Superposition model analysis of zero field splitting for Mn²⁺ in ZnX₂(OPPh₃)₂ (X = Cl, Br) and ammonium tetra fluorozincate (II) dihydrate single crystals

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ABSTRACT

The Newman superposition model has been used to investigate the substitution of Mn^{2+} for Zn^{2+} site in Dichlorobis (triphenylphosphine oxide) zinc (II), Dibromobis (triphenylphosphine oxide) zinc (II) Ammonium Tetra Fluorozincate (II) Dihydrate (ATFD) single crystals. The calculated values of zero field splitting parameter b^0_2 at room temperature fit the experimental one taken from the literature with average intrinsic parameters b_2 (Cl) = -0.0267 cm⁻¹, b_2(Br) = -0.0500 cm⁻¹, b_2 (F) = -0.0531 cm⁻¹ and, b_2 (O) = -0.0280 cm⁻¹ taken t_2 = 7 and t_4 = 10 for Mn^{2+} doped in Dichlorobis (triphenylphosphine oxide) zinc (II), Dibromobis (triphenylphosphine oxide) zinc (II) and Ammonium Tetra Fluorozincate (II) Dihydrate single crystals. The superposition model analysis shows that for large values of b_2^0, b_2^2, b_4^0, b_4^2 and b_4^4 intrinsic parameters $\bar{b}_2$ and $\bar{b}_4$ can be estimated with suitable error but for small values of these parameters it is very difficult to predict the correct sign and magnitude. The present study about superposition model is very useful to get information about the zero field splitting of Mn^{2+} ions in some host single crystals.

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INTRODUCTION

Electron Paramagnetic Resonance (EPR) is regarded as an effective method to study the local geometry and local properties in the vicinity of impurity ions doped in the single crystals. Many EPR investigations resulting in the determination of spin-Hamiltonian parameters of S-state ions in various single crystals have been reported in the literature[1-2]; few attempts have been made to relate these to the crystalline environment of the substituted ion, apart from using its point symmetry to restrict the number of parameters. In order to understand the various characteristics of transition-metal complex molecules, it is important to establish the inter-relations between electronic and molecular structure. Newman proposed the empirical superposition model (SPM) relating the fine structure constants to the actual arrangements of the ligands around the impurity ion[3-4] and usually the zero-field splitting

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(ZFS) parameters $b_2{}^0$, $b_2{}^2$, $b_4{}^0$, $b_4{}^2$ and $b_4{}^4$ are quite sensitive with respect to small structural changes, where Mn^{2+} ions are coordinated by florine and chlorine in single crystals. The objective of this paper is to study the local distortion produced by substitution of Mn^{2+} in place of host ions Zn^{2+} in Dichlorobis (triphenylphosphine oxide) zinc (II) and Dibromobis (triphenylphosphine oxide) zinc (II) and Ammonium Tetra Fluorozincate (II) Dihydrate single crystal which can lead to variation of magnetic properties.

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 symmetrically 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

$$b_n{}^m = \sum K_n{}^m (\theta_i, \phi_i) \ \bar{b}_n (R_i) \tag{1}$$

where the summation is taken over all ligands. R_i, θ_i and Φ_i are the spherical coordinates of the ith 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[4] and Rudowicz[5]. 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

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

where R_o is the normal distance of the metal ion-ligand and R_i of the ith 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

$$b^0{}_2 = \sum_i [(3\cos^2\theta_i - 1)/2][R_0/R_i]^{t_2} \ \bar{b}_2[M,O] \tag{3}$$

$$b^2{}_2 = \sum_i [(3\sin^2\theta_i \cos2\phi_i)/2][R_0 / R_i]^{t_2} \ \bar{b}_2[M,O] \tag{4}$$

$$b^0{}_4 = \sum_i [(35\cos^4\theta_i - 30\cos^2\theta_i + 3)/8][R_0/R_i]^{t_4} \ \bar{b}_4[M,O] \tag{5}$$

$$b^2{}_4 = \sum_i [5/2(7\cos^2\theta_i - 1) \sin2\theta_i \cos2\phi_i][R_0/R_i]^{t_4} \ \bar{b}_4[M,O] \tag{6}$$

$$b^4{}_4 = \sum_i [(35\sin^4\theta_i \cos4\phi_i)/8][R_0/R_i]^{t_4} \ \bar{b}_4[M,O] \tag{7}$$

