

Zero field splitting parameter of Mn^{2+} in ZnFS single crystals

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Abstract

A theoretical investigation of crystal field parameters and zero-field splitting parameter of Mn^{2+} doped zinc fluosilicate $ZnSiF_6 \cdot 6H_2O$ (ZnFS) single crystals is carried out with the help of superposition model and the perturbation theory. The zero-field splitting parameter determined agrees well with the experimental value obtained from EPR study. The theoretical study performed here supports the experimental conclusion that Mn^{2+} ions enter interstitially in ZnFS single crystal.

Keywords: A. Inorganic compounds; A. Single crystal; D. Crystal fields; D. Optical properties; D. Electron paramagnetic resonance.

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I. Introduction

Electron paramagnetic resonance (EPR) studies provide information about structural distortions and local site symmetry of transition ions incorporated in different host systems [1-3]. With the help of microscopic spin-Hamiltonian (MSH) theory, the spin Hamiltonian (SH) parameters obtained from EPR are correlated with optical and structural parameters. These studies indicate that the spin Hamiltonian parameters of transition ions (d^5) in crystals are very sensitive to local distortions. Hence, the SH theory is widely employed in crystals.

The crystal-field (CF) parameters of d^5 ion may be evaluated using superposition model (SPM) [4, 5]. The zero field splitting (ZFS) parameters are then obtained using CF parameters [6]. Mn^{2+} ion of iron group is quite interesting because of its ground state $^6S_{5/2}$ [7-10]. The electron spins in external magnetic field orient freely having high order interaction with crystalline electric field [11, 12].

Fluosilicate hexahydrates of several bivalent metals are considered to be isomorphous with a large number of salts having general formula MG_6LR_6 , where M is a bivalent metal, G may be water or ammonia, L is a quadrivalent element like Si, Sn, Ti or Zr, and R may be Cl, F or CN. These crystals have a rhombohedrally distorted CsCl-type packing and similar cell dimensions [13].

EPR study of Mn^{2+} doped zinc fluosilicate $ZnSiF_6 \cdot 6H_2O$ (ZnFS) single crystals has been done at 5K and 222.4 GHz frequency and spin Hamiltonian parameters have been evaluated [14]. The substitutional and interstitial sites may be considered for Mn^{2+} ion in the ZnFS crystal. It was confirmed from EPR [14] that Mn^{2+} ion enters the lattice of ZnFS interstitially. In this investigation, the CF parameters are determined using SPM and these parameters with MSH theory then give ZFS parameter for Mn^{2+} ions at the interstitial site in ZnFS single crystal at 5K. The ZFS parameter D obtained employing SPM gives reasonable agreement with the experimental value [14].

II. Crystal Structure

The ZnFS single crystals are colourless hexagonal prisms at room temperature with hexagonal cell parameters $a = 0.9363$ nm, $c = 0.9690$, space group $R\bar{3}$ [13]. The F atoms are at the corners of regular or nearly regular octahedron. The water molecules are also at the corners of nearly regular octahedron. These octahedra are packed according to a rhombohedrally distorted CsCl-type structure. The densest packing is in columns of alternate cations and anions along the threefold axis (Fig. 1). Three hydrogen bonds connect each pair of adjacent octahedra in a column, while one hydrogen bond connects an octahedron to each of its six neighboring octahedra in other columns. The oxygen coordination around Zn^{2+} is shown in Fig. 1. The site symmetry around Mn^{2+} ions may be considered as approximately axial, as suggested by EPR study of Mn^{2+} : ZnFS [14].

