

## Superposition Model Study of Fe<sup>3+</sup> doped VO<sub>2</sub> Single Crystal

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**Abstract:** Theoretical study of crystal field parameters and zero field splitting parameters of Fe<sup>3+</sup> doped VO<sub>2</sub> single crystals are done using superposition model and the perturbation theory. The above parameters are determined without and with local distortion. These parameters are in reasonable agreement with the experimental values when local distortion is taken into account. The theoretical study supports the experimental observation that Fe<sup>3+</sup> substitutes for V<sup>4+</sup> in VO<sub>2</sub> crystal.

**Keywords:** inorganic compounds, single crystal, crystal fields, electron paramagnetic resonance.

### 1. Introduction

Electron paramagnetic resonance (EPR) is an important technique to obtain local site symmetry and zero field splitting (ZFS) parameters of transition ions introduced in crystals [1,2]. Fe<sup>3+</sup> ion has half filled 3d shell in the iron group and its ground state is <sup>6</sup>S (S = 5/2). The Hamiltonian of a 3d<sup>5</sup> ion may be expressed in terms of the free-ion Hamiltonian, crystal field Hamiltonian, the spin-orbit and spin-spin couplings, respectively.

As known the crystal fields have important role in spin-orbit mechanism, the superposition model (SPM), is used to obtain the crystal field (CF) parameters [3, 4]. Since the positions of various ligands in the crystal are required in this model, the relation between the model and the theories of local distortion in crystals are important to find ZFS parameters for the 3d<sup>5</sup> system [5, 6].

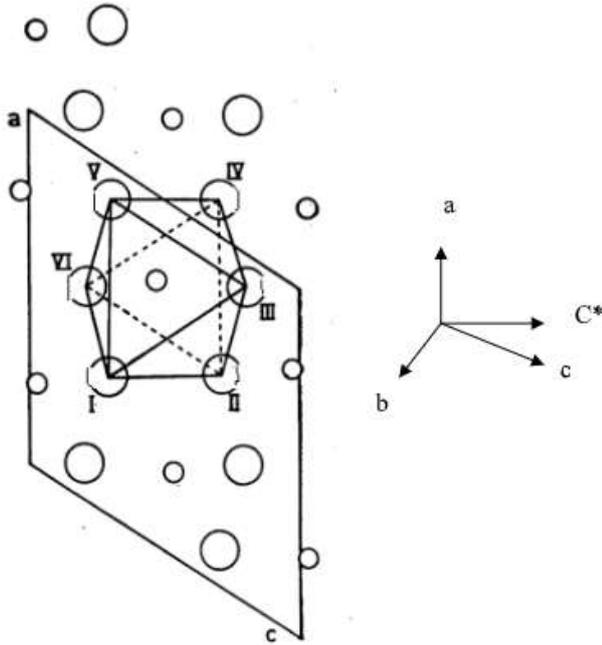
Perturbation procedures have been used to investigate theoretically the spin Hamiltonian parameters of 3d<sup>5</sup> ions by many workers [7-10]. In Hamiltonian, cubic field and the diagonal part of free-ion Hamiltonian are normally considered as unperturbed terms and the rest as the perturbation terms [11].

Vanadium dioxide (VO<sub>2</sub>) single crystal undergoes a first-order phase transition at 340 K from metallic to the semiconducting phase as the temperature is reduced. These two phases possess tetragonal ( $D_{4h}^{14}$ ) and monoclinic ( $C_{2h}^5$ ) crystal structures above and below 340 K, respectively [12, 13]. The physical properties of VO<sub>2</sub>, as well as the phase transition temperature are influenced by doping ions.

