



Superposition Model analysis of Zero field splitting for Mn²⁺ in (NH₄)₂SbF₅ and (TEA)₂BX₄(B = Zn, Ni) (X = Cl, Br) single crystals.

KEYWORDS

EPR; Superposition model; ZFS parameters.

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ABSTRACT

The Newman superposition model has been used to investigate the substitution of Mn²⁺ for Sb³⁺ site in Ammonium Pentafluoroantimonate (III) and for Zn²⁺ site in Tetra Ethyl Ammonium (TEA) single crystal. 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 $b_2(F) = -0.059 \text{ cm}^{-1}$ for fluorine and $b_2(Cl) = -0.0443 \text{ cm}^{-1}$ for chlorine taken $t_2 = 7 \pm 2$ and $t_4 = 10 \pm 2$ for Mn²⁺ doped in Ammonium Penta fluoro antimonite (III) single crystal. The values of b_2 determined for Mn²⁺ doped in tetra ethyl ammonium are -0.0443 cm^{-1} single crystal. 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 b_2 and b_4 can be estimated with suitable error but for small values of these spin – Hamiltonian 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 parameters ions in some host single crystals.

1. 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 crystal. 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 ligands around the impurity ions [3-4] and usually the zero-field splitting (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 Mn²⁺ ions are coordinated by fluorine and chlorine in single crystals.

The objective of this paper is to study the local distortion produced by substitution Mn²⁺ in place of host ions Sb³⁺ in Ammonium Penta fluoro antimonate (III) and Zn²⁺ in Tetra Ethyl Ammonium in single crystal which can lead to variation of magnetic properties.

2. SUPERPOSITION MODEL

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

The total ZFS experienced at an ion in a crystal is due to its nearest neighboring ions. 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

$$b_n = \sum K(\theta_i, \Phi_i) \bar{b}_n(R_i) \quad (1)$$

where the summation is taken over all ligands. R_i , θ_i and Φ_i are the spherical coordinates of the i^{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 [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

$$\bar{b}_n(R_i) = (R_0/R_i)^{t_n} \bar{b}_n(R_0) \quad (2)$$

where R_0 is the normal distance of the metal ion-ligand and R_i of the i^{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

$$b_2^0 = \sum_i^{t_2} [(3\cos^2\theta_i - 1)/2][R_0/R_i] \bar{b}_2[M,O] \quad (3)$$

$$b_2^2 = \sum_i^{t_2} [(3\sin^2\theta_i \cos 2\Phi_i)/2][R_0/R_i] \bar{b}_2[M,O] \quad (4)$$

$$b_4^0 = \sum_i^{t_4} [(35\cos^4\theta_i - 30\cos^2\theta_i + 3)/8][R_0/R_i] \bar{b}_4[M,O] \quad (5)$$

$$b_4^2 = \sum_i^{t_4} [5/2(7\cos^2\theta_i - 1)\sin 2\theta_i \cos 2\Phi_i][R_0/R_i] \bar{b}_4[M,O] \quad (6)$$

$$b_4^4 = \sum_i^{t_4} [(35\sin^4\theta_i \cos 4\Phi_i)/8][R_0/R_i] \bar{b}_4[M,O] \quad (7)$$

3. Result & Discussion

Mn²⁺ doped Penta Fluoroantimonate (III)

The crystal structure of (NH₄)₂ SbF₅ has been investigated by R.R. Ryan and D.T. Cromer [6] by a three dimension single crystal X-ray diffraction study. The structure was refined in the orthorhombic space group Cmcm. The cell constants are $a = 6.497\text{\AA}$, $b = 14.162\text{\AA}$, $c = 6.772\text{\AA}$ and

$\alpha = \beta = \gamma = 90^\circ$. the structure consist of isolated SbF_5^{2-} ions with the approximate square pyramid. It is found that five fluorines from halogens molecules with nearly D_{4h} symmetry square parameter surround sb. Using the atomic position given for $(\text{NH}_4)_2 \text{SbF}_5$ with the lattice constants the values of metal – F bond distances, the angle θ_i that Metal –F bond makes with the c- axis and ϕ_i are calculated and given in table 1.

