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Theoretical and Experimental EPR Study of VO^{2+}-Doped Ammonium Hydrogen Tartrate

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Abstract: We studied the electron paramagnetic resonance (EPR) spectra of VO^{2+} ions in ammonium hydrogen tartrate (AHT) single crystals at room temperature. We determined the spin Hamiltonian parameters and the molecular bonding coefficients of the complex both in theoretical and experimental ways. The results indicate that the vanadium ion forms a tetragonally compressed octahedron and has a double bond with one of the oxygens in the axial position. This is the reason why the paramagnetic centre in the host crystal is axially symmetric as in most of the vanadyl ion-containing complexes.

Keywords: Ammonium Hydrogen Tartrate; EPR; Molecular Bonding Coefficients; VO^{2+} Ions.

1 Introduction

The electron paramagnetic resonance (EPR) spectroscopic technique is a useful tool to study the magnetic behaviour, site symmetry, bonding nature, and dynamics of paramagnetic centres. There are many methods to have such centres in the host crystal lattices. One of the methods is doping transition metal ions to the crystal centres [1–4].

Vanadium has an electronic configuration [Ar]3d^{3}4s^2 and is a stable cation existing in di-, tri-, and tetravalent states in complexes [5–7]. The tetravalent state of the vanadium ion has only one unpaired electron in the ground-state configuration. Usually, in solids or in solutions, vanadium coordinates to five or six oxygens [8]. One of the oxygens is bound to vanadium ion by a strong double covalent bond and forms vanadyl (VO^{2+}) ion. Therefore, most of the complexes having VO^{2+} ions possess C_{4v} symmetry and show axial symmetry in paramagnetic centres [9].

Some researchers have studied tartrate-containing complexes such as di-sodium tartrate [10] and diammonium d-tartrate [5] doped with VO^{2+} by EPR spectroscopy in recent years. The title complex in our study, ammonium hydrogen tartrate (AHT) or ammonium bitartrate, is used as baking powder [11]. Some other researchers have studied different physical properties of the AHT such as Fourier transform infrared (FT-IR) and Raman spectra [12]; magnetic susceptibility [13]; electrical conductivity [14]; and thermal, optical, and dielectric properties [15]. However, there is no EPR spectroscopic report for the AHT complex in the literature.

One can study the bonding nature and magnetic behaviour of the complex by the EPR method after doping with VO^{2+} ions. In this study, we tried to identify the dynamics of the paramagnetic centre in AHT complex by using EPR technique. We calculated the spin Hamiltonian parameters and the molecular bonding coefficients of the complex both in theoretical and experimental ways.

2 Experimental

AHT single crystals were grown from a saturated solution of ammonia with tartaric acid in stoichiometric proportion. An aqueous solution of 1 wt% of vanadyl(IV) sulphate was added as dopant to the saturated solution of AHT. After about 3 weeks, colourless single crystals were obtained by using slow evaporation method. The crystal system of AHT is orthorhombic and belongs to the space group $P2_12_12_1$ having four molecules per unit cell with the following parameters: $a = 7.648$, $b = 11.066$, and $c = 7.843$ Å [16]. EPR spectra of the AHT:VO^{2+} single crystal were recorded on a Varian E109 Century series X-band EPR spectrometer. We used a diphenylpicrylhydrazyl (dpph) sample ($g = 2.0036$) to make corrections to the g values.

3 Results and Discussion

We recorded the EPR spectra of the AHT:VO^{2+} single crystal at room temperature. The nuclear spin of the vanadium

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is 7/2, and vanadyl ion has a single electron of spin 1/2 in its d orbitals. The interaction between these spins results hyperfine splitting giving an octet in an EPR spectrum [17]. Since there are four molecules in the unit cell of the AHT:VO^{2+} complex, we can expect 32 peaks in the EPR spectrum. However, the positions of the sites in the complex depending on the crystal planes cause the complex to feel different external magnetic fields. If two of the sites feel the same magnetic field, there will be an octet instead of 16 peaks in the EPR spectrum as if there was a single site. But this time, the intensity of the lines increases twice. Both of the sites have the same *g* values and same hyperfine splitting constants (*A*). If two of the sites feel different magnetic fields, there will be 16 peaks having nearly the same *g* but different *A* values in the EPR spectrum. In this case, still some of the lines overlap and increase the intensity of the peaks [10].

