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Zero field splitting parameter of Mn^{2+} doped guanidine zinc sulphate crystal -a theoretical study

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Abstract.

A theoretical investigation of crystal field parameters (CFP) and zero-field splitting (ZFS) parameter D of Mn^{2+} doped guanidine zinc sulphate (GZS) crystals at room temperature (RT) is done with the help of superposition model and the perturbation theory. The ZFS parameter D determined here is in good agreement with the experimental value reported earlier. The conclusion of experimental study that Mn^{2+} substitutes for Zn^{2+} in GZS is supported by our theoretical investigation. The values of D without and with local distortion are 11174.3×10^{-4} cm^{-1} and 702.4×10^{-4} cm^{-1}, respectively, while the experimental value is 702.0×10^{-4} cm^{-1}.

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

1. Introduction

Electron paramagnetic resonance (EPR) studies are useful for the knowledge of structural distortions and local site symmetry of transition ions in crystals [1-7]. EPR spectra of these ions are frequently analyzed with the help of microscopic spin-Hamiltonian (MSH) theory. Using this theory, the spin Hamiltonian (SH) parameters from EPR can be correlated with optical absorption and structural parameters. Both the experimental and theoretical studies indicate that the spin Hamiltonian parameters of transition ions (d^5 (^{6}S)) in crystals are very sensitive to local distortion. Therefore, the SH theory is widely used in crystals.

The crystal-field (CF) parameters of d^5 ion are obtained using superposition model (SPM) [8, 9]. The zero field splitting (ZFS) parameters are determined using CF parameters [10]. Mn^{2+} ion is important as its ground state is ^{6}S$_{5/2}$ [11-15]. The electron spin is affected by high order interaction of crystalline electric field and in external magnetic field the orientation of spins is free [16]. As S state ions have large spin–lattice relaxation time, Mn^{2+} ion gives well resolved EPR lines [15-19] at room temperature (RT).

In the present paper, the CF parameters are determined using SPM and these parameters with MSH theory give ZFS parameter for Mn^{2+} ion at the substitutional Zn^{2+} site in guanidine zinc sulphate (GZS) crystal at RT.

2. Crystal Structure

The crystal structure of GZS, Zn[C(NH$_2$)$_3$]$_2$(SO$_4$)$_2$ belongs to space group $I\bar{4}2d$ with unit cell dimensions a = 0.9515 nm and c = 1.4351 nm, and there exist four molecules per unit cell (Z = 4) [20]. A network of zinc and sulphate ions constitutes the main feature of the structure. Four oxygen ions form a distorted tetrahedral environment around the Mn^{2+} ion, as shown in Fig. 1.
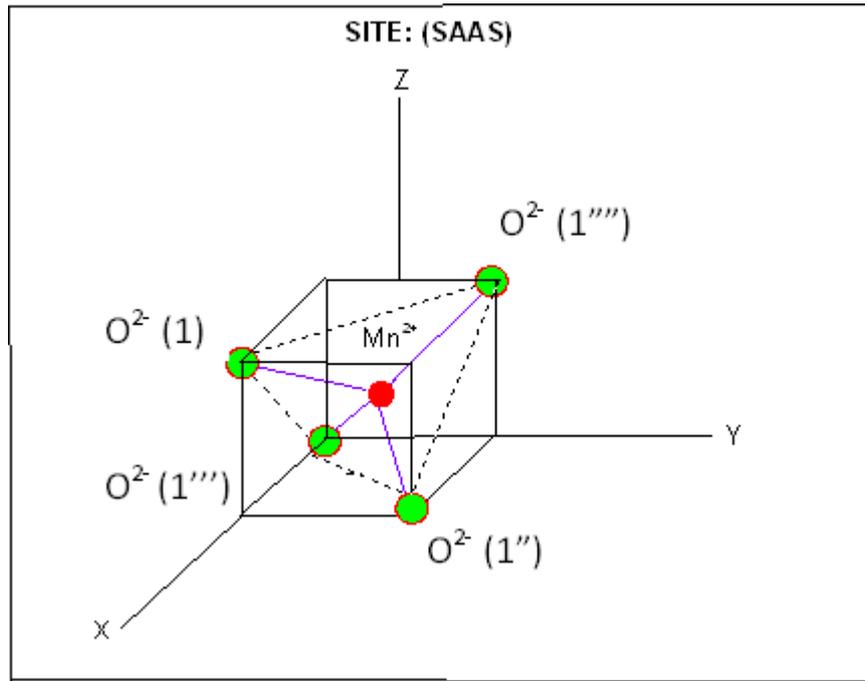
Fig. 1 Environment around Mn^{2+} ion.

