

Zero Field Splitting Study of Cr³⁺ Doped Nickel Maleate Tetrahydrate

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Abstract: The superposition model is used to determine the zero field splitting parameters (ZFSPs) D and E of Cr³⁺ ion doped nickel maleate tetrahydrate (NiMTH), Ni (C₄H₃O₄)₂.4H₂O. The comparison of these ZFSPs with the experimental values from electron paramagnetic resonance (EPR) shows good agreement between them. The energy band positions of optical absorption spectra of Cr³⁺ in NiMTH single crystal computed with CFA package are similar to the experimental band positions, though only two experimental bands are reported.

Keywords: A. Organic compounds; B. Crystal growth; D. Crystal fields; D. Electron paramagnetic resonance, D. Optical properties.

I. INTRODUCTION

The information about the local site symmetry and zero field splitting (ZFS) parameters of metal ions in crystals is successfully provided by Electron paramagnetic resonance (EPR) [1-3]. This technique also gives information about the charge compensation in the transition ion doped crystals [4]. Further, ordering of the energy levels and crystal field parameters are obtained by the optical absorption study [5]. The nature of bonding in various crystals is also obtained by EPR study [6]. The electronic configuration of Cr³⁺ is 3d³ and ground state, ⁴A₂ [7].

EPR of Cr³⁺ ion doped in nickel maleate tetrahydrate (NiMTH), Ni (C₄H₃O₄)₂.4H₂O crystal at room temperature has been done earlier [8]. Cr³⁺ ion can enter the crystal of NiMTH by substituting at Ni²⁺ ion site, or it can sit at any structural vacancy site. This is quite interesting to find the site of this paramagnetic impurity. In the present study, the superposition model (SPM) is used to obtain zero field splitting parameters (ZFSPs) for Cr³⁺ ion in NiMTH. The result obtained for Cr³⁺ ion to be at the site of Ni²⁺ ion is in agreement with the experiment.

II. MATERIALS AND METHODS

NiMTH single crystals are triclinic [9] with the space group $P\bar{1}$ and contain one molecule in the unit cell. The unit cell parameters are $a = 7.309(3) \text{ \AA}$, $b = 9.134(2) \text{ \AA}$, $c = 5.170(2) \text{ \AA}$; $\alpha = 104.65(3)^\circ$, $\beta = 92.88(3)^\circ$ and $\gamma = 108.40(2)^\circ$. The Nickel atom has six coordination with oxygen atoms, the two oxygen atoms are from water molecules and other four oxygen atoms from hydrogen maleate ion, as shown in Fig.1. The metal coordination can be described as a distorted octahedron. The Cr³⁺ ion site symmetry is approximately orthorhombic.