The EPR spectrum of Mn^{2+} in $(\text{NH}_4)_2 \text{SbF}_5$ single crystal have been studied by L. Sreerama Chandra Parsad and S. Subramanian [7] and the value of ZFS parameter b_2^0 reported is 0.0359 cm^{-1} In order to apply the superposition model for the case considered in this paper, we used the values of $b_2(R_0)$, R_0 and t_2 given previously in the literature. Heming and Lehman [8] determined the values of $b_2(R_0) \approx -0.05 \text{ cm}^{-1}$ and $t_2 \approx 7$. These data were tested by Wen – Chen Zeng [9], who studied the zero – field splitting and a local geometry for Mn^{2+} in LiTaO_3 . He was able to obtain consistant result assuming the data given [8] with the reference distance being $R_0 = 0.20 \text{ nm}$ [10]. We used the above given data in our analysis. As a first step we calculated the value of b_2^0 spin – Hamiltonian parameter for the structure data obtained from X – ray measurement done for pure $(\text{NH}_4)_2 \text{SbF}_5$ or R.R. Ryan and D.T. Cromer [6]. we obtained the value $b_2^0 = -0.0146 \text{ cm}^{-1}$. It is certainly substainally different from the value measured by experimentally [7]. Therefore it is obvious that the local symmetry around Mn^{2+} doping $(\text{NH}_4)_2 \text{SbF}_5$ is modified. The reason for this modification lies, as it seems, in both the different valencies between Mn^{2+} and Sb^{3+} and different ionic radii. In order to obtain some information about local distortions of the crystal lattice around the paramagnetic Mn^{2+} ion, we again used the superposition model but this time we allowed for both radial and angular changes in the positions of the florine 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_2^0 (Table2) and that determine experimental. The convergence of our calculations were assured by imposing two conditions:

The structure data for pure $(\text{NH}_4)_2 \text{SbF}_5$ were taken as a set of starting parameters.

A minimum Mn^{2+} and F- distance was assumed to be 0.2 nm based on the knowledge of the ionic radii of Mn^{2+} and F-.

In this way we were able to fit the experimental data on b_2^0 with the structural data given in (Table 1) and using $b_2 = -0.059 \text{ cm}^{-1}$. In these calculations the charge compensation should occur due to charge difference. This may take place locally, in which case the magnetic parameters are affected and the charge compensation take place sufficiently await from the impurity such that magnetic parameters are not affected. We have made SPM calculations by taking into account the charge compensation effect of bond angles only and assuming that bond length to remain unchanged as doping with Mn^{2+} in place Sb^{3+} . Using equation (3-7) along with the values of θ_i , ϕ_i and M – F bond distances (table 1). $R_0 = 0.20 \text{ nm}$, $t_2 = 7 \pm 2$, $t_4 = 10 \pm 2$, the values of intrinsic parameters $b_2 = -0.059 \text{ cm}^{-1}$ and $b_4 = -0.00147 \text{ cm}^{-1}$, 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 \bar{b}_2 and \bar{b}_4 are very close to that of Mn^{2+} in other host single crystals [1,2] and maintain the inequality $b_2 \geq 4b_4$ [3,4]

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.)
$(\text{NH}_4)_2 \text{SbF}_5$	Sb – F (1)	0.1915	86.01	89.91
	Sb – F (2)	0.2074	42.05	14.60
	F (1) – F (2)	0.2551	53.52	46.41
$(\text{TEA})_2 \text{BX}_4$ (B = Zn, Ni) (X = Cl, Br)	Ni – Cl	0.2252	50.53	5.73

Table 2: Spin Hamiltonian and intrinsic parameters obtained for Mn^{2+} in Host single crystals

