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Theoretical investigation of zero field splitting parameters for Mn^{2+} centres in L-asparagine monohydrate

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ABSTRACT

Zero-field splitting (ZFS) parameters D and E are calculated using the point-charge model (PCM) and superposition model (SPM) for Mn^{2+} centre in L-asparagine monohydrate (LAM) single crystal. The calculated ZFS parameters obtained using these two models are compared with the experimental values for interstitial site of Mn^{2+}. The SPM and PCM give ZFS parameters similar to those of experimental ones. This supports the notion that the impurity ion occupies interstitial site in LAM.

1. Introduction

For an orbital singlet ground state ($|\Gamma_o\rangle$), there is no orbital contribution to the magnetic moment because the average component of orbital angular momentum **L** in any direction is zero (i.e. the matrix element $\langle\Gamma_o|\mathbf{L}|\Gamma_o\rangle \equiv 0$) [1]. Hence only the spin momentum **S** contributes to the magnetic properties of transition-metal ions. Theoretical studies on the perturbation procedures of d^5 (^6S) ions suggested that various mechanisms contribute to the ground state splitting of the magnetic ions interacting with the lattices and the Hamiltonian of a d^5 ion can be written as sum of the free-ion Hamiltonian $\mathcal{H}_o$, crystal field $\mathcal{H}_{cf}$ and the spin–orbit and spin–spin couplings i.e. H_{so} and H_{ss}, respectively.

For an orbital singlet ground state, the spin–orbit interaction ($\mathcal{H}_{so}$), spin–spin interaction ($\mathcal{H}_{ss}$) and the Zeeman electronic interaction $\mathcal{H}_{ze}$ can be treated as perturbations. Perturbation involving the spin–orbit interaction is called spin–orbit (SO) mechanism while perturbation involving the spin–spin interaction is called the spin–spin (SS) mechanism [2]. The SS mechanism contributes values to the spin Hamiltonian parameters much smaller in magnitude than those due to the SO mechanism [3–5]. Because of the weakness of spin–spin interaction, important effect is expected only due to the spin–orbit interaction.

There are three alternative perturbation procedures available for SO mechanism [6]. These perturbation procedures correlate the spin Hamiltonian parameters with the crystal field ones in different ways and are shown to be equivalently correct. As the crystal fields have an important role in evaluations for SO mechanism, two models, the point-charge model (PCM) and superposition model (SPM), are generally used to calculate the crystal field parameters B_{kq}. These models have been widely used as quite reliable for determining the probable site of dopant [7–9]. These two models can establish relations between the crystal field parameters and crystal structure properties. The superposition model [10] has been shown to be quite successful in explaining the crystal field splitting of $4f^n$ ions and $3d^5$ ions.

As the resultant orbital angular momentum is zero in Mn^{2+} and only the electron spin is responsible for its paramagnetisum, the zero field splitting (ZFS) of this ion is quite sensitive to even small structural changes. The EPR and optical absorption are two powerful tools to study the dynamic aspects of crystalline state, site symmetry of the impurity and nature of bonding in crystals [11,12]. EPR of Mn^{2+} impurity has been widely studied [13–15]. In view of great interest in these studies, a suitable theoretical method, which would enable easy predictions of the ZFS parameters for the $3d^5$ system, would be helpful to researchers. This has motivated us to perform theoretical study of ZFS parameters using spin Hamiltonian involving higher-order perturbation terms and crystal field models.

EPR and optical study of Mn^{2+}doped L-asparagine monohydrate ($C_4H_8N_2O_3 \cdot H_2O$) (LAM) single crystal at 77 K was reported [16].

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There is interstitial possibility only for the site of Mn^{2+} centre in the single crystal of LAM. In the present paper, the ZFS parameters for Mn^{2+} ion in LAM, under the assumption that it is located at interstitial site, are calculated using point-charge model and superposition model. The theoretical results obtained from the point-charge model and superposition model are compared with the experimental data considering the preferred site of Mn^{2+} in LAM crystal. The results derived using both the models are consistent with the experimental observation.

2. Crystal structure

The crystal structure of LAM is orthorhombic [17], it belongs to space group $P2_12_12_1$ and contains four molecules in a unit cell, $Z = 4$. Cell parameters are $a = 5.593$, $b = 9.827$ and $c = 11.808$ Å. Molecule is in the zwitterions form and linked together by seven distinct hydrogen bonds to form a three dimensional network. The molecular structure of LAM is illustrated in Fig. 1(a).