3. Theoretical Investigation

The Mn^{2+} ion in GZS crystal substitutes at Zn^{2+} site [21]. The SH of 3d^5 ion in crystal field of axial symmetry is given as [2, **22**, **23**]

$$\mathcal{H} = \quad g\,\mu_B B.S \quad + D\{S_z^2 - \frac{1}{3}S(S+1)\}$$

$$+\left(\frac{a}{6}\right)[S_X^4 + S_Y^4 + S_Z^4 - \frac{1}{5}S(S+1)(3S^2+3S-1)]$$

$$+\frac{F}{180}\{35S_Z^4 - 30S(S+1)S_Z^2 + 25S_Z^2 - 6S(S+1) + 3S^2(S+1)^2\}$$

$$+ \quad A(I.S) \tag{1}$$

where the first term gives 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 represent the second order axial, fourth-rank cubic and fourthrank axial ZFS terms [2]. The fifth term provides 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 used in case of Mn^{2+} ions [2, 24, 25].

The Hamiltonian for a d^5 ion is given as

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

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

gives the crystal field Hamiltonian. $\mathcal{H}_0$ and $\mathcal{H}_{so}$ represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Since the spin-spin coupling is very small [26-28], its contribution has been neglected in Eq. (2). The crystal field of SO interaction is considered as perturbation term [29,30]. The strong-field scheme calculation for F-state ions was given by Macfarlane [31]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given by [30]

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

(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 taken in Eq. (3) as other perturbation terms are negligible [32]. The parameters B, C and ξ, in terms of the average covalency parameter N, are given as, $B = N^4 B_0$, $C = N^4 C_0$ and $\xi = N^2 \xi_0$, where B_0 and C_0 are the Racah parameters and ξ_0, the spin-orbit coupling parameter, for free ion [33, 34]. $B_0 = 960\ cm^{-1}$, $C_0 = 3325\ cm^{-1}$, $\xi_0 = 336$ cm^{-1} [2] for Mn^{2+} ion are used here. N can be obtained with the help of equation

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

(4)

By using SPM the CF parameters for Mn^{2+} in GZS crystal are calculated and substituting these in Eq. (3) ZFS parameter D is obtained. Similar method has been used for finding ZFS parameters by many other workers [35].

To understand the crystal-field splitting, the SPM is effectively used. This model has also been applied for $3d^n$ ions [8, 32, 36]. The crystal field parameters, using this model, are found from the equations [37]

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

(5)

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

(6)

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

(7)

in which R_0 is the reference distance, in general chosen as the average value of all four bond lengths (for axial symmetry).

4. Results and Discussion

The average value of two out of four Mn^{2+}-O bond lengths are given as $R_{10} = 0.20936$ nm and the average value of the rest two bond lengths are also given as $R_{20} = 0.20936$ nm. ΔR_1 and ΔR_2 represent the distortion parameters. $\bar{A}_2$, $\bar{A}_4$ and t_k are the intrinsic parameter and power law exponent, respectively. In tetrahedral

coordination, $\overline{A_4}(R_0) = (-27/16)Dq$ [10]. For $3d^5$ ions, $\dfrac{\overline{A_2}}{A_4}$ is in the range 8-12 [32, 36]. The power law exponent for Mn^{2+} ion is taken as $t_2 = 3$, $t_4 = 7$. Semi-ab initio calculations are performed for other transition metal ions to obtain the intrinsic parameter values in SPM,

The values of *B, C* and *Dq* are obtained (for oxygen ligands) [38] using optical study [39] as 917, 2254 and 756 cm^{-1}, respectively. First no local distortion is considered and the value of D is estimated. For this, taking $\dfrac{\overline{A_2}}{A_4} = 8$ and $R_0 = 0.215$ nm, the sum of ionic radii of $Mn^{2+} = 0.08$ nm and $O^{2-} = 0.135$ nm, which is slightly larger than the average distance of four ligands; the B_{kq} parameters are obtained as: $B_{20} = -66319.5$ cm^{-1}, $B_{40} = 43026.6$ cm^{-1}, $B_{44} = 25713.3$ cm^{-1} and the value of D as: D = 11174.3×10^{-4} cm^{-1}. EPR study gives the experimental value of D as: D = 702.0×10^{-4} cm^{-1} [40]. From above it is found that the theoretical value is larger than the experimental one.

Now, taking local distortions as $\Delta R_1 = 0.04794$ nm and $\Delta R_2 = 0.00002$ nm, $R_0 = 0.215$ nm and ratio $\dfrac{\overline{A_2}}{A_4} = 8$, the B_{kq} parameters are obtained as: $B_{20} = -56109.5$ cm^{-1}, $B_{40} = 24233.6$ cm^{-1}, $B_{44} = 25696.1$ cm^{-1} and the value of D as: D = 702.4×10^{-4} cm^{-1}, in reasonable agreement with the experimental one: D = 702.0×10^{-4} cm^{-1}.

5. Conclusions

Axial symmetry zero-field splitting parameter D for Mn^{2+} in GZS crystal has been determined using superposition model and perturbation theory. The theoretical D is in reasonable agreement with the experimental one when local distortion is taken into consideration. This theoretical investigation suggests that Mn^{2+} ion occupies substitutional Zn^{2+} site supporting the conclusion drawn from the experimental EPR study.

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