The relatively high transition temperature of VO<sub>2</sub> gives convenience for electron paramagnetic resonance (EPR) studies [14-16]. EPR studies of Fe<sup>3+</sup> in VO<sub>2</sub> single crystals have been done in the temperature range 4.2–350 K [17]. The detailed spin Hamiltonian parameters have been determined at 150K, monoclinic phase [17]. It was concluded from EPR study [17] that Fe<sup>3+</sup> ion substitutes at V<sup>4+</sup> site in the crystal lattice. In the present study, the ZFS parameters D and E are calculated for the Fe<sup>3+</sup> ion at substitutional V<sup>4+</sup> site as well as at interstitial site in VO<sub>2</sub> crystal using CF parameters found from SPM and perturbation expressions [18]. The aim of the study is to confirm whether Fe<sup>3+</sup> ion substitutes at V<sup>4+</sup> site in the crystal or enters the lattice interstitially and about the distortion produced in the lattice. The results obtained for the Fe<sup>3+</sup> ion at substitutional site in VO<sub>2</sub> are in reasonable agreement with the experimental ones when local distortion is taken into account.

### 2. Crystal Structure

The low-temperature phase of VO<sub>2</sub> has 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 important feature of the monoclinic (M) phase is the presence of V<sup>4+</sup>-V<sup>4+</sup> pairs, pointing in a direction very close to the symmetry axis. The separation of adjacent vanadium ions is in the range of 2.65 Å to 3.12 Å. The distortion to the monoclinic phase as the temperature is lowered results in doubling of the unit cell, and consequently the presence of four molecules per unit cell [19]. The semiconducting phase has a distorted rutile structure. Though there are four vanadium ions per unit cell, due to the presence of a center of symmetry, there are only two magnetically inequivalent sites as in the rutile structure. The crystal structure of VO<sub>2</sub> with symmetry adopted axis system (SAAS) is shown in Fig.1..



Large circles-O atoms, small circles-V atoms

Fig. 1. Crystal structure of VO<sub>2</sub> with symmetry adopted axis system (SAAS).

### 3. Calculations of CF and ZFS Parameters

The EPR spectrum can be analyzed with the spin Hamiltonian [20, 21],

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

where  $g$  is the spectroscopic splitting factor,  $\mu_B$  is the Bohr magneton and  $B$  is the external magnetic field.  $D$  and  $E$  are the second rank axial and rhombic ZFS parameters, whereas  $a$  is the fourth rank cubic one,  $A$  and  $B$  give hyperfine terms [22- 24]. 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 perpendicular 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).

From symmetry considerations, in the monoclinic phase of VO<sub>2</sub>, out of the four impurity ions that substitute for vanadium ions there should be two magnetically inequivalent sets of Fe<sup>3+</sup> ions, each set consisting of two magnetically equivalent ions. Then, the observed four sets of Fe<sup>3+</sup> EPR spectra corresponding to four magnetically inequivalent but physically equivalent ions can be described by the same spin-

Hamiltonian parameters. The most intense Fe<sup>3+</sup> EPR lines were referred to as belonging to spectrum *A* while weaker Fe<sup>3+</sup> EPR lines were referred to as belonging to spectrum *B*. Spectrum *A* is due to those Fe<sup>3+</sup> ions which substitute for V<sup>4+</sup> ions such that the valence of the nearest V<sup>4+</sup> ion increases to V<sup>5+</sup> for charge compensation. On the other hand, spectrum *B* is due to those Fe<sup>3+</sup> ions, which substitute for V<sup>4+</sup> ions, where the charge compensation is being provided by the non-stoichiometry in VO<sub>2</sub>. The spectrum

*B* was not investigated in detail due to its low intensity [17].

The Z axis of SAAS 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 four sites (Fig. 1). This shows that Fe<sup>3+</sup> substitutes for V<sup>4+</sup> in the crystal lattice of VO<sub>2</sub>. The ionic radius of Fe<sup>3+</sup> ion 0.064 nm [25] is slightly larger than the ionic radius of V<sup>4+</sup> (0.058 nm), implying thereby that Fe<sup>3+</sup> ion can go at the location of V<sup>4+</sup> with some distortion.

The ZFS parameters of Fe<sup>3+</sup> ion located at V<sup>4+</sup> sites in Fig. 1 are determined with the help of perturbation theory [26, 27] and are then compared with the experimental values.

