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Theoretical investigation of zero field splitting parameter of Cr³⁺ doped diammonium hexaaqua magnesium sulfate



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ARTICLE INFO

Article history:

Received 25 June 2014

Received in revised form

20 August 2014

Accepted 29 August 2014

Available online 8 September 2014

Keywords:

Inorganic compounds

Crystal fields

Electron paramagnetic resonance

Optical properties

ABSTRACT

The zero field splitting parameter D of Cr³⁺ doped diammonium hexaaqua magnesium sulfate (DHMS) are calculated with perturbation formula using crystal field (CF) parameters from superposition model. The theoretically calculated ZFS parameters for Cr³⁺ in DHMS single crystal are compared with the experimental value obtained by electron paramagnetic resonance (EPR). The theoretical ZFS parameter D is similar to that from experiment. The energy band positions of optical absorption spectra of Cr³⁺ doped DHMS single crystal are calculated with CFA package, which are in good match with experimental values.

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1. Introduction

The superposition model (SPM) has been successfully applied to obtain crystal field parameters of Cr³⁺ ion in crystals [1]. Very specific energy level structure of Cr³⁺ ion with spin doublet and spin quartet level gives an opportunity to reveal static and dynamic properties of Cr³⁺ impurities [2,3]. The Cr³⁺ ion is extensively used as a probe for studying the structure and the local symmetry of new materials. The theoretical studies on the spin Hamiltonian parameters of d³ ion have been the subject of considerable amount of work. Various mechanisms have been suggested to contribute to ground state splitting of magnetic ion interacting with lattice [4].

Cr³⁺ is one of the most investigated metal ions with 3d³ electronic configuration. Its ground state is ⁴A₂. Transition ions doped crystals are important due to their interesting spectroscopic properties making them suitable for lasers and optical fibers. The mostly used perturbation procedure treats cubic field and diagonal parts of free ion Hamiltonian as unperturbed Hamiltonian, leaving the perturbation as the spin-orbit coupling, the low symmetry field, and off diagonal part of free ion Hamiltonian. This procedure was used by Macfarlane for F state ion which gives better results [5].

EPR and optical study of Cr³⁺ in DHMS single crystal at liquid nitrogen temperature has been reported [6]. There are two possibilities of Cr³⁺ ion entering the lattice of DHMS, substitution in place of Mg²⁺ ion and/or structural vacancy. This is interesting

to determine the site of this paramagnetic impurity. It is reported [6] that Cr³⁺ ion substitutes the Mg²⁺ ion with charge compensation in DHMS.

We present, in this paper, the calculated ZFS parameters for Cr³⁺ ion using perturbation formula and crystal field (CF) parameters obtained from superposition model. The result derived from theoretical study is consistent with the experimental observation.

2. Crystal structure

The DAHAMS single crystal is monoclinic with space group P21/a. The unit cell parameters are $a=0.9316$ nm, $b=1.258$ nm, $c=0.6202$ nm with $Z=2$ and angle $\beta=107.09^\circ$ [7,8]. The magnesium atom has six-coordination, surrounded by six oxygen atoms with octahedral structure, as shown in Fig. 1. The site symmetry at Cr³⁺ ion in the crystal is axial or tetragonal.

3. Theoretical investigations

The ZFS parameter D of Cr³⁺ ion in DHMS is calculated using the microscopic spin Hamiltonian theory [9] and CF parameters obtained from SPM. The calculated value is then compared with the experimental one. For Cr³⁺ ions at tetragonal or axial symmetry the effective spin Hamiltonian taking into account the ZFS and Zeeman terms can be written as follows [10]:

$$\mathcal{H} = D \left\{ S_z^2 - \frac{1}{3} S(S+1) \right\} + \mu_B g_{\parallel} B_z S_z + \mu_B g_{\perp} (B_x S_x + B_y S_y) \quad (1)$$

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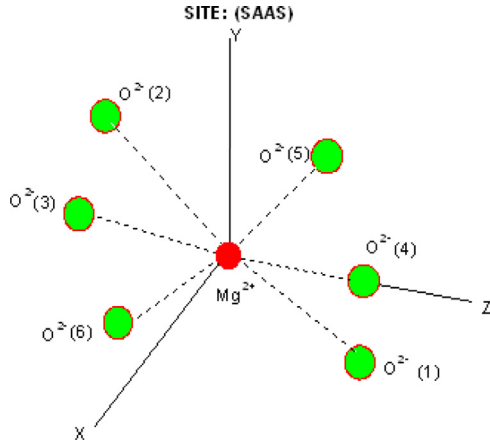


Fig. 1. Crystal structure of DHMS in which symmetry adopted axis system (SAAS) is shown.

where g_{\parallel} and g_{\perp} are the spectroscopic splitting factors, μ_B is the Bohr magnetron and B is the external magnetic field. The parameter D is the second rank axial ZFS parameter.

