



RESEARCH ARTICLE

Estimation of the covalent binding parameters and the ground state wave functions in complexes doped with vanadyl ion

Indrajeet Mishra

Abstract

Steven's model has been used for computing the covalent binding parameters in octahedral complexes doped with transition metal ions. This model is further used to interpret the g-factors in various single crystals containing paramagnetic VO^{2+} ions. Theoretical expressions were given for the g-factors of Vanadyl ions in the crystalline field of cubic nature with components of tetragonal symmetry. The g-factors have been given in terms of covalent binding parameters K_{\parallel} and K_{\perp} taking into account the tetragonal crystalline field and covalent binding. Computations show that K_{\perp} should be less than 0.064 in order to fit the experimental g-values. Crystal field theory has determined the ground state wave functions (GSWF) for VO^{2+} ions in different single crystals. It is found that GSWF is in d_{xy} state with a slight admixture of excited states $d_{x^2-y^2}$, d_{xz} and d_{yz} . The hyperfine interaction parameter P and Fermi contact term X have also been calculated.

Keywords: Electron Paramagnetic Resonance; binding parameters; spin-orbit interaction; spin-Hamiltonian; fermi contact term; hyperfine interaction parameter; parametric angle.

INTRODUCTION

Vanadyl complexes have been the subject of interest to different researchers due to fact that the electronic state of VO^{2+} ion having vanadium ion V^{4+} and a closed shell oxide O^{2-} is $3d^1$. A number of workers Assour *et al.* (1965); Assour (1965); Radhakrishna (1983); Selvin (1965); Manoogian and Mackinnon (1967); Rao *et al.* (1968); Manoharan and Rogers (1968); Flowers *et al.* (1973); Jain (1979); Oversluisen and Metselaar R (1982) have done earlier EPR studies of Vanadyl ion doped in different single crystals because tetravalent vanadium exists as a stable Vanadyl. It is found that the configuration of a single unpaired electron of Vanadyl ion is similar to the d^1 configuration of Ti^{3+} or d^9 configuration of

Cu^{2+} . It was shown by Tapramaz *et al.* (2000) that in Vanadyl ion V-O bond has considerable covalent bonding nature which is inversely proportional to the EPR parameters g_{\parallel} and g_{\perp} . Earlier investigations show that VO^{2+} ion always occurs coordinated to other groups, whether in the solid state or in the solution form. This ion's electronic state is mainly dependent on the $3d^1$ electron. Hence the energy levels of VO^{2+} ion can be taken as that of the V^{4+} ion. 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 earlier by Gerritsen and Lewis (1960) that expressions of g- factors in the parallel and perpendicular orientations, as given by Bleaney *et al.* (1955) 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.* (1950). The model for covalent bonding given by Stevens (1953) may be a better tool for the explanation of experimental g-values in the presence of tetragonal crystalline field. In the present study I try to find out whether the g-values determined from the EPR experiment and also the bonding character for VO^{2+} ion doped different single crystals can be explained by Steven's (1953) model of covalent bonding. It is clear from the theoretical observations that in order to have better fit the experimental g-factors, one of the covalent binding

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factors should be taken as less than one. If EPR parameters g and A are known by experiment, then spectroscopic and magnetic character can be obtained from ground state wave functions. The hyperfine splitting parameter P and Fermi contact term X can be evaluated using g and A values. In the present work, using crystal field theory, the covalent binding factors and ground state wave functions along with P and X of VO^{2+} ion in different single crystal lattices.

Theory and Calculation

If Vanadyl ion VO^{2+} doped in a single crystal is subjected in the octahedral symmetry of crystalline field having tetragonal distortion because of surrounding ligands. In such a field the equivalent Hamiltonian operator is given as follow (Abragam and Bleaney 1970):

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

In the above equation (1) term B_4 represents the magnitude of the octahedral field and the remaining two terms give the tetragonal distortions for the second and fourth degree in the potential, respectively. The expressions of g_{\parallel} and g_{\perp} for $(d\varepsilon)^5$ in an octahedral field with tetragonal distortion were given by Stevens (1953). The states in the ground state doublet for d electron can be expressed as:

$$|\Psi_+\rangle = \cos\beta|b,-\rangle - \sin\beta|c,+\rangle \quad (2)$$

$$|\Psi_-\rangle = \cos\beta|a,+\rangle + \sin\beta|c,-\rangle \quad (3)$$

where β is defined as:

