Boson Journal of Modern Physics (BJMP)
ISSN: 2454-8413

SCITECH
RESEARCH ORGANISATION

Volume 3, Issue 1
February 25, 2017

Boson Journal of Modern Physics
www.scitecresearch.com

Crystalline Field Effect on bonding Parameters of VO2+ Ion

Ram Kripal[1], Sanjay Misra[2] and Awadhesh Kumar Yadav[3]

[1, 2, 3]Department of Physics, University of Allahabad, Allahabad, 211 002, India

E-mail: [1]ram_kripal2001@rediffmail.com; [2]ssopam@gmail.com, [3]aky.physics@gmail.com.

Abstract

The interpretation of g factor of the VO^{2+} ion doped in defferent single crystals is made using the Stevens model where the symmetry of the crystalline field is tetragonal. The bonding parameters $K_{\parallel}$ and $K_{\perp}$, choosing the different parametric angle β, are determined. The value of $K_{\perp}$ should be less than 0.048 in order to have a better fit to the experimental g values.

Keywords: Electron paramagnetic resonance; parametric angle; Bonding parameters.

Introduction

Electron paramagnetic resonance (EPR) provides a great deal of information about the magnetic properties of paramagnetic ion in different host lattices. This method also provides a detailed description of the ground state wave function of paramagnetic ions and enables one to understand the nature of the electric field symmetry produced by the ligands around the metal ion. VO^{2+} ion has only one electron, i.e., it has $3d^1$ configuration which allows paramagnetic resonance to be observed at ambient temperature. The VO^{2+} 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 resonance studies. The paramagnetic VO^{2+} ion in different host lattices is studied and reported [1–10].

On the basis of the theoretical analysis of the behavior of $3d^1$ single electron in VO^{2+} ion doped single crystals, the ground state wave function and nature of bonding are estimated with the help of EPR data. In the present investigation, the experimental g values are explained by the Stevens model of covalent bonding in the presence of tetragonal crystalline field. It is seen that a better fit of the experimental g factor is obtained by taking one of the bonding parameters less than 0.048.

1. Theoretical Aspect

When VO^{2+} ion is doped in a crystal lattice, it experiences crystal field of octahedral symmetry having tetragonal distortion due to ligands around the metal ion. For this the Hamiltonian can be written as [11],

$$\mathcal{H} = B_4(O_4^0 + 5O_4^4) + B_2^0 O_2^0 + B_4^2 O_4^0 \tag{1}$$

where B_4 is the magnitude of the octahedral field and other terms are the tetragonal distortions of second and fourth degree. We can take into account the tetragonal field in a potential in the form[12],

$$V = A_2^0 r^2 Y_2^0 + A_4^0 r^4 Y_4^0 + A_4^4 r^4 (Y_4^4 + Y_4^{-4}) \tag{2}$$

where the first and second term incorporate the tetragonal component.

The lower states and their energies are:

Doublet: $\frac{1}{\sqrt{2}}(|+1\rangle+|-1\rangle)$

Singlet: $\frac{1}{\sqrt{2}}(|+2\rangle+|-2\rangle)$

Energy:

$$-\sqrt{\frac{1}{14}}a-\sqrt{\frac{8}{63}}c$$

$$\sqrt{\frac{2}{7}}a+\sqrt{\frac{1}{126}}c-\sqrt{\frac{5}{9}}d \qquad (3)$$

where $a = -\sqrt{\frac{5}{14\pi}}r^{-2}A_2^0$

c = $3/\sqrt{14\pi}r^{-4}A_4^0$

d = $3/\sqrt{14\pi}r^{-4}A_4^4$

Stevens [12] has shown that states $|-1\rangle$ and $|+1\rangle$ etc. do not exhibit a purely d-nature due to pi- bonding between d-electron and the surrounding p-electron of oxygen atoms. We have two lower states due to a combined effect of the tetragonal field (with negative Δ) and the spin – orbit interaction

$$|+1\rangle = \cos\beta\,|-1\rangle\,|-1/2\rangle-\sin\beta\,|0\rangle\,|+1/2\rangle$$

$$|-1\rangle = \cos\beta\,|+1\rangle\,|+1/2\rangle+\sin\beta\,|0\rangle\,|-1/2\rangle \qquad (4)$$

where

$$\tan 2\beta=\frac{\sqrt{2}}{(1/2)\lambda_1+\Delta}\lambda_1$$

λ_1 is reduced spin orbit interaction. The expressions for g- factors are given below as

$$g_{\parallel} = 2\left|\sin^2\beta-(1+K\ )\cos^2\beta\right|$$

$$(5)$$

$$g_{\perp} = 2\left|\sqrt{2}K\ \ \sin\beta\cos\beta+\sin^2\beta\right|$$

where K is defined as

K = <+1|L_z|+1>

and it is assumed that covalent bonding is isotropic. If we assume that bonding is anisotropic we can write

$$g_{\parallel} = 2\left|\sin^2\beta-(1+K_{\parallel})\cos^2\beta\right|$$

$$(6)$$

$$g_{\perp} = 2\left|\sqrt{2}K_{\perp}\sin\beta\cos\beta+\sin^2\beta\right|$$

where

$K_{\parallel}$ = <+1|L_z|+1> and K⊥ = √2 <+1|L_x|+0>

From above equations we can estimate the nature of bonding inVO^{2+} ion doped different lattices with the help of EPR data and parametric angle β.

