

**SINGLE CRYSTAL EPR STUDY OF VO(II) IN MAGNESIUM RUBIDIUM SULPHATE  
HEXAHYDRATE: A CASE OF TWO INTERSTITIAL SITES**

**H. Anandalakshmi**

Engineering Chemistry Section, FEAT, Annamalai University, Chidambaram

*Article History: Received 14<sup>th</sup> January, 2015, Accepted 30<sup>th</sup> Jan, 2015, Published 31<sup>st</sup> January, 2015*

**ABSTRACT**

Single crystal EPR studies of VO(II) –doped magnesium rubidium sulphate hexahydrate have been studied at room temperature. The results show that the paramagnetic impurity has entered the lattice at two interstitial sites. The EPR of VO(II) has been studied in a variety of lattices, which fall into two categories, those in which the VO(II) ion is free to rotate (at least at normal temperature) and those in which it is preferentially oriented Vanadyl complexes have been the subject of interest over recent years. The spin Hamiltonian parameters obtained from single crystal data suggest orthorhombic nature and interstitial substitution for the impurity. The two sites have slightly different spin Hamiltonian parameters.

**Keywords:** Interstitial, Substitutional behaviour, Spin Hamiltonian, Crystallography.

**1. INTRODUCTION**

EPR spectroscopy is the one of the fine probes to study inorganic metal complexes having at least one unpaired electron on the metal ion. EPR studies are carried out on paramagnetic impurities doped either in diamagnetic or paramagnetic host lattices [1, 2]. The occurrence of paramagnetic impurity in paramagnetic host results in broadening of the resonance lines due to the host-impurity interaction, such as dipolar-dipolar. Hence more often, paramagnetic impurities doped in diamagnetic lattices, are preferred. Vanadium belongs to the first series transition metal group and readily reacts to form a number of oxocations, the simplest being the vanadyl ion, VO(II). The interesting behaviour of the VO(II) ion in different crystalline matrices is due to the differential orientations of the V=O ion. Since, vanadyl ion is one of the few most stable molecular paramagnetic transition metal ions having  $t_{2g}^1 e_g^0$  configuration, it is widely used as an EPR probe for the studies such as phase transitions, distortion, strength and magnitude of crystal fields, relaxation time, etc. Even though the vanadium can exist in several oxidation states, the tetravalent vanadyl ion has been well studied due to the interesting result furnished by the orientation of the V = O band in lattice [3]. Also it is found that the VO(II) ion has fixed preferential orientations in different symmetries with and without water molecules of oxygen ligands. Since the

vanadyl ion is found to have interesting changes on the EPR spectrum in different crystalline field environments, we have studied VO(II) impurity ions in the Magnesium Rubidium Sulphate Hexahydrate (hereafter abbreviated as MRSH) lattice.

The EPR of VO(II) has been studied in a variety of lattices, which fall into two categories, those in which the VO(II) ion is free to rotate (at least at normal temperature) and those in which it is preferentially oriented Vanadyl complexes have been the subject of interest over recent years [4-6].

Tutton's salts are thoroughly investigated by mineralogists, chemists and physicians in different points of view and described many physical and chemical properties. In the present work, MRSH lattice falls under the category of Tutton's salt, has been selected for detailed single crystal EPR analysis by doping a paramagnetic ion. In order to understand the substitutional behaviour of MRSH, a paramagnetic ion, i.e., vanadyl has been incorporated and the results are presented below.

**2. METHODS**

Magnesium Rubidium Sulphate Hexahydrate (MRSH) single crystals are grown at room temperature by slow evaporation of aqueous magnesium sulphate with rubidium sulphate hexahydrate in equimolar ratio of 1:1. To this, a few drops of vanadyl sulphate solution is added as paramagnetic impurity. Light green colour crystals are obtained within 20 days. Single crystals of VO(II)/MRSH are studied at room temperature using JEOL JES TE100 ESR spectrometer having a modulation of 100 kHz and operating at X-band frequency. DPPH (diphenyl picryl

*Corresponding author: Dr. H. Anandalakshmi, Asst. Professor,  
Engineering Chemistry Section, FEAT, Annamalai University,  
Chidambaram*

hydrazine) with a g value of 2.0023 is used for g factor calculations.

