

Modeling of Cr³⁺ doped VO₂ Single Crystal

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Abstract

Crystal field parameters (CFPs) and zero field splitting parameters (ZFSPs) of Cr³⁺ doped VO₂ single crystal are obtained employing superposition model (SPM). The possible substitutional and interstitial sites for Cr³⁺ ion in VO₂ together with distortion are considered for computation. The obtained ZFSPs are in reasonable agreement with the experimental values when distortion is taken into consideration. The optical energy band positions for Cr³⁺ in VO₂ are calculated using CFPs determined from SPM and CFA package. The results indicate that Cr³⁺ ions substitute VO₂ lattice at V⁴⁺ sites.

Keywords: Superposition model; Crystal field; zero-field splitting; Optical spectroscopy; Cr³⁺ ions in VO₂.

Date of Submission: 15-06-2022

Date of acceptance: 30-06-2022

I. Introduction

Electron paramagnetic resonance (EPR) technique provides local site symmetry and zero field splitting (ZFS) of transition ions incorporated in crystals [1, 2]. Since the crystal fields have important role in spin-orbit mechanism, the superposition model (SPM) is employed to find the crystal field (CF) parameters (CFPs) and zero field splitting parameters (ZFSPs) [3-5].

VO₂ crystal undergoes a single phase transition at 68°C between a high temperature metallic phase having a rutile structure, and a low temperature insulating phase having a distorted rutile structure of monoclinic symmetry (M1). In V_{1-x}Cr_xO₂ (x > 0.5%), however, three structurally distinct insulating phases, having different distortions from the rutile structure, are observed as the temperature is reduced [6, 7]. To know the lattice position and ionic state chromium is incorporated in VO₂ crystal, the Electron Paramagnetic Resonance (EPR) study was done on crystals with chromium concentrations (x < 0.3%) so that the crystal structure is that of monoclinic VO₂ (M1) [8].

Two chromium spectra corresponding to two centers A and B were reported at high frequency and helium temperatures [8]. The three $\Delta m = 1$ transitions characteristic of a Cr³⁺ ion (S = 3/2) are observed. The relative intensity of the center B spectrum with respect to that of center A decreases with increasing Cr concentration x, and is about 10% for x = 0.1%. For center A, the charge unbalance due to the substitution of a Cr³⁺ ion in place of a V⁴⁺ ion is compensated by ionization of the nearest neighbour V⁴⁺ into V⁵⁺. This produces an axial perturbation along the [001] axis, responsible for the z axis to be in this direction. Center B is observed in crystals of lower concentrations and the degree of stoichiometry is of the order of the Cr concentration (x < 0.1%). This center corresponds to charge compensation by associated stoichiometry defects. Thus the perturbation produced by the associated defect is axial along [110]. It is supported by the similarity of center B to Cr³⁺ in TiO₂ and SnO₂ [9, 10]. The z axis of center A is close to [001], whereas that of center B is close to [110]. Center A corresponds to the Cr³⁺ ions occupying vanadium positions at the centers of the unit cells, while the other center B to the vanadium positions at the corners of the unit cells [11]. The spin-Hamiltonian parameters (g, D, and E) were determined for both the centers A and B [8].

The present paper discusses the superposition model (SPM) investigation of the crystal field parameters (CFPs) and the zero field splitting parameters (ZFSPs) for Cr³⁺ ions incorporated in VO₂. The aim is to find the ZFSPs for Cr³⁺ ions at all possible substitutional and interstitial sites, to find the CFPs for Cr³⁺ ions and to understand the structural distortion about the Cr³⁺ ions at different sites. The optical energy band positions for Cr³⁺ in VO₂ are obtained using CFPs and CFA package. The determined CFPs and ZFSPs may be useful in future investigations for technological applications of such crystals.