$$\tan 2\beta = \frac{\sqrt{2\lambda}}{(\lambda/2) - \Delta}$$

Here λ is the spin-orbit coupling constant and the energy gap between the states Γ_3 and Γ_3 is Δ . In the present investigation for d electrons $|a\rangle$, $|b\rangle$ and $|c\rangle$ become $|1\rangle$, $|-1\rangle$ and $(\frac{1}{\sqrt{2}}(|2\rangle - |2\rangle))$. The expressions for g -factors are given as

$$g_{\parallel} = 2|\sin^2\beta - (1 + \kappa)\cos^2\beta| \quad (4)$$

$$g_{\perp} = 2|\sqrt{2\kappa}\sin\beta\cos\beta + \sin^2\beta| \quad (5)$$

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 assumed to be anisotropic in nature, the g -factors are determined as follows:

$$g_{\parallel} = 2|\sin^2\beta - (1 + \kappa_{\parallel})\cos^2\beta| \quad (6)$$

$$g_{\perp} = 2|\sqrt{2\kappa_{\perp}}\sin\beta\cos\beta + \sin^2\beta| \quad (7)$$

Where κ_{\parallel} and κ_{\perp} are the covalent binding parameters are defined by the following relations:

$$\kappa_{\parallel} = \langle 1|L_z|1\rangle \text{ and } \kappa_{\perp} = \sqrt{2} \langle 1|L_x|0\rangle \text{ with } \kappa = \langle a|L_z|a\rangle.$$

The above equations (4) and (5) can be used for the estimation of the binding parameters along with experimental values g -factors taken from the different research papers mentioned in Table 1.

The 2D term splits into three singlets and one doublet in an octahedral field with tetragonal distortion. The splitting of 2D term is shown in Figure 1. It is found that the form of spin-orbit coupling matrix has form $\langle \psi_i|\lambda L.S|\psi_j\rangle$ (Poole and Farach 1972). The wave function of the ground state can be easily written by using the first-order perturbation theory and following Zapirov and Chirkin (1968). In the present case wave function is as follows:

$$|\pm\rangle = \pm C_1|\pm 2, \pm \frac{1}{2}\rangle \mp C_2|\mp 2, \pm \frac{1}{2}\rangle \pm C_3|\mp 1, \mp \frac{1}{2}\rangle \quad (8)$$

The coefficient C_1 , C_2 and C_3 gives the admixture of d_{xy} state with slight admixture of excited states $d_{x^2-y^2}$, d_{xy} states to the ground state d_{xy} due to the spin-orbit coupling. If we know these coefficients C_1 , C_2 and C_3 the ground state can be easily calculated. These constants are determined by solving the following equations-

$$C_1^2 + C_2^2 + C_3^2 = 1 \quad (9)$$

$$g_{\parallel} = 2(3C_1^2 - C_2^2 - 2C_3^2) \quad (10)$$

and

$$g_{\perp} = 4C_1(C_2 - C_3) \quad (11)$$

The coefficients C_1 , C_2 and C_3 are easily determined by substituting the experimental values of g_{\parallel} and g_{\perp} in the equations (10) and (11) along with the equation (9). Now in equation (8) the values of constants C_1 , C_2 and C_3 are substituted to obtain the ground state wave function. The hyperfine structure constants are now calculated using the estimated ground state wave function (Abragam and Bleaney 1970).

$$A_{\parallel} = P \left[g_{\parallel} \left(X + \frac{15}{7} \right) \left(1 - 2C_3^2 - \frac{3}{7}(1 + 4C_2C_3) \right) \right] \quad (12)$$

$$A_{\perp} = P \left[\frac{11}{14} g_{\perp} - 2C_1C_2 \left(X + \frac{9}{7} \right) \right] \quad (13)$$

The values of calculated coefficients C_1 , C_2 and C_3 along with the experimental values g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} for different diamagnetic lattices taken from different references (Table 1) are substituted in equations (12) and (13) to get hyperfine interaction parameter P and Fermi contact term X . The calculated ground state wave functions along with the values of P , X , binding factors and parametric angle β are given in Table 1. The values of P and X are determined in both cases i.e. positive and negative values of A_{\parallel} and A_{\perp} . In case $A_{\parallel} / A_{\perp} < 0$, the obtained values of P and X do not match with the results using molecular orbital theory therefore, these values are not included in the present work. The reasonable values for P and X are taken for the small unpairing or polarization due to inner electron as a result of an interaction with an unpaired d electron.