For a transition ion the crystal field can be written as follows:

$$\mathcal{H}_c = \sum B_{kq} C_q^{(k)} \quad (2)$$

where B_{kq} are the CF parameters and $C_q^{(k)}$ are the Wybourne spherical tensors or operators. For orthorhombic crystal field, $B_{kq} \neq 0$ only with $k=2, 4$; $q=0, 2, 4$. The crystal-field theory has been extensively applied to the study of the spin Hamiltonian parameters of transition metal ions in crystals [11,12]. SPM and point-charge model are generally used to calculate the CF parameters [9,13]. Moreover, the exchange charge model (ECM) is also a powerful and reliable tool for analysis and interpretation of the crystal field effects in rare-earth and transition metal doped crystals [14]. In the present study, we have calculated the CF parameters B_{kq} using SPM. Newman [1] proposed superposition model for CF based on the following four assumptions: (1) the CF at a paramagnetic ion can be expressed as an algebraic sum of contributions from other ions in the crystal. (2) When the paramagnetic ion is at the origin of a chosen coordinates frame, all the major CF contributions from every single ion in the crystal are axially symmetric with respect to its position vector. (3) Only neighboring or coordinated ions need to be counted for their CF contributions. (4) CF contributions from single ion (ligand) are transferable across different host crystals. The first assumption implies the validity of the superposition principle in describing the CF while the axial symmetry assumption (2) allows to freely transforming one coordinate frame to another. However, a more restrictive form of assumption (3) is often adopted in which only the nearest neighboring ions are considered and the term 'ligand' just refers to single ion. The last assumption (4) on ligand transferability means that the CF contributions from a single ligand depend only on the ligand type and its distance from the paramagnetic ion. In order to carry out a SPM analysis of the CF splitting, an almost pre-requisite condition is to have a reliable set of polar coordinates (R_L, θ_L, ϕ_L) for all the ligands concerned as obtained from the X-ray data of the host crystal. If transition metal ions are doped as impurities, they will probably induce certain amount of local distortion or lattice relaxation due to the mismatch in the ionic charge, ionic size and/or inter-ionic bonding. If there is sufficient number of CF parameters, we may apply linear or non-linear least-squares fit to those CF parameters to obtain the fitted values of the SPM intrinsic parameters and the power-law exponents. Newman and Siegel [15] made a critical analysis of the experimental spin-Hamiltonian parameters for Mn^{2+} and Fe^{3+} in CaO and MgO crystals verifying that the CF for 3d ions satisfies the

superposition principle and provides explicit values of the SPM parameters for the EPR data. Yeung and Newman [16] developed a rigorous lattice relaxation model on the basis of the Kanzaki's lattice statics method [17] to calculate the locally distorted ligand positions for the Eu^{2+} at the orthorhombic sites in various alkali halides. Yeung [18] applied the similar approach to a reliable set of ligand distances as calculated for the alkaline earth oxides to obtain sets of SPM intrinsic parameters ($R_0=2.0 \text{ \AA}$) for Mn^{2+} and Fe^{3+} doped MgO, CaO and SrO: $\bar{b}_2 = (-1552 \pm 48) \times 10^{-4} \text{ cm}^{-1}$ (for Fe^{3+}) and $(-6440 \pm 113) \times 10^{-4} \text{ cm}^{-1}$ (for Mn^{2+}) with fixed $t_2=16$ for both ions. $\bar{b}_4 = (9.9 \pm 0.8) \times 10^{-4} \text{ cm}^{-1}$ (for Fe^{3+} and Mn^{2+}) with fixed $t_4=(16 \pm 4)$ for both ions. For separate fitting of t_2 , the fitted values were 17.7 and 14.4 for Mn^{2+} and Fe^{3+} , respectively. Yeung and Newman [19] had successfully employed the superposition model to analyze the EPR parameters for the strain-induced ground state 4A_2 splitting of $Al_2O_3:Cr^{3+}$ and obtained reliable sets of intrinsic crystal field parameters.

In DHMS single crystal, the local symmetry around Cr^{3+} ion is tetragonal. In this symmetry, the ZFS parameter D can be written as follows [10]:

$$D = \frac{1}{2} \left[\epsilon \left(|E'(^4F \downarrow ^4A_{2g} \downarrow ^4B_1) \rangle \right) - \epsilon \left(|E''(^4F \downarrow ^4A_{2g} \downarrow ^4B_1) \rangle \right) \right] \quad (3)$$

Diagonalization of the full Hamiltonian matrices gives the energy levels and eigen vectors as functions of B_{kq} , B , C and ξ ; where B_{kq} are defined above, B and C are the Racah parameters describing electron–electron repulsion and ξ is the spin–orbit coupling parameter. 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 N can have value between zero and one. 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 [20–22] and spin–orbit coupling parameter as follows:

$$B = N^4 B_0, \quad C = N^4 C_0, \quad \xi = N^2 \xi_0 \quad (4)$$

where B_0 and C_0 are the Racah parameters in free state and ξ_0 is free state spin-orbit coupling parameter. For Cr^{3+} ion, $B_0=830 \text{ cm}^{-1}$, $C_0=3430 \text{ cm}^{-1}$ and $\xi_0=276 \text{ cm}^{-1}$ are used [21].

Using the values of Racah parameters ($B=676 \text{ cm}^{-1}$, $C=3371 \text{ cm}^{-1}$) evaluated from optical study, the average covalency parameter $N=0.972$ is obtained [10] from

$$N = \left[\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}} \right] / 2 \quad (5)$$

The SPM expresses the CF parameters [1,23] as follows:

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

where the co-ordination factor $K_{kq}(\theta_j, \varphi_j)$ is an explicit function of the angular position of the ligand [23]. The intrinsic parameter $\bar{A}_k(R_j)$ is given by the following equation:

$$\bar{A}_k(R_j) = \bar{A}_k(R_0) \left(\frac{R_0}{R_j} \right)^{t_k} \quad (7)$$

where R_j is the distance between the d^n ion and ligand, $\bar{A}_k(R_0)$ is the intrinsic parameter of the reference crystal, t_k is the power-law exponent and R_0 is reference distance between metal and ligand. According to SPM, for axial symmetry, the relation between the local structure parameters and CF parameters can be expressed as follows [10]:

$$B_{20} = -2\bar{A}_2 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_2} - 4A_2 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_2} \quad (8)$$

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