

Theoretical Zero Field Splitting Parameters of Cr³⁺ doped Dipotassium Tetrachloropalladate

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ABSTRACT

Zero field splitting parameters (ZFSPs) *D* and *E* of Cr³⁺ ion doped dipotassium tetrachloropalladate (DTP) crystal are calculated using the superposition model. The calculated ZFSPs for Cr³⁺ in DTP crystal are compared with the experimental ones obtained by electron paramagnetic resonance (EPR). Theoretical ZFSPs are in reasonable agreement with the experimental values. The energy band positions of optical absorption spectra of Cr³⁺ in DTP crystal computed with CFA package are in good match with the experimental results.

KEYWORDS: A. Inorganic compounds; D. Crystal fields; D. Electron paramagnetic resonance, D. Optical properties.

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I. INTRODUCTION

Electron paramagnetic resonance (EPR) provides information about the local site symmetry and zero field splitting parameters (ZFSPs) of transition ions in crystals [1]. It also helps to identify the defects responsible for the charge compensation in the impurity ions doped crystals [2]. EPR technique is a very important tool for the study of dynamical aspects of the crystalline state and bonding in crystals [3]. The optical absorption study gives the energy levels and crystal field parameters. Cr³⁺ is one of the most studied transition metal ions. Its electronic configuration is 3d³ and ground state ⁴A₂ [4]. In the mostly used perturbation procedure, cubic field and diagonal parts of free ion Hamiltonian are treated as unperturbed Hamiltonian, while the spin-orbit coupling, the low symmetry field, and off diagonal part of free ion Hamiltonian as the perturbation. This procedure was used by Macfarlane for F state ions giving better results [5].

EPR of Cr³⁺ doped impurity in dipotassium tetrachloropalladate (DTP) crystal at liquid nitrogen temperature has been reported earlier [6]. There are two possibilities of Cr³⁺ ion entering the crystal of DTP; substitution at K⁺ ion site and/or structural vacancy. This is interesting to determine the site of this paramagnetic impurity. In the present investigation, the ZFSPs for Cr³⁺ ion are calculated using superposition model (SPM) considering Cr³⁺ ion to be present at the site of K⁺ ion. The result obtained is consistent with the experimental observation.

II. CRYSTAL STRUCTURE

DTP single crystals are tetragonal [7]. These belong to the space group P4/mmm and contain one molecule in the unit cell (Z = 1). The unit cell parameters are: a = 7.0259(2), c = 4.0797(2) Å. The Pd - Cl bond length is 2.3066(2) Å. Above and below the [PdCl₄]²⁻ plane, excess densities of 2.3(3)e Å⁻³ are found at 0.47 Å from the Pd nucleus which indicates an enhancement of the d_{z²} orbital population. The potassium ion is six coordinated by chlorine atoms as shown in Fig.1. The site symmetry at Cr³⁺ ion is approximately orthorhombic.

