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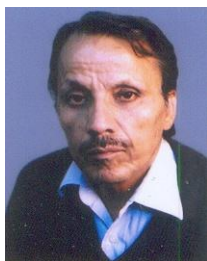
## GROUND STATE WAVE FUNCTION AND CRYSTALLINE FIELD EFFECT ON EPR PARAMETERS OF VO<sup>2+</sup>ION

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### ABSTRACT

The ground state wave function of VO<sup>2+</sup> ion doped in different host lattices is estimated with the help of EPR data. From these data also evaluated other parameters a, b, c, u, v, w and f<sub>x</sub>, f<sub>y</sub>, f<sub>z</sub>. The |x<sup>2</sup>-y<sup>2</sup>> is found to be the predominant ground state. The Fermi contact term K and hyperfine interaction parameter P<sub>hf</sub> in different host lattices are calculated with the help of (A<sub>i</sub> -f<sub>i</sub>) diagram. Further, based on this method correct signs and directions of the spin Hamiltonian parameters g and A are assigned.

**Keywords:** Ground state wave function; Electron paramagnetic resonance; Fermi contact term; Hyperfine interaction parameter.

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### INTRODUCTION

Electron paramagnetic resonance (EPR) yields a great deal of information about the magnetic properties of paramagnetic ion in different single crystals and it also provides a detailed description of the ground state wave function of paramagnetic ions. EPR study can provide valuable information on the effective ligand field symmetry and orbital geometry as well as on the bonding of transition metal ions. It is used in the study of the biochemistry of metalloproteinase and inorganic metal complexes having at least one unpaired electron on the metal ion [1-2]. Presently, EPR is used as a tool for the characterization of transition metal ions and rare earth impurities in non linear optical and laser crystals [3-5]. Vanadium is an important trace element in nature that has been studied with EPR spectroscopy in different states. The common valance states of vanadium are +2, +3, +4, +5 [6-8]. The +5 state is diamagnetic and the +3 state, although paramagnetic, is usually not

observed by EPR due to internal electric field effects. +2 state is oxydatively unstable and easily yields the oxycation, VO<sup>2+</sup>. Due to the remarkable stability and interesting spectral as well as magnetic properties of complex oxycations of the types MO<sup>n+</sup> and MO<sup>n+</sup><sub>2</sub>, where M refers for the metal ion, a theoretical speculation has been presented about their electronic structure [9]. One of the simplest examples of this type is VO<sup>2+</sup>. It is formulated as having V<sup>4+</sup>, with the electronic structure 3d<sup>1</sup>, and an oxide ion. The paramagnetic behaviour of the vanadyl ion arises from single unpaired electron and its EPR spectrum is quite analogous to that of Cu<sup>2+</sup> ion [10-11]. In its tetravalent state, vanadium V<sup>4+</sup> exists as VO<sup>2+</sup> ion with a single unpaired electron bound to an oxygen atom by a strong double bond so the VO<sup>2+</sup> ion is the most stable cation among a few molecular paramagnetic transition metal ions which is used extensively as an impurity probe for electron paramagnetic studies.

In the present investigation, on the basis of theoretical analysis of the behaviour of  $3d^1$  single electron in  $VO^{2+}$  ion doped in different single crystals the ground state wave function and parameters  $a, b, c, u, v, w, f_x, f_y, f_z$  are estimated with the help of EPR data. These EPR data are also used to evaluate the hyperfine interaction parameter  $P$  and Fermi contact term  $K$  in the presence of rhombic symmetry crystalline field. It is interesting to have a knowledge of the ground state wave function of paramagnetic ion doped in different host lattices to get information about the signs as well as magnitudes of EPR parameters  $g$  and  $A$  and to evaluate the fine structure constant [12]. The Fermi contact term  $K$ , which is dimensionless constant, represents the amount of unpaired electron density at the vanadium nucleus and the hyperfine interaction parameter is important because of the fact that it enables to determine nuclear spins, magnetic and quadrupole moments of stable and radioactive nuclei and to explain the nature of chemical bonding in complexes [13-14]. The paramagnetic  $VO^{2+}$  ion in different host lattices is studied and reported [15-32] but they have not assigned the correct signs and directions to spin Hamiltonian parameters which plays very important role in the determination of ground state wave function and the value of  $K$  and  $P$  of different host lattices to decide the signs as well as directions of the spin Hamiltonian parameters [33].

