by six water molecules along with the values of  $R_i$  and  $\theta_i$  given in Table, and  $t_2 = 7$  for  $Mn^{2+}$ ,  $R_o = 0.22$  nm as the reference distance for  $Mn^{2+}$  surrounded by water molecules and taking  $\bar{b}_2 = -0.05 cm^{-1} [11]$ , zero-field splitting parameter  $b_2^0$  is evaluated as  $265.9 \times 10^{-4} cm^{-1}$ . Though SPM predicts the correct sign but calculated value of  $b_2^0$  is greater than experimental value. It has been suggested by Barriuso et al.[5] and Duan et al [6] that if  $R$  (metal-ligand bond distance) is greater than the normal Mn-ligand bond distance, the introduction of

substitutional  $Mn^{2+}$  gives rise to an inward relaxation while the opposite occurs for R less than the normal Mn-ligands bond distance. Thus, it is a good approximation to take the value of R as the mean of the Mn-ligand bond distance and metal –ligand bond distance in the pure host to take into account the lattices relaxation.

We have made SPM calculations for  $Mn^{2+}$  in  $Zn(ClO_4)_2 \cdot 6H_2O$  by taking into account the relaxation effects of bond lengths only and assuming the bond angles to remain unchanged on doping with  $Mn^{2+}$  in place of  $Zn^{2+}$ .

We have used  $R_{av} = 2.1762 \text{ \AA}$  for M - water molecules. The calculated value of  $b_2^0$  is fairly matched with experimental value  $125.7 \pm 1.0 \times 10^{-4} \text{ cm}^{-1}$  by taking  $b_2^0 = -0.0219 \text{ cm}^{-1}$ . Hence, we find a close agreement

between theoretical and experimental value of  $b_2^0$ . The superposition theory analysis given here is based on the assumption of identical structure around guest and host ions and only the immediately co-ordinated ions have been considered. Using e.q. (3-7) we have calculated the second and fourth order zero field spatially parameters  $b_2^2, b_4^0, b_4^2, b_4^3$  and  $b_4^4$ . The intrinsic parameters  $\bar{b}_2$  and  $\bar{b}_4$  are very close to that of  $M_4^{2+}$  in the other single crystal [7-14].

## Conclusion

The ionic radii of  $Mn^{2+}$  and  $Zn^{2+}$  is comparable, So  $Mn^{2+}$  an substituting the  $Zn^{2+}$  cation site perhaps does not cause appreciable local distortion in  $Zn(ClO_4)_2 \cdot 6H_2O$  single crystal. Hence by using SPM theory suggested by Newman and Urban, it is possible to reproduce ZFS parameters  $b_2^0, b_2^2, b_4^0, b_4^2$  and  $b_4^4$  for  $Mn^{2+}$  doped in these single crystals at room temperature using the values of intrinsic parameters of  $\bar{b}_2$  and  $\bar{b}_4$  calculated in the present study. The superposition model analysis shows that for large values of ZFS parameters  $b_2^2, b_4^0, b_4^2, b_4^3$  and  $b_4^4$ . Intrinsic parameters  $\bar{b}_2$  and  $\bar{b}_4$  can be estimated with suitable errors but for small values of these spin-Hamiltonian parameters it is very difficult to predict the correct sign and magnitude. Hence we can conclude from the present study that superposition model is very useful to get information about the zero field splitting of parameters ions in host single crystals.

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