II. Crystal structure

The low-temperature phase of VO₂ is monoclinic structure with a = 0.5743 nm, b = 0.4517 nm, c = 0.5375 nm, $\beta = 122.61^\circ$, Z = 4, space group C_{2h}⁵ [12]. The distinguished feature of the monoclinic (M1) phase is the presence of V⁴⁺-V⁴⁺ pairs, pointing in a direction close to the symmetry axis. The separation of adjacent vanadium ions lies in the range 2.65 Å-3.12 Å. The insulating phase has a distorted rutile structure. Though there are four vanadium ions per unit cell, because of a center of symmetry, there are only two magnetically

inequivalent sites as in the rutile structure. The crystal structure of VO₂ with symmetry adopted axis system (SAAS) is shown in Fig.1.

The laboratory axes (x, y, z) are parallel to the modified crystallographic axes a, b, c*. The local site symmetry axes, i. e. the symmetry adopted axes (SAA) are the mutually normal directions of metal-ligand bonds. The Z-axis of SAAS is along the crystal c*-axis and the other two axes (X, Y) lie in the ab plane (Fig.1). The Z axis of SAAS for center A is along the metal-ligand bond V-O (III) and the two other axes (X, Y) are normal to the Z axes for all the sites (Fig. 1). The Z axis of SAAS for center B is along the metal-ligand bond V-O (corner) and the two other axes (X, Y) are perpendicular to the Z axis (Fig. 1). This shows that Cr³⁺ substitutes for V⁴⁺ in the crystal lattice of VO₂ with approximately orthorhombic symmetry. The ionic radius of Cr³⁺ ion 0.061 nm [13] is slightly larger than the ionic radius of V⁴⁺ (0.058 nm), this means that Cr³⁺ ion can go at the place of V⁴⁺ with some distortion.

The crystal structure data in spherical polar coordinates for the Cr³⁺ ions in VO₂ on the basis of fractional positions of ligands [12] are shown in Table 1A and 1B for centers A and B. These data are used for SPM/ZFS and SPM/CF computations for VO₂: Cr³⁺.

III. SPM calculations of ZFSPs

The energy levels of transition ions incorporated in crystals are obtained by the spin Hamiltonian having electronic Zeeman (Ze) and ZFS terms [14, 15, 16]:

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

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 and $O_k^q(S_x, S_y, S_z)$ represent the extended Stevens operators (ESO) [17, 18]. B_k^q and b_k^q give the related ZFSPs, $f_k = 1/3$ and $1/60$ are the scaling factors for $k = 2$ and 4 , respectively. The ZFS terms in (1) for Cr³⁺ ion with $S = 3/2$ at orthorhombic symmetry sites can be found as [19, 20, 21]:

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

The conventional orthorhombic ZFSPs (D, E) and (B_k^q, b_k^q) have relations as:

$$b_2^0 = D = 3 B_2^0, \quad b_2^2 = 3 B_2^2. \quad (3)$$

Employing SPM [19-21], the ZFSPs for a ML_n complex can be obtained (in ESO notation) for any symmetry as:

$$b_k^q = \sum_i \bar{b}_k(R_0) \left(\frac{R_0}{R_i} \right)^{t_k} K_k^q(\theta_i, \varphi_i), \quad (4)$$

where (R_i, θ_i, φ_i) are the spherical polar coordinates of the i -th ligand. The intrinsic parameters \bar{b}_k provide the strength of the k -th rank ZFS contribution from a ligand positioned at the distance R_i , whereas the coordination factors K_k^q give the geometrical information. K_k^q with $k = 1$ to 6 in the ESO notation evaluated in [22] are retabulated in Appendix A1 of [23]. The distance dependence of the intrinsic parameters for a ML_n complex is shown in (5) [19-21, 23], where t_k are the power-law exponents and R_0 is the reference distance [23, 24-27].