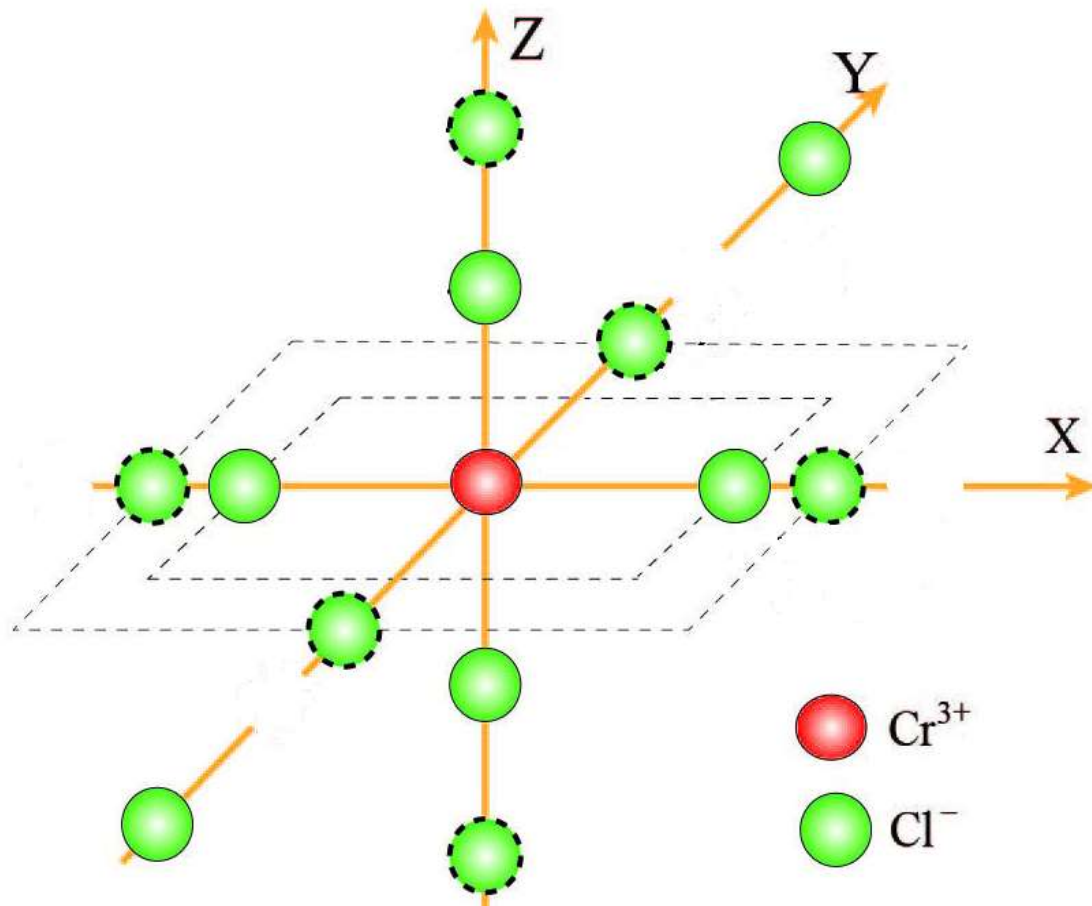


Fig. 1. Local structure of Cr^{3+} centre on K^+ site in DTP where symmetry adopted axis system (SAAS) is shown.

III. THEORETICAL INVESTIGATIONS

EPR spectra of Cr^{3+} doped single crystals of DTP were analyzed using the spin Hamiltonian in a crystal field of orthorhombic symmetry. The ground state of transition ion in crystals can be described using the spin Hamiltonian having Zeeman electronic (Ze) and ZFS terms [8, 9].

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

where g is the spectroscopic splitting factor, μ_B is the Bohr magneton, \mathbf{B} is the applied magnetic field, \mathbf{S} is the effective spin operator, B_k^q and b_k^q are zero field splitting parameters (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. The ZFS terms in Eq. (1) for Cr^{3+} 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) and conventional zero field splitting parameters D and E are obtained using SPM as [10-14]:

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

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

For Cr³⁺ (3d³, S = 3/2) ions, there exist crystal field parameters (CFPs) of the rank k = 2 and 4, while ZFSPs only of the rank k = 2.

IV. RESULT AND DISCUSSION

The Cr³⁺ ion substitutes the K⁺ ion in DTP and has similar ligands environment. From crystal structure the local symmetry around Cr³⁺ ion is C₁, for which the 14 CF parameters B_{kq} are admitted by group theory. As some of CF parameters in C₁ symmetry are very small [15], the calculations are done on the approximation of orthorhombic symmetry and 5 appreciable CF parameters are determined. For octahedral coordination of Cr³⁺ ion in LiNbO₃ having Cr³⁺ - O²⁻ bond, t₂ = - 0.12 and $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$ [13] were used for calculating b₂⁰ and b₂². Here for chlorine ligands in octahedral coordination with Cr³⁺, t₂ = 0.92 and $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$ are used for calculating b₂⁰ and b₂² to have results similar to the experimental ones.

The position of Cr³⁺ ion and spherical coordinates of ligands are given in Table 1. The conventional ZFSPs D and E of Cr³⁺ ion in DTP crystal are determined using Eqs. (3) and (4). The reference distance of 2.00Å is taken for the evaluation of ZFSPs [11], and the calculated conventional ZFSPs are D = -89 ×10⁻⁴ cm⁻¹, E = 45×10⁻⁴ cm⁻¹. For orthorhombic symmetry, the ratio b₂² / b₂⁰ should be within the range (0, 1) [16]. In the present study, the ratio b₂² / b₂⁰ = -1.517 and E/D = -0.506 which is not consistent with above. The calculated ZFSPs, and experimental ZFSPs for Cr³⁺ ion are given in Table 2. The theoretical ZFSPs thus obtained are not in agreement with the experimental values [6]. Therefore, using above values of t₂ and reference distance, the conventional ZFSPs D and E are calculated for Cr³⁺ at the K⁺ site with distortion with position K⁺(-0.1300, -0.0010, -0.4400). The calculated conventional ZFSPs now are D = 89 ×10⁻⁴ cm⁻¹, E = 19×10⁻⁴ cm⁻¹, which are in good agreement with the experimental ones. The ratio b₂² / b₂⁰ = 0.638 and E/D = 0.213 which is consistent with above range [16]. Further, using above values of t₂ and reference distance, the conventional ZFSPs D and E are determined for Cr³⁺ at the structural vacancy site but the values obtained are quite different from the experimental ones. To save the space, these data are not being provided here.

Table 1. Coordinates of Cr³⁺ ion together with spherical co-ordinates (R, θ, φ) of ligands in DTP single crystal.

