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Theoretical investigation of zero field splitting parameters for Mn^{2+} centers in ammonium tartrate

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ABSTRACT

Zero-field splitting (ZFS) parameters *D* and *E* for Mn^{2+} centers in ammonium tartrate single crystal are calculated with perturbation formulae using the superposition model. The theoretically calculated ZFS parameters for Mn^{2+} at site I and site II of ammonium ion are compared with the experimental values obtained by electron paramagnetic resonance (EPR) at room temperature. The superposition model gives the ZFS parameters similar to those from experiment. The energy band positions of optical absorption spectrum of Mn^{2+}in ammonium tartrate are calculated using the CFA package and crystal field parameters from superposition model. These are in good agreement with experimental energy band positions.

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1. Introduction

Theoretical studies in the past few decades on the spin Hamiltonian of d^5 (^6S) ions suggested that various mechanisms contribute to the ground state splitting of the magnetic ions interacting with the lattices. The Hamiltonian of a d^5 ion can be written as the sum of the free-ion Hamiltonian, the crystal field, the spin–orbit and spin–spin couplings. As usual, the crystal field can be written as the sum of cubic part and a low symmetry component.

Because of the weakness of spin–spin coupling, important effect is expected due to the spin–orbit interaction. This effect is called a spin–orbit (SO) mechanism. Blume and Orbach [1] treated the calculation within the ground d^5 configuration taking spin–orbit coupling and low symmetry component of the crystal field as a part of perturbation. For calculation of spin–orbit coupling effect in d^5 configuration, one may treat the total crystal field as one of the perturbation terms together with spin–orbit interaction [2] or make the calculation in the strong-field as done by Macfarlane for F-state ions [3]. Perturbation involving the spin–spin interaction is the spin–spin mechanism [4] (SS), which contribute values to the spin Hamiltonian parameters much smaller in magnitude than those due to the SO mechanism [5–7].

Three alternative perturbation procedures for the SO mechanism are shown to be equivalently correct [8]. The calculation of the crystal field parameters plays a crucial role in the evaluation of contributions of SO mechanism. Two models, namely the point-charge model and the superposition model, are generally used to calculate the crystal field parameters. These two models can establish relations between the crystal field parameters and crystal structure properties. The superposition model [9] has been shown to be quite successful in explaining the crystal field splitting of $4f^n$ ions. More recently, this model has been employed to deal with some $3d^n$ ions (e.g. Cr^{3+} in Al_2O_3 [10], Fe^{2+} in garnets [11] and Mn^{2+} in $BiVO_4$) [12] and the results are satisfactory.

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. EPR of Mn^{2+} impurity has been widely studied in a variety of single crystals [13–15], as the zero field splitting of this ion is sensitive to even small distortion in the lattice [16]. The EPR study of Mn^{2+} impurity in ammonium tartrate (AT) single crystal at room temperature has been reported [17]. There are two possibilities for the site of Mn^{2+} center in the single crystal of ammonium tartrate—substitution at ammonium ion and/or structural vacancy. It is interesting and worthwhile to determine the site of this paramagnetic impurity. It was proposed that Mn^{2+} ion substitutes ammonium ion with charge compensation.

In this paper, we present the calculated ZFS parameters for Mn^{2+} ion under the assumption that this ion is present at two sites of ammonium ion, using the point-charge model and the superposition model. The result derived from the superposition model is consistent with the experimental observation.

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2. Theoretical investigation

In this section, the ZFS parameters of Mn^{2+} ions located at site I and site II in AT (Fig. 1) are calculated using the microscopic spin Hamiltonian (MSH) theory. These calculated values are then compared with the experimental results.

The spin Hamiltonian (SH) in the conventional form [18,19] for the spin $S=5/2$ ground state of Mn^{2+} ion is taken as [20]

$$\begin{aligned}\mathscr{H} &= g\mu^B \boldsymbol{B}\cdot S + D\left\{Sz^2-\frac{1}{3}S(S+1)\right\}+E(Sx^2-Sy^2)\\ &+\left(\frac{a}{6}\right)\left[Sx^4+Sy^4+Sz^4-\frac{1}{5}S(S+1)(3S^2+3S-1)\right]\\ &+\frac{F}{180}\{35Sz^4-30S(S+1)Sz^2+25Sz^2-6S(S+1)+3S^2(S+1)^2\}\\ &+\frac{K}{4}[\{7Sz^2-S(S+1)-5\}](S^{+2}+S^{-2})\\ &+(S^{+2}+S^{-2})\{7Sz^2-S(S+1)-5\}+\mathcal{A}SzIz+\mathcal{B}(SxIx+SyIy) \qquad (1)\end{aligned}$$