As a general case, when there is more than one site in a paramagnetic centre, the number of lines in the EPR spectrum increases as well. The sites have nearly the same *g* values, while *A* values may change slightly. This is the case for some lines at some orientations overlapping in the spectrum for the AHT:VO^{2+} complex. Figure 1 shows one of such spectra at an orientation in the *bc* plane. To determine the principal *g* and *A* values of the single crystal, one must take the EPR spectra in all three mutually perpendicular axes. When taking the spectra in one axis, generally one rotates the crystal from 0° to 180° in the external applied magnetic field. It will be very difficult to follow the same line, say for the magnetic spin quantum number $m = -7/2$, in all spectra for a single axis in anisotropic cases. To handle the problem, we used a simple numerical technique explained in [18]. Figure 2 shows the line positions and fitted curves. One can easily find the g^2 values for a specific line with respect to rotation angle in each plane after the fitting process [19].

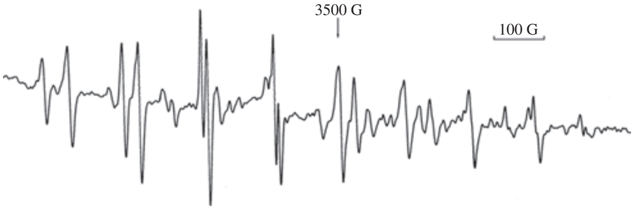

Figure 1: EPR spectrum of AHT:VO^{2+} single crystal. The magnetic field is in the *bc* plane making 10° from the *b*-axis.

Including only electronic Zeeman and hyperfine interactions, one can describe the EPR spectra of the single crystal in terms of the following spin Hamiltonian:

$$H = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}. \quad (1)$$

After calculations described in [18], we constructed **g** and **A** tensors and diagonalised them to find the principal *g* and *A* values. One can find both the results of our work and some other tartrate containing complexes in Table 1.

If we examine Figure 2 carefully, we can see four chemically identical but magnetically not identical sites in the complex. It means that the sites align in different directions in the unit cell of the complex. All sites in the single crystal show nearly axial symmetry as is the case for paramagnetic vanadyl ions in orthorhombic crystal systems. The single-crystal EPR spectra also show that

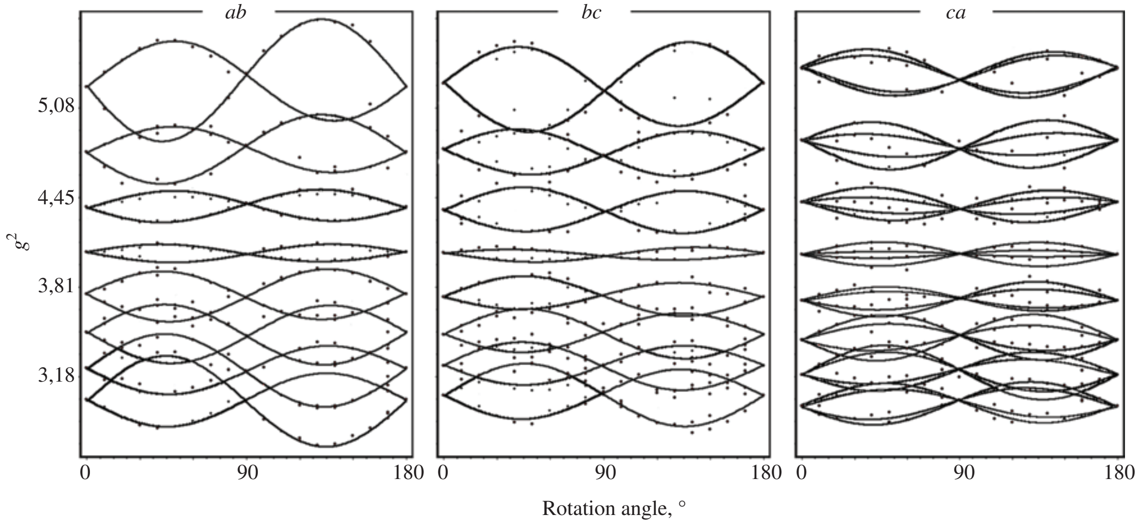

Figure 2: Angular variation of g^2 values of AHT:VO^{2+} single crystal.