### Crystal structure

Tutton's salts have the general formula  $M''M_2'(XO_4)_2 \cdot 6H_2O$ , where  $M''$  is a divalent cation like Co, Cu, Ni, Mg, Zn;  $M'$  is a monovalent cation like K, Cs, Rb,  $NH_4$  and X was S or Se. Tutton's salts have monoclinic crystal structure with space group  $P_{21/n}$ . The lattice parameters of MRSH ( $M''$  was Mg,  $M'$  was Rb and X was S) are :  $a=0.613$ ,  $b=1.223$ ,  $c=0.909$  nm,  $B = 104.780$  and  $Z=2$ [7]. Magnesium ion is surrounded by six water molecules in the form of a compressed octahedron in MRSH lattice. In all Tutton's salts, the shortest Mg-O bond is unique, whereas the longest bond depends on the nature of  $M'$  and  $M''$ [7].

### 3.RESULTS AND DISCUSSION

Single crystals of optimum size with well defined axes have been selected for crystal rotations, carried out in the three planes for every ten degrees of rotations. EPR spectra are recorded by rotating the crystal along the three mutually perpendicular axes, a, b and  $c^*$ . Here axes a and b are crystallographic axes, where as axis  $c^*$  is perpendicular to the ab plane. In other words, single crystal rotations are done in the three mutually orthogonal planes namely ab,  $bc^*$  and  $ac^*$  to obtain spin Hamiltonian parameters. Initially, the crystal is mounted along axis b and a typical EPR spectrum of VO(II)/MRSH in  $ac^*$  plane is given in Fig 1. This EPR spectrum consists of a number of overlapping angular dependent eight line hyperfine patterns, each produced by ions located at specific site. This spectrum corresponds to the orientation, when the applied magnetic field (B) is making an angle of 10 degrees with axis  $c^*$ . As the paramagnetic impurity is vanadyl ion, one expects an octet spectrum due to the interaction of electron spin ( $S=1/2$ ) with  $^{51}V$  nucleus ( $I=7/2$ ). One can easily notice two strong octets and a few octets of lower intensity. The approximate ratios of the intensities of the EPR lines corresponding to the VO(II) sites for three octets are found to be approximately 12:6:1. This reveals the presence of three vanadyl sites with different population in the unit cell. The two strong octets are marked by a-h (represented as Site I) and a'-h' (represented as Site II). Only these two sites are followed during crystal rotations, since the other resonances became very weak. EPR spectrum of VO(II)/MRSH at another orientation of the crystal in  $ac^*$  plane is shown in Fig.2. The unit cell of MRSH contains two molecules. Generally, since these two sites are magnetically inequivalent, they will coincide along a crystallographic axis.

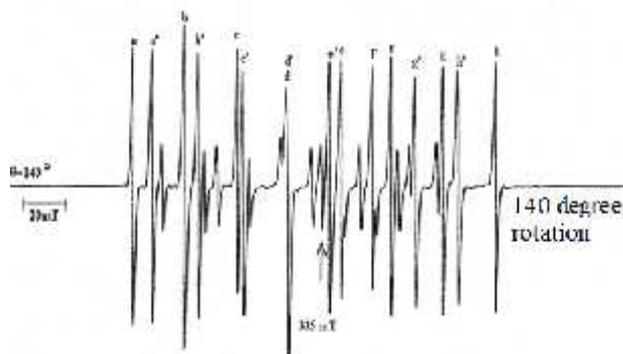
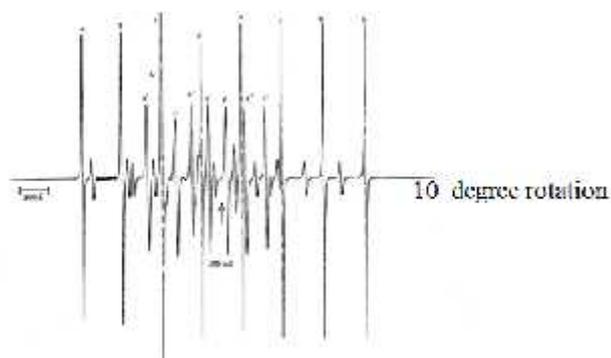


Fig 1&2: The above two figures show the single crystal EPR spectrum of VO(II)/MRSH in  $ac^*$  plane, where the applied magnetic field makes an angle of 10 and 140 degrees respectively with axis  $c^*$ . Here also, Sites I and II are marked by a-h and a'-h'.  $\nu = 9.09014$  GHz.

