

Modeling of Mn²⁺ Doped YAP Single Crystals at Axial Symmetry Site

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Abstract: A theoretical investigation of crystal field parameters (CFP) and zero-field splitting (ZFS) parameter D of Mn²⁺ doped yttrium aluminium perovskite (YAP) single crystals is done employing superposition model and the perturbation theory. The ZFS parameter D determined here is in good match with the experimental value. The theoretical investigation supports the conclusion of experimental study that Mn²⁺ substitutes for Y³⁺ in YAP single crystal. The values of D without and with local distortion are $52 \times 10^{-4} \text{ cm}^{-1}$ and $77.5 \times 10^{-4} \text{ cm}^{-1}$, respectively. The experimental value reported earlier is $77.5 \times 10^{-4} \text{ cm}^{-1}$.

Keywords: A. Inorganic compounds; A. Single crystal; D. Crystal fields; D. Optical properties; D. Electron paramagnetic resonance.

1. Introduction

Electron paramagnetic resonance (EPR) studies provide structural distortions and local site symmetry of transition ions in various host systems [1-5]. With the help of microscopic spin-Hamiltonian (MSH) theory, the spin Hamiltonian (SH) parameters obtained from EPR are correlated with optical and structural parameters. Both the experimental and theoretical investigations suggest that the spin Hamiltonian parameters of transition ions (d^5) in crystals are very sensitive to local distortion. Thus, the SH theory is largely used in crystals.

The crystal-field (CF) parameters of d^5 ion may be determined employing superposition model (SPM) [6, 7]. The zero field splitting (ZFS) parameters are then determined using CF parameters [8]. Mn²⁺ ion of iron group is important due to its ground state being $^6S_{5/2}$ [9-12]. The electron spins have high order interaction with crystalline electric field and in external magnetic field show free orientation [13]. As S state ions have large spin-lattice relaxation time, Mn²⁺ provides well resolved EPR lines [12-14] at room temperature (RT).

EPR study of Mn²⁺ doped YAP single crystals has been done and spin Hamiltonian parameters determined [15]. The substitutional and interstitial site locations may be considered for Mn²⁺ ion in the YAP crystal. It was found [15] that Mn²⁺ ion enters the lattice of YAP substitutionally at Y³⁺ site. In the present investigation, the CF parameters are determined employing SPM and these parameters with MSH theory then give ZFS parameters for Mn²⁺ ions at the substitutional Y³⁺ site

in YAP single crystal at RT. The value of ZFS parameter D obtained with the help of SPM show reasonable matching with the experimental one [15].

2. Crystal Structure

The YAP single crystal has a perovskite-like orthorhombic structure with lattice parameters $a = 0.5330(2) \text{ nm}$, $b = 0.7375(2) \text{ nm}$, $c = 0.5180(2) \text{ nm}$; space group Pnma-D_{2h}^{16} [16]. The oxygen coordination around Y³⁺ is shown in Fig. 1. The site symmetry around Mn²⁺ ions may be considered as approximately axial, as suggested by EPR investigation of Mn²⁺: YAP [15].

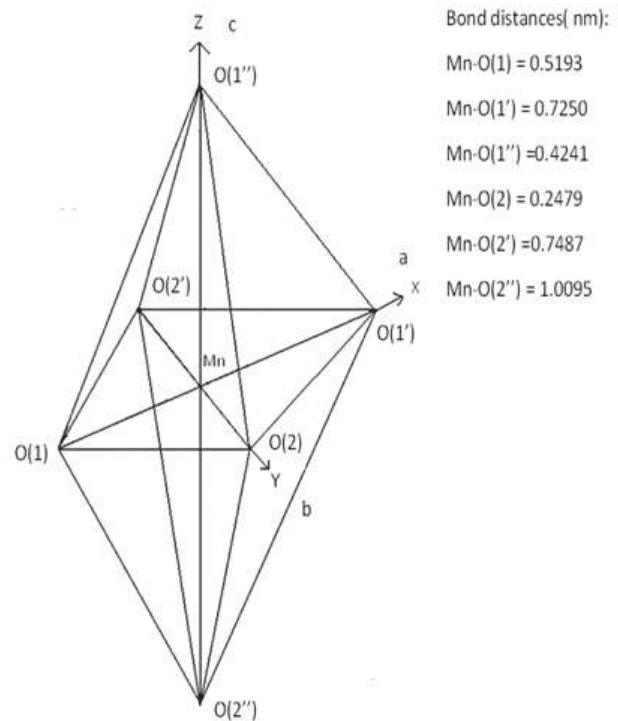


Fig. 1: Coordination around Mn²⁺ in YAP single crystal.

3. Theoretical Investigation

The Mn²⁺ ion in YAP single crystal substitutes at Y³⁺ site [15]. The SH of $3d^5$ ion in crystal field of axial symmetry is given as [17-19]

$$\mathcal{H} = g \mu_B B \cdot S + D(S_z^2 - S(S+1)) + \left(\frac{a}{6}\right)[S_x^4 + S_y^4 + S_z^4 - \frac{1}{5}S(S+1)(3S^2 + 3S - 1)]$$

$$+ \frac{F}{180} (35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2) + A(I.S) \tag{1}$$

where the first term gives electronic Zeeman interaction, B is the external magnetic field, g is the spectroscopic splitting factor and μ_B is Bohr magneton. The second, third, and fourth terms are the second order axial, fourth-rank cubic and fourth-rank axial ZFS terms [5]. The fifth term is the hyperfine interaction term. S, D, a, F are the effective spin vector, second order axial, fourth-rank cubic and fourth-rank axial ZFS parameters, respectively. An isotropic approximation for the electronic Zeeman interaction is used in case of Mn^{2+} ions [5, 20, 21].