Results and Discussion

If VO^{2+} ion is doped in different single crystals, then observed EPR spectra are usually described by a very strong octahedral ligand field with tetragonal distortion due to covalent bonding between central metal ion and the surrounding ligands. The calculated values of A_{\parallel} and A_{\perp} and ground state wave functions, X and P are given in Table 1. In the presence of a tetragonal field, there is no shifting of the doublet in t_{2g} and higher doublet e_g ; therefore, covalent binding factors are found to be less than 1. Since λ is not exactly known, multiple values of K_{\parallel} , K_{\perp} and parametric angle β have been determined. Angle β can not be fixed here as exact value for λ is not known. If λ is exactly known the parametric angle β can be fixed and the parameters corresponding to fixed β will give the proper result for the system. The present study computation shows that by taking value of $K_{\perp} < 0.064$ the best fit to the experimental g values can be obtained. If the value of covalent binding factor is small then an electron will migrate to its neighboring atoms.

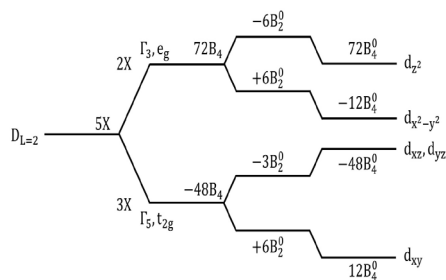


Figure 1: Energy level splitting of $2D$ state of vanadium V^{4+} with octahedral field in Configuration d^1 by tetragonal distortion

The parameters g_{\parallel} and g_{\perp} depends upon nature of covalent binding and the factors K_{\parallel} and K_{\perp} . This dependency confirms the inverse relation between K_{\parallel} and g_{\parallel} . If the value of K_{\parallel} decreases then g_{\parallel} increases and covalency decreases, indicating that the complex will have more ionic character. At the same time there is direct proportionality between and showing different nature of the binding for a particular system. The present work shows that rate of decrease of K_{\parallel} is more than K_{\perp} so that compound can be considered to be more ionic in nature. Therefore there will be more migration of electrons to neighboring atoms indicating that there must be the possibility of transfer of net amount of charge, which is also observed in the crystal field theory for ionic compounds.

The ground state wave functions of different complexes doped with VO^{2+} estimated in present study is of the d_{xy} type with some admixture of excited states d_{x-y}^2 , d_{xz} and d_{yz} . The same result was also obtained by Kivelson and Lee (1964) using theory of Ballhausen and Gray (1962). ESR spectra of complexes used in my study also confirm that ground state is d_{xy} . Spectra also support my calculations. Parameter X shows the contribution of unpaired s -electron to the hyperfine structure splitting. According to Abragam (1950) hyperfine splitting is originated from interaction because of configuration. Major contribution to the hyperfine structure splitting by virtue of core polarization parameter (Fermi contact term) is due to unpaired s -electron therefore, slight admixture in ground state wave function is necessary for the explanation of splitting. A regular variation in P with covalency was observed by Wieringen (1955). There is direct relation between ionic character of crystal and splitting. The single crystal with more ionic character shows larger splitting. If $A_{\parallel} / A_{\perp} > 0$ the estimated values of P and X are more suitable because the condition P/P_0 is satisfied only for the positive ratio of A_{\parallel} and A_{\perp} . Here P_0 having a value of $200 \times 10^{-4} \text{ cm}^{-1}$ is free ion hyperfine interaction. A relation between P and P_0 is given by the relation:

$$\frac{P}{P_0} \propto \frac{\lambda}{\lambda_0}$$

In above relation λ is spin-orbit coupling constant for paramagnetic ion in a crystal, λ_0 is the free ion value. It is found that $\lambda < \lambda_0$.

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Table 1: Ground state wave function, hyperfine interaction parameter P, Fermi contact term X, Covalent binding factors K_{\parallel} , K_{\perp} and parametric angle β for Vanadyl ion in different crystals