However, this is not the case with the present system. Hence, these two sites are not only magnetically inequivalent but also chemically. The isofrequency plot in the  $ac^*$  plane for both the sites is shown in Fig.3. In this figure, open circles correspond to experimental resonances for site I and solid circles correspond to resonances for site II. In previous cases of VO(II) in Tutton's salts [12], it has been reported that the two sites observed are orthogonal to each other, in the sense that resonance in an isofrequency plot corresponds to different planes for the two sites. However, in the present case, isofrequency plot (Fig. 3) corresponds to  $ac^*$  plane for both the sites. This implied that the two sites are not orthogonal to each other. The crystal is then mounted along axis a and two EPR spectra of VO(II)/MRSH in  $bc^*$  plane at indicated orientations are given in Figs 4 and 5. Here also more than two sites are noticed and the two intense ones only followed in this plane also. The isofrequency plot in  $bc^*$  plane is shown in Fig 6. Here also, as mentioned above, open circles correspond to experimental resonances for site I and solid circles correspond to experimental resonances for site II. This also confirms that the two sites are not orthogonal to each other, as both of them belong to  $bc^*$  plane. EPR spectra of VO(II)/MRSH recorded at room temperature for two different orientations in the ab plane are shown in Figs.7 and 8. The isofrequency plot in ab plane is shown in Fig. 9. Here also, as mentioned above, open circles correspond to experimental resonances for site I and solid circles correspond to resonances for site II. This isofrequency plot further confirms that the two sites are not orthogonal to each other, as both of them belong to ab plane.

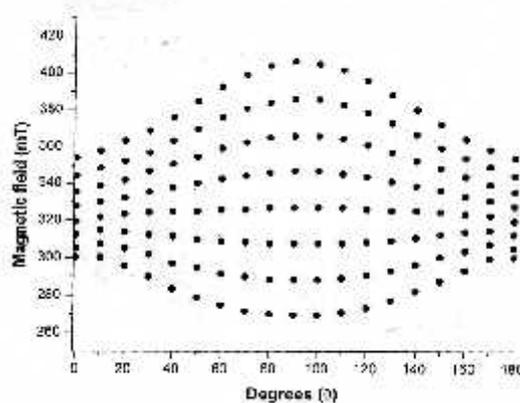


Fig.3: Isofrequency plot for VO(II)/MRSH in  $ac^*$  plane showing two magnetically inequivalent sites. Here and in Figs. 6 and 9, circles correspond to experimental points and lines correspond to theoretical ones, as calculated from the program EPR-NMR with the data given in Table.1. Moreover, solid lines and open circles represent resonances for Site I and dotted lines and solid circles correspond to resonances for Site II.  $\nu=9.09014$ GHz.

Moreover, solid lines and open circles represent resonances for Site I and dotted lines and solid circle correspond to resonances for Site II.  $\nu=9.09014\text{GHz}$ .