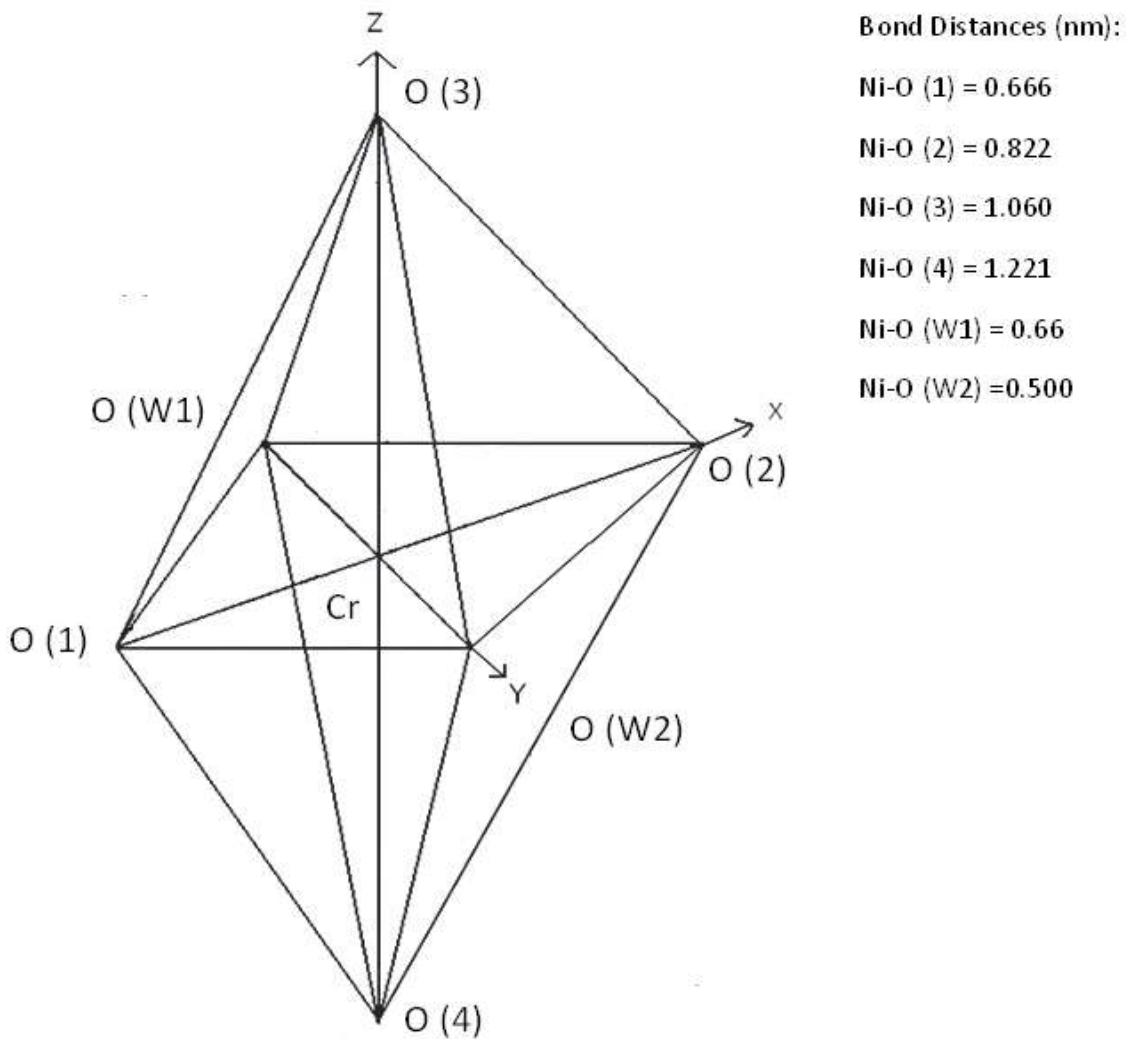


Fig1. Crystal structure of NiMTH with symmetry adopted axis system (SAAS).

EPR spectra of Cr³⁺ doped NiMTH single crystals have been analyzed with the help of spin Hamiltonian of orthorhombic symmetry. The ground state of Cr³⁺ ion doped crystal can be described with the spin Hamiltonian [10, 11],

$$\mathcal{H} = \mathcal{H}_{ZE} + \mathcal{H}_{ZFS} = \mu_B B \cdot g \cdot S + \sum B_k^q O_k^q = \mu_B B \cdot g \cdot S + \sum f_k b_k^q O_k^q \quad (1)$$

in which *g* is the spectroscopic splitting factor, μ_B is the Bohr magneton, *B* is the applied magnetic field and *S* is the effective spin operator. B_k^q as well as b_k^q are ZFSPs in extended Stevens operators O_k^q notation. The $f_k = 1/3$ and $1/60$ represent the scaling factors for $k = 2$ and 4 , respectively. The ZFS terms in Eq. (1) for Cr³⁺ ion ($S = 3/2$) at orthorhombic symmetry sites are expressed as

$$\mathcal{H} = B_2^0 O_2^0 + B_2^2 O_2^2 = \frac{1}{3} b_2^0 O_2^0 + \frac{1}{3} b_2^2 O_2^2 = D(S_z^2 - \frac{1}{3} S(S+1)) + E(S_x^2 - S_y^2) \quad (2)$$

The ZFSPs in Eq. (2) are obtained using SPM [12, 13]. The exchange charge model (ECM) is also a reliable technique for analysis of the crystal field (CF) effects in rare-earth and transition metal ion doped crystals [14]. In the present investigation, however, the CF parameters B_{kq} are calculated using SPM. Newman [15] proposed SPM for CF, in which a pre-requisite condition is to have a reliable set of polar coordinates (R_L, θ_L, Φ_L) for all the ligands in the crystal as obtained from the X-ray data. If transition metal ions are doped as impurities, they will probably introduce some local distortion due to the mismatch in the ionic charge and ionic size. Newman & Siegel [16] critically analyzed the experimental spin-Hamiltonian parameters for Mn²⁺ and Fe³⁺ doped crystals and verified that the CF for 3d ions satisfies the superposition principle and gives explicit values of the SPM parameters for the EPR data. Yeung & Newman [17] developed a rigorous lattice relaxation model [18] to find the locally distorted ligand positions for the Eu²⁺ at the orthorhombic symmetry sites in various alkali halide crystals. Yeung [19] applied a similar approach to find sets of SPM intrinsic parameters for Mn²⁺ and Fe³⁺ doped MgO, CaO and SrO. Yeung & Newman [20] successfully used the superposition model to strain-induced ground state ⁴A₂ splitting of Al₂O₃: Cr³⁺.

