



A theoretical analysis of zero-field splitting parameters of Mn^{2+} doped dicadmium diammonium sulfate $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ single crystal

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ABSTRACT

The superposition model (SPM) and crystallographic data are utilized to determine the zero-field splitting (ZFS) parameters (ZFSPs) for Mn^{2+} ions in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ single crystal, assuming that the Mn^{2+} ions locate at either Cd^{2+} or NH_4^+ site. The SPM results has been verified by the fourth-order perturbation formulae analysis. Experimental suggestions about Mn^{2+} ions substituting at Cd^{2+} sites have been confirmed theoretically for the first time.

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1. Introduction

Dicadmium diammonium sulfate $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ crystal, abbreviated as CAS hereafter, is one of the langbeinite-type crystals having the general formula $X_2Y_2(\text{SO}_4)_3$, where X is a divalent metal, e.g. Cd, Zn, Mg, Ca and Y is ammonium (NH_4) or a monovalent metal, e.g. K, Tl, Rb, Cs [1,2]. CAS has been the subject of many investigations [3–10] since its discovery by Jona and Pepinsky [3]. The ferroelectricity of CAS below 90 K was found out as well [3]. The disordering of the SO_4 ion in the high temperature phase was suggested based on Raman, infrared and far-infrared studies since no mode softening was observed [4]. Electron paramagnetic resonance (EPR) investigations of Mn^{2+} doped CAS single-crystal were reported in [5–7]; first at room temperature [5], whereas more detailed study [6] included also the crystal structure of Mn^{2+} :CAS. No change in space group symmetry at 80 K could be observed [6], in spite of the fact that a monoclinic ferroelectric phase of CAS below 90 K was suggested [2,3]. The structural phase transitions in CAS were studied by EPR in [7] and [8,9]. The studies [7–10], reporting a proton NMR, indicated some dynamical disordered arrangements related to ammonium and sulfate ions. Also, the authors [7] suggested that the phase transition occurred because of the freezing of the sulfate rotations, while the structural change was considered as a result of some motional change of the sulfate group in [6]. The

zero-field splitting (ZFS) parameters (ZFSPs) of Mn^{2+} in CAS were measured by EPR at room temperature [5–7].

In the present paper, first theoretical analysis of the ZFSPs of Mn^{2+} ions in CAS has been carried out. The ZFSPs have been calculated for different paramagnetic centers formed by Mn^{2+} ions at possible sites, namely, Cd^{2+} site and NH_4^+ site, in CAS crystal. We employ two theoretical methods: the superposition model (SPM) [11–13] and the fourth-order perturbation formulae on the basis of the dominant spin–orbit coupling mechanism [14]. The outcomes of both methods are consistent with the experimental results and they support earlier suggestions [5–7] that Mn^{2+} ions substitute for Cd^{2+} ions in CAS crystal.

2. Crystal structure

CAS crystal has cubic symmetry with the space group $P2_13$ (T^4) and contain four formula units per unit cell at room temperature. The cubic lattice parameters were reported to be $a = 1.0350$ nm [3,2] and 1.0362 nm [6]. Positional parameters and thermal parameters of CAS at room temperature were reported in [2,6]. Single unit cell of CAS is shown in Fig. 1 with the orientation of the crystallographic axes a , b , and c . The body diagonal of the cubic unit cell is parallel to the symmetry Z -axis [5] (see Fig. 1). CAS undergoes a first-order phase transition from the high-temperature cubic phase ($P2_13$) to the low-temperature monoclinic phase ($P2_1$) [2,15]. CAS is isomorphous to the langbeinite $\text{K}_2\text{Mg}_2(\text{SO}_4)_3$. The NH_4^+ and Cd^{2+} lie on the threefold axes, and the SO_4 tetrahedra are in general positions [8].