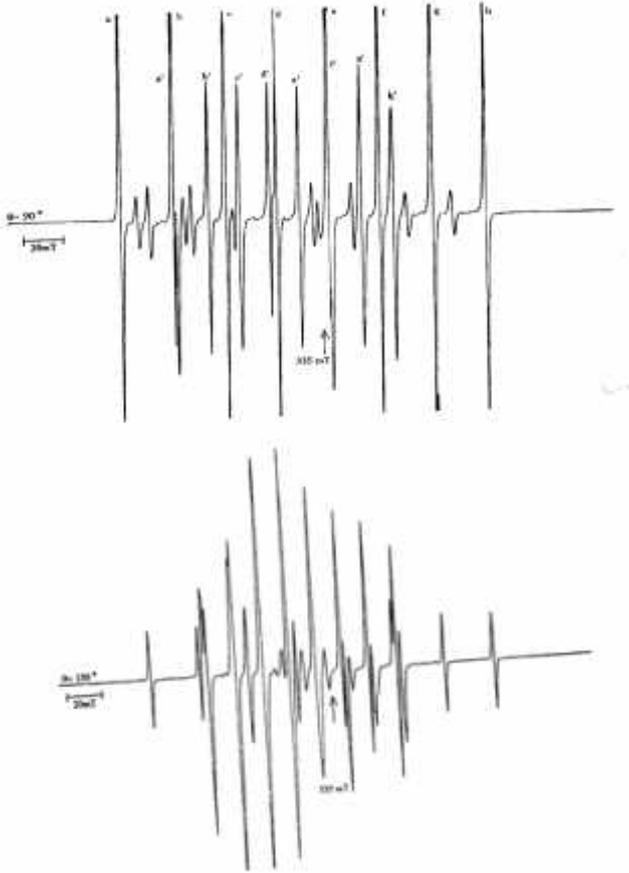


Fig.4 &5 shows single crystal EPR spectrum of VO(II)/MRS when the applied magnetic field (B) is  $90^\circ$  and  $150^\circ$  away from axis  $c^*$  in  $bc^*$  plane.  $\nu = 9.08969\text{GHz}$ .

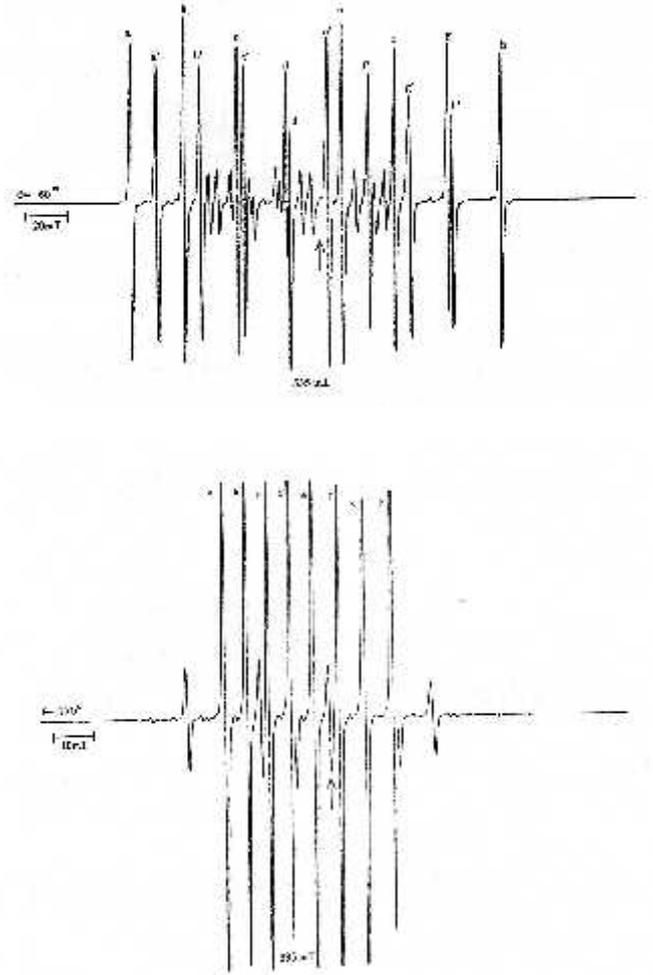


Fig.7&8 shows typical orientation in  $ab$  plane at 60 and 170 degrees of rotation, for VO(II)/MRS, at which sites I and II make nearly identical angle with B, resulting in only eight lines. Here a-h corresponds to both the Sites. The other octet corresponds to Site III that is not followed.  $\nu = 9.08670\text{GHz}$ .