Eq. (4) gives conventional ZFSPs, D and E as [23]:

$$b_2^0 = D = \frac{\bar{b}_2(R_0)}{2} \left[\left(\frac{R_0}{R_i} \right)^{t_2} \sum_i (3 \cos^2 \theta_i - 1) \right] \quad (5)$$

$$b_2^2 = 3E = \frac{b_2^2}{3} = \frac{\bar{b}_2(R_0)}{2} \left[\left(\frac{R_0}{R_i} \right)^{t_2} \sum_i \sin^2 \theta_i \cos 2\varphi_i \right]$$

Cr³⁺ ion in VO₂ may be supposed to enter the lattice substitutionally at the V⁴⁺ ion site, and the interstitial site having similar ligand arrangement. The local symmetry at Cr³⁺ ion site is assumed to be approximately orthorhombic. In octahedral coordination of Cr³⁺ ion for LiNbO₃ having Cr³⁺-O²⁻ bond, $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$ and $t_2 = -0.12$ [28] have been used to find b_2^0 and b_2^2 . Since Cr³⁺ ion in VO₂ has distorted octahedral coordination

(Fig.1) with oxygens as ligands, the b_k^q in the present study are determined using the parameters $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$ and $t_2 = -1.95$ for center A and $\bar{b}_2(R_0) = 2.34 \text{ cm}^{-1}$ and $t_2 = -1.5775$ for center B, respectively.

The location of metal ion and spherical coordinates of ligands given in Table 1A and 1B are used for calculation. The conventional ZFSPs, D and E of Cr³⁺ ion in VO₂ crystal are obtained using (5). The reference distance of 0.176 nm was taken for the determination of ZFSPs [29], and the evaluated values of conventional ZFSPs are: for center A, $|D| = 0.4009 \text{ cm}^{-1}$ and $|E| = 0.0387 \text{ cm}^{-1}$ and for center B, $|D| = 0.4709 \text{ cm}^{-1}$ and $|E| = 0.0904 \text{ cm}^{-1}$. The ratio b_2^2/b_2^0 should be within the range (0, 1) for orthorhombic symmetry [30]. In the present investigation, the ratio $|b_2^2|/|b_2^0| = 0.289$ and $|E|/|D| = 0.096$ for center A and $|b_2^2|/|b_2^0| = 0.575$ and $|E|/|D| = 0.191$ for center B, which agrees with above for b_2^2/b_2^0 . However, the value of $|E|$ does not agree with the experimental value. Therefore, with above values of t_2 and reference distance, the ZFSPs $|D|$ and $|E|$ are obtained for Cr³⁺ at the V⁴⁺ site with distortion having position V⁴⁺ (0.242, 1.001, 0.112). for center A and V⁴⁺ (0.7142, -0.31, -0.09) for center B. The conventional ZFSPs found now are $|D| = 0.4009 \text{ cm}^{-1}$, $|E| = 0.0416 \text{ cm}^{-1}$ for center A and $|D| = 0.4710 \text{ cm}^{-1}$, $|E| = 0.0167 \text{ cm}^{-1}$ for center B, being in reasonable agreement with the experimental ones. The ratio $|b_2^2|/|b_2^0| = 0.311$ and $|E|/|D| = 0.103$ for center A and $|b_2^2|/|b_2^0| = 0.106$ and $|E|/|D| = 0.035$ for center B is consistent with [30]. Further, with above values of t_2 and reference distance, the conventional ZFSPs $|D|$ and $|E|$ are evaluated for Cr³⁺ at the interstitial site but the values found are quite inconsistent with the experimental values and hence these data have not been given here.

The calculated and experimental ZFSPs for Cr³⁺ ion doped VO₂ are presented in Table 2. From Table 2, it is seen that the ZFSPs $|D|$ and $|E|$ show reasonable agreement with the experimental ones [8] when the distortion is taken into account.

IV. SPM calculations of CFPs

The CF energy levels of transition ions doped crystals [31-34], in terms of CF Hamiltonian \mathcal{H}_{CF} [13, 35], employing Wybourne operators [14, 35], are given by:

$$\mathcal{H}_{CF} = \sum_{kq} B_{kq} C_q^{(k)} \quad (6)$$

Using SPM [19-21], the CFPs in (6) for a ML_n complex are found as:

$$B_{kq} = \sum_i \bar{A}_k \left(\frac{R_0}{R_i} \right)^{t_k} K_{kq}(\theta_i, \varphi_i). \quad (7)$$