As discussed in introduction section the spin Hamiltonian of a d<sup>5</sup> (<sup>6</sup>S state) ion can be given as sum of free ion ( $\mathcal{H}_0$ ), spin-orbit coupling ( $\mathcal{H}_{so}$ ), spin-spin coupling ( $\mathcal{H}_{ss}$ ) and crystal field ( $\mathcal{H}_c$ ) Hamiltonians,

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_{so} + \mathcal{H}_{ss} + \mathcal{H}_c \quad (2)$$

$$\mathcal{H}_c = \sum B_{kq} C_q^{(k)} \quad (3)$$

where  $B_{kq}$  are the CF parameters and  $C_q^{(k)}$  are the Wybourne spherical tensor operators. For the crystal field of orthorhombic symmetry,  $B_{kq} \neq 0$  only with  $k = 2, 4, q = 0, 2, 4$ . The crystal-field theory has been widely used to study the spin Hamiltonian parameters of transition ions introduced in crystals [28-31]. In the present study, the CF parameters,  $B_{kq}$  are determined using SPM [26].

In VO<sub>2</sub> crystal the local field symmetry around Fe<sup>3+</sup> ions is taken to be orthorhombic (OR-I) [17, 25]. In OR-I symmetry, the ZFS parameters  $D$  and  $E$  are obtained as [31]

$$D = \left( \frac{3\zeta^2}{70P^2D} \right) [-B_{20}^2 - 21\zeta B_{20} + 2B_{22}^2] + \left( \frac{\zeta^2}{63P^2G} \right) [-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2]$$

$$E = \left( \frac{\sqrt{6}\zeta^2}{70P^2D} \right) [2B_{20} - 21\zeta]B_{22} + \left( \frac{\zeta^2}{63P^2G} \right) [3\sqrt{10}B_{40} + 2\sqrt{7}B_{44}]B_{42}$$

(4) (5)

where  $P = 7B+7C$ ,  $G = 10B+5C$ ,  $D = 17B+5C$ .  $B$  and  $C$  are Racah parameters, giving electron-electron repulsion and  $\zeta$  is the spin-orbit coupling parameter. It is noted that the values of  $B$  and  $C$  for transition ion in a crystal are less than those of the free ion. By taking the average covalency parameter  $N$ , we write the Racah parameters [26, 32] and spin-orbit coupling parameter as  $B = N^4B_0$ ,  $C = N^4 C_0$ ,  $\zeta = N^2\zeta_0$ , where  $B_0$  and  $C_0$  are Racah parameters for free ion and  $\zeta_0$  is free ion spin-orbit coupling parameter. For free  $Fe^{3+}$  ion,  $B_0 = 1130 \text{ cm}^{-1}$ ,  $C_0 = 4111 \text{ cm}^{-1}$  and  $\zeta_0 = 589 \text{ cm}^{-1}$  are taken [26].

Using the values of Racah parameters ( $B = 810 \text{ cm}^{-1}$ ,  $C = 3400 \text{ cm}^{-1}$ ) evaluated from optical study of the  $Fe^{3+}$  ion with O ligand [33], the average parameter  $N$  is obtained from  $N = (\sqrt{B/B_0} + \sqrt{C/C_0})/2$ .

The CF parameters in SPM are found [31, 34] as

$$B_{kq} = \sum_j \overline{A}_k(R_j) K_{kq}(\theta_j, \phi_j)$$

(6)

Here the co-ordination factor  $K_{kq}(\theta_j, \phi_j)$  is an explicit function of the angular position of the ligand. The intrinsic parameter  $\overline{A}_k(R_j)$  is given by

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

where  $R_j$  is the distance of the  $d^n$  ion from the ligand,  $\overline{A}_k(R_0)$  is the intrinsic

parameter of the reference crystal,  $R_0$  is the reference distance between metal and ligand ion and  $t_k$  is the power law exponent. For  $Fe^{3+}$ -doped crystals,  $t_2 = 3$  and  $t_4 = 5$  are used [30]. We have also taken the same values in our calculation. As the co-ordination around  $Fe^{3+}$  ion is octahedral,  $\overline{A}_4$  is determined as [35]

$$\overline{A}_4(R_0) = \frac{3}{4} Dq$$

Using optical study [33], the value of  $Dq = 1350 \text{ cm}^{-1}$ .

