
ESTIMATION OF THE COVALENT BINDING FACTORS IN VO²⁺ DOPED SINGLE CRYSTALS

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ABSTRACT

The Steven's model is made to interpret the g-factors in various single crystals doped with paramagnetic ion VO²⁺. This model has been used for the evaluation of covalent binding factors K_{\parallel} and K_{\perp} in different Vanadyl ions complexes with tetragonal symmetry of crystalline field. Using cubic nature for the crystalline field and covalent binding, g-factors are determined in the terms of binding parameters K_{\parallel} and K_{\perp} with the help of self developed computer program. Computations of binding factors show that one of the covalent binding parameters K_{\perp} should be less than 0.095 in order to fit the best experimental g-values.

KEYWORDS:

: Electron Paramagnetic Resonance; binding parameters; spin-orbit interaction; Fermi contact term; hyperfine interaction parameters; parametric angle.

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INTRODUCTION

Electron Paramagnetic Resonance (EPR) studies of vanadyl ion in different single crystals has been reported earlier [1-7] in order to study the structure as well as the relation between temperature and structure of vanadyl complexes in various host lattices. Vanadyl ion is found to be most stable cation among the few molecular paramagnetic transition metal ions, therefore a large number of paramagnetic resonance absorption studies as well as optical and magnetic studies have been done in the complexes doped with VO²⁺ ion. Due to its higher stability, vanadyl ion is used extensively as an impurity probe to study defect properties, structural changes and host lattice effects on molecular ion using EPR studies [8]. Vanadyl complexes have been the subject of interest to a number of workers over recent years [9-10] in different crystalline field environments. The different earlier research works [1-5] show that VO²⁺ ion always occurs co-ordinated to other groups whether in the solid state or in the solution form. The electronic state of this ion is highly dependent on the 3d¹ electron of vanadium. This is why the energy levels of VO²⁺ ion can be taken as that of the V⁴⁺ ion. The d¹ configuration of Ti³⁺ and d⁹ configuration of Cu²⁺ is similar to that of the single unpaired electron vanadyl ion linked to the

V^{4+} ion. The V-O bond has larger covalent character in vanadyl ion [11]. This covalency is inversely proportional to the EPR parameters g_{\parallel} and g_{\perp} . Therefore, it is interesting to see whether it is possible to explain the experimental data obtained from the EPR spectra of VO^{2+} ion doped in different diamagnetic lattices as well as to find the bonding character of vanadium complexes on the basis of theoretical analysis of the behavior of a single $3d^1$ electron.

It was suggested by Gerritsen and Lewis [12] that the simple expressions of g-factors in the parallel and perpendicular orientations as given by Bleaney et al. (1955) [13] could not explain the experimental g values due the presence of the crystalline field of lower symmetry and the factors not taken into analysis by Bleaney et al (1955) [13]. Steven's model [14] for covalent bonding seems to be a better tool for the explanation of experimental g-values in the presence of tetragonal crystalline field. Using experimental g-factors. In the present work it is tried to observe whether the g-values determined from the EPR experiment and also the bonding character for VO^{2+} ion in different single crystals can be explained by Steven's model (1953) [14] of covalent bonding. It is clear from the different theoretical observations that in order to have better fit the experimental g-factors one of the covalent binding factors should be taken as less than one. In table 1 the covalent binding factors K_{\parallel} and K_{\perp} along with the parametric angle δ are given. In my study for best fit to the observed g-values K_{\perp} should be less than 0.095. The following section gives the theoretical expressions of g-factors for covalent binding in the presence of tetragonal field. The discussion will be given in the subsequent section.

THEORY

In this section of the paper the theoretical expressions for g-factors are given in the presence of a tetragonal crystalline field and covalent binding for the present work. The expressions for g_{\parallel} and g_{\perp} for $(d\varepsilon)^5$ in strong cubic field having some tetragonal component were given by Steven's [14] by taking $(d\varepsilon)^5$ as a positive hole in the $d\varepsilon$ shell. For the present work these expressions are slightly modified. These formulas are also used to interpret the g-factors of different single crystals.

In most of the cases the symmetry of the crystalline field is predominantly cubic, with small distortions. The splitting in the orbital states because of the cubic field is larger than that due to the terms with lower symmetry. In my case, the non-cubic component of the crystalline field consists of a tetragonal component which can be seen from observed EPR spectra. First of all, using the first order perturbation theory the matrix of cubic field splitting is diagonalized and thereafter the effect of tetragonal symmetry terms is considered. The "spin-operator technique" [15-16] is used for estimating the energy of lower states.