where g is the isotropic spectroscopic splitting factor, μ^B—the Bohr magneton, $\boldsymbol{B}$—the external field. The parameters D and E are the second-rank axial and rhombic ZFS parameters, whereas a, F and K are the fourth-rank cubic, axial and rhombic ones, respectively. For relationships between the conventional ZFS parameters and those in the (extended) Stevens notation refer to Refs. [18,19]. It may also be useful to consult the review [18] on the spin Hamiltonian formalisms, the review [19a] on the often confused interrelations between the CF and ZFS quantities and the note [19b] on the incorrect orthorhombic ZFSPs relations. The last two terms in Eq. (1) represent the hyperfine ($I=5/2$) interaction. The F and K ZFS terms are omitted here as their effect are small [19a,21,22]. The isotropic approximation used for the electronic Zeeman interaction is generally valid for Mn^{2+} ions [21,23]. The two approximations in question may slightly affect the fitted value of a [24]. 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 [25]. The laboratory axes (x, y, z) determined from EPR spectra are found to coincide with the crystallographic axes (CA). The z-axis of the local site symmetry axes, i.e. the symmetry adapted axes (SAA) is along the metal oxygen bond and the other two axes (x, y) are perpendicular to the z-axis.

The crystal field theory has been extensively applied to study the spin Hamiltonian parameters [26–30] of d^5 ions. These works discuss contributions from different mechanisms to ZFS of the d^5 (^6S) ion. With these formulae ZFS parameters are determined by the electrostatic, spin–orbit coupling and the crystal field parameters of the d^5 ion in a crystal. When the transition metal ion substitutes a host ion, the electrostatic and spin–orbit coupling parameters for the transition metal–ligand bonds with equal ligand ions are similar. Therefore, the electrostatic and spin–orbit coupling parameters of Mn^{2+} ion for site I are similar to those of Mn^{2+} ion for site II, because Mn^{2+} at both sites have same kind of ligand (oxygen ions). However, the local ionic arrangement around Mn^{2+} at both sites is different. This difference provides different crystal fields; consequently ZFS parameters of Mn^{2+} ion at both sites are different.

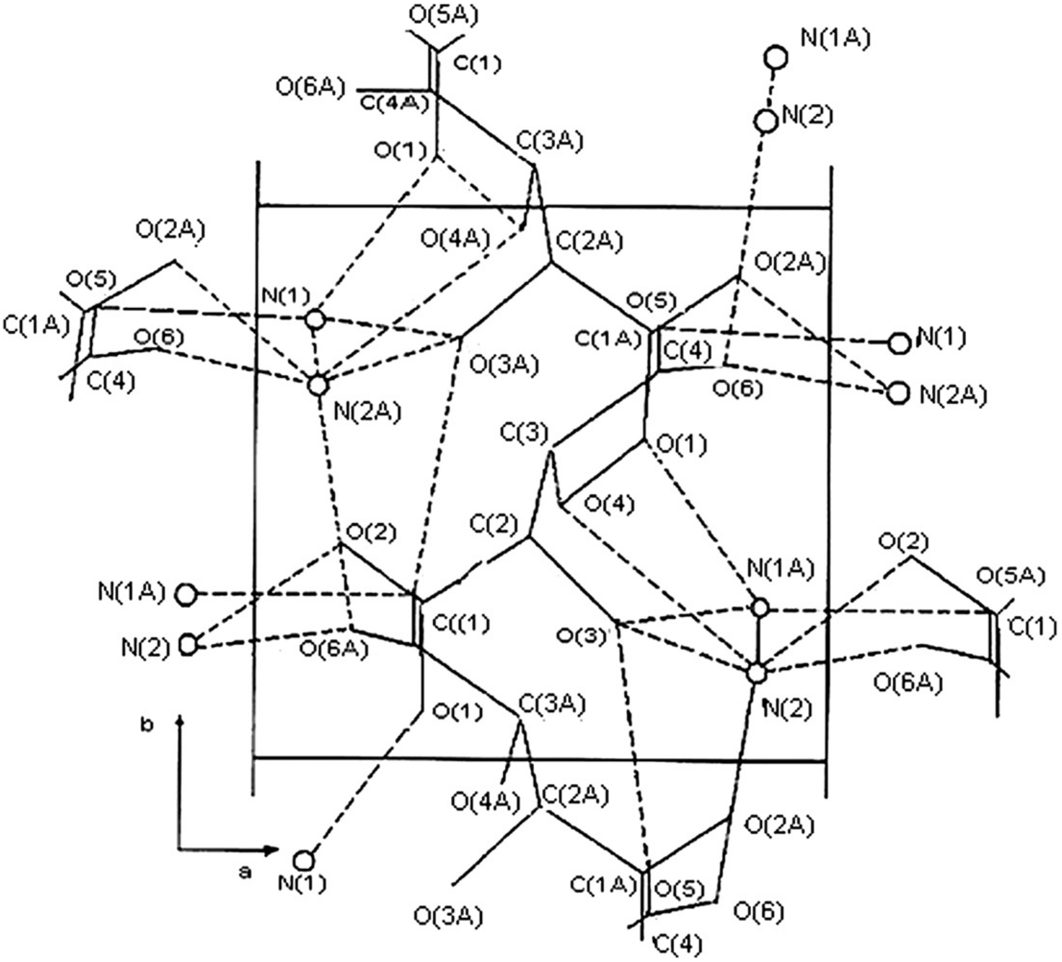

Fig. 1. Crystal structure of ammonium tartrate projected down the c-axis.

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