RESULT & DISCUSSION

Mn^{2+} doped Dichlorobis (triphenylphosphine oxide) zinc (II)

The crystal structure of $ZnCl_2(OPPh_3)_2$ has been investigated by Bertrand, J.A. Kalyanaraman[6] by a three dimesion single crystal X-ray diffaraction study. The structure was refined in the orthorhombic. The unit cell constants are $a = 32.95(1)A^0$, $b = 20.702(6)A^0$, $c = 9.792(3)A^0$ and $\alpha = \beta = \gamma = 90^o$ space group Fdd2, and $Z = 8$. The environment of the metal atom in each case approximates to a tetrahedral arrangement of two oxygens and two halide ions. Using the atomic position given for $ZnCl_2(OPPh_3)_2$ with the lattice constants the values of metal – Cl bond distances and metal – O bond distance, the angle θ_i that Metal –Cl and Metal - O bond makes with the c- axis and φ_i are calculated and given in TABLE 1.

The EPR spectrum of Mn^{2+} in $ZnCl_2(OPPh_3)_2$ single crystals have been studied by Charles A. et al[7] and the value of ZFS arameter $b^0{}_2$ reported is 0.172 cm^{-1} In order to apply the superposition model for the case considered in this paper, we used the values of $b_2(R_o)$, R_o and t_2 given previously in the literature. Heming and Lehman[8] determined the values of $b_2(R_o) \approx -0.05$ cm^{-1} and $t_2 \approx 7$. These data were

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TABLE 1 : Polar co-ordinates of M-O bond in single crystals

Host	M-O Bond	R_i (nm)	θ_i (deg.)	ϕ_i (deg.)
ZnCl₂(OPPh₃)₂	Zn-Cl	.2186	58.63	-57.31
	Zn - O	.1966	131.52	30.50
	Zn – Br(1)	.2397	40.85	-18.42
ZnBr₂(OPPh₃)₂	Zn – Br (2)	.2339	177.63	62.20
	Zn – O (1)	.2087	39.48	50.97
	Zn – O(2)	.1988	70.30	-42.57
	Zn – F(1)	0.2046	80.91	47.91
	Zn – F (2)	0.1949	79.75	-46.40
Ammonium Tetra Fluorozincate (II) Dihydrate	Zn – F (3)	0.2055	80.91	47.91
	Zn – F(4)	0.2058	79.75	-46.40
	Zn – O(1)	0.2149	17.8	-2.06
	Zn – O(2)	0.2111	17.8	-2.06
ZnCl₂(OPPh₃)₂	Zn-Cl	.2186	58.63	-57.31
	Zn - O	.19662	131.52	30.50
	Zn – Br(1)	.23966	40.85 ± 2	-18.42
ZnBr₂(OPPh₃)₂	Zn – Br (2)	.2339	177.63 ± 2	62.20
	Zn – O (1)	.20874	39.48 ± 2	50.97
	Zn – O(2)	.19879	70.3 ± 2	-42.57
	Zn – F(1)	0.2046	80.91	47.91
	Zn – F (2)	0.1949	79.75	-46.4
	Zn – F (3)	0.2055	80.91	47.91
(NH₄)₂ZnF₄.2H₂O	Zn – F(4)	0.2058	79.75	-46.4
	Zn – O(1)	0.2149	17.8	-2.06
	Zn – O(2)	0.2111	17.8	-2.06

tested by Wen – Chen Zeng[9], who studied the zero – field splitting and a local geometry for Mn²⁺ in LiTaO₃. He was able to obtain consistant results assuming the data given[8] with the reference distance being R_o (Cl)= 0.20 nm and R_o (O)= 0.22 nm[10]. We used the above given data in our analysis. As a first step we calculated the value of b^0_2 spin – Hamiltonain parameter for the structure data obtained from X – ray measurement done for pure ZnCl₂(OPPh₃)₂. we obtained the value b^0_2 = - 0.0299 cm⁻¹. It is certainly substially different from the value measured by experimentally[7]. Therefore it is obvious that the local symmetry around Mn²⁺ doping ZnCl₂(OPPh₃)₂ is modified. In order to obtain some information about local distortions of the crystal lattice around the paramagnetic Mn²⁺ ion, we again used the superposition model but this time we allowed for average radial values and angular values remains constant in the position of Clorine ligands and Oxygen ligands.