where R_0 is the reference distance; R_i , θ_i , φ_i are the polar coordinates of the i^{th} ligand and K_{kq} are the coordination factors [31]. To find B_{kq} ($k = 2, 4$; $q = 0, 2, 4$); $\bar{A}_2 = 40, 400 \text{ cm}^{-1}$, $t_2 = 1.3$, $\bar{A}_4 = 11, 700 \text{ cm}^{-1}$ and $t_4 = 3.4$ are taken [31]. The calculated B_{kq} parameters are shown in Table 3. The ratio $B_{22}/B_{20} = 0.200$ for center A and $B_{22}/B_{20} = -0.245$ for center B, which indicates that B_{kq} parameters are standardized [30]. Using B_{kq} parameters in Table 3 and CFA program [32, 33], the CF energy levels of Cr³⁺ ion in VO₂ single crystals are computed by diagonalizing the complete Hamiltonian containing 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 given in Table 4. As optical study data on Cr³⁺: VO₂ could not be found in literature, the experimental energy values for Cr³⁺: NiMTH having similar ligands [36] are considered here for comparison. From Table 4, it is observed that the theoretical and experimental band positions are in reasonable agreement. Thus the theoretical study of Cr³⁺ ions in VO₂ lattice at V⁴⁺ sites supports the experimental observation [8, 36].

V. Summary and Conclusions

The zero-field splitting (ZFS) parameters (ZFSPs) and crystal field (CF) parameters (CFPs) are found employing superposition model (SPM) for Cr³⁺ ions in VO₂ single crystals. Cr³⁺ ions in VO₂ lattice at V⁴⁺ ion sites, interstitial site and distortion models are considered for calculation. The obtained conventional ZFSPs for Cr³⁺ ion at V⁴⁺ sites in VO₂ crystal show reasonable agreement with the experimental values when distortion is taken into account. It is concluded that the Cr³⁺ ions substitute the VO₂ lattice at V⁴⁺ ion sites. The CF energy values for Cr³⁺ ions at V⁴⁺ sites determined using CFA package and CFPs are in reasonable agreement with the experimental ones. Hence the theoretical results support the experimental observation. Modeling approaches

employed in this study may be applicable in future to correlate EPR and optical data for different ion-host systems.

Acknowledgement

The author is thankful to the Head, Department of Physics for providing the departmental facilities and to Prof. C. Rudowicz, Faculty of Chemistry, A. Mickiewicz. University, Poznan, Poland for CFA program.

References

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Table and figure captions:

Table 1A. Fractional coordinates of Cr³⁺ ion (center A) and spherical co-ordinates (R, θ , ϕ) of ligands in VO₂ crystal.

Table 1B. Fractional coordinates of Cr³⁺ ion (center B) and spherical co-ordinates (R, θ , ϕ) of ligands in VO₂ crystal.

Table 2. Calculated and experimental ZFSPs of Cr³⁺ doped VO₂ single crystal for centers A and B together with reference distance.

Table 3. B_{kq} parameters of Cr³⁺ doped VO₂ single crystal for centers A and B with distortion.

Table 4. Experimental and calculated (CFA package) energy band positions (centers A and B) of Cr³⁺ doped VO₂ single crystal.

Fig1. Crystal structure of VO₂ with symmetry adopted axis system (SAAS).

Table 1A

Position of Cr ³⁺	Ligands	Spherical co-ordinates of ligands		
		R ^Å	θ°	ϕ°
ND: Substitutional (0.242, 0.975, 0.025)	O(1)	3.7837	75.6	76.7
	O(1')	5.6045	102.4	69.8
	O(1'')	3.2564	63.0	31.3
	O(2)	1.7617	36.0	-56.5
	O(2')	8.1227	102.0	64.2
	O(2'')	4.3584	76.8	-14.9
WD: substitutional (0.242, 1.001, 0.112)	O(1)	3.7510	82.7	77.1
	O(1')	5.7482	106.9	70.2
	O(1'')	2.9573	70.0	33.7
	O(2)	1.6537	54.6	-58.8
	O(2')	8.2299	105.2	64.5
	O(2'')	4.0299	82.4	-13.2

ND = No distortion, WD = With distortion.

