EPR Spectra of VO^{2+} Doped in $Na_2C_4H_4O_6$ Single Crystals

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EPR spectra of VO^{2+} ions in di-sodium tartrate, $[Na_2C_4H_4O_6]$, single crystal and powder spectra have been studied at room temperature. The angular variation of the EPR spectra has shown that three different VO^{2+} complexes are located in different chemical environments, and each environment contains two magnetically inequvalent sites. The spin Hamiltonian parameters are determined, and these parameters have been used to assess the bonding coefficients of the VO^{2+} ion in the di-sodium tartrate lattice. The parallel and perpendicular components of axially symmetric g and hyperfine tensors are evaluated. The results are discussed.

Key words: EPR; Vanadil Ion; Di-sodium Tartrate.

1. Introduction

EPR technique was used to determine the local structure of crystals by doping transition metal ions into a host lattice as impurity. It is known that the local symmetry and bond shape of a paramagnetic centre can be clearly determined by this technique. Also this technique gives valuable information about the environmental symmetry of transition metal ions together with the bonding ligands. Among these, the VO^{2+} ion has been widely used as a probe to study the symmetry of crystal fields. Many workers have studied the EPR spectra of VO^{2+} ions in different diamagnetic host lattices. When VO^{2+} is doped in a diamagnetic crystal as an impurity it can have various ligands in its environment. Some of these environments were clearly resolved. In recent years, many papers have been published on magnetically and chemically distinct VO^{2+} ion complexes in single crystals [1 – 6]. When the number of distinct metal ion complexes in a single host crystal is large, the resolution of the spectra is not easy, and some techniques for the resolution must be utilised [7 – 14]. The difficulty in the resolution of the spectra arises basically from the overlapping of a large number of lines in different orientations. In this work we have undertaken the resolution and identification of VO^{2+} spectra in di-sodium tartrate (DST) single crystal. Many lines in the single crystal spectra were observed, and a numerical technique was used to evaluate the spectra as given in [10, 12].

2. Experimental

Single crystals of doped DST were grown by slow evaporation of a saturated aqueous solution of commercial DST in polycrystalline form by adding a very small amount of $VOSO_4$ to the solution to provide VO^{2+} ions as dopants. Single crystals grown in two weeks were chosen for the investigation. The crystal structure of DST is monoclinic with space group $P2_1/n$ [15]. There are two molecules in a unit cell. The unit cell dimensions are $a = 4.999$ Å, $b = 6.348$ Å, $c = 10.135$ Å and $\beta = 97.49^\circ$.

The EPR spectra were recorded with a Varian E-109 C model X-band EPR spectrometer using 2 mW microwave power and 100 kHz magnetic field modulation. The single crystals were glued on a Lucit pillar and rotated in three mutually perpendicular planes (*xy*, *xz*, *yz*, respectively). The spectra were recorded with 10° steps. The g factors were obtained by comparison with a diphenylpicrylhydrazyl sample with $g = 2.0036$.

3. Results and Discussion

The VO^{2+} ion has a $3d^1$ electron configuration. The EPR spectra of the vanadyl ions can be satisfactorily explained in terms of the unpaired electron interacting with the ^{51}V nucleus ($I = 7/2$) [16]. The EPR spectra of VO^{2+} ions in DST single crystals consist of many anisotropic hyperfine lines, as shown in Figs. 1a and 1b. The number of lines and line widths vary with