Hence, the value of  $\overline{A}_4(R_0) = 1012.5 \text{ cm}^{-1}$ . For  $3d^5$  ions

the ratio  $\frac{\overline{A}_2}{\overline{A}_4}$  lies between 8 to 12 [26, 36, 37]. In this

study, this ratio is taken as 10, which gives  $\overline{A}_2 = 10125 \text{ cm}^{-1}$ .

#### 4. Results and Discussion

The CF parameters  $B_{kq}$  of  $Fe^{3+}$  ion at  $V^{4+}$  sites are calculated using SPM with the help of parameters  $\overline{A}_2$  and  $\overline{A}_4$  as well as arrangement of O ions about  $Fe^{3+}$  ion (Fig. 1). Atomic coordinates in  $VO_2$  crystal along with bond length  $R$  (without and with distortion) and angle  $\theta, \varphi$  (one site) are given in Table 1. The calculated CF parameters using Eq. (6) and transformation S5 for standardization [24] and ZFS parameters together with reference distance  $R_0$  are presented in Table 2. Table 2 shows that the value of  $R_0 = 0.123 \text{ nm}$  slightly less than the lowest of six ligand distances from the central metal ion ( $0.1761 \text{ nm}$ ) together with local distortion provide ZFS parameters for  $V^{4+}$  sites in reasonable agreement with the experimental values [17]. The ZFS parameters obtained using  $R_0 = 0.123 \text{ nm}$  and without local distortion are less than the experimental values. For comparison the interstitial sites for  $Fe^{3+}$  ions were also studied but the ZFS parameters are found to be inconsistent with the experimental ones and so are not being presented here to save the space.

**Table 1.** Atomic coordinates in VO<sub>2</sub> crystal along with bond length R (without and with distortion) and angle  $\theta$ ,  $\varphi$  (one site).

Position of Fe <sup>3+</sup>	Ligands			Spherical co-ordinates of ligands		
	x	y	z	R(nm)	$\theta^{\circ}$	$\varphi^{\circ}$
	(Å)					
	Without distortion					
Site I: Substitutional V (0.242, 0.975, 0.025)	O(1)	-0.142	-0.765	0.175	0.3783 R <sub>1</sub>	87.34 $\theta_1$ 92.15 $\varphi_1$
	O(1')	-0.342	-0.765	-0.225	0.3833 R <sub>2</sub>	93.36 $\theta_2$ 95.12 $\varphi_2$
	O(1 <sup>*</sup> )	-0.342	-0.265	0.275	0.3256 R <sub>3</sub>	85.15 $\theta_3$ 96.04 $\varphi_3$
	O(2)	0.148	-0.285	0.265	0.1761 R <sub>4</sub>	81.34 $\theta_4$ 85.12 $\varphi_4$
	O(2')	-0.632	-1.665	-0.315	0.8122 R <sub>5</sub>	92.22 $\theta_5$ 94.46 $\varphi_5$
	O(2'')	-0.632	0.215	0.185	0.4358 R <sub>6</sub>	87.56 $\theta_6$ 98.34 $\varphi_6$
	With distortion					
	O(1)					0.2105 R <sub>1</sub> + $\Delta$ R <sub>1</sub>
	O(1')					0.2133 R <sub>2</sub> + $\Delta$ R <sub>2</sub>
	O(1 <sup>*</sup> )					0.1856 R <sub>3</sub> + $\Delta$ R <sub>3</sub>
	O(2)					0.1762 R <sub>4</sub> + $\Delta$ R <sub>4</sub>
	O(2')					0.5922 R <sub>5</sub> + $\Delta$ R <sub>5</sub>
	O(2 <sup>*</sup> )					0.2158 R <sub>6</sub> + $\Delta$ R <sub>6</sub>

Employing above CF parameters and CFA program [38, 39] with OR-I symmetry of the crystal field the optical spectra of Fe<sup>3+</sup> doped VO<sub>2</sub> crystals are calculated. The energy levels of the impurity ion are obtained by diagonalization of the complete Hamiltonian within the

3d<sup>N</sup> basis of states in the intermediate crystal field coupling scheme. The calculated energy values are presented in Table 3 together with the experimental values for comparison [40]. A reasonable agreement is obtained between the two. Thus, the inference drawn on the basis of SPM supports the experimental result that Fe<sup>3+</sup> ions substitute at V<sup>4+</sup> site in the crystal [17].