The Hamiltonian for a d^5 ion is given as

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{cf} + \mathcal{H}_{so}$$

where $\mathcal{H}_{cf} = \sum_{kq} B_{kq} C_q^k$ (2)

represents the crystal field Hamiltonian. \mathcal{H}_0 and \mathcal{H}_{so} represent free ion Hamiltonian and spin-orbit (SO) coupling, respectively. Since the spin-spin coupling is very small [22-24], its contribution has been neglected in Eq. (2). The crystal field of SO interaction is considered as perturbation term [25, 26]. The strong-field scheme calculation for F-state ions was done by Macfarlane [27]. The SO contribution to the ZFS parameter D for $3d^5$ ions in axial symmetry is given by [30]

$$D^{(4)}(SO) = \left(\frac{\xi^2}{63F^2G} \right) [14B_{44}^2 - 5B_{40}^2] - \left(\frac{3\xi^2}{70F^2D} \right) B_{20} [B_{20} - 14\xi] \tag{3}$$

where $P = 7(B+C)$, $G = 10B+5C$ and $D = 17B+5C$. P, G, and D are the energy separations between the excited quartets and the ground sextet. Racah parameters B and C give the electron-electron repulsion. Only fourth order term is taken in Eq. (3) as other perturbation terms are negligible [28]. The parameters B, C and ξ , in terms of the average covalency parameter N, are given as, $B = N^4B_0$, $C = N^4C_0$ and $\xi = N^2\xi_0$, where B_0 and C_0 are the Racah parameters and ξ_0 , the spin-orbit coupling parameter, for free ion [29, 30]. $B_0 = 960 \text{ cm}^{-1}$, $C_0 = 3325 \text{ cm}^{-1}$, $\xi_0 = 336 \text{ cm}^{-1}$ [5] for Mn^{2+} ion are used in our calculation. Using equation

$$N = \left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}} \right) / 2, \tag{4}$$

N can be found.

By using SPM the CF parameters for Mn^{2+} in YAP single crystal are determined and then from Eq. (3) ZFS parameter D is obtained. Similar method has been employed for finding ZFS parameters by several earlier workers [31].

In order to explain the crystal-field splitting, the SPM is effectively applied. This model has also been used for $3d^n$ ions [6, 28, 32]. The crystal field parameters, using this model, are found from the equations [33]

$$B_{20} = -2\bar{A}_2 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_2} - 4\bar{A}_2 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_2} \tag{5}$$

$$B_{40} = 16\bar{A}_4 \left(\frac{R_0}{R_{10} + \Delta R_1} \right)^{t_4} + 12\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4} \tag{6}$$

$$B_{44} = 2\sqrt{70}\bar{A}_4 \left(\frac{R_0}{R_{20} + \Delta R_2} \right)^{t_4} \tag{7}$$

In which R_0 is the reference distance, generally taken as the average value of all four bond lengths (for axial symmetry).

4. Results and Discussion

The average of two out of four Mn^{2+} -O bond lengths are found as $R_{10} = 0.6340 \text{ nm}$ and the average value of the rest two bond lengths are obtained as $R_{20} = 0.4865 \text{ nm}$.

ΔR_1 and ΔR_2 give the distortion parameters. \bar{A}_2 , \bar{A}_4 and t_k represent the intrinsic parameter and power law exponent, respectively. In octahedral coordination,

$$\bar{A}_4(R_0) = (3/4)Dq \tag{8}$$

For $3d^5$ ions, the ratio $\frac{\bar{A}_2}{\bar{A}_4}$

lies in the range 8-12 [28, 32]. The power law exponent for Mn^{2+} ion is taken as $t_2 = 3$, $t_4 = 7$. Semi-ab initio calculations are done for other transition metal ions to obtain the intrinsic parameter values in SPM,

The values of B, C and Dq are determined using optical study [34] as 917 , 2254 and 756 cm^{-1} , respectively. First no local distortion is considered and the value of

D is estimated. For this, taking $\frac{\bar{A}_2}{\bar{A}_4} = 10$ and $R_0 = 0.220$

nm, which is less than the sum of ionic radii of $Mn^{2+} = 0.080 \text{ nm}$ and $O^{2-} = 0.140 \text{ nm}$, the B_{kq} parameters are obtained as: $B_{20} = -2570.76 \text{ cm}^{-1}$, $B_{40} = 31.79683 \text{ cm}^{-1}$,

$B_{44} = 36.68096 \text{ cm}^{-1}$ and the value of D as: $D = 52 \times 10^{-4} \text{ cm}^{-1}$. EPR study provides the experimental value of D as: $D = 77.5 \times 10^{-4} \text{ cm}^{-1}$ [15]. From above it is found that the theoretical value is less than the experimental one.

Now, taking local distortions as $\Delta R_1 = 0.0478 \text{ nm}$ and $\Delta R_2 = 0.0310 \text{ nm}$, $R_0 = 0.220 \text{ nm}$ and ratio $\frac{A_2}{A_4} = 10$, the

B_{kq} parameters are obtained as: $B_{20} = -3410.49 \text{ cm}^{-1}$, $B_{40} = 62.05459 \text{ cm}^{-1}$, $B_{44} = 75.65475 \text{ cm}^{-1}$ and the value of D as: $D = 77.5 \times 10^{-4} \text{ cm}^{-1}$, in good match with the experimental one: $D = 77.5 \times 10^{-4} \text{ cm}^{-1}$.

5. Conclusions

Axial symmetry zero-field splitting parameter D for Mn^{2+} in YAP single crystal has been obtained using superposition model and perturbation theory. The theoretical D is in good match with the experimental one when distortion is taken into account. This investigation indicates that Mn^{2+} ion occupies substitutional Y^{3+} site supporting the inference drawn from the experimental EPR study.

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