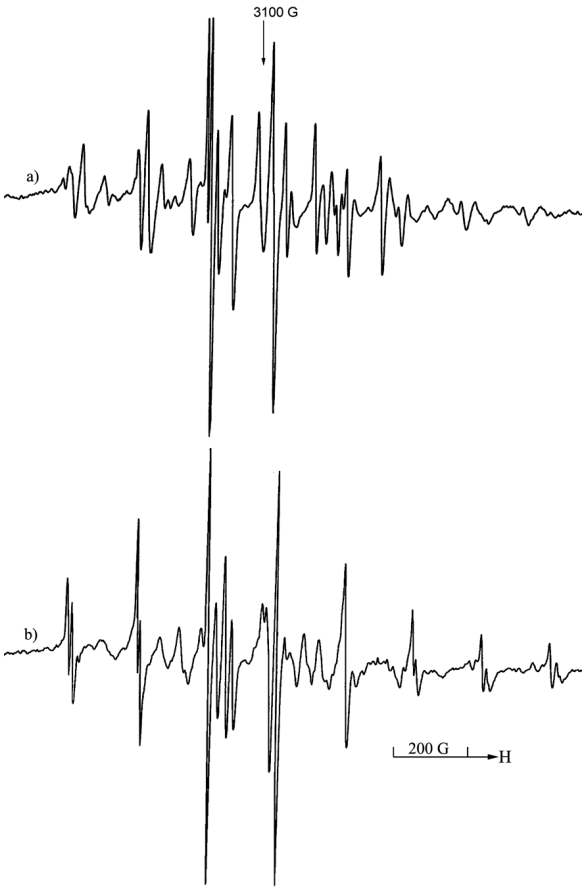

Fig. 1. EPR spectrum of VO^{2+} doped DST single crystal. The magnetic field is in the *zx* plane making a) 50° and b) 80° with the *x* axis.

the orientation of magnetic field. A group of lines observed in one orientation partly or totally disappear in some other orientations of the magnetic field. The angular variations of $g_k^2(\theta)$ and $a_k^2(\theta)$ are

$$g_k^2(\theta) = g_{ii}^2 \cos^2\theta_i + g_{jj}^2 \sin^2\theta_j + 2g_{ij}^2 \sin\theta_i \cos\theta_j, \quad (1a)$$

$$a_k^2(\theta) = a_{ii}^2 \cos^2\theta_i a g_{jj}^2 \sin^2\theta_j + 2a_{ij}^2 \sin\theta_i \cos\theta_j, \quad (1b)$$

where *i*, *j*, and *k* represent the *x*, *y* and *z* axes. They are used to resolve the spectra by using the curve fitting procedure [17]. In a DST single crystal, the distance between the EPR lines can not be measured precisely due to varying hyperfine splittings from low to high fields. Therefore one has to take into account the second order shifts. For this contribution, a special solution of the spin-Hamiltonian has to be taken for the $g^2(\theta)$ and $A^2(\theta)$ values. At any orientation, the solution of the spin Hamiltonian for the magnetic field to the second order approximation is given by

$$H_{M_1} = \frac{h\nu}{g\beta} - aM_1 - \frac{a^2[I(I+1) - M_1^2]}{2H_o}, \quad (2)$$

where H_o is $h\nu/g\beta$ [18]. Equation (2) has been used to obtain g and A values of each site for all orientation, and then the g and A tensors were formed and diagonalised. The results are given in Table 1, where are $g_\perp = (g_x + g_y)/2$, $g_\parallel = g_{zz}$, $g_{iso.} = (2g_\perp + g_\parallel)/3$, $A_\perp = (A_{xx} + A_{yy})/2$, $A_\parallel = A_{zz}$, and $A_{iso.} = (2A_\perp + A_\parallel)/3$.

Figure 2 shows that at any arbitrary orientation, six groups of eight hyperfine lines in the single crystal are observed. The lines can be distinguished from each other in all planes. Especially when the magnetic field is in the *zx* plane 48 lines become clearly observable. The intensities of all complexes seem to be almost equal when observed in all orientations, which mean that the formations of complexes are equally probable. Nevertheless, six groups of lines have been clearly observed.

The spectra show that the vanadium ion of the V^{4+}–O^{2+} group replaces Na^+ in the host lattice, because V^{4+} is more active and smaller. The radii are 0.98 Å for Na^+ and 0.61 Å for V^{4+}. VO^{2+} coordinates with five O atoms of the tartrate group. The charge compensation for this replacement may be fulfilled by a proton vacancy of the tartrate group. VO^{2+} may replace Na^+ in the host lattice because there are three types of oxygen atoms and invariance of the symmetry. The crystal data of DST show three Na^+ ions with different Na–O bond distances [15]. Therefore, VO^{2+} complexes are located in three different chemical environments, and each environment contains two chemically equivalent and magnetically distinct sites, which is compatible with the monoclinic crystal symmetry. Similar studies were made by many workers [7–13, 18, 19], who found different complex centers in different host lattices. The principle **g** and **A** values of all groups have nearly axial symmetry. Table 1 includes the orientations of parallel components of the axially symmetric g and hyperfine A values in spherical coordinates with respect to the crystalline axes system. θ is the polar and ϕ the azimuthal angle with respect to the crystalline axis, where θ is the angle between parallel components of g or A and the z axis, and ϕ is the projection of parallel components of g or A in xy plane and the x axis.