**Table 2.** Crystal field parameters and zero field splitting parameters of Fe<sup>3+</sup> doped VO<sub>2</sub> single crystal.

Site	Crystal- field parameters (cm <sup>-1</sup> )					Zero-field splitting parameters ( $\times 10^{-4}$ cm <sup>-1</sup> )			
	R <sub>0</sub> (nm)	B <sub>20</sub>	B <sub>22</sub>	B <sub>40</sub>	B <sub>42</sub>	B <sub>44</sub>	D	E	E / D
	Without distortion								
Site I									
$\frac{A_2}{A_4} = 10$	0.123	-4685.0	-5849.64	441.3671	481.2109	3894.86	762	313	0.411
	With distortion								
Site I									
$\frac{A_2}{A_4} = 10$	0.123	13307.77	-10623.8	1321.554	1397.736	5062.664	1426	433	0.304
	Exp. 1426 314 0.220								

**Table 3.** Experimental and calculated (CFA package) energy band positions of Fe<sup>3+</sup> doped VO<sub>2</sub> single crystal.

Transition from ${}^6A_{1g}(S)$	Observed wave number ( $\text{cm}^{-1}$ )	Calculated wave number ( $\text{cm}^{-1}$ )
${}^4T_{1g}(G)$	10000	${}^4T_{2g}(G)$ 13500
${}^4E_g(G)$	21740	21495, 21604
${}^4T_{2g}(D)$	25120	23366, 23518, 23666, 23793, 24554, 24609
${}^4E_g(D)$	27500	26920, 27842
${}^4T_{1g}(P)$	30970	29305, 29342, 30801, 31132, 31519, 31886
${}^6T_{1u}(6t_{1u\beta}-2t_{2g\beta})$	35800	34960, 35184, 35245, 35418, 35806, 35869
${}^6E_g(1t_{2u\beta}-2t_{2g\beta})$	40500	40420, 40510
${}^6T_{2u}(6t_{1u\beta}-4e_g\beta)$	46200	45477, 45944, 46120, 46221, 46512, 47064

## 5. Conclusions

CF parameters and ZFS parameters for  $\text{Fe}^{3+}$  ion doped  $\text{VO}_2$  have been obtained using superposition model and perturbation theory, respectively. The computed ZFS parameters are in reasonable agreement with the experimental values. The calculated optical spectra are also in reasonable agreement with the experimental one. Thus, the inference drawn on the basis of superposition model supports the experimental result that  $\text{Fe}^{3+}$  ions substitute at  $V^{4+}$  site in  $\text{VO}_2$  crystal