The conventional ZFSPs *D* and *E* for 3d³ ion at orthorhombic symmetry site can be obtained [21-24] as

$$D = b_2^0 = \frac{b_2(\bar{R}_0)}{2} \left[\left(\frac{R_0}{R_i} \right)^{t_2} \sum_i (3 \cos^2 \theta_i - 1) \right] \quad (3)$$

$$E = \frac{b_2^2}{3} = \frac{b_2(\bar{R}_0)}{2} \left[\left(\frac{R_0}{R_i} \right)^{t_2} \sum_i \sin^2 \theta_i \cos 2\phi_i \right] \quad (4)$$

For Cr^{3+} ($3d^3$, $S = 3/2$) ions the CFPs exist for the rank $k = 2$ and 4, whereas the ZFSPs for $k = 2$ only.

III. RESULTS AND DISCUSSION

Cr^{3+} ion in NiMTH can be considered to enter the lattice at two sites, namely, the Ni^{2+} ion site, and the structural vacancy site having similar ligand arrangement. The local symmetry at Cr^{3+} ion site is approximately orthorhombic. In octahedral

coordination of Cr^{3+} ion for LiNbO_3 having $\text{Cr}^{3+}\text{-O}^{2-}$ bond, $\bar{b}_2(\bar{R}_0) = 2.34 \text{ cm}^{-1}$ and $t_2 = -0.12$ [25] have been used to calculate

b_2^0 and b_2^2 . Since Cr^{3+} ion in NiMTH has distorted octahedral coordination (Fig.1) with oxygen ligands, the parameters $\bar{b}_2(\bar{R}_0) = 2.34 \text{ cm}^{-1}$ and $t_2 = -0.96$ are used for calculating b_k^q in the present study. The value of t_2 different from -0.12 has also been used by other workers [24].

The location of metal ion and spherical coordinates of ligands are given in Table 1. The conventional ZFSPs, D and E of Cr^{3+} ion

Table 1. Fractional coordinates of Cr^{3+} ion and spherical co-ordinates (R, θ, ϕ) of ligands in NiMTH single crystal.

Position of Cr^{3+}	Ligands	Spherical co-ordinates of ligands		
		$R^{\text{\AA}}$	θ°	ϕ°
ND: Substitutional (0, 0, 0)	O(1)	2.0616	69.4	76.7
	O(2)	3.3347	108.3	59.9
	O(3)	5.7968	107.6	61.2
	O(4)	7.4630	97.5	66.4
	O(W1)	2.0078	144.0	-42.5
	O(W2)	2.1407	52.2	20.5
WD: substitutional (0, 0, 0)	O(1)	2.0873	89.1	86.3
	O(2)	3.5924	118.9	65.5
	O(3)	6.0265	114.0	64.4
	O(4)	7.6228	102.6	68.9
	O(W1)	2.7584	147.1	-42.4
	O(W2)	2.1438	73.1	11.0

ND = No distortion, WD = With distortion.

in NiMTH crystal are evaluated using Eqs. (3) and (4). The reference distance of 0.130 nm (approximately the sum of ionic radii of Ni^{2+} , 0.069 nm and Cr^{3+} , 0.063 nm [24]) was taken for the evaluation of ZFSPs [22], and the obtained values of conventional ZFSPs are $D = -1072 \times 10^{-4} \text{ cm}^{-1}$ and $E = -167 \times 10^{-4} \text{ cm}^{-1}$. The ratio b_2^2/b_2^0 should lie within the range (0, 1) for orthorhombic symmetry [26]. In this work, the ratio $b_2^2/b_2^0 = 0.468$ and $E/D = 0.156$, which is in agreement with above. But the values of D and E are differ much from the experimental values. Therefore, using above values of t_2 and reference distance, the conventional ZFSPs D and E are calculated for Cr^{3+} at the Ni^{2+} site with distortion having position Ni^{2+} (-0.0410, 0.0300, 0.1337). The calculated conventional ZFSPs now are $D = 954 \times 10^{-4} \text{ cm}^{-1}$, $E = 178 \times 10^{-4} \text{ cm}^{-1}$, which are in reasonable agreement with the experimental values. The ratio $b_2^2/b_2^0 = 0.558$ and $E/D = 0.186$ which is consistent with given range [26]. Further, using above values of t_2 and reference distance, the conventional ZFSPs D and E are determined for Cr^{3+} at the structural vacancy site but the values obtained are quite different from the experimental ones. Therefore, these data have not been provided here.