In the presence of a cubic field with a tetragonal distortion the equivalent Hamiltonian operator is given by:

$$\mathcal{H} = B_4(O_4^0 + 5O_4^4) + B_2^0 O_2^0 + B_4^0 O_4^0 \quad (1)$$

Here B_4 is the magnitude of cubic field; second and third terms represent the tetragonal distortion of the second and fourth order in the potential, respectively. The energy levels and wave functions for the lower states are given below:

$$\begin{array}{l}
 \text{State} \\
 \text{Doublet} \quad |2^a\rangle \equiv |\tilde{O}\rangle \\
 \text{Singlet} \quad \pm|\mp 1\rangle \equiv |\pm \tilde{1}\rangle
 \end{array} \quad (2a)$$

$$\begin{array}{l}
 \text{Energy} \\
 -3B_2^0 - 48B_4^0 \\
 6B_2^0 + 12B_4^0
 \end{array} \quad (2b)$$

States are given in terms of $|L_z\rangle$ and $|\tilde{I}_z\rangle$ where \tilde{I} is the fictitious orbital momentum. According to Stevens [14] the states $|1\rangle$ and $|-1\rangle$ do not show a purely d-nature due to π -bonding between d-electrons and the surrounding p-electrons of the environment. Due to the combined effect of the tetragonal field with negative Δ and spin-orbit interaction two lower states are obtained as below:

$$\begin{aligned}
 \Psi_1 &= \text{Cos}\delta|-1\rangle\left|-\frac{1}{2}\right\rangle - \text{Sin}\delta|0\rangle\left|\frac{1}{2}\right\rangle \\
 \Psi_2 &= \text{Cos}\delta|1\rangle\left|\frac{1}{2}\right\rangle - \text{Sin}\delta|0\rangle\left|-\frac{1}{2}\right\rangle
 \end{aligned} \quad (3)$$

$$\text{Where, } \tan 2\delta = \frac{\sqrt{2\lambda_1}}{(\lambda_1/2) + \Delta} \quad (4)$$

and λ_1 is the reduced value for spin-orbit interaction with Δ as the energy difference between the states Γ_5 and Γ_3 . The g-factors are obtained as

$$\begin{aligned}
 g_{\parallel} &= 2|\text{Sin}^2\delta - (1 + \kappa)\text{Cos}^2\delta|, \\
 g_{\perp} &= 2|\sqrt{2}\kappa\text{Sin}\delta\text{Cos}\delta + \text{Sin}^2\delta|
 \end{aligned} \quad (5)$$

Where κ is defined as $\kappa = \langle a|L_z|a\rangle$ and it is assumed that covalent binding is isotropic, that is, same in all directions. If covalent binding is anisotropic, then expressions for g-factors will be as:

$$\begin{aligned}
 g_{\parallel} &= 2|\text{Sin}^2\delta - (1 + \kappa_{\parallel})\text{Cos}^2\delta|, \\
 g_{\perp} &= 2|\sqrt{2}\kappa_{\perp}\text{Sin}\delta\text{Cos}\delta + \text{Sin}^2\delta|
 \end{aligned} \quad (6)$$

$$\text{Where } \kappa_{\parallel} = \langle 1|L_z|1\rangle \text{ and } \kappa_{\perp} = \sqrt{2} \langle 1|L_x|0\rangle$$

RESULTS AND DISCUSSION

In general, the EPR spectra of VO^{2+} in single crystal are described by a strong octahedral field having tetragonal distortion due to covalent bonding between the central metal ion and surrounding ligand. Using equation (6) the covalent binding factors κ_{\parallel} and κ_{\perp} were estimated. The values of these factors for different single crystals [17-34] with parametric angle δ satisfying experimental g-values are given in Table 1. In presence of tetragonal field, the covalent binding factors are found to be less than one, because no shifting of doublet in t_{2g} and higher doublet e_g . The multiple values of [35] of κ_{\parallel} , κ_{\perp} and δ have been estimated as exact value of λ_1 is not known. In case of exact value parametric angle δ can be fixed so that corresponding

parameters with respect to δ is obtained. The theoretical calculations show that experimental values of g-factors can be obtained if κ_{\perp} is less than 0.095. The larger migration of an electron to its neighboring atom may be explained by less value of covalent binding factor [36]. However, covalency is inversely proportional to g_{\parallel} and g_{\perp} . Also, g_{\parallel} varies inversely to covalent binding factor κ_{\parallel} , that is, if κ_{\parallel} is decreased g_{\parallel} will be increase and so covalency will decrease indicating more ionic character of the complex [37]. The more ionic the crystal is larger will be splitting [38-39]. However direct proportionality between g_{\perp} and κ_{\perp} will give a different nature to the complex as for as binding is considered. The rate of decrease of κ_{\parallel} is more than κ_{\perp} and therefore taking more ionic nature for the complex will be appropriate. Therefore, the migration of electron to its neighboring atoms will take place. These assumptions indicate that crystal field theory for ionic complex must be modified by considering a definite amount of charge transfer.