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## References

- [1] F. E. Mabbs, D. Collison, D. Gatteschi Electron Paramagnetic Resonance of d Transition Metal Compounds, Elsevier, Amsterdam, 1992.
- [2] J. A. Weil, J. R. Bolton, Electron Paramagnetic Resonance: Elementary Theory and Practical Applications, 2nd ed., Wiley, New York, 2007.
- [3] M. I. Bradbury, D. J. Newman, Ratios of crystal field parameters in rare earth salts, Chem. Phys. Lett. **1** (1967) 44-45, doi.org/10.1016/0009-2614(67)80063-0.
- [4] D. J. Newman, On the g-shift of S-state ions, J. Phys. C: Solid State Phys. **10** (1977) L315-L318.
- [5] E. Siegel and K. A. Müller, Local position of  $\text{Fe}^{3+}$  in ferroelectric  $\text{BaTiO}_3$ , Phys. Rev. B **20** (1979) 3587-3595, doi.org/10.1103/PhysRevB.20.3587.
- [6] Y. Y. Yeung, Local distortion and zero-field splittings of  $3d^5$  ions in oxide crystals, J. Phys. C: Solid State Phys. **21** (1988) 2453-2461.
- [7] T. H. Yeom, S. H. Choh, M. L. Du, A theoretical investigation of the zero-field splitting parameters for an  $\text{Mn}^{2+}$  centre in a  $\text{BiVO}_4$  single crystal, J. Phys.: Condens. Matter **5** (1993) 2017-2024.
- [8] M. L. Du, M. G. Zhao, The eighth-order perturbation formula for the EPR cubic zero field splitting parameter of  $d^5(%)$  ion and its applications to  $\text{MgO: Mn}^{2+}$  and  $\text{MnCl}_2 \cdot 2\text{H}_2\text{O}$ , J. Phys. C: Solid State Phys. **18** (1985) 3241- 3247.
- [9] W. L. Yu, Cubic zero-field splitting of a  ${}^6S$  state ion, Phys. Rev. **B 39**(1989) 622-632, doi.org/10.1103/PhysRevB.39.622.
- [10] M. G. Brik, C. N. Avram, N. M Avram, Calculations of spin Hamiltonian parameters and analysis of trigonal distortions in  $\text{LiSr}(\text{Al,Ga})\text{F}_6:\text{Cr}^{3+}$  crystals, Physica **B 384**(2006) 78-81, doi.org/10.1016/j.physb.2006.05.155.
- [11] Z. Y. Yang, An investigation of the EPR zero-field splitting of  $\text{Cr}^{3+}$  ions at the tetragonal site and the  $\text{Cd}^{2+}$  vacancy in  $\text{RbCdF}_3:\text{Cr}^{3+}$  crystals, J. Phys.: Condens. Matter **12** (2000) 4091-4096.
- [12] G. Andersson, Studies on Vanadium Oxides II. The Crystal Structure of Vanadium Dioxide, Acta Chem. Scand. **10** (1956) 623-626.
- [13] W. Bruckner, H. Oppermann, W. Reichelt, E. I. Terukov, F. A Chudnovskii, and E. Wolf, Vanadium Oxide (Academie-Verlag, Berlin, 1983), p. 252.
- [14] J. P. D'Haenens, D Kaplan, P. Merenda, Electron spin resonance in  $\text{V}_{1-x}\text{Cr}_x\text{O}_2$ , J. Phys. C: Solid State Phys. **8**(1975)2267-2273.
- [15] D. L. Carter and A. Okaya, Electron Paramagnetic Resonance of  $\text{Fe}^{3+}$  in  $\text{TiO}_2$  (Rutile), Phys. Rev. **118** (1960) 1485-1490.
- [16] P. O. Andersson, E. L. Kolberg, and A. Jelensky, Extra EPR Spectra of Iron-Doped Rutile, Phys. Rev. **B 8** (1973) 4956-4965.
- [17] S. K. Misra, S. I. Andronenko, R. R. Andronenko, Variable-temperature EPR study of  $\text{Fe}^{3+}$  in  $\text{VO}_2$  single crystals, Phys. Rev. B **57**(1998)8203-8210.