Position of Cr ³⁺	Ligands	Spherical co-ordinates of ligands		
		R ^Å	θ ⁰	φ ⁰
ND: Substitutional (0, 0, 0)	Cl(1)	3.2191	129.3	-49.1
	Cl(2)	5.7686	110.7	72.4
	Cl(3)	4.0622	120.1	0.0
	Cl(4)	8.1157	104.5	63.4
	Cl(5)	3.5129	90.0	0.0
	Cl(6)	8.8514	117.4	63.4
WD: substitutional (0, 0, 0)	Cl(1)	3.5180	59.3	32.7
	Cl(2)	2.5245	135.3	66.2
	Cl(3)	5.9334	72.4	38.5
	Cl(4)	4.7192	112.4	53.4
	Cl(5)	5.9334	72.4	38.5
	Cl(1)	4.7192	112.4	53.4

ND = No distortion, WD = With distortion.

Table 2. Calculated and conventional zero field splitting parameters together with reference distance and experimental ZFSPs for Cr³⁺ doped DTP single crystal.

	$R_0^{\text{\AA}}$	Calculated ZFS parameters (cm ⁻¹)			Conventional ZFS parameters ($\times 10^4$ cm ⁻¹)		
		b_2^0	b_2^2	b_2^2/b_2^0	D	E	E/D
ND	2.00	-0.0089	0.0135	-1.517	-89	45	-0.506
					89 ^e	19 ^e	0.213
WD	2.00	-0.0089	-0.0057	0.638	89	19	0.213
					89 ^e	19 ^e	0.213

ND = No distortion, WD = With distortion, K⁺(-0.1300, -0.0010, -0.4400)

^e = experimental.

The CFPs for Cr³⁺ in crystals can be obtained by the following formula [15]

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

where $R_0 = 2.00 \text{ \AA}$ (reference distance); R_i, θ_i, ϕ_i are the polar coordinates of the i^{th} ligand and K_{kq} is the coordination factor [2]. For obtaining B_{kq} ($k = 2, 4; q = 0, 2, 4$), $\bar{B}_2 = 40, 400 \text{ cm}^{-1}$, $t_2 = 1.3$, $\bar{B}_4 = 11, 700 \text{ cm}^{-1}$ and $t_4 = 3.4$ are taken from [2]. The calculated B_{kq} parameters are presented in Table 3. Employing these B_{kq} parameters and CFA program [17-18], the optical spectra of Cr³⁺ doped DTP crystals are calculated. The energy levels of the Cr³⁺ ion are determined by diagonalizing the complete Hamiltonian within the $3d^N$ basis of states in the intermediate crystal field coupling scheme. The calculated energy values are shown in Table 4 together with the experimental values [6] for comparison. There is good agreement between these two. Thus the theoretical study supports the experimental investigation [6].

Table 3. B_{kq} parameters to be used in CFA program for calculating optical absorption spectra.

	$R_0^{\text{\AA}}$	Calculated $B_{kq}^{\text{cm}^{-1}}$ Parameters used for CFA package					
		B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	B_{22}/B_{20}
WD	2.00	-29237.0	-3129.67	-391.279	-119.151	-6034.04	0..107

WD = With distortion.

Table 4. Observed and calculated energy band positions of Cr³⁺ doped DTP single crystal from CFA package.

Transition from ⁴ A _{2g} (F)	Experimentally observed band (cm ⁻¹) [6]	Calculated energy band from CFA (cm ⁻¹)
² E _g (G)	12121, 12578	11750, 12469
² T _{1g} (G)	15151, 15723, 17094	15906, 16435, 17361
⁴ T _{2g} (F)	18115, 18518, 20618	18877, 19182, 19261, 19870, 21566, 21624
⁴ T _{1g} (F)	24096	23827, 25096, 25228, 26138, 26737, 26992
² T _{1g} (aD)	40000	37753, 39729, 41676
² E _g (bD)	47619	44141, 50872

Input parameters: Numbers of free ion parameters = 5, number of d shell electrons = 3, number of fold for rotational site symmetry = 1; Racah parameters in A, B and C, spin-orbit coupling constant and Trees correction are 0, 521, 2861, 276 and 70 cm⁻¹, respectively; number of crystal field parameters = 5; crystal field parameters B₂₀ = -29237.0, B₂₂ = -3129.67, B₄₀ = -391.67, B₄₂ = -119.151, B₄₄ = -6034.04 cm⁻¹; spin-spin interaction parameter, M0 = 0.0000; spin-spin interaction parameter, M2 = 0.2021; spin-other-orbit interaction parameter, M00 = 0.0159; spin-other-orbit interaction parameter, M22 = 0.2021; magnetic field, B = 0.0 Gauss; angle between magnetic field B and z-axis = 0.00 degree.

V. CONCLUSIONS:

The theoretical study of ZFSPs has been done using superposition model. The conventional ZFSPs for the Cr³⁺ ion doped DTP are similar to the experimental values. The calculated optical spectra energy values using CFPs and CFA program are in agreement with the experimental ones. The Cr³⁺ ions are concluded to enter the lattice substitutionally by replacing K⁺ site and are electrically bound to neighboring vacancies necessary for the charge compensation. Thus our results support the conclusion obtained from the experimental data.

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