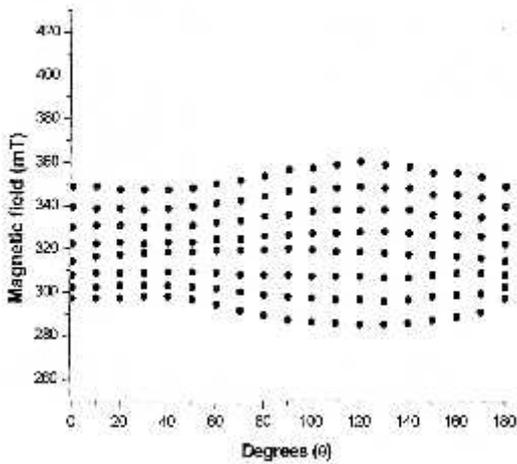


Fig. 6. Angular variation of the hyperfine lines for VO(II)/MRS single crystals at RT in the  $bc^*$  plane for Sites I and II.  $\nu = 9.08969\text{GHz}$ .

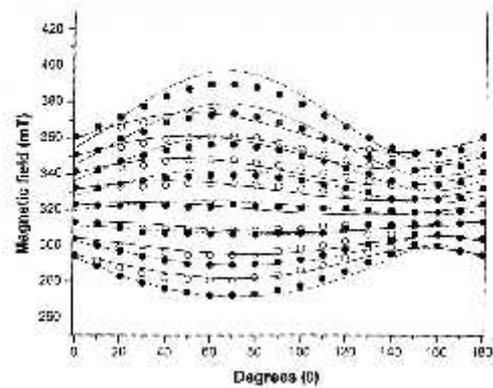


Fig. 9 Angular variation of resonance lines for the two sites for the single crystal of VO(II)/MRS in  $ab$  plane at room temperature.  $\nu = 9.08670\text{GHz}$ .

**Table-2: Spin Hamiltonian Matrices parameter calculated using program EPR-NMR[10]**

g/A Matrices		Eigen Values		Direction Cosines		
				a	B	c*
Site I :						
g matrix :						
1.954	-0.009	0.023	1.996	0.116	-0.975	-0.191
	1.993	0.010	1.978	-0.703	0.055	-0.709
		1.956	1.929	0.702	0.217	-0.679
A matrix (mT) :						
9.67	2.01	-4.77	19.08	-0.482	-0.369	0.794
	9.36	-3.30	7.82	0.184	-0.929	-0.321
		14.65	6.78	0.857	-0.008	0.516
Site II						
g matrix :						
1.981	0.004	-0.017	1.998	0.018	0.978	0.207
	1.996	0.013	1.987	0.944	0.051	-0.327
		1.939	1.930	-0.330	0.201	-0.922
A matrix (mT)						
9.12	-1.08	3.67	18.57	0.375	-0.300	0.877
	7.61	-3.29	7.61	0.916	0.268	-2.99
	15.88	6.43	-0.145	0.915	0.375	

**Table-3: Spin Hamiltonian parameters of VO(II) ion in MRSH and in similar hosts. A values are given in units of mT.**

Lattice	gzz	gxx,gyy	Azz	Axx,Ayy	Ref
ZMTH					
Site I	1.935	1.982, 1.982	16.3	6.3, 6.3	[11]
Site II	1.935	1.967, 1.967	16.9	6.3, 6.3	
MPPH					
Site I	1.930	1.980, 1.977	18.69	7.25, 8.09	[12]
Site 2	1.930	1.980, 1.976	18.75	6.82, 8.48	
Powder	1.933	1.985, 1.985	18.60	7.42, 7.42	
MRSH					
Site I	1.929	1.996, 1.978	19.1	6.78, 7.82	Present Study
Site II	1.930	1.998, 1.987	18.6	6.43, 7.61	
Powder	1.927	1.976, 1.976	19.79	7.6, 7.6	

The l ZMTH – Zinc maleate tetrahydrate;  
are c MPPH – Magnesium potassium phosphate hexahydrate

single unpaired electron with the  $^{51}\text{V}$  nucleus whose nuclear spin is  $7/2$ , with 99.76% natural abundance. The spin Hamiltonian parameters (g and A) for the two sites are calculated from the isofrequency plots using program EPR-NMR[10] by assuming an orthorhombic spin-Hamiltonian.