The calculations were performed using a computer programme so that R_i, θ_i and φ_i parameters were adjusted for the best fit measured by least mean square deviation between the calculated values of b^0_2 (TABLE 2) and that determine experimental. The convergence of our calculations were assured by imposing two conditions:

a) The structure data for pure ZnCl₂(OPPh₃)₂ were taken as a set of starting parameters.

b) A minimum Mn²⁺ and Cl⁻ distance was assumed to be 0.20 nm based on the knowledge of the ionic radii of Mn²⁺ and Cl⁻.

c) A minimum Mn²⁺ and O⁻ distance was assumed to be 0.22 nm based on the knowledge of the ionic radii of Mn²⁺ and O⁻.

In this way we were able to fit the experimental data on b^0_2 with the structural data given in (TABLE 1) and using b_2 = -0.052 cm⁻¹. We have made SPM calculations by taking into account the charge relax-

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TABLE 2 : Spin hamiltonian and intrinsic parameters obtained for Mn²⁺ in host single crystals

Host	Spin Hamiltonian Parameters in cm⁻¹	Intrinsic Parameters in cm⁻¹
$ZnCl_2(OPPh_3)_2$	$b_2^{\ 0} = -0.1720$	$\left\{\begin{array}{l}\overline{b_2}(Cl) = -0.0267 \\ \overline{b_2}(O) = -0.1000\end{array}\right\}$
	$b_2^{\ 2} = -.2264$	$\left\{\begin{array}{l}\overline{b_2}(Cl) = -0.0267 \\ \overline{b_2}(O) = -0.1000\end{array}\right\}$
	$b_4^{\ 0} = 0.0622$	$\left\{\begin{array}{l}\overline{b_4}(Cl) = -0.006 \\ \overline{b_4}(O) = -0.050\end{array}\right\}$
	$b_4^{\ 2} = -0.2314$	$\left\{\begin{array}{l}\overline{b_4}(Cl) = -0.006 \\ \overline{b_4}(O) = -0.050\end{array}\right\}$
	$b_4^{\ 4} = -0.0892$	$\left\{\begin{array}{l}\overline{b_4}(Cl) = -0.006 \\ \overline{b_4}(O) = -0.050\end{array}\right\}$
$ZnBr_2(OPPh_3)_2Br)$	$b_2^{\ 0} = -0.0126$ $b_2^{\ 2} = -0.1047$ $b_4^{\ 0} = 0.0041$ $b_4^{\ 2} = 0.0031$ $b_4^{\ 4} = -0.0071$	$b_2 = -0.0500$ $\overline{b_2} = -0.0500$ $\overline{b_4} = -0.0130$ $\overline{b_4} = -0.0130$ $\overline{b_4} = -0.0130$
Ammonium Tetra Fluorozincate (II) Dihydrate	$b_2^{\ 0} = 0.0358$	$\left\{\begin{array}{l}\overline{b_2}(F) = -0.0531 \\ \overline{b_2}(O) = -0.0280\end{array}\right\}$
	$b_2^{\ 2} = -0.2059$	$\left\{\begin{array}{l}\overline{b_2}(F) = -0.0531 \\ \overline{b_2}(O) = -0.0280\end{array}\right\}$
	$b_4^{\ 0} = -0.0342$	$\left\{\begin{array}{l}\overline{b_4}(Cl) = -0.0132 \\ \overline{b_4}(O) = -0.0070\end{array}\right\}$
	$b_4^{\ 2} = -0.0274$	$\left\{\begin{array}{l}\overline{b_4}(Cl) = -0.0132 \\ \overline{b_4}(O) = -0.0070\end{array}\right\}$
	$b_4^{\ 4} = -0.1996$	$\left\{\begin{array}{l}\overline{b_4}(Cl) = -0.0132 \\ \overline{b_4}(O) = -0.0070\end{array}\right\}$

