A Theoretical Analysis of Zero Field Splitting of Mn$^{2+}$ in Ammonium Oxalate Monohydrate

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The superposition model has been used to investigate the substitution of Mn$^{2+}$ in ammonium oxalate monohydrate. The zero field splitting parameters $D$ and $E$ calculated by the superposition model are compared with the experimental values $D_{\text{exp}}$ and $E_{\text{exp}}$, respectively, for Mn$^{2+}$ obtained by electron paramagnetic resonance. Both the zero field splitting parameters $D$ and $E$ calculated theoretically are in good agreement with the experimental values $D_{\text{exp}}$ and $E_{\text{exp}}$. The result indicates that the Mn$^{2+}$ ion substitutes for the NH$^+_4$ ion in ammonium oxalate monohydrate.

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1. Introduction

Electron paramagnetic resonance (EPR) studies of paramagnetic impurities in ammonium oxalate monohydrate (AOM) single crystals have been reported [1]. There are two possibilities for site of the Mn$^{2+}$ centre in this crystal, namely substitution in place of NH$^+_4$ and interstitial. It is interesting to determine the site of this impurity. It was indicated [1] that Mn$^{2+}$ enters the lattice substitutionally in place of NH$^+_4$.

The superposition model was introduced to separate the physical and geometrical information existing in lanthanide crystal field parameters [2]. Its field of application was extended in regard to systems and types of phenomenological parameterization. Its application to the spin Hamiltonian parameter of $d^5$ ion ground states has been developed [3]. Some success in applying this model to the orbit lattice interaction has been achieved. The usual problem in applying this model lies in finding the positions of the ligands. Hence the link between the model and the theories of local distortion in crystals is of considerable interest.

In this paper, we present the calculated zero-field splitting (ZFS) parameters, using superposition model for the Mn$^{2+}$ ion present at NH$^+_4$ site. The result derived from this model is found to be consistent with experimental observations.

2. Crystal structure

The crystal structure [4] of AOM (NH$_4$)$_2$C$_2$O$_4$·H$_2$O is orthorhombic with the space group $P2_12_12_1$, containing two formula units per unit cell. The unit cell dimensions are $a = 8.04 \AA$, $b = 10.27 \AA$ and $c = 3.82 \AA$. Distances within the oxalate group are: C–C = (1.581 ± 0.01) Å; O$_1$–C = (1.25 ± 0.02) Å; and O$_2$–C = (1.32 ± 0.02) Å, the angle O–C–O = (129 ± 2)$^\circ$. The angle between the O–C–O plane and (001) is 14$^\circ$ and thus the angle between the two O–C–O planes of an oxalate group is 28$^\circ$. The surroundings of NH$_4^+$ ion are shown in Fig. 1.

![Fig. 1. Surroundings of NH$_4^+$ ion in ammonium oxalate monohydrate.](image)

3. Theoretical investigation

Theoretical studies on the spin-Hamiltonian parameters of $d^5$ ions have been the subject of a considerable amount of work [5–13]. The lack of orbital angular momentum in $^6S$ ground state leads to considerable difficulty in explaining the observed effects of the crystal field. Various mechanisms have been suggested to contribute to ground-state splitting of the magnetic ions interacting with the lattice. The experimental results for the resonance field of Mn$^{2+}$ in AOM single crystals can be analyzed with the
usual spin Hamiltonian [1, 14–16]:
\[
H = g_\mu_B B \cdot S + D \left( S_x^2 - \frac{1}{3} S(S+1) \right) + E(S_z^4 - S_y^4) + \frac{a}{2} \left[ S_x^2 + S_y^2 + S_z^2 - \frac{1}{5} S(S+1)(3S^2 + 3S - 1) \right] + \frac{F}{180} \left[ 35S_4^4 - 30S(S+1)S_2^2 + 25S_2^6 \right] - 6S(S+1) + 35(S^2 + S_1^2) + K \left\{ \left[ 7S_2^2 - S(S+1) - 5 \right] (S_x^4 + S_y^4) + (S_z^4 + S_3^4) \left[ 7S_2^2 - S(S+1) - 5 \right] \right\} + \mathcal{A} S_2 I_z + B(S_x I_x + S_y I_y). \tag{1}
\]