S. No.	Crystal Lattices	Ground state wave function	$P \times (10^{-4} \text{ cm}^{-1})$	X	K_{\parallel}	K_{\perp}	β
1.	Potassium Alum {KAl(SO ₄) ₂ .12H ₂ O} (Rao et al. 1968)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0061 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0086 \left \mp 1, \mp \frac{1}{2} \right\rangle$	126.1952	0.9533	1.377 1.112 0.889 0.643	0.022 0.037 0.042 0.049	96°45' 97° 97°15' 97°30'
2.	Cs Alum {Cs Al(SO ₄) ₂ .12H ₂ O} (Manoogian and MacKinnon 1967)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0063 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0094 \left \mp 1, \mp \frac{1}{2} \right\rangle$	115.1922	0.9372	1.089 0.889 0.632 0.432 0.336	0.009 0.015 0.026 0.035 0.030	96°15' 96°30' 96°45' 97° 97°15'
3.	Tri Sodium Citrate Pentahydrate {Na ₃ C ₆ H ₅ O ₇ .5H ₂ O} (Bhaskar et al. 1982)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0069 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0089 \left \mp 1, \mp \frac{1}{2} \right\rangle$	117.668	0.9077	1.082 0.858 0.658 0.457 0.320	0.016 0.019 0.026 0.029 0.036	96° 96°15' 96°30' 96°45' 97°
4.	L-asparagine monohydrate (Kripal et al. 2009)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0068 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0077 \left \mp 1, \mp \frac{1}{2} \right\rangle$	114.978	0.8459	1.202 0.950 0.758 0.657 0.420 0.233	0.034 0.039 0.046 0.049 0.056 0.067	95°15' 95°30' 95°45' 96° 96°15' 96°30'
5.	Tri Sodium Citrate Dihydrate (Karabulut et al. 2005)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0071 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0079 \left \mp 1, \mp \frac{1}{2} \right\rangle$	120.8095	0.8566	1.072 0.850 0.658 0.457 0.225	0.0094 0.016 0.027 0.031 0.036	96°15' 96°30' 96°45' 97° 97°15'
6.	K Zn Cl (SO ₄).3H ₂ O (PZCST) (Raju et al. 2003)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0057 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0049 \left \mp 1, \mp \frac{1}{2} \right\rangle$	114.659	0.7928	0.0196 0.0223 0.0289 0.0320	0.0048 0.0088 0.016 0.020	96°30' 96°45' 97° 97°15'
7.	Cs ₂ Co (SO ₄) ₂ .6H ₂ O (Tutton Salt) (Narasimhulu and Rao 1997)	$\pm \left(\frac{1}{\sqrt{2}} \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right) \right)$ $\mp 0.0058 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0047 \left \mp 1, \mp \frac{1}{2} \right\rangle$	116.8774	0.7519	1.113 0.888 0.654 0.463 0.355	0.0098 0.017 0.021 0.027 0.039	95°15' 95°30' 95°45' 96° 96°15'

8.	MgRb ₂ (SO ₄) ₂ .6H ₂ O (Tutton Salt) (Jain and Venkateshwarlu 1979)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0055 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0036 \left \mp 1, \mp \frac{1}{2} \right\rangle$	119.9095	0.8308	1.2033 0.944 0.833 0.565	0.018 0.033 0.034 0.039	95°30' 95°45' 96° 96°15'
9.	(NH ₄) ₂ C ₂ O ₄ .H ₂ O (Jain and Venkateshwarlu 1979)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0055 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0090 \left \mp 1, \mp \frac{1}{2} \right\rangle$	120.8085	0.8886	1.068 0.846 0.647 0.435 0.236	0.0078 0.014 0.022 0.036 0.039	96°30' 96°45' 97° 97°15' 97°30'
10.	GeO ₂ (Siegel 1964)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0058 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0046 \left \mp 1, \mp \frac{1}{2} \right\rangle$	113.8894	0.9406	1.122 0.888 0.732 0.644 0.533	0.016 0.024 0.044 0.048 0.054	96°30' 96°45' 97° 97°15' 97°30'
11.	(NH ₄) ₂ Mg (SO ₄) ₂ .6H ₂ O (Narayana et al. 1976)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0061 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0086 \left \mp 1, \mp \frac{1}{2} \right\rangle$	115.2888	0.8306	1.078 0.858 0.669 0.499 0.326	0.006 0.016 0.022 0.026 0.032	95°45' 96° 96°15' 96°30' 96°45'
12.	K ₂ Mg (SO ₄) ₂ .6H ₂ O (Kasturirengan et al. 1975)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0066 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0036 \left \mp 1, \mp \frac{1}{2} \right\rangle$	128.526	0.8819	1.212 0.956 0.754 0.522 0.348	0.0028 0.0086 0.016 0.020 0.026	96°45' 97° 97°15' 97°30' 98°
13.	ZnSO ₄ .7H ₂ O (Kasiviswanath 1977)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0047 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0044 \left \mp 1, \mp \frac{1}{2} \right\rangle$	125.2928	0.9376	1.086 0.869 0.668 0.498 0.316	0.009 0.017 0.021 0.024 0.032	95°45' 96° 96°15' 96°45' 97°
14.	KMgCl(SO ₄).3H ₂ O (Kainite) (Dhanuskodi et al. 2001)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0068 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0079 \left \mp 1, \mp \frac{1}{2} \right\rangle$	118.2628	0.9636	1.388 1.112 0.868 0.656 0.461 0.288	0.022 0.026 0.033 0.038 0.044 0.049	95°30' 95°45' 96° 96°15' 96°30' 96°45'
15.	Cd (NH ₄) ₂ (SO ₄) ₂ .6H ₂ O (CdASH) (Satyanarayana and Radhakrishna 1985)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right\rangle - \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\mp 0.0061 \left(\left \pm 2, \pm \frac{1}{2} \right\rangle + \left \mp 2, \pm \frac{1}{2} \right\rangle \right)$ $\pm 0.0087 \left \mp 1, \mp \frac{1}{2} \right\rangle$	127.449	0.8466	1.068 0.836 0.624 0.434 0.266	0.008 0.015 0.022 0.032 0.038	97° 97°15' 97°30' 97°45' 98°