The calculated and experimental ZFSPs for Cr^{3+} ion are given in Table 2. From Table 2, it is noted that the conventional ZFSPs are in reasonable agreement with the experimental ones [8] when distortion is taken into account.

Table 2. Calculated and experimental ZFSPs of Cr³⁺ doped NiMTH single crystal and reference distance.

	Calculated ZFS parameters (cm ⁻¹)				Conventional ZFS parameters (×10 ⁻⁴ cm ⁻¹)		
	R ₀ ^Å	b ₂ ⁰	b ₂ ²	b ₂ ² / b ₂ ⁰	D	E	E/D
ND	1.30	-0.1072	-0.0502	0.468	-1072	-167	0.186
					-954 ^e	-288 ^e	0.302
WD	1.30	-0.0954	-0.0534	0.559	-954	-178	0.186
					-954 ^e	-288 ^e	0.302

ND = No distortion, WD = With distortion, Ni²⁺ (-0.0410, 0.0300, 0.1337)

^e = experimental.

The CFPs for Cr³⁺ in crystals can be obtained by the following SPM formula [27]

$$B_{kq} = \sum_i \bar{B}_k \left(\frac{R_0}{R_i} \right)^{t_k} K_{kq}(\theta_i, \phi_i) \tag{5}$$

where R₀ = 1.30 Å is the reference distance for the site; R_i, θ_i, φ_i are the polar coordinates of the ith ligand and K_{kq} represent the coordination factors [20]. To compute B_{kq} (k = 2, 4; q = 0, 2, 4), we take $\bar{B}_2 = 40, 400 \text{ cm}^{-1}$, t₂ = 1.3, $\bar{B}_4 = 11, 700 \text{ cm}^{-1}$ and t₄ = 3.4 from [20]. The obtained B_{kq} parameters are given in Table 3. The ratio B₂₂/B₂₀ = 0.289, which indicates that B_{kq} parameters

Table 3. B_{kq} parameters of Cr³⁺ doped NiMTH single crystal.

	R ₀ ^Å	Calculated B _{kq} ^{cm-1} Parameters used for CFA package					B ₂₂ /B ₂₀
		B ₂₀	B ₂₂	B ₄₀	B ₄₂	B ₄₄	
WD	1.30	-15048.1	-4348.18	882.3335	3880.517	-27005.2	0.289

WD = With distortion.

are standardized [26]. Using these B_{kq} parameters and CFA program [28, 29], the optical spectra of Cr³⁺ doped NiMTH crystals are calculated. The energy levels of Cr³⁺ ion are determined by diagonalizing the complete Hamiltonian within the 3d^N basis of states in the intermediate crystal field. The complete Hamiltonian includes the Coulomb interaction (in terms of the Racah parameters B and C), Trees correction, the spin-orbit interaction, the crystal field Hamiltonian, the spin-spin interaction and the spin-other orbit interaction. The calculated energy values are shown in Table 4. The experimental energy values are also given here, though only two band positions have been observed experimentally. From Table 4, it is found that there is good agreement between theoretical and experimental band position values. Thus the theoretical investigation carried out for Cr³⁺ at Ni²⁺ site supports the experimental observation [5].

Table 4. Experimental and calculated (CFA package) energy band positions of Cr³⁺ doped NiMTH single crystal.

Transition from ${}^4A_{2g}(F)$	Experimentally observed band (cm ⁻¹) [8]	Calculated energy band from CFA (cm ⁻¹)
${}^2E_g(G)$		12878, 12995
${}^2T_{1g}(G)$		14456, 15049, 16236
${}^4T_{2g}(F)$	17725	17736, 17745, 19192, 20172, 20220, 21386
${}^4T_{1g}(F)$	24505	23709, 24424, 24503, 27241, 27931, 28783
${}^2T_{1g}(aD)$ ${}^2E_g(bD)$		37287, 37774, 38229 42091, 42733

(Racah parameters A , B and C , spin-orbit coupling constant and Trees correction are 0, 668, 2672 (= 4B), 276 and 70 cm⁻¹, respectively)

IV. CONCLUSIONS

The theoretical study of ZFSPs has been done using superposition model. The calculated conventional ZFSPs for Cr³⁺ ion doped NiMTH crystal show reasonable agreement with the experimental values. It is concluded that the Cr³⁺ ions enter the lattice substitutionally by replacing Ni²⁺. For the charge compensation, they are electrically bound to neighboring vacancies. Thus the theoretical results obtained support the conclusion drawn from the experimental study.

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