3. Theoretical investigation

In this section, the ZFS parameters of Mn^{2+} ions located at interstitial site is calculated using the microscopic spin Hamiltonian (MSH) theory. The usual spin Hamiltonian describing the experimental EPR spectrum of Mn^{2+} in LAM is given by [15]

$$\begin{aligned} H = {} & \mu_B BgS + D\left(S_Z^2 - \frac{1}{3}S(S+1)\right) + E(S_x^2 - S_y^2) \\ & + \frac{a}{6}\left[S_x^2 + S_y^2 + S_z^2 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)\right] \\ & + AS_zI_z + B(S_xI_x + S_yI_y) \end{aligned} \tag{1}$$

where the first term is the Zeeman interaction term, the second and third are the axial and rhombic zero field splitting terms, the fourth is the cubic field splitting term and fifth and sixth are the hyperfine terms, respectively. In LAM, the local symmetry around Mn^{2+} ions is orthorhombic. In orthorhombic symmetry, the ZFS parameters D and E are given by [6]

$$\begin{aligned} D^{(4)}(\mathrm{SO}) = {} & \frac{3\xi^2}{70P^2D}(-B_{20}^2 - 21B_{20} + B_{22}^2) \\ & + \frac{\xi^2}{63P^2G}(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2) \end{aligned} \tag{2}$$

$$E^{(4)}(\mathrm{SO}) = \frac{\sqrt{6}\xi^2}{70P^2D}(2B_{20} - 21\xi_d)B_{20} + \frac{\xi^2}{63P^2G}(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44})B_{42} \tag{3}$$

where $P = 7B + 7C$, $G = 10B + 5C$, $D = 17B + 5C$. B and C are Racah parameters, ξ is the spin–orbit coupling parameter. Meanwhile, the first-, second-, third-, fifth-order perturbations of D and E are zero, and sixth-order term is small enough to be negligible. Thus only fourth order term is considered here. The two-particle parameters B and C describe electron–electron repulsion. In fact, the values of B and C for transition metal ion in a crystal are less than those of the free ion. The average covalency parameter N takes into account the covalency, where o < N < 1 ($N = 1$ for pure ionic bond). The parameter N depends on the property of the metal–ligand bond. By considering the average covalency parameter N, we can write the Racah parameters [18–20] as

$$B = N^4B_0, \qquad C = N^4C_0 \tag{4}$$

Table 1
The spherical co-ordinates of oxygen and nitrogen in LAM at room temperature.

R (Å)	Cos θ
5.16(N)	0.6831
2.22(N)	0.5416
5.79(O)	0.9565
6.66(O)	0.8398
4.24(O)	0.6423
4.91(O)	0.8605

where B_0 and C_0 are Racah electrostatic parameters in free state. In crystals, the spin–orbit coupling parameter [19,20] ξ can also be written in terms of average covalency parameter N

$$\xi = N^2\xi_0 \tag{5}$$

For transition metal ion in a crystal, the crystal field can be written as

$$\mathcal{H}_{\mathrm{cf}} = \sum\nolimits_{k,q} B_{kq}C_q^{(k)} \tag{6}$$

where $C_q^{(k)}$ are the orbital angular momentum operators and B_{kq} are the crystal field parameters. For the rhombic crystal field, $B_{kq} \neq 0$ only for $k = 2, 4$; $q = 0, 2, 4$. The crystal field parameters B_{kq} are closely related to the structure of LAM and these parameters are calculated using two models, namely: PCM and SPM.

3.1. Point-charge model

The crystal-field parameters using PCM are given by

$$\begin{aligned} & B_{kq} = (-1)^q \sum\nolimits_i eq_i < r^k > \frac{C_q^k(\theta_i, \phi_i)}{R_i^{k+1}} \\ & C_q^k = \sqrt{4\pi + 1)}Y_q^k \end{aligned} \tag{7}$$

where R_i, θ_i, Φ_i are the spherical co-ordinates of the i^{th} ligand, q_i is the equivalent charge of the i^{th} ligand and Y_q^k are the spherical harmonics, e is the electronic charge, r the radial co-ordinate of the $3d^5$ electron for Mn^{2+} ion in crystal, and $<r^k>$ is the expectation value of r^k. The expectation value $<r^k>$for the d^n ion in crystal is

$$\langle r^2 \rangle = N^2 \langle r^2 \rangle_0, \qquad \langle r^4 \rangle = N^2 \langle r^4 \rangle_0 \tag{8}$$

where $\langle r^k \rangle_0$ is the expectation value of r^k for the free ion. The non-zero crystal field parameters derived from Eq. (7) are given in Appendix A.

3.2. Superposition model

The SPM expresses the crystal field parameters [6] as

$$B_{kq} = \sum\nolimits_j \overline{A_k}(R_j)K_{kq}(\theta_j, \phi_j) \tag{9}$$

where the co-ordination factor $K_{kq}(\theta_j, \phi_j)$ is an explicit function of the angular position of the ligand (see Table 1 in Appendix B). The intrinsic parameter $\overline{A_k}(R_j)$ is given by

$$\overline{A_k}(R_j) = \overline{A_k}(R_0)\left(\frac{R_0}{R_j}\right)^{t_k}$$

where R_j is the distance between the d^n ion and the ligand, $\overline{A_k}(R_0)$ is the intrinsic parameter of the reference crystal, and t_k is the power law exponent. The crystal field splitting of an ion in the same bond is usually similar for different crystals. Likewise, the superposition model parameters of the bond in different crystals are similar to each other. The expressions for non-zero crystal field parameters derived from Eq. (9) for Mn^{2+} ion are given in Appendix B.