Table 1: The principal values of **g** and **A** tensors of VO^{2+} ions observed in different single crystals ($\Delta g = \pm 0.005$ and $\Delta A = \pm 5 \times 10^{-4}$ cm^{-1}).

Complex	Site	$g_{\parallel}$	$g_{\perp}$	g_{iso}	$A_{\parallel}$ (10^{-4} cm^{-1})	$A_{\perp}$ (10^{-4} cm^{-1})	A_{iso} (10^{-4} cm^{-1})	Ref.
AHT	I	1.941	1.992	1.975	198.0	93.58	128.4	This work
	II	1.946	1.990	1.975	173.2	94.34	120.6	This work
	III	1.942	1.993	1.976	191.9	97.42	128.9	This work
	IV	1.946	1.990	1.975	175.7	101.4	126.2	This work
DADT	I	1.940	1.990	1.973	197.0	79.00	118.3	[5]
DST	I	1.894	1.984	1.954	180.2	78.00	112.2	[10]

DADT, diammonium d-tartrate; DST, disodium tartrate.

the VO^{2+} group localises interstitially and make a defection in the host lattice. It coordinates with two bidentate tartrate dianions in the equatorial plane and an aqua molecule in the axial position opposite to the oxide. The proton vacancy in tartrate dianions provides the charge compensation in the complex [10]. The value of the ratio $g_{\parallel}/g_{\perp}$ is greater than unity and hence indicates the tetragonal distortion of the vanadyl ions in AHT single crystals [20]. The distortion is along V=O direction and removes the degeneracy of the ground state of vanadyl ion with its d$_{xy}$ orbital lying lowest.

The g_i ($i = \parallel, \perp$) values and the molecular bonding coefficients are related to each other [21]:

$$g_{\parallel} = g_e\left(1 - \frac{4\lambda\beta_1^2\beta_2^2}{\Delta_{\parallel}}\right), \tag{2}$$

$$g_{\perp} = g_e\left(1 - \frac{\lambda\gamma^2\beta_2^2}{\Delta_{\perp}}\right), \tag{3}$$

where g_e (2.0023) is the free electron g factor, and λ is the spin-orbit coupling coefficient for the VO^{2+} ion. We take $\lambda = 170$ cm^{-1} for VO^{2+} ion [22]. β_1^2, β_2^2, and γ^2 are the molecular orbital bonding coefficients characterising in-plane σ, in-plane π, and out-of-plane π-bonding, respectively, for the central transition metal ion with the ligands. The denominators are optical absorption bands assigned to $\Delta_{\perp} = {}^2B_{2g} \to {}^2E_g$, and $\Delta_{\parallel} = {}^2B_{2g} \to {}^2B_{1g}$ transitions for the title complex [8]. Since there is no optical absorption report for the AHT:VO^{2+} complex, we used the two bands $\Delta_{\perp} = 10{,}762$ cm^{-1}, and $\Delta_{\parallel} = 16{,}621$ cm^{-1} reported for vanadyl-doped diammonium d-tartrate complex, which is similar to the structure under study [5].

On the other hand, the relation between A_i ($i = \parallel, \perp$) values and the molecular bonding coefficients is as follows [21, 22]:

$$A_{\parallel} = -P\left[\kappa + \frac{4}{7}\beta_2^2 + (g_e - g_{\parallel}) + \frac{3}{7}(g_e - g_{\perp})\right], \tag{4}$$

$$A_{\perp} = -P\left[\kappa - \frac{2}{7}\beta_2^2 + \frac{11}{14}(g_e - g_{\perp})\right], \tag{5}$$

where κ is the Fermi contact term and indicates the 4s