Table 1B

Position of Cr ³⁺	Ligands	Spherical co-ordinates of ligands		
		R ^Å	θ°	ϕ°
ND: Substitutional (-0.242, -0.975, -0.025)	O(1)	5.6045	77.5	69.8
	O(1')	3.7837	104.3	76.7
	O(1'')	7.7531	76.9	83.8
	O(2)	8.1227	77.9	64.2
	O(2')	1.7617	143.9	-56.5
	O(2'')	9.9553	82.7	-85.0
WD: substitutional (0.7142, -0.31, -0.09)	O(1)	5.1296	72.3	-35.6
	O(1')	4.4088	97.7	-55.1
	O(1'')	7.6191	74.0	-44.5
	O(2)	5.6692	68.8	-67.5
	O(2')	6.0801	100.1	15.1
	O(2'')	9.9871	80.7	-46.8

ND = No distortion, WD = With distortion.

Table 2

	$R_0^{\text{\AA}}$	Calculated ZFS parameters (cm ⁻¹)			Conventional ZFS parameters (×10 ⁻⁴ cm ⁻¹)		
		$ D_2^2 $	$ D_4^2 $	$ D_4^2 / D_2^2 $	$ D $	$ E $	$ E / D $
Center A							
ND	1.76	0.4009	0.1162	0.289	4009	387	0.096
					4009*	417*	0.104
WD	1.76	0.4009	0.1249	0.311	4009	416	0.103
					4009*	417*	0.104
Center B							
ND	1.76	0.4709	0.2712	0.575	4709	904	0.191
					4709*	167*	0.035
WD	1.76	0.4710	0.0501	0.106	4710	167	0.035
					4709*	167*	0.035

ND = No distortion, WD = With distortion
 * = experimental.

Table 3

	$R_0^{\text{\AA}}$	Calculated B_{kq} cm ⁻¹ Parameters used for CFA package					
		B_{20}	B_{22}	B_{40}	B_{42}	B_{44}	B_{22}/B_{20}
Center A							
WD	1.76	-25700.8	-5160.02	-5118.41	-14696.3	-66350.3	0.200
Center B							
WD	1.76	-20048.7	4926.782	234.8519	-1429.55	157.73	-0.245

WD = With distortion.

Table 4

Transition from	Experimentally observed band (cm ⁻¹) [36]	Calculated energy band from CFA (cm ⁻¹)	
		Center A	Center B
² A _{2g} (F)			
² E _g (G)		10509, 10539	10202, 10592
² T _{1g} (G)		12048, 12106, 12430	11368, 11790, 12440
⁴ T _{2g} (F)	17725	12539, 15144, 15851, 17294, 23972, 24714	15434, 15761, 16019, 16796, 17238, 18697
⁴ T _{1g} (F)	24505	25071, 27359, 27927, 28020, 35421, 36223	24057, 25585, 25683, 28307, 28712, 30532
² T _{1g} (aD)		38460, 39472, 41540	36013, 36334, 39600
² E _g (bD)		42498, 43437	43660, 46308

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

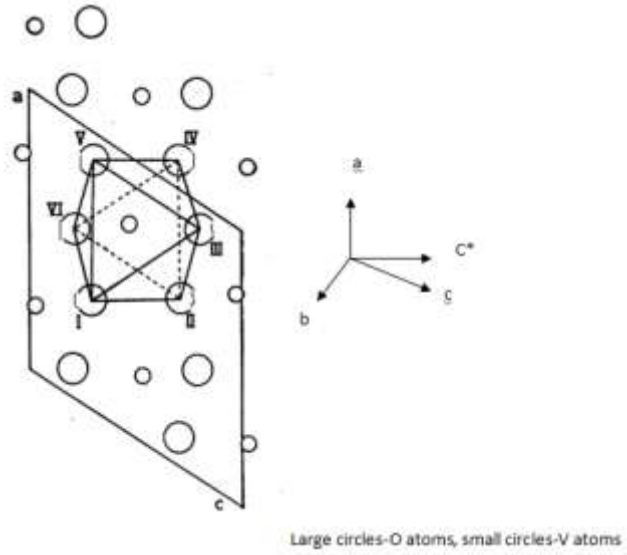


Fig. 1.