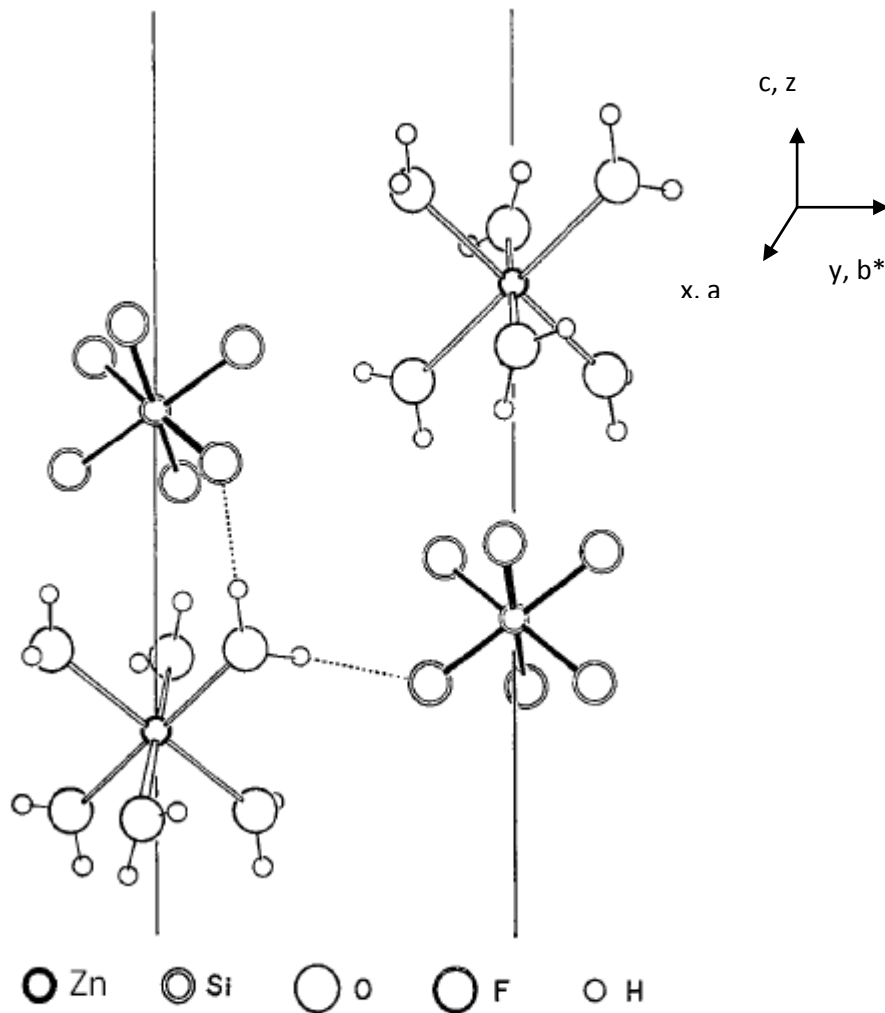


Fig. 1: Coordination around Zn^{2+} in ZnFS single crystal.

III. Theoretical Investigation

The Mn^{2+} ion in ZnFS single crystal substitutes at interstitial site [14]. The SH of $3d^5$ ion in crystal field of axial symmetry is given as [15-17]

$$\begin{aligned}
 \mathcal{H} = & g \mu_B B \cdot S + D(S_z^2 - S(S+1)) \\
 & + \left(\frac{\alpha}{6}\right) [S_x^4 + S_y^4 + S_z^4 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1)] \\
 & + \frac{F}{180} (35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2) \\
 & + A(I \cdot S)
 \end{aligned} \tag{1}$$

where the first term provides electronic Zeeman interaction, B is the external magnetic field, g is the spectroscopic splitting factor and μ_B is Bohr magneton. The second, third, and fourth terms give the second order axial, fourth-rank cubic and fourthrank axial ZFS terms [9]. The fifth term represents the hyperfine

interaction term. S , D , a , F are the effective spin vector, second order axial, fourth-rank cubic and fourth-rank axial ZFS parameters, respectively. An isotropic approximation for the electronic Zeeman interaction is considered for Mn^{2+} ions [9, 18, 19].

The Hamiltonian for a d^5 ion is given by

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{cf} + \mathcal{H}_{so}$$

where $\mathcal{H}_{cf} = \sum_{kq} B_{kq} C_q^k$ (2)

gives the crystal field Hamiltonian whereas \mathcal{H}_0 and \mathcal{H}_{so} represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. As the spin-spin coupling is very small [20-22], its contribution has been neglected in Eq. (2). The crystal field of SO interaction is considered as perturbation term [23-25]. The strong-field scheme calculation for F-state ions was carried out by Macfarlane [26]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given by [24]

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

where $P = 7(B+C)$, $G = 10B+5C$ and $D = 17B+5C$. P , G , and D represent the energy separations between the excited quartets and the ground sextet. Racah parameters B and C give the electron-electron repulsion. Only fourth order term is considered in Eq. (3) since other perturbation terms are negligible [24, 26]. The parameters B , C and ξ , in terms of the average covalency parameter N , are written as, $B = N^4B_0$, $C = N^4C_0$ and $\xi = N^2\xi_0$, where B_0 , C_0 and ξ_0 are the Racah parameters and the spin-orbit coupling parameter for free ion [27, 28], respectively. $B_0 = 960 \text{ cm}^{-1}$, $C_0 = 3325 \text{ cm}^{-1}$, $\xi_0 = 336 \text{ cm}^{-1}$ [9] for Mn^{2+} ion are taken in this calculation. Using equation

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

N can be evaluated.