Here \( g \) is the spectroscopic splitting factor, \( \mu_B \) is the Bohr magneton, \( B \) is the external field and \( S \) is the electron spin operator. The parameters \( a \), \( D \), and \( E \) are the cubic, axial, and rhombic ZFS parameters, respectively. The first term represents the electronic Zeeman interaction, the second and third terms represent axial and rhombic components of the zero-field splitting, the fourth term represents fourth-rank cubic ZFS term [14], the fifth term represents axial fourth-rank ZFS term, the sixth term represents rhombic fourth-rank ZFS term, the seventh and eighth terms are the hyperfine interaction terms (\( I = 5/2 \)). The fifth and sixth terms in spin Hamiltonian (1) have been omitted here as their effect is small [15, 17, 18]. Due to this there may be a little error in the value of \( g \) [19].

The direction of the maximum overall splitting of EPR spectrum is taken as the z axis and that of the minimum as the x axis [20]. The (\( x, y, z \)) system is parallel to the crystallographic axes. The local site symmetry axes, i.e., the symmetry adapted axes (SSA) in the present case are the nearly orthogonal directions of \( \text{NH}_4^- \) O bonds [4].

The effect of the spin–orbit interaction is considered as a part of the perturbation to the free ion Hamiltonian. However, the spin–spin interaction is neglected because its contribution to the spin-Hamiltonian parameters is much smaller than that due to the spin–orbit interaction [21–23]. In a rhombic symmetry, the ZFS parameters \( D \) and \( E \) are written as [24, 25]:
\[
D^{(4)}(\text{SO}) = (3 \zeta^2/70P^2D) \left( -B_{20}^2 - 21\zeta B_{20} + 2B_{22}^2 \right) + \left( \zeta^2/63P^2G \right) \left( -5B_{10}^2 - 4B_{22}^2 + 14B_{44}^2 \right), \tag{2}
\]
\[
E^{(4)}(\text{SO}) = (\sqrt{6} \zeta^2/70P^2D) \left( 2B_{20} - 21\zeta B_{22} \right) + \left( \zeta^2/63P^2G \right) \left( 3\sqrt{10}B_{40} + 2\sqrt{7}B_{44} \right) B_{42}. \tag{3}
\]

where \( P = 7B + 7C \), \( G = 10B + 5C \), and \( D = 17B + 5C \); \( B \) and \( C \) are the Racah parameters. Since the first-, second-, third-, and fifth-order perturbations of \( D \) and \( E \) are zero, only the fourth-order perturbations are considered. The sixth-order term is so small that it is usually negligible. The formula for the fourth-order ZFS parameter \( F \) is given by Yu [20].

The two-particle operator parameters \( B \) and \( C \) describe electron–electron repulsion. By considering the covalency effect and by introducing the average covalency parameters \( N \), we can express the Racah parameters \( B \) and \( C \) in terms of \( N \) [27, 28]:
\[
B = N^4B_0, \quad C = N^4C_0, \tag{4}
\]
where \( B_0 \) and \( C_0 \) denote the Racah electrostatic parameters in the free state. The spin–orbit coupling would also be reduced in a crystal [28], i.e.
\[
\zeta_d = N^2\zeta_0^d. \tag{5}
\]

The following values for free Mn\(^{2+} \) ion are used:
\[
B_0 = 960 \text{ cm}^{-1}, \quad C_0 = 3325 \text{ cm}^{-1} [17],
\]
\[
\zeta_0^d = 337 \text{ cm}^{-1} [29, 30], \quad N = 0.9773.
\]

The crystal-field parameters \( B_{kq} \) are related to the crystal structure. The superposition model is used to calculate the ZFS parameters for Mn\(^{2+} \) at the \( \text{NH}_4^- \) site.

The superposition model has been shown to be quite successful in explaining the crystal-field splitting of the \( 4f^n \) ions [31]. Recently, this model has been employed to deal with some \( 3d^n \) ions [32–34] and the results have been found satisfactory.