The powder spectrum of DST, recorded at room temperature, is shown in Figure 3. The spectrum consists of parallel and perpendicular components of the

Table 1. Principal values of **g** and hyperfine (**A**) tensors for paramagnetic vanadyl complexes in DST single crystals at room temperature ($\Delta g = \pm 0.005$ G and $\Delta A = \pm 1$).

Complex no	Site	$g_\parallel$	$g_\perp$	$g_{\text{iso.}}$	**g** tensor		$A_\parallel$	$A_\perp$	$A_{\text{iso.}}$	**A** tensor	
					θ	ϕ		10^4 cm^{-1}		θ	ϕ
I	1	1.894	1.984	1.954	92°	166°	180.2	78.0	112.2	92°	164°
	2	1.895	1.984	1.954	85°	164°	180.0	78.2	112.2	85°	164°
II	1	1.894	1.977	1.949	29°	20°	184.6	68.0	106.9	29°	21°
	2	1.894	1.977	1.949	29°	37°	186.1	70.5	109.0	30°	32°
III	1	1.902	1.991	1.961	30°	155°	160.0	74.4	102.9	27°	169°
	2	1.900	1.990	1.960	31°	154°	168.0	74.2	105.5	30°	158°
Powder		1.922	1.984	1.963	–	–	183.0	70.7	108.1	–	–