### Theory

The ground state of atomic  $V^{4+}$  has five fold orbital degeneracy and is described by the term  ${}^2D$ . A predominantly cubic crystalline field splits this degeneracy into a lower orbital  $\Gamma_5$  and an upper orbital doublet  $\Gamma_3$ . The additional splitting of the orbital levels is caused by the non-cubic part of the crystalline field. A component of tetragonal symmetry splits the doublet into two singlets, and the triplet into a singlet and a doublet. This doublet is split into two singlets by the crystalline field of rhombic symmetry so that the degeneracy of the orbital levels is completely removed. The position of upper two singlets is also modified by the crystalline field of lower symmetry. The energy level splittings are shown in Fig.1.

The ground state wave function in crystalline field of rhombic symmetry can be written as,

$$1/2 \sqrt{5} f(r) (ax^2 + by^2 + cz^2) \quad (1)$$

with the condition

$$a + b + c = 0 \quad (2)$$

$$a^2 + b^2 + c^2 = 6$$

The wave function of the orbital triplet may be represented as

$$\sqrt{15} f(r) yz, \sqrt{15} f(r) zx, \sqrt{15} f(r) xy \quad (3)$$

their energies above the ground state will be denoted by  $E_x, E_y, E_z$ . Spin orbit coupling admixes some of the triplet wave function to the ground state and therefore, two components of the ground doublet take the general form

$$1/2 \sqrt{15} M f(r) \{ (ax^2 + by^2 + cz^2 + iRxy) 1 + (iPyz - Qzx) m \} \quad (4)$$

$$1/2 \sqrt{15} M f(r) \{ (iPyz + Qzx) 1 + (ax^2 + by^2 + cz^2 - irxy) m \}$$

where  $l, m$  are the two spin functions quantized along the  $z$ -axis and  $M$  is a normalizing

factor, given by

$$M^2 = 1 + (P^2 + Q^2 + R^2)/12 \quad (5)$$

For vanadium ion  $\lambda/E_x, \lambda/E_y, \lambda/E_z$  is positive and denoted by  $u, v, w$ , respectively. One can have correct to the first order in  $\lambda$ ,

$$P = u (b - c)$$

$$Q = v (c - a) \quad (6)$$

$$R = w (a - b)$$

The expressions for  $g$  values in terms of  $P, Q, R$  are

$$g_x = 2 + 2/3 P (b-c)$$

$$g_y = 2 + 2/3 Q (c-a) \quad (7)$$

$$g_z = 2 + 2/3 R (a-b)$$

With the help of Eq.(4) one can express them directly in term of  $a, b, c$ . The magnetic hyperfine structure can be expressed simultaneously in terms of hyperfine interaction parameter and the Fermi contact term  $K$ , which represents the admixture of configurations with unpaired  $s$ -electron, in the form.

$$A_x/P_{hf} = -K + 2/3 P (b-c) + 1/7 (2a^2 - 4 + Rc - Qb) = -K + f_x$$

$$A_y/P_{hf} = -K + 2/3 Q (c-a) + 1/7 (2b^2 - 4 + Pa - Rc) = -K + f_y \quad (8)$$

$$A_z/P_{hf} = -K + 2/3 R (a-b) + 1/7 (2c^2 - 4 + Qb - Pa) = -K + f_z$$

The expressions for  $g$  values contain unknown parameters  $u, v, w$ , and  $a, b, c$ .  $a, b, c$  are related by