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|}
\hline
\( k \) & \( q \) & \( K_{k,-q} \) \\
\hline
2 & 0 & 3 \cos^2 \theta - 1 \\
2 & 1 & -(1/2)\sqrt{6} \sin 2\theta \exp(-i\phi) \\
2 & 2 & (1/2)\sqrt{6} \sin^2 \theta \exp(-i2\phi) \\
2 & 4 & 35 \cos^4 \theta - 30 \cos^2 \theta + 3 \\
4 & 1 & -2\sqrt{5} \sin \theta (7 \cos^3 \theta - \cos \theta) \exp(-i\phi) \\
4 & 2 & \sqrt{70} \sin^2 \theta (7 \cos^2 \theta - 1) \exp(-i2\phi) \\
4 & 3 & -2\sqrt{35} \sin^4 \theta \cos \theta \exp(-i3\phi) \\
4 & 4 & (1/2)\sqrt{70} \sin^4 \theta \exp(-i4\phi) \\
\hline
\end{tabular}
\caption{Expressions of \( K_{k,-q} \) \( [K_{k,-q} = (-1)^q K_{k,q}] \).}
\end{table}

The superposition model expresses the crystal-field parameters as [25, 31, 35]:
\[
B_{kq} = \sum \mathcal{A}_{k}(R_{ij}) K_{kq}(\theta_j, \phi_j). \tag{6}
\]

In this equation the various symbols have the following meanings: \( R_{ij} \) are the distances between the magnetic ion Mn\(^{2+} \) and the ligand ion \( j \). \( R_0 \) is the reference point, normally chosen near a value of the \( R_{ij} \)'s. \( \theta_j \) is the angle between the EPR main axis, the Mn\(^{2+} \) ion and the ligand ion \( j \) [36]. Summation is taken over all ligands. The coordination factor \( K_{kq}(\theta_j, \phi_j) \) are the explicit functions of angular position of ligand given in Table I (Table III from [25]). The intrinsic parameter \( \mathcal{A}_{k}(R_j) \) is given by the power law [25, 31], i.e.
\[
\mathcal{A}_{k}(R_j) = \mathcal{A}_{k}(R_0)(R_0/R_j)^{\delta k}, \tag{7}
\]
where \( R_j \) is the distance between the \( d^n \) ion and the ligand ion, and \( \mathcal{A}_{k}(R_0) \) is intrinsic parameter of the reference crystal. The symbol \( \delta k \) is power law exponent. The crystal-field parameters \( B_{kq} \) can be obtained using the
superposition model given by Eq. (6) and are as follows:

$$B_{20} = \frac{\mathcal{A}_2(R_0)}{\mathcal{A}_4(R_0)}[(R_0/R_1)^{1/2}(3\cos^2\theta_1 - 1) + (R_0/R_1)^{1/2}(3\cos^2\theta'_1 - 1) + (R_0/R_2)^{1/2}(3\cos^2\theta_2 - 1) + (R_0/R_2)^{1/2}(3\cos^2\theta'_2 - 1)],$$

$$B_{22} = \sqrt{6}\frac{\mathcal{A}_2(R_0)}{\mathcal{A}_4(R_0)}[(R_0/R_1)^{1/2}\sin^2\theta_1\cos(2\phi_1) + (R_0/R_1)^{1/2}\sin^2\theta'_1\cos(2\phi'_1) + (R_0/R_2)^{1/2}\sin^2\theta_2\cos(2\phi_2) + (R_0/R_2)^{1/2}\sin^2\theta'_2\cos(2\phi'_2)]/2,$$

$$B_{40} = \frac{\mathcal{A}_4(R_0)}{\mathcal{A}_4(R_0)}\times[(R_0/R_1)^{1/4}(35\cos^3\theta_1 - 30\cos^2\theta_1 + 3) + (R_0/R_1)^{1/4}(35\cos^3\theta'_1 - 30\cos^2\theta'_1 + 3) + (R_0/R_2)^{1/4}(35\cos^3\theta_2 - 30\cos^2\theta_2 + 3) + (R_0/R_2)^{1/4}(35\cos^3\theta'_2 - 30\cos^2\theta'_2 + 3)],$$