Using SPM the CF parameters for Mn^{2+} in ZnFS single crystal are determined and then from Eq. (3) ZFS parameter D is evaluated. Similar method has been employed for finding ZFS parameters by various earlier workers [29].

In order to interpret the crystal-field splitting, the SPM is effectively employed. This model has also been applied for $3d^n$ ions [26, 30]. The crystal field parameters, using this model, are found from the equations [31]

$$B_{20} = -2\bar{A}_2 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_2} - 4\bar{A}_2 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_2} \tag{5}$$

$$B_{40} = 16\bar{A}_4 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_4} + 12\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4} \tag{6}$$

$$B_{44} = 2\sqrt{70}\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4} \tag{7}$$

where R_0 is the reference distance, generally taken as the average value of all four bond lengths (for axial symmetry).

IV. Results and Discussion

The average of two out of four Mn^{2+} -O bond lengths are found as $R_{10} = 0.6749 \text{ nm}$ and the average value of the rest two bond lengths are obtained as $R_{20} = 0.6782 \text{ nm}$. ΔR_1 and ΔR_2 are the distortion parameters. \bar{A}_2 , \bar{A}_4 and t_k are the intrinsic parameter and power law exponent, respectively. In octahedral coordination,

$\overline{A_4}(R_0) = (3/4)Dq$ [6]. For $3d^5$ ions, the ratio $\frac{\overline{A_2}}{\overline{A_4}}$ lies in the range 8-12 [26, 30]. The power law exponent

for Mn^{2+} ion is taken as $t_2 = 3$, $t_4 = 7$. Semi-ab initio calculations are carried out for other transition metal ions to get the intrinsic parameter values in SPM,

The values of B, C and Dq are found from optical absorption study [32] as 917, 2254 and 756 cm^{-1} , respectively.

First no local distortion is considered and the value of D is determined. For this, taking $\frac{\overline{A_2}}{\overline{A_4}} = 10$ and $R_0 = 0.220$

nm, which is the sum of ionic radii of $Mn^{2+} = 0.080 \text{ nm}$ and $O^{2-} = 0.140 \text{ nm}$, the B_{kq} parameters are found as: $B_{20} = -1166.69 \text{ cm}^{-1}$, $B_{40} = 6.115439 \text{ cm}^{-1}$, $B_{44} = 3.584896 \text{ cm}^{-1}$ and the value of D as: $|D| = 18.77 \times 10^{-4} \text{ cm}^{-1}$. EPR study provides the experimental value of D as: $|D| = 61527.57 \times 10^{-4} \text{ cm}^{-1}$ [14]. From above it is seen that the theoretical value is smaller than the experimental one.

Now, taking local distortions as $\Delta R_1 = 0.51207 \text{ nm}$ and $\Delta R_2 = 0.48991 \text{ nm}$, $R_0 = 0.220 \text{ nm}$ and ratio $\frac{\overline{A_2}}{\overline{A_4}} = 10$,

the B_{kq} parameters are obtained as: $B_{20} = -64079.7 \text{ cm}^{-1}$, $B_{40} = 94466.94 \text{ cm}^{-1}$, $B_{44} = 28172.57 \text{ cm}^{-1}$ and the value of D as: $|D| = 61527.2 \times 10^{-4} \text{ cm}^{-1}$, in good match with the experimental one: $|D| = 61527.57 \times 10^{-4} \text{ cm}^{-1}$. The substitutional site was also studied but the value of D was quite different from the experimental value and hence the data is not being given here.

V. Conclusions

Axial symmetry zero-field splitting parameter D for Mn^{2+} in ZnFS single crystal has been evaluated using superposition model and perturbation theory. The theoretical D matches well with the experimental value when distortion is taken into account. This study shows that Mn^{2+} ion occupies interstitial site which supports the conclusion drawn from the experimental EPR study.

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