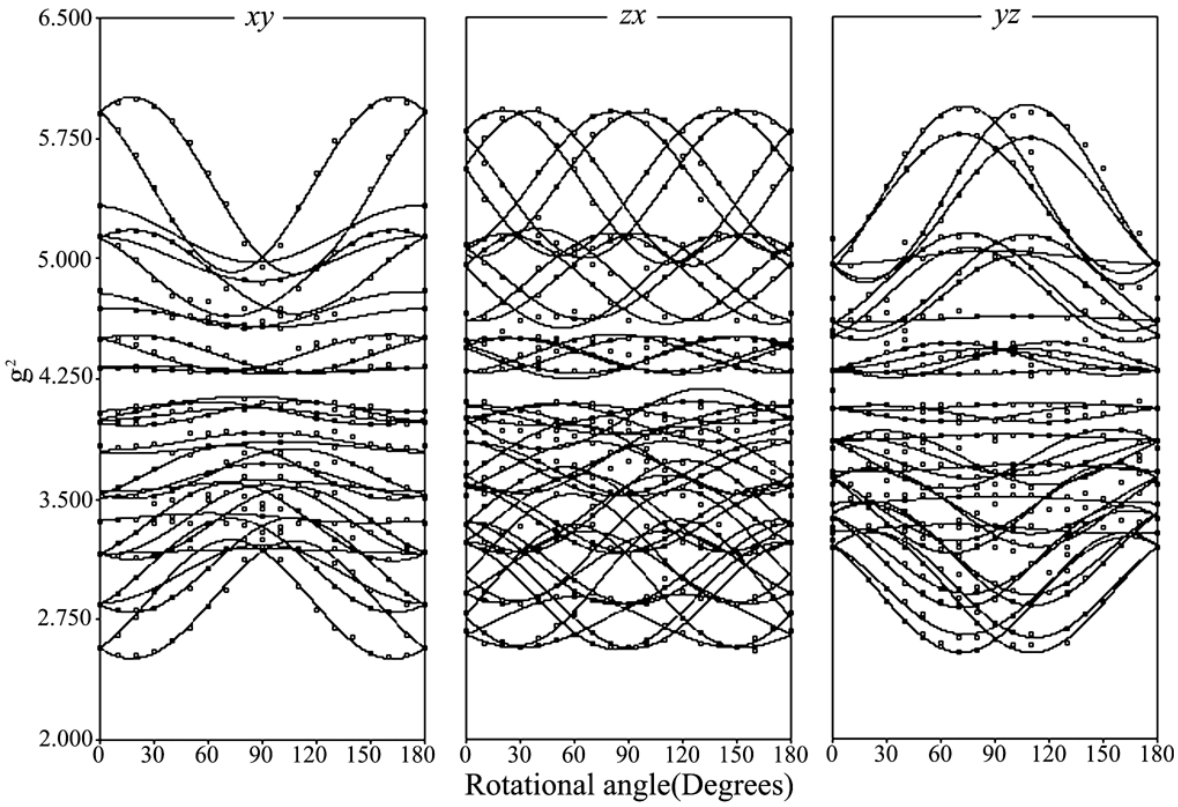

Fig. 2. Variations of g^2 values of all lines in three mutually perpendicular planes of VO^{2+} doped DST single crystal.

VO^{2+} complex clearly. The measured values results of the analysis are $g_\perp = 1.9845$, $g_\parallel = 1.9220$, $A_\perp = 75.71$ G, and $A_\parallel = 196.42$ G, where $\parallel$ and $\perp$ show the parallel and perpendicular components of the **g** and **A** tensors with respect to the V–O direction of the octahedron. From these values the isotropic or average values are $g_{\text{iso.}} = 1.9640$ and $A_{\text{iso.}} = 115.94$ G. In Table 1, it can be seen that each complex center is similar to the g and A values of the powder spectrum of the compound.

The parallel components of the **g** and the **A** tensors are not collinear due to the distortion of octahedrons around the vanadium atoms in the environments where they are settled. The distortion probably takes place along the $V = O$ directions, and the degeneracy of the ground state d_{xy} of the vanadium atom in $3d^1$ configuration splits into $d_{x^2-y^2}$, d_{xz} and d_{yz} states [20].

The degree of distortion can be estimated from the Fermi contact terms κ, and the P parameter, which are related to the radial distribution of the wave function of the ions given as $P = g_e g_N \beta_e \beta_N \langle r^{-3} \rangle$. The Fermi contact term is directly related to the isotropic hyperfine

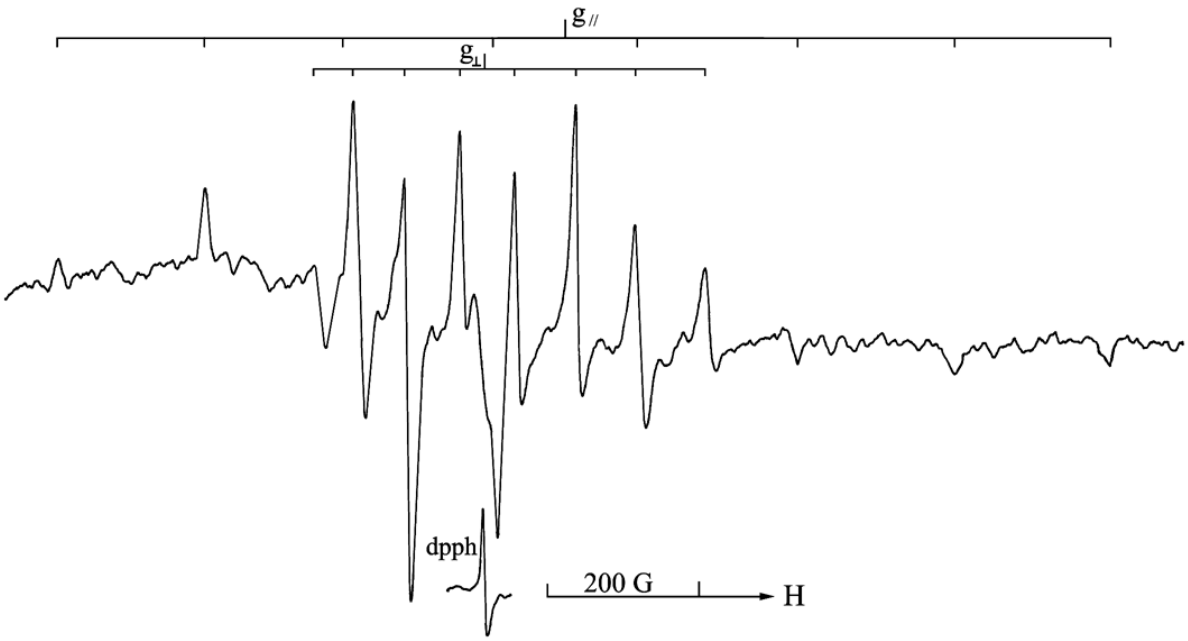

Fig. 3. Powder spectrum of VO^{2+} doped DST.

coupling and represents the amount of unpaired electron density at the nucleus.