2. Results & Discussion

The covalent bonding parameters $K_{\parallel}$ and $K_{\perp}$ were determined with the help of EPR data of VO^{2+} ion doped in different single crystals given in Table 1 [13, 14, 15]. The values of these parameters $K_{\parallel}$ and $K_{\perp}$ with the parametric angle β shown in Table 2 satisfy the experimental g values.

In the presence of tetragonal crystalline field the covalent bonding parameters are less than 1 as there is no shifting of doublet in t_{2g} and higher doublet e_g. The result shows that the value of one covalent bonding factor $K_{\perp}$ should be less than 0.048 in order to have a better fit to the experimental g value [12]. The covalency is inversely proportional to the g value [16] and the value of $g_{\parallel}$ depends on the $K_{\parallel}$. If $K_{\parallel}$ decreases, $g_{\parallel}$ increases and covalency decreases showing that, the character of the complex will be more ionic. $g_{\perp}$ depends on the $K_{\perp}$ and is directly proportional to it. Hence, its value will increase if $K_{\perp}$ increases; giving different nature to the complex as far as bonding is concerned.

Table 1 E PR parameters for VO^{2+} ion in selected crystal lattices with tetragonal symmetry

S.N	Crystal Lattices	EPR Parameters				
		$g_{\parallel}$	**$g_{\perp}$**	**$A_{\parallel}$**	**$A_{\perp}$**	**[Ref.]**
1.	Germanium Dioxide $GeO_2 : VO^{2+}$	1.9290	1.9771	175	68	[13]
2.	Cesium Cadmium Sulfate Hexahydrate $Cs_2Cd(SO_4)_2.6H_2O$ $: VO^{2+}$	1.9210	1.9871	177	70	[13]
3.	Magnesium Ammonium Sulphate Hexahydrate $Mg(NH_4)_2(SO_4)_2$ $.6H_2O: VO^{2+}$	1.9141	1.9790	180	73	[13]
4.	Ammonium Selenate $(NH_4)_2.SeO_4: VO^{2+}$	1.9220	1.9821	187	73	[13]
5.	Zinc Cesium Sulphate Hexahydrate $ZnCs_2(SO_4)_2.6H_2O$ $: VO^{2+}$	1.9350	1.9861	182	73	[13]
6.	Potassium Succinate $C_4H_4KO_4: VO^{2+}$	1.9261	1.9781	178	69	[13]
7.	Zinc lactate trihydrate $Zn(C_3H_5O_3)_2\cdot 3H_2O: VO^{2+}$	1.9236	1.9999	197	90	[14]

8. Zinc ammonium phosphate hexahydrate $ZnNH_4PO_4·6H_2O$: VO^{2+}					[15]
Site I	1.9668	1.9867	172	66	
Site II	1.9698	1.9909	149	57	

Table 2. The value of covalent bonding Parameters ($K_\parallel$ & K⊥) and the parametric angle β for VO^{2+} doped in some single crystals.

S.N. Crystal Lattices	**$K_\parallel$**	**K⊥**	**β**
1. Germanium Dioxide			
	0.984	0.002	96.31
	0.901	0.004	96.40
	0.856	0.006	96.45
2. Cesium Cadmium Sulphate Hexahydrate			
	0.953	0.044	96.69
	0.850	0.046	96.81
	0.800	0.048	96.87
3. Magnesium Ammonium Sulphate Hexahydrate			
	0.981	0.023	96.91
	0.961	0.025	96.97
	0.853	0.027	97.10
4. Ammonium Selenate	0.966	0.026	96.60
	0.907	0.028	96.70
	0.847	0.030	96.77
5. Zinc Cesium Sulphate Hexahydrate	0.924	0.029	96.10
	0.839	0.031	96.19
	0.785	0.032	96.25
6. Potassium Succinate			

	0.995	0.009	96.45
	0.921	0.011	96.51
	0.799	0.014	96.65
7. Zinc lactate trihydrate			
	0.979	0.031	96.10
	0.970	0.038	96.20
	0.963	0.042	96.30
8. Zinc ammonium phosphate hexahydrate			
Site I	0.937	0.004	94.10
	0.921	0.008	94.20
	0.915	0.012	94.30
Site II	0.980	0.006	94.10
	0.943	0.008	94.20
	0.811	0.011	94.30

The rate of decrease of $K_{\parallel}$ is more than $K\perp$ so that the compound can be approximately considered to be more ionic. Thus electron will migrate to neighboring atom suggesting that the net amount of charge transfer should also be considered in the crystal field theory of ionic complex.