Host	Spin Hamiltonian Parameters in $\times 10^{-4} \text{ cm}^{-1}$	Intrinsic Parameters in cm^{-1}
$(\text{NH}_4)_2 \text{SbF}_5$	$b_2^0 = -359.1$	$\bar{b}_2 = -0.059$
	$b_2^2 = -114.4$	$\bar{b}_2 = -0.059$
	$b_4^0 = 58.9$	$\bar{b}_4 = -0.00147$
	$b_4^2 = -16.91$	$\bar{b}_4 = -0.00147$
	$b_4^4 = -11.54$	$\bar{b}_4 = -0.00147$
$(\text{TEA})_2 \text{BX}_4$ (B = Zn, Ni) (X = Cl, Br)	$b_2^0 = -81.60$	$\bar{b}_2 = -0.0443$
	$b_2^2 = -67.42$	$\bar{b}_2 = -0.0443$
	$b_4^0 = 57.25$	$\bar{b}_4 = -0.00110$
	$b_4^2 = -35.12$	$\bar{b}_4 = -0.00110$
	$b_4^3 = -13.07$	$\bar{b}_4 = -0.00110$
	$b_4^4 = -19.13$	$\bar{b}_4 = -0.00110$

Mn²⁺ doped in Tetra Ethyl Amonium (TEA)₂ BX₄ (B = Zn, Ni) (X = Cl, Br)

The crystal structure of (TEA)₂ BX₄ (B = Zn, Ni) (X = Cl, Br) has been investigated by G.D. Stucky et al [11] and J.R. Wiesner et. Al. [12] the Orthorhombic at room temperature. The unit cell dimention are $a = b = 9.05\text{\AA}$ and $c = 15.01\text{\AA}$ and $\alpha = \beta = \gamma = 90^\circ$ it is found that four chlorin molecules with near tetragonal symmetry surrounded zinc. Using the atomic position given for (TEA)₂ BX₄ with lattice constants, the value of bond distance R_r , the θ_1 and ϕ_1 are calculated in table 1.

M. Kahrizi et al has reported the EPR of Mn²⁺ in (TEA)₂ BX₄ (B = Zn, Ni) (X = Cl, Br) in the literature [13]. Using equations (3-7) along with the values of R_r , the θ_1 and ϕ_1 given for the structural data obtained from X-ray measurements done for pure (TEA)₂ BX₄ by G, D Stucky [11] $t_2 = 7$, $t_4 = 10$ for Mn²⁺, $R_o = 0.20$ nm is the references distance for Mn²⁺ surrounded by chlorine [12] and taking $b_2 = -0.05$ cm⁻¹ [8] $b_4 = -0.0125$ cm⁻¹ [3,4] zero field splitting parameters are evaluated as $b_0^2 = -0.00259$ cm⁻¹, $b_2^2 = -0.1652$ cm⁻¹ and $b_4^0 = 0.00613$ cm⁻¹. The SPM predicts the correct sign for b_4^0 but opposite sign for b_2^2 and b_2^2 and the calculated values are different than experimental values. It has been suggested by M.T. Barriuso et. al. [14] and Mie – Ling Duan et. Al. [15] 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 acctont the lattice relaxation. Using equation (3-7) along with the values of θ_1 , ϕ_1 and M - F bond distances (table 1). $R_o = 0.20$ nm, $t_2 = 7 \pm 2$, $t_4 = 10 \pm 2$, the values of intrinsic parameters $b_2 = -0.0443$ cm⁻¹ and $b_4 = -0.00110$ cm⁻¹, the second and fourth order zero field splitting parameters are calculated and given in table

(2). 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 b_2 and b_4 are very close to that of Mn²⁺ in other host single crystal given in the literature [16-25].

4. CONCLUSIONS

The ionic radii of Mn²⁺, Sb³⁺ and Ni²⁺ are comparable, so Mn²⁺ on substituting the Sb³⁺ and Ni²⁺ cation site perhaps does not cause appreciable local distortion in (NH₄)₂ SbF₅ and (TEA)₂ single crystals. Hence by using SPM theory suggested by Newman and Urban [3], it is possible to reproduce ZFS parameters b_2^0 , b_2^2 , b_4^0 , b_4^2 and b_4^4 for Mn²⁺ doped in these single crystal at room temperature using the values of intrinsic parameters of b_2 and b_4 calculated in the present study. The superposition model analysis shows that for large values of ZFS parameters b_2^0 , b_2^2 , b_4^0 , b_4^2 and b_4^4 , intrinsic parameters b_2 and 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 param-eter ions in host single crystals.

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