ation effect of bond angles only and assuming that bond length to remain unchanged as doping with Mn²⁺ in place zn²⁺. Using equation (3-7) along with the values of θ_i, φ_i and M - Cl bond distances (TABLE 1). $R_o = 0.20$ nm, $t_2 = 10$, $t_4 = 10$, M - O bond distances $R_o = 0.22$ nm. The calculated value of b_2^0 fairly matched with experimental value of 0.172 cm-1 if for clorine $\overline{b_2}$ (Cl) = -0.0267 and for Oxygen $\overline{b_2}$ (O) = -0.1000 cm-1 which is in the range[8]. Hence we find close agreement between theoretical and experimental values. The second and fourth order zero field splitting parameters are calculated and given in TABLE (2). The values of ZFS parameters $b_2^{\ 0}$, $b_2^{\ 2}$, $b_4^{\ 0}$, $b_4^{\ 2}$ and $b_4^{\ 4}$ and intrinsic parameters $\overline{b_2}$ and $\overline{b_4}$ b_4 are very close to that of Mn²⁺ in other host single crystals[1,2] and maintain the inequality

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$\overline{b_2} \geq 4$[3,4]

Mn²⁺ doped in dibromobis (triphenylphosphine oxide) zinc (II)

The crystal structure of $ZnBr_2(OPPh_3)_2$ has been investigated by Allen F.H., Rogers D. et al[11] the crystal in $ZnCl_2(OPPh_3)_2$ are triclinic with a = 10.188(1) A°, b = 9.987(1)A° and c = 11.189(1)A° and α =114.58°, β = 121.29°, γ = 89.82°, Z = 1, the space group is P1. The environment of the metal atom in each case approximates to a tetrahedral arrangements of two oxygen and two bromide ions. Using the atomic position given for $ZnBr_2(OPPh_3)_2$ with lattice constants, the values of bond distance R_i, the θ_i and φ_i are calculated and given in TABLE 1. A. Charles has reported the EPR of Mn²⁺ in $ZnBr_2(OPPh_3)_2$ in the literature[7]. Using equations (3-7) along with the values of R_i, θ_i and φ_i given for the structural data obtained from X-ray measurements done for pure $ZnBr_2(OPPh_3)_2$ by Allen F.H., Rogers D.[11] $t_2 = 7$, $t_4 = 10$ for Mn²⁺, R_o (Br)= 0.20 nm, R_o (O)= 0.22 nm are the reference distances for Mn²⁺ surrounded by bromine and oxygen and taking $\overline{b_2}$ = -0.05 cm⁻¹[8] $\overline{b_4}$ = - 0.0125 cm⁻¹[3,4] zero field splitting parameter b_2^0 is evaluated as b_2^0 = +.00276 cm⁻¹. The SPM predicts the correct sign for b_2^0 but the calculated value is different than experimental value. 0.523cm⁻¹ It has been suggested by MT Barriuso et. al.[12] and Mie – Ling Duan et. Al.[13] if R (metal – ligand bond distance) is greater than the normal Mn²⁺– ligand bond distance, the introduction of substitutional Mn²⁺ 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 distance in the pure host to take into account the lattice relaxation. Using equation (3-7) along with the values of θ_i, φ_i and M -Br bond distances and M-O bond distance (TABLE 1). R_o (Br)= 0.20 nm, R_o (O)= 0.22nm,t_2 = 7, t_4 = 10, the values of intrinsic parameters $\overline{b_2}$ = -0.05 cm⁻¹ and $\overline{b_4}$ = -.0125 cm⁻¹, the second and fourth order zero field splitting param-

eters are calculated and given in TABLE (2) which lies in the range from -0.0267 cm⁻¹ to -0.1000 cm⁻¹[14]. The calculated values of ZFS parameters b_2^0, b_2^2 and b_4^0 are fairly matched with experimental values and the intrinsic parameters $\overline{b_2}$ and $\overline{b_4}$ are very close to that of Mn²⁺ in other host single crystal given in the literature[15-23].