16.	Zn (NH ₄) ₂ (SO ₄) ₂ .6H ₂ O (Mishra . and Jian- Sheng Sun. 1990).	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0059 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0086 \left \mp 1, \mp \frac{1}{2} \right $	117.8706	0.8812	1.0189 0.846 0.666 0.424 0.265	0.0052 0.012 0.018 0.024 0.028	96°45' 97° 97°15' 97°30' 97°45'
17.	Mg KPO ₄ .6H ₂ O (MPPH) (Deepa et al. 2005)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0059 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0087 \left \mp 1, \mp \frac{1}{2} \right $	118.886	0.8898	1.238 0.978 0.746 0.536 0.354	0.024 0.028 0.033 0.037 0.044	95°45' 96° 96°15' 96°30' 96°45'
18.	MPSH (Anandalakshmi et al 2000)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0052 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0096 \left \mp 1, \mp \frac{1}{2} \right $	112.868	0.8102	0.846 0.549 0.302 0.092	0.0012 0.0075 0.014 0.019	96° 96°15' 96°30' 96°45'
19.	ZPPH (Ravikumar et al. 2001)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0060 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0077 \left \mp 1, \mp \frac{1}{2} \right $	114.8668	0.7766	0.763 0.489 0.347 0.222 0.030	0.005 0.013 0.016 0.021 0.033	94°45' 95° 95°15' 95°30' 95°45'
20.	CPPH (Sougandi et al.2002)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0058 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0065 \left \mp 1, \mp \frac{1}{2} \right $	115.8081	0.7582	1.096 0.768 0.478 0.390 0.027	0.018 0.025 0.031 0.033 0.036	94°15' 94°30' 94°45' 95° 95°15'
21.	CSPH (Sougandi et al.2003)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0066 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0081 \left \mp 1, \mp \frac{1}{2} \right $	119.3722	0.7446	0.666 0.488 0.387 0.0325 0.0266 0.0066	0.022 0.029 0.034 0.039 0.041 0.045	97° 97°15' 97°30' 97°45' 98° 98°15'
22.	(CoMTH) H ₂ Co(C ₄ H ₂ O ₄) ₂ .4H ₂ O (Gopal et al.2001)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0053 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0048 \left \mp 1, \mp \frac{1}{2} \right $	114.8886	0.8844	1.188 0.899 0.558 0.336 0.099	0.006 0.018 0.022 0.027 0.033	94°30' 94°45' 95° 95°15' 95°30'
23.	(NH ₄) ₂ C ₄ H ₄ O ₆ (Tapramaz et al.2000)	$\pm \left(\frac{1}{\sqrt{2}} \right) \left(\left \pm 2, \pm \frac{1}{2} \right - \left \mp 2, \pm \frac{1}{2} \right \right)$ $\mp 0.0072 \left(\left \pm 2, \pm \frac{1}{2} \right + \left \mp 2, \pm \frac{1}{2} \right \right)$ $\pm 0.0056 \left \mp 1, \mp \frac{1}{2} \right $	113.8885	0.9288	1.123 0.879 0.664 0.465 0.299	0.0028 0.0086 0.014 0.022 0.026	96°30' 96°45' 97° 97°15' 97°30'

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