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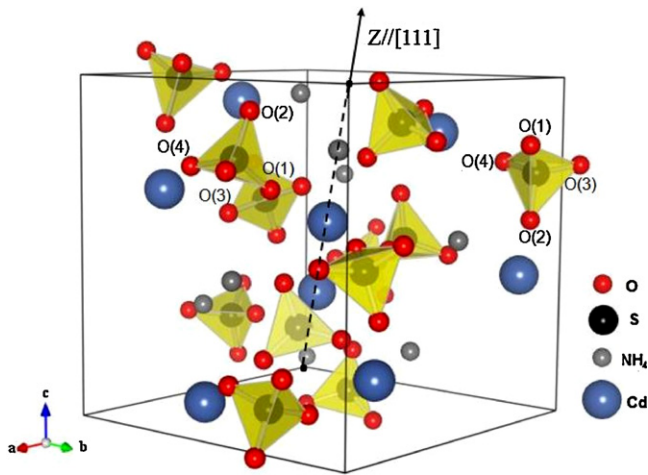


Fig. 1. Unit cell of $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)$ (CAS) crystal. Orientation of the crystallographic axes a , b , and c and the symmetry axis (Z -axis) parallel to the body diagonal of the cubic unit cell are shown.

Table 1

Bond distances and coordination angles of ligands used for SPM calculations of ZFS parameters for Mn^{2+} ions at Cd^{2+} site in CAS.

Host Cd sites		Substitutional sites		Angle θ_i (°)
Metal-oxygen	R_{hi} (nm)	Dopant Mn^{2+} -oxygen	R_i (nm)	
Cd-O(1)	0.382873	Mn-O(1)	0.368873	46.7902
Cd-O(2)	0.425824	Mn-O(2)	0.411824	36.0849
Cd-O(3)	0.451958	Mn-O(3)	0.437958	64.8707
Cd-O(4)	0.224573	Mn-O(4)	0.210573	59.8448

Table 2

Bond distances and coordination angles of ligands used for SPM calculations of ZFS parameters for Mn^{2+} ions at NH_4^+ site in CAS.

Host NH_4 sites		Substitutional sites		Angle θ_i (°)
Metal-oxygen	R_{hi} (nm)	Dopant Mn^{2+} -oxygen	R_i (nm)	
NH_4 -O(1)	0.367858	Mn-O(1)	0.327358	49.3410
NH_4 -O(2)	0.29626	Mn-O(2)	0.25576	57.8399
NH_4 -O(3)	0.513286	Mn-O(3)	0.472786	52.8615
NH_4 -O(4)	0.434782	Mn-O(4)	0.394282	26.5269

3. Theoretical analysis

3.1. The coordinates of the ligand ions

The bond distances and corresponding coordination angles of ligands have been determined and tabulated for host Cd site in Table 1 and for host NH_4 site in Table 2. The distance of a ligand is usually different from the cation–anion distance in the host lattice because of the mismatch of the radius of the substitution atom r_s and that of the host atom r_h . Ligand distance can be reasonably approximated using the following formula [16]: $R_i \approx R_{hi} + (1/2)(r_s - r_h)$, where R_i and R_{hi} represent the ligand and cation–anion distances, respectively. Using the data: $r_i(\text{Mn}^{2+}) = 0.067$, $r_h(\text{Cd}^{2+}) = 0.092$ [17], and $r_h(\text{NH}_4^+) = 0.148$ [18] (in nm), and the cation–anion distances in Tables 1 and 2 yield R_i values given in Tables 1 and 2.

3.2. Superposition model analysis

Experimental spectra of Mn^{2+} doped CAS can be analyzed by utilizing the spin Hamiltonian, suitable for the spin $S = 5/2$ systems at trigonal type I symmetry sites (D_3 , C_{3v} , D_{3d}), consisting of the

Zeeman electronic terms and the ZFS terms (without considering the hyperfine terms) [19–22]:

$$H = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \sum f_k b_k^q O_k^q = g_{\perp} \mu_B (B_x S_x + B_y S_y) + g_{\parallel} \mu_B B_z S_z + f_k (b_2^0 O_2^0 + b_4^0 O_4^0 + b_4^3 O_4^3) \quad (1)$$

where \mathbf{g} is the spectroscopic splitting factor, μ_B – Bohr magneton, \mathbf{B} – the applied magnetic field, \mathbf{S} – the effective spin operator, and b_k^q are ZFSPs associated with the extended Stevens operators O_k^q , whereas $f_k = 1/3$, and $1/60$ are the scaling factors for $k=2$, and 4 , respectively [23,24].