$$B_{42} = \sqrt{10}\frac{\mathcal{A}_4(R_0)}{\mathcal{A}_4(R_0)}\times[(R_0/R_1)^{1/4}\sin^2\theta_1(7\cos^2\theta_1 - 1)\cos(2\phi_1) + (R_0/R_1)^{1/4}\sin^2\theta'_1(7\cos^2\theta'_1 - 1)\cos(2\phi'_1) + (R_0/R_2)^{1/4}\sin^2\theta_2(7\cos^2\theta_2 - 1)\cos(2\phi_2) + (R_0/R_2)^{1/4}\sin^2\theta'_2(7\cos^2\theta'_2 - 1)\cos(2\phi'_2)],$$

$$B_{44} = \sqrt{70}\frac{\mathcal{A}_4(R_0)}{\mathcal{A}_4(R_0)}\times[(R_0/R_1)^{1/4}\sin^4\theta_1\cos(4\phi_1) + (R_0/R_1)^{1/4}\sin^4\theta'_1\cos(4\phi'_1) + (R_0/R_2)^{1/4}\sin^4\theta_2\cos(4\phi_2) + (R_0/R_2)^{1/4}\sin^4\theta'_2\cos(4\phi'_2)]/2.$$

The parameters $t_2$, $t_4$, $\mathcal{A}_2(R_0)$ and $\mathcal{A}_4(R_0)$ may be obtained from other crystals having similar Mn$^{2+}$–O$^{2−}$ bonds [26, 30]. A lot of work has indicated that $\mathcal{A}_2(R_0)/\mathcal{A}_4(R_0)$ is constant for 3d$^n$ ions and the value of $\mathcal{A}_2(R_0)/\mathcal{A}_4(R_0)$ for 3d$^n$ ions is 8–12 [32, 37–40]. Other values of the superposition-model parameters and the Mn$^{2+}$–O$^{2−}$ bond distances adopted are $t_2 = 3$, $t_4 = 7$ [26, 30], $R_0 = 2.02$ Å, $\mathcal{A}_2(R_0) = -1535.6$ cm$^{-1}$ and $\mathcal{A}_4(R_0) = -1535.63$ cm$^{-1}$. The above values are close to the true values of Yu [26] and reasonable for the estimation of ZFS parameters for Mn$^{2+}$ doped AOM. Yeom et al. [38] used $R_0 = 2.1$ Å in Mn$^{2+}$ doped BiVO$_4$ for the estimation of ZFS parameters and obtained good agreement with the experimental values but in our case this value ($R_0 = 2.1$ Å) yields large deviation from the experimental ZFS parameters.

4. Results and discussion

The $B_{4q}$ parameters obtained using Eqs. (8)–(12) are: $B_{20} = -3787.66$ cm$^{-1}$, $B_{22} = 6934.961$ cm$^{-1}$, $B_{40} = 169.0939$ cm$^{-1}$, $B_{42} = -287.492$ cm$^{-1}$, $B_{44} = -21.1269$ cm$^{-1}$. The ZFS parameters for the Mn$^{2+}$ centre at NH$_4^+$ site in AOM are then calculated substituting these $B_{4q}$ parameters in Eqs. (2),(3) and are given in Table II. The experimental values are also shown in Table II for comparison. The calculated values of the second-order axial and rhombic ZFS parameters at the NH$_4^+$ site turn out to be very similar to the values obtained from the experiment [1].

5. Conclusion

The EPR ZFS parameters have been investigated using the superposition model. The experimental ZFS parameters for the Mn$^{2+}$ ion in AOM single crystal are more similar to the calculated ZFS parameters at the NH$_4^+$ site. We conclude that the Mn$^{2+}$ ion substitutes the NH$_4^+$ ion in AOM. Our result supports the inference derived from experimental study.

<p>| Values of ZFS parameters [10$^{-4}$ cm$^{-1}$] |</p>
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The calculated ZFS parameters using superposition model may be used to identify the site of the Mn$^{2+}$ centre. From the above comparison of the ZFS parameters we conclude that the Mn$^{2+}$ ion substitutes the NH$_4^+$ ion. Our calculation based on the superposition model supports the reported experimental results.

References