Mn (II) doped ammonium tetra fluorozincate (II) dihydrate (ATFD)

The crystal structure of $(NH_4)_2ZnF_4.2H_2O$ has been investigated by E. Balasiva Subramanian et al.[24]. The crystal is orthorhombic belonging to $P22_12_1$ at room temperature. The unit cell dimensions are a= 5.288(2) A°, b = 7.550(3)A°, c = 12.689(10)A° and α = β = γ = 90°. it is found that four flourines from halogens and two oxygens of the water molecules with nearly D_{4th} symmetry octahedrally surround zinc. Using the atomic positions given for $(NH_4)_2ZnF_4.2H_2O$ with the lattice constants, the values of metal – O bond distances, the angles φ_i are calculated and given in TABLE 1. The F_1-Zn-F_3 direction is nearly perpendicular to the F_2-Zn-F_4 direction and it makes an angle of 48.6° with the a-axis. The O_1-Zn-O_2 bond direction makes an angle of 17.8° with the c-axis. It is found that the four fluorines and the zinc are in one plane that makes an angles of 18° with the ab plane and the O_1-Zn-O_2 bond axis is perpendicular to the ZnF_4 plane. This is one of the rare systems where Zinc is octahedrally surrounded by four halogens and two water molecules.

E. Balasivasubramanian et al. reported that EPR of Mn²⁺ in ATFD includes only the extreme sextets of the fine structure quintets of one of the sites located at the X-band frequency due to overlapping of the spectra of two sites. Also, the symmetry experimental values of b_2^0 is reported as 388 x 10⁻⁴ cm⁻¹[24].

We have reported earlier in literature[2] the SPM calculation for Mn²⁺ in $(NH_4)_2ZnF_4.2H_2O$ by taking into account the relaxation effects of bond lengths only and assuming the bond angles to remain unchanged on doping with Mn²⁺ in place of Zn. We have used R_{av} = 2.0135 $\overset{0}{A}$ for F-atoms and R_{av} =

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2.165 $\overset{0}{A}$ for atoms[2]. The calculated value of b^0_2 is fairly matched with experimental value 0.0388 cm^{-1}[4], if for fluorine $\overline{b_2}$ (F) = -0.0531 cm^{-1} and for oxygen $\overline{b_2}$ (O) = -0.0280 cm^{-1} which lie in the range from -0.0267 to -0.1000cm^{-1}[14]. Using equation[4-7] we have calculated the second and fourth order zero field splitting parameters b^2_2, b^0_4, b^2_4 and b^4_4 given in TABLE [2]. The intrinsic parameters $\overline{b_2}$ (F), (o), (F) and (o) are very close to that of in other lost single crystals[15-23]. Hence, we find close agreement between theoretical and experimental values of ZFS parameters of Mn^{2+} in the host single crystals.

CONCLUSIONS

The ionic radii of Mn^{2+}, and Zn^{2+} are comparable, so Mn^{2+} on substituting the Zn^{2+} cation site perhaps does not cause appreciable local distortion in $ZnCl_2(OPPh_3)_2$, $ZnBr_2(OPPh_3)_2$ and $(NH_4)_2ZnF_4.2H_2O$ single crystals. Hence by using SPM theory suggested by Newman and Urban[3], it is possible to reproduce ZFS parameters b^0_2, b^2_2, b^0_4, b^2_4 and b^4_4 for Mn^{2+} doped in these single crystals at room temperature using the values of intrinsic parameters $\overline{b_2}$ and $\overline{b_4}$ calculated in the present study. The superposition model analysis shows that for large values of ZFS parameters b^0_2, b^2_2, b^0_4, b^2_4 and b^4_4, intrinsic parameters and 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 parameter ions in host single crystals.

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