Here the symbols have their usual meaning. The quadrupole and nuclear Zeeman interaction terms are ignored. The spin Hamiltonian parameters thus obtained are given in Table-2. It is clear from the table that the two sites have slightly different spin Hamiltonian parameters and a major difference is noticed in the principal value of A. The g and A matrices are coincident, as evidenced from direction cosines. This is also further confirmed that the maxima and minima occurred at the same angle for g and A values in the isofrequency plots. The three principal values of g and A show orthorhombicity, as expected from the isofrequency plots. For comparison, a selected literature data of vanadyl impurities in a few related host lattices are given in Table-3.

In order to confirm the spin Hamiltonian parameters obtained from single crystal data, isofrequency plots have been simulated using program EPR-NMR and data given in Table-2. The calculated isofrequency plots are also given in Figs. III 3, 6 and 9. In these figures solid lines correspond to theoretical ones for Site I and dotted lines correspond to resonances for Site II

Single crystal EPR studies of VO(II) in MRSH have been carried out systematically at room temperature. The EPR spectrum indicates the presence of more than two sites. However, only two intense sites have been analyzed, since the other sites have very low intensity to follow during crystal rotations. The spin Hamiltonian parameters obtained from single crystal data suggest orthorhombic nature and interstitial substitution for the impurity. The two sites have slightly different spin Hamiltonian parameters. The isofrequency plots have been simulated to confirm these values. The principal values of g and A match well indicating the coincidence of these two matrices. An important observation being that the two sites are not perpendicular to each other, as noticed in all previous systems. This also resulted in obtaining a single site even in powder spectrum. The powder data matched fairly well with single crystal data. Other orbital mixing parameters agree with the standard values.

#### 4. REFERENCES :

- [1] Gopal, .N.O, Narasimhulu .K.V. and Lakshmana Rao .J, Physical B 307 (2001) 117.
- [2] Natarajan .B, Deepa .S, Mithira .S, R V S S N Ravikumar and Sambasiva Rao .P, Phys. Scr. 76 (2007) 253.
- [3] Aoki.K, Nagamo .K and Iitaka .Y, Acta Cryst. B 27 (1971) 11.

- [4] Sougandi .I, Rajendiran .T.M, Venkatesan .R and Sambasiva Rao .P, Proc. Indian Acad. Sci. (Chem..Sci), 114 (2002) 473
- [5] Ch. Linga Raju, Narasimhulu .K.V., Gopal .N.O. Rao .J.L and Reddy B.C.V., Journal of Molecular structure 754 (2005) 100.
- [6] Ram Kripal and Pragya Singh, Journal of Magnetism and Magnetic Materials 307 (2006) 308.
- [7] Sankar .B, Naarajan .B, Mithira .S, Anandalakshmi .H and Sambasiva Rao .P Cryst. Res. Technol. 42 (2007) 173.
- [8] Chandrasekhar Rao .A, Mithira .S, Natarajan .B, Ravikumar, R.V.S.S.S.N. Anandalakshmi .H and Sambasiva Rao.P, Journal of Physics and Chemistry of Solids 68 (2007) 305.
- [9] Kannan .K.K and Viswamitra M.A. Kristallogr.Z., 122 (1965) 161.
- [10] EPR-NMR Program developed by Clark .F, Dickson .R.S, Fulton, D.B, Isoya .J, Lent .A, McGavin D.G. Mombourquette .M.J, Nuttall, R.H.D., Rao P.S, Rinnerberg .H, Tennant .W.C, Weil, J.A. (1996) University of Saskatchewan, Saskatoon, Canada.
- [11] C. Shiyamala, S. Mithra and P. Sambasiva Rao, spectrochimica Acta.
- [16] S.Deepa, K. Velavan, I. Sougandi, R. Venkatesan and P.Sambasiva Rao, spectrochimica Acta A61 (2005) 2482