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Table 1 Values of the covalent bonding factors K_{\parallel} and K_{\perp} with parametric angle δ in different crystals

S. No.	Crystal Lattices	K_{\perp}	K_{\parallel}	δ	Reference
1.	Ammonium Alum {NH ₄ Al (SO ₄) ₂ .24H ₂ O}	0.030 0.035 0.040 0.047 0.053 0.062	1.629 0.988 0.662 0.455 0.239 0.061	95°45' 96° 96°15' 96°30' 96°45' 97°	[17]
2.	Rb Alum {Rb Al (SO ₄) ₂ . 12H ₂ O}	0.010 0.018 0.028 0.034 0.037	1.145 0.889 0.689 0.339 0.074	96°14' 96°49' 97°30' 97°52' 98°59'	[18]
3.	L-asparagine monohydrate	0.022 0.010 0.007 0.006	1.485 0.933 0.833 0.736	96°14' 96°49' 97°30' 97°52'	[19]
4.	Sodium Citrate	0.041 0.033 0.020 0.010 0.007 0.004	1.324 0.966 0.604 0.324 0.245 0.144	95°45' 96° 96°15' 96°30' 96°45' 97°	[20]
5.	Tutton Salts	0.031 0.040 0.047 0.051 0.057 0.062	1.631 0.985 0.663 0.495 0.215 0.061	96°28' 96°44' 97°14' 97°32' 97°46' 98°2'	[21]
6.	Tri Sodium Citrate Pentahydrate {Na ₃ C ₆ H ₅ O ₇ .5H ₂ O}	0.061 0.063 0.068 0.072 0.061	1.148 0.951 0.612 0.319 0.074	95°24.5' 95°48' 95°48' 96°14' 96°32'	[22]
7.	Calcium Fumarate Trihydrate	0.031 0.037 0.041 0.047 0.051 0.061	1.174 0.898 0.730 0.357 0.162 0.041	96°49' 97°8' 97°20' 97°40.5' 97°54.5' 98°28'	[23]
8.	CoMTH Cobalt Maleate Tetrahydrate	0.030 0.036	1.173 0.897	96°29' 96°47.5'	[24]

		0.040 0.050 0.056 0.060	0.729 0.356 0.161 0.042	96°59.5' 97°32' 97°46' 98°2'	
9.	Potassium Oxlate Monohydrate (POM) (COOK) ₂ .H ₂ O	0.004 0.006 0.007 0.012 0.020	0.585 0.522 0.461 0.397 0.116	96°35' 96°42' 96°48' 96°55.5' 97°16'	[25]
10.	Lactate Trihydrate (ZLT) [Zn (CH ₃ CHOHCOO) ₂ .3H ₂ O]	0.001 0.002 0.004 0.008 0.010 0.020	0.918 0.804 0.660 0.595 0.277 0.002	96°11.5' 96°15.5' 96°29.5' 96°35.5' 96°46' 97°2'	[26]
11.	KHC ₂ O ₄	0.002 0.004 0.006 0.008 0.010	0.477 0.413 0.353 0.294 0.234	95°23' 95°27.5' 95°32.5' 95°37' 95°43.5'	[27]
12.	TiO ₂	0.001 0.004 0.008 0.010 0.020 0.025	0.688 0.648 0.584 0.445 0.384 0.087	96°29' 96°47.5' 96°59.5' 97°32' 97°46' 98°	[28]
13.	GeO ₂ (amorphous)	0.010 0.015 0.020 0.025 0.031 0.036	1.047 0.798 0.642 0.424 0.292 0.108	96°2' 96°16' 96°29.5' 96°44.5' 96°56' 97°13'	[29]
14.	FeRb ₂ (SO ₄) ₂ .6H ₂ O (Tutton Salt)	0.010 0.016 0.022 0.028 0.036	1.187 0.766 0.537 0.398 0.204	96°1' 96°17' 96°59.5' 97°32' 97°46'	[30]
15.	NaKC ₄ H ₄ O ₆ .6H ₂ O	0.001 0.003 0.005 0.008 0.011 0.020	0.914 0.804 0.660 0.592 0.274 0.234	96°36' 96°41' 96°45' 96°51.5' 97°16' 97°20.5'	[30]
16.	MgSO ₄ .7H ₂ O	0.060 0.063 0.066 0.071	1.447 1.147 0.948 0.604	94°52' 95°0.5' 95°19.5' 95°38'	[30]

		0.075 0.079	0.317 0.076	95°57.5' 96°23.5'	
17.	MASH	0.060 0.066 0.070 0.075 0.080 0.085	1.027 0.889 0.687 0.492 0.227 0.074	96°23' 96°47.5' 97°3' 97°28' 97°46' 98°2.5'	[31]
18.	Cs ₂ Mg (SO ₄) ₂ .6H ₂ O	0.030 0.040 0.045 0.051 0.056 0.060	1.628 0.980 0.660 0.468 0.215 0.062	96°15' 96°47.5' 97°8.5' 97°22' 97°42' 97°57'	[32]
19.	Mg (H ₂ O)6H ₂	0.066 0.069 0.071 0.075 0.080 0.082	1.066 0.928 0.807 0.483 0.295 0.207	96°21.5' 96°30' 96°39.5' 97°3' 97°20' 97°29'	[32]
20.	CoASH	0.030 0.034 0.039 0.045 0.052 0.060	1.273 0.947 0.788 0.456 0.199 0.052	98°46' 99°7' 99°21.5' 99°54.5' 100°16' 100°32'	[33]
21.	CASH	0.030 0.040 0.050 0.070 0.080 0.090	1.153 0.818 0.616 0.383 0.284 0.194	96°21' 96°29.5' 96°38.5' 97°3' 97°20' 98°28'	[34]

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