3. Conclusion

The nature of bonding of VO^{2+} ion doped in different single crystals has been evaluated. This result shows that the value of one covalent bonding parameter should be less than 0.048 in order to have a better fit to the experimental g value. The rate of decrease of $K_{\parallel}$ more than $K\perp$ shows that the compound can be approximately considered more ionic.

Acknowledgements

The authors are thankful to the Head of Physics Department for providing departmental facilities.

References

[1] Yerli, Y. Zerenturk, A. Ozdogan, K. (2007). EPR of VO^{2+} in double formate, $Ba_2Zn(HCOO)_6(H_2O)_4$ single Spectrochim. Acta A, 68 , 147-149.

[2] Natarajan, B., Mithira, S., Deepa, S., Rao, P. S. (2007). EPR and optical investigation of VO(II) in Zn(C3H3O4)2(H2O)2 single crystals: An interstitial site, J. Phys. Chem. Solids 68,1995-2002.

[3] Karabulut, B., Tufan, A. (2006). An EPR and optical absorption study of VO^{2+} ions in sodium hydrogen oxalate monohydrate ($NaHC_2O_4 \cdot H_2O$) single crystals Spectrochim. Acta A, 65, 742-748.

[4] Velavan, K., Sougandi, I., Venkatesan, R., Rao,P. S. (2005). Observation of three sites for vanadyl in a biomineral, zinc sodium phosphate hexahydrate: an EPR investigation , J. Phys. Chem. Solids 66, 15-20.

[5] Deepa, S., Velavan, K., Sougandi, I., Venkatesan, R., Rao, P. S. (2005). Single crystal EPR study of VO(II) in magnesium potassium phosphate hexahydrate: a case of two substitutional vanadyl ions, Spectrochim. Acta A, 61, 2482-2487.

[6] Gopal, N. O., Narasimhulu, K.V., Rao, J. L. (2001). EPR and optical absorption studies on VO^{2+} ions doped in cobalt maleate tetrahydrate single crystals, Physica B 307, 117-124.

[7] Shiyamala, C., Ranjendiran, T.M. (2002). Host Lattice Effect on Paramagnetic Impurity: Single Crystal EPR Study of VO(II)-Doped Biomineral Cadmium Ammonium Phosphate Hexahydrate, Crys. Res. Technol. 37, 841-848.

[8] Dhanuskodi, S., Jeyakumari, A. P. (2001). EPR studies of VO^{2+} ions in kainite single crystals, Spectrochim. Acta A, 57, 971-975.

[9] Natarajan, B., Mithira, S., Deepa, S., Ravi Kumar, R.V.S.S.N., Rao, P. S. (2006). Identification of doped paramagnetic vanadyl impurity in dipotassium diaquabis (malonato-κ^2O, O′) zincate dihydrate single crystal using EPR and optical techniques, Radiat. Eff. Defects Solids, 161, 177-187.

[10] Tapramaz, R., Karabulut, B., Koksal, F. (2000). EPR spectra of VO^{2+} and Cu^{2+} ions in di-ammonium d-tartrate single Crystals, J. Phys. Chem. Solids 61, 1367-1372.

[11] Abragam, A., Bleaney, B., Electron Paramagnetic Resonance of Transition Ions, Clarendon, Oxford, 1970.

[12] Stevens, K.W. H. (1953). On the Magnetic Properties of Covalent XY_{6} Complexes Proc. Roy. Soc. A 219, 542-555.

[13] Bansal, R. S. (1990). Electron Paramagnetic Resonance Studies of Doped Single Crystals, Ph. D. Thesis submitted to M.D University, Rohtak, India, p. 133.

[14] Kripal, R., Singh, P. (2006). EPR and optical absorption studies on VO^{2+} ions in zinc lactate trihydrate J. Magn. Magn. Mat. 307, 308-312.

[15] Kripal, R., Misra, M. G, Lipinski, I. E. and Rudowicz, C. (2012). Electron paramagnetic resonance and optical study of VO^{2+}-doped zinc ammonium phosphate hexahydrate single crystals Phys. Scr. 86, 045602 (9pp).

[16] Misra, B. N., Kripal, R. (1977). Covalent Bonding Parameters of Complexes with Paramagnetic ions, Z. Phys. Chem.(Leipzig), 258, 605-608.