The parallel and perpendicular components of the hyperfine interactions $A_{\|}$ and $A_{\perp}$ are related to the molecular orbital coefficients by the expressions [21],

$$A_{\|} = -P\Big[\kappa + \frac{4}{7}\beta_2^2 + (g_e - g_{\|}) + \frac{3}{7}(g_e - g_{\perp})\Big], \quad (3)$$

$$A_{\perp} = -P\Big[\kappa - \frac{2}{7}\beta_2^2 + \frac{11}{14}(g_e - g_{\perp})\Big]. \quad (4)$$

The isotropic EPR parameters, $g_{\text{iso.}}$ and $A_{\text{iso.}}$ can be determined from the anisotropic parameters, using the relations $g_{\text{iso.}} = (2g_{\perp} + g_{\|})/3$ and $A_{\text{iso.}} = (2A_{\perp} + A_{\|})/3$.

Using these equations with the expression [3] and [4] one gets

$$A_{\text{iso.}} = -P\kappa - (g_e - g_{\text{iso.}})P, \quad (5)$$

where P is the dipolar interaction constant between the magnetic moment of the electron and the Vanadium nucleus. It is taken as 126 cm^{-1}, Ballhausen and Gray [20]. g_e (=2.0023) is the free electron g value, β_2^2 the covalency ratio of $V = O$ bonds. Combining (3) and (4), and eliminating κ one gets an expression for β_2^2 in terms of the principal values of the **g** and **A** tensors:

$$\beta_2^2 = -\frac{7}{6}\Big[\big((A_{\|} - A_{\perp})/P\big) + (g_e - g_{\|}) - \frac{5}{14}(g_e - g_{\perp})\Big]. \quad (6)$$

Table 2. Fermi contact terms and molecular orbital coefficients of the vanadyl complexes in various lattices.

Complex	Site	β_2^2	κ	Reference
I-$Na_2C_4H_4O_6$	1	0.83	0.84	[a]
	2	0.83	0.84	[a]
II-$Na_2C_4H_4O_6$	1	0.96	0.79	[a]
	2	0.96	0.81	[a]
III-$Na_2C_4H_4O_6$	1	0.69	0.77	[a]
	2	0.76	0.79	[a]
$(NH_4)_2Mg(SO_4)_2.6H_2O$		0.91	0.86	[16]
I-$Cd(NH_4)_2(SO_4)_2.6H_2O$	1	1	0.85	[11]
	2	1	0.85	[11]
I-$Mg(NH_4)_2(SO_4)_2.6H_2O$	1	1	0.85	[11]
	2	1	0.85	[11]
Powder $Na_2C_4H_4O_6$		0.96	0.81	*a*

[a] present work.

Computed κ and β_2^2 values are given in Table 2. The parameters of the first and third complex are approximately in the same range, and close to the values given in the cited papers. The deviation of β_2^2 from unity represents the degree of admixture of the ligand orbitals and increase in the degree of covalency. The second

complex and powder crystal have a smaller κ, and β_2^2 is almost unity. The value of β_2^2 shows that the bonding is nearly ionic and therefore makes a poor π bonding to the ligands [20].

4. Conclusions

EPR studies of VO^{2+} di-sodium tartrate single crystals were carried out at room temperature. The EPR parameters of the complexes are given, and hence the structure is discussed. The large numbers of lines in the spectra were resolved. The spectral features clearly indicate the monoclinic symmetry of the crystal lattice. Three vanadyl complexes have been identified, corresponding to two vanadyl sites having distinct orientations. The detailed EPR analysis shows that the vanadyl ions occupy substitutional positions of Na^+ ions in the crystal lattice. The VO^{2+} bond is nearly ionic. The deviation of β_2^2 from unity shows mixing of ligand orbitals due to the presence of a low symmetry ligand field.

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