ZFSPs in Eq. (1) can be estimated using SPM approach outlined recently in [25,26]. The explicit SPM expressions for ZFSPs for a fourfold coordinated $3d^5$ ion in the Mn-O_4 complex in CAS are derived as

$$D_{SPM} = b_2^0 = \frac{\bar{b}_2(R_0)}{2} \left[\left(\frac{R_0}{R_1} \right)^{t_2} (3 \cos^2 \theta_1 - 1) + \left(\frac{R_0}{R_2} \right)^{t_2} (3 \cos^2 \theta_2 - 1) + \left(\frac{R_0}{R_3} \right)^{t_2} (3 \cos^2 \theta_3 - 1) + \left(\frac{R_0}{R_4} \right)^{t_2} (3 \cos^2 \theta_4 - 1) \right] \quad (2)$$

$$b_4^0 = \frac{\bar{b}_4(R_0)}{8} \left[\left(\frac{R_0}{R_1} \right)^{t_4} (35 \cos^4 \theta_1 - 30 \cos^2 \theta_1 + 3) + \left(\frac{R_0}{R_2} \right)^{t_4} (35 \cos^4 \theta_2 - 30 \cos^2 \theta_2 + 3) + \left(\frac{R_0}{R_3} \right)^{t_4} (35 \cos^4 \theta_3 - 30 \cos^2 \theta_3 + 3) + \left(\frac{R_0}{R_4} \right)^{t_4} (35 \cos^4 \theta_4 - 30 \cos^2 \theta_4 + 3) \right] \quad (3)$$

$$b_4^3 = 35 \bar{b}_4(R_0) \left[\left(\frac{R_0}{R_1} \right)^{t_4} \sin^3 \theta_1 \cos \theta_1 + \left(\frac{R_0}{R_2} \right)^{t_4} \sin^3 \theta_2 \cos \theta_2 + \left(\frac{R_0}{R_3} \right)^{t_4} \sin^3 \theta_3 \cos \theta_3 + \left(\frac{R_0}{R_4} \right)^{t_4} \sin^3 \theta_4 \cos \theta_4 \right]$$

Two data sets [27,28] of the model parameters, i.e. the intrinsic parameters $\bar{b}_k(R_0)$ and the power law exponents t_k , suitable for Mn^{2+} in CAS exist in literature (Table 5). These sets were adopted in our calculations together with three values of the reference distance R_0 taken as: (a) $R_0 = a_0/4$, where a_0 is the lattice parameter, (b) R_0 values from [27,28] for Mn^{2+} , and (c) $R_0 \approx R_{avg}$ [29,30].

3.3. The fourth-order perturbation formula of ZFS parameter D

Second-rank ZFS parameter $b_2^0 = D$ can also be calculated using the fourth-order perturbation formula on the basis of the dominant spin–orbit coupling mechanism [14]

$$D_{PT} = b_2^0 = \frac{3\zeta^2}{70p^2d} (-B_{20}^2 - 21\zeta B_{20}) + \frac{\zeta^2}{126p^2g} (-10B_{40}^2 + 7B_{43}^2) \quad (4)$$

with

$$p = 7B + 7C \quad g = 10B + 5C \quad d = 17B + 5C \quad (5)$$

where B and C are the Racah parameters. B_{kq} are the crystal-field parameters (CFPs) in Wybourne notation. They can be expressed using the superposition model as [14,31]:

$$B_{kq} = \sum_j \bar{A}_k(R_j) K_{kq}(\theta_j, \phi_j) \quad (6)$$

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