- [18] W. L. Yu, M.G. Zhao, Spin-Hamiltonian parameters of  $6S$  state ions, *Phys. Rev. B* **7** (1988) 9254-9267, doi.org/10.1103/PhysRevB.37.9254.
- [19] J. P. D'Haenens, D. Kaplan, and J. Tuchendler, Electron spin resonance in chromium doped  $VO_2$ , *Solid State Commun.* **15** (1974) 635-638.
- [20] A. Abragam, B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions*, Clarendon Press, Oxford, 1970.
- [21] C. Rudowicz, Concept of spin Hamiltonian, forms of zero field splitting and electronic Zeeman Hamiltonians and relations between parameters used in EPR. A critical review, *Magn. Reson. Rev.* **13** (1987) 1-89.
- [22] C. Rudowicz, H. W. F. Sung, Can the electron magnetic resonance (EMR) techniques measure the crystal (ligand) field parameters?, *Physica B* **300** (2001) 1- 26, doi.org/10.1016/S0921-4526(01)00568-3.
- [23] C. J. Radnell, J. R. Pilbrow, S. Subramanian, M. T. Rogers, Electron paramagnetic resonance of  $Fe^{3+}$  ions in  $(NH_4)_2SbF_5$ , *J. Chem. Phys.* **62** (1975) 4948-4952.
- [24] C. Rudowicz, R. Bramley, On standardization of the spin Hamiltonian and the ligand field Hamiltonian for orthorhombic symmetry, *J. Chem. Phys.* **83** (1985) 5192- 5197.
- [25] B. N. Figgis, M. A. Hitchman, *Ligand Field Theory and its Applications*, Wiley, New York, 2000.
- [26] T. H. Yeom, S. H. Choh, M. L. Du and M. S. Jang, EPR study of  $Fe^{3+}$  impurities in crystalline  $BiVO_4$ , *Phys. Rev. B* **53** (1996) 3415-3421, doi.org/10.1103/PhysRevB.53.3415.
- [27] C. Rudowicz, S. K. Misra, SPIN-HAMILTONIAN FORMALISMS IN ELECTRON MAGNETIC RESONANCE (EMR) AND RELATED SPECTROSCOPIES, *Appl. Spectrosc. Rev.* **36** (2001) 11-63.
- [28] Z. Y. Yang, C. Rudowicz, Y. Y. Yeung, Microscopic spin-Hamiltonian parameters and crystal field energy levels for the low  $C_3$  symmetry  $Ni^{2+}$  centre in  $LiNbO_3$  crystals, *Physica B* **348** (2004) 151-159, doi.org/10.1016/j.physb.2003.11.085 .
- [29] Z. Y. Yang, Y. Hao, C. Rudowicz, Y. Y. Yeung, Theoretical investigations of the microscopic spin Hamiltonian parameters including the spin-spin and spin-other-orbit interactions for  $Ni^{2+}(3d^8)$  ions in trigonal crystal fields, *J. Phys.: Condens. Matter* **16** (2004) 3481-3494.
- [30] T. H. Yeom, Y. M. Chang, S. H. Choh, C. Rudowicz, Experimental and Theoretical Investigation of Spin-Hamiltonian Parameters for the Low Symmetry  $Fe^{3+}$  Centre in  $LiNbO_3$ , *Phys. Stat. Sol.* **b185** (1994) 409-415, doi.org/10.1002/pssb.2221850211.
- [31] C. Rudowicz, Z. Y. Yang, Y. W. Lun, Crystal field analysis for  $3d^4$  and  $3d^6$  ions with an orbital singlet ground state at orthorhombic and tetragonal symmetry sites, *J. Phys. Chem. Solids* **53** (1992) 1227-1236, doi.org/10.1016/0022-3697(92)90043-D.
- [32] C. K. Jorgensen, *Modern Aspects of Ligand Field Theory*, North- Holland, Amsterdam, 1971, p.305.
- [33] T. H. Yeom, Superposition model calculation of zero-field splitting of  $Fe^{3+}$  in  $LiTaO_3$  crystal, *J. Phys: Coondens. Matter* **13**(2001)10471-10476.
- [34] D. J. Newman, B. Ng, The superposition model of crystal fields, *Rep. Prog. Phys.* **52**(1989)699-763.
- [35] D. J. Newman, B. Ng (Eds.), *Crystal Field Handbook*, Cambridge University Press, Cambridge, 2000.
- [36] D. J. Newman, D. C. Pryce, W. A. Runciman, Superposition model analysis of the near infrared spectrum of Fe (super 2+) in pyrope-almandine garnets, *Am. Miner.* **63** (1978) 1278-1281.
- [37] A. Edgar, Electron paramagnetic resonance studies of divalent cobalt ions in some chloride salts, *J. Phys. C: Solid State Phys.* **9** (1976) 4303-4314.
- [38] P. Gnutek, Z. Y. Yang and C. Rudowicz, Modeling local structure using crystal field and spin Hamiltonian parameters: the tetragonal  $Fe_{K^{3+}}-O_{I^{2-}}$  defect center in  $KTaO_3$  crystal, *J. Phys.: Condens. Matter* **21**, 455402 (2009)(11pp).
- [39] Y. Y. Yeung, C. Rudowicz, Crystal Field Energy Levels and State Vectors for the  $3d^N$  Ions at Orthorhombic or Higher Symmetry Sites, Issue 1, *J. Comput. Phys.* **109** (1993) 150-152.
- [40] D. M. Sherman, The Electronic Structures of  $Fe^{3+}$  Coordination Sites in Iron Oxides; Applications to Spectra, Bonding and Magnetism, *Phys. Chem. Minerals* **12**(1985)161-175.