Eq.(2) and can be expressed in terms of single parametric angle  $\phi$  as,

$$\begin{aligned} a &= \cos \phi + \sqrt{3} \sin \phi \\ b &= \cos \phi - \sqrt{3} \sin \phi \\ c &= -2 \cos \phi \end{aligned} \quad (9)$$

These three parameters a, b, c will be evaluated with the help of EPR data. The  $|xz\rangle$  and  $|yz\rangle$  levels may be treated as close since the uniaxial symmetry leading to rhombic part of the crystals is usually small. Therefore we can take easily  $u = v$  and from this approximation we can find the value of other parameters using expressions (6), (7) and (9).

$$\begin{aligned} \sin 2\phi &= g_y - g_x / 4\sqrt{3}u \\ \text{and} & \end{aligned} \quad (10)$$

Table 1. E PR parameter for vanadyl ion in selected crystals lattices.

S.N.	Crystal lattices	$g_x$	$g_y$	$g_z$	$A_x$	$A_y$	$A_z$	Ref.
1.	diaquabis [malanato(1-)-k <sup>2</sup> O,O <sup>-</sup> ] zinc [DAMBZ]	1.98	1.972	1.937	78.49	56.99	169.13	[15]
2.	dipotassium diaquabis (malonato-k <sup>2</sup> O,O <sup>-</sup> )zincate dihydrate [PMZD]	1.978	1.972	1.936	66.53	62.88	170.44	[16]
3.	kainite crystal [PMCST]	1.958	1.937	1.987	102.5	74.23	184.75	[17]
4.	magnesium potassium phosphate hexahydrate site1 site2 [MPPH]	1.98	1.9774	1.9276	67.74	75.59	174.64	[18]
5.	zinc ammonium trihydrogen bis(orthophosphate) monohydrate [ZATM]	1.9802	1.9765	1.9296	63.73	79.23	175.20	
6.	potassium titanium phosphate [KTP]	1.978	1.974	1.925	69.14	72.88	181.27	[19]
7.	cadmium formate dihydrate [CFD]	1.982	1.965	1.934	64.2	21.2	178.3	[20]
8.	potassium zinc chloro sulphate trihydrate site1. site2. [PZCST]	1.9684	1.9562	1.9929	76	68	195	[21]
9.	cadmium sodium sulphate hexahydrate site1. [CSSH] site2.	1.998	1.972	1.92	61	108	173	[22]
10.	zinc sulphate heptahydrate [ZSH] site1. site2.	1.995	1.983	1.94	52	114	174	
		1.984	1.975	1.938	61.30	70.08	173.89	[23]
		1.982	1.978	1.94	64.29	70.64	173.518	
		1.986	1.985	1.945	71.86	74.19	192.49	[21]
		1.993	1.985	1.954	71.67	73.82	182.30	

$A_x, A_y$  and  $A_z$  are in the unit of ( $\times 10^{-4} \text{cm}^{-1}$ )

$$\cos 2\phi = (g_y + g_x - 4 / 4u) - 2$$

From these two equations, a quadratic equation in terms of u is obtained and u can be easily determined. Putting the value of u in Eq.(10) we can evaluate the value of  $\sin 2\phi$  and  $\cos 2\phi$ . With the help of Eqs.(7), (8) and (9) we can evaluate parameters a, b, c, P, Q, R and  $f_x, f_y, f_z$ . When a graph is plotted between the  $f_i$  ( $i = x, y, z$ ) and hyperfine structure constant  $A_i$  ( $i = x, y, z$ ) with proper signs and directions, the points must lie on straight line [33]. The intersection of the line on  $f_i$  axis gives the value of Fermi contact term K and the slope of the line gives the value of hyperfine interaction parameter  $P_{hf}$ .

Table 2. Ground state wave function for vanadyl ion in selected host lattices.

S.N.	Ground state wave function
1.	$1.7784 x^2 - 1.6816 y^2 - 0.0979 z^2$
2.	$1.7657 x^2 - 1.6962 y^2 - 0.0694 z^2$
3.	$1.7873 x^2 - 1.6708 y^2 - 0.1164 z^2$
4. site1.	$1.7494 x^2 - 1.7141 y^2 - 0.0325 z^2$
site2.	$1.7562 x^2 - 1.7068 y^2 - 0.0494 z^2$
5.	$1.7556 x^2 - 1.7074 y^2 - 0.0481 z^2$
6.	$1.8189 x^2 - 1.6295 y^2 - 0.1893 z^2$
7.	$1.7710 x^2 - 1.6831 y^2 - 0.0939 z^2$
8. site1.	$1.9595 x^2 - 1.3262 y^2 - 0.6333 z^2$
site2.	$1.8760 x^2 - 1.5383 y^2 - 0.3377 z^2$
9. site1.	$1.7925 x^2 - 1.6644 y^2 - 0.1280 z^2$
site2.	$1.7602x^2 - 1.7024 y^2 - 0.0578 z^2$
10. site1.	$1.7419 x^2 - 1.7220 y^2 - 0.1991 z^2$
site2.	$1.8299 x^2 - 1.6138 y^2 - 0.2161 z^2$

Table 3. Fermi contact term, hyperfine interaction parameter, the percent ratio of hyperfine interaction parameter (Phf) to the value for free ion (Pi).

S.N.	Fermi contact term K	Hyperfine interaction parameter P	$P_{hf}/P_f$ %
1.	0.83	108.25	54.13
2.	0.78	116.37	58.19
3.	0.98	111.13	55.57
4. site1.	0.85	112.61	56.30
site2.	0.82	114.70	57.35
5.	0.81	119.13	59.56
6.	0.65	118.03	59.02
7.	0.73	144.17	72.08
8. site1.	0.82	136.24	68.12
site2.	0.90	114.23	57.11
9. site1.	0.77	121.65	60.83
site2.	0.78	123.02	61.51
10. site1.	0.76	115.05	57.53
site2.	0.81	125.94	62.97

P is in the unit of ( $\times 10^{-4} \text{cm}^{-1}$ )

Table 4. Theoretically investigated EPR parameters.

S.No.		u	w	$f_i$		
				$f_x$	$f_y$	$f_z$
1.		0.01194	0.0078	0.3179	0.2129	-0.6419
2.		0.01247	0.0080	0.3032	0.2274	-0.6447
3.		0.02607	0.0016	0.3112	0.1735	-0.6027
4.	site1.	0.01064	0.0088	0.2877	0.2498	-0.6505
	site2.	0.01081	0.0088	0.2949	0.2417	-0.6503
5.		0.01199	0.0093	0.2927	0.2403	-0.6560
6.		0.01302	0.0083	0.362741	0.156399	-0.63814
7.		0.01877	0.00088	0.3077	0.2017	-0.5920
8.	site1.	0.00625	0.0111	0.5300	0.0989	-0.5411
	site2.	0.0052	0.0102	0.4333	0.0876	-0.6230
9.	site1.	0.01017	0.0077	0.3357	0.1986	-0.6373
	site2.	0.00998	0.0075	0.3004	0.2385	-0.6390
10.	site1.	0.00725	0.0068	0.2847	0.2638	-0.6325
	site2.	0.00537	0.0069	0.3816	0.1584	-0.6175

### Result and discussion

Different combinations have been tried giving different directions to  $g_i$  and  $A_i$  values and assigning positive and negative signs to  $A_i$  in order to have a straight line on the  $A_i$ - $f_i$  diagram. The  $A_i$ - $f_i$  diagram thus obtained is shown in Fig. 2. With the help of proper signs and directions of the spin Hamiltonian parameters given in Table 1, the ground state wave function along with hyperfine interaction parameter, Fermi contact term and parameters  $u, v, w, f_x, f_y, f_z$  for the selected host lattices are obtained. These are given in Tables 2, 3 and 4, respectively.

The various points on the  $A_i$  -  $f_i$  diagram lie on straight line in maximum cases but due to some inaccuracy in the experimental data a considerable scatter of the points from straight line are obtained. The ground state wave function of selected host lattices is predominately  $|x^2-y^2\rangle$  and the value of hyperfine interaction parameter in all the cases is lower than the value of the free ion [34]. This indicates that the value of  $r^{-3}$  in crystals is less as compared with the free ion. Since the EPR spectrum of  $VO^{2+}$  ion is quite analogous to the  $Cu^{2+}$  and the spin-orbit coupling decreases for  $Cu^{2+}$  in crystals [35], there will be similar decrease in the spin-orbit coupling and therefore a reduction in the orbital contribution to the  $g$  values. The value of  $P_{hf}/P_f$  is minimum in case of DABMZ indicating that the covalency is maximum because of the fact that the covalency is inversely proportional to the values of

$P_{hf}/P_f$  i.e. the covalency decreases as  $P_{hf}/P_f$  increases and vice versa. With the help of these the order of covalency may be written as,  $CFD > PZCSTsite1. > ZSHsite2. > CSSHsite2. > CSSHsite1. > ZATM > KTP > PMZD > ZSH site1. > MPPHsite2. > PZCSTsite2. > MPPHsite1. > PMCST > DAMBZ$ .

Similarly, we can write the order of decrease of Fermi contact term  $K$  [36]. From Table 2 it can be seen that the ground state wave function comes out to be  $|x^2-y^2\rangle$  type in all the selected host lattices while in DABMZ, PMZD, PMCST, MPPH, CAD, PZCST, CSSH, ZSH systems the ground state has been given to be  $|xy\rangle$  type. However, the parameters  $K$  and  $P$  obtained theoretically in this investigation are well comparable with the experimental values given by earlier workers. This shows that the interpretation of ground state wave function in these systems to be of  $|xy\rangle$  type seems less appropriate.

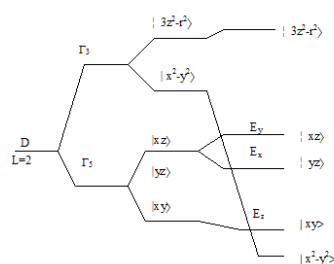


Fig. 1. Energy level splitting of  $VO^{2+}$  ion in crystalline field of lower symmetry

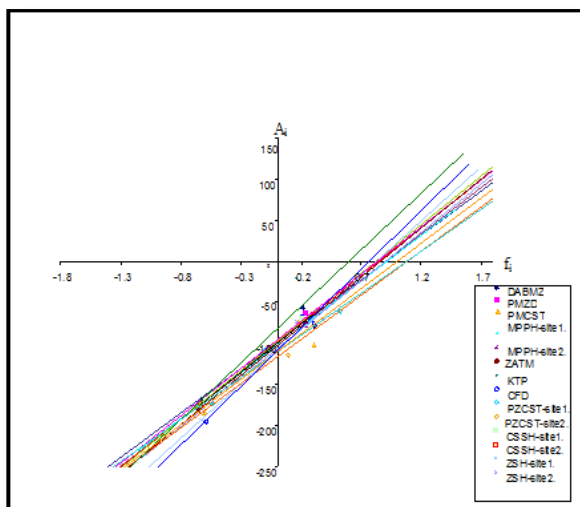


Fig. 2. ( $A_i - f_i$ ) diagram of  $VO^{2+}$  ion doped in different single crystals.

### Conclusion

Ground state wave function of  $VO^{2+}$  ion doped in different single crystals is evaluated and the results show that the ground state is of  $|x^2 - y^2\rangle$  type. The parameters  $u, v, w, a, b, c$  and  $f_x, f_y, f_z$  are also determined. The hyperfine interaction parameter  $P$  and Fermi contact term  $K$  are calculated with the help of  $A_i - f_i$  diagram. Using the value of hyperfine interaction parameter in different host lattices and the value for free ion the order of covalency is determined. Further, from this method the correct signs and directions are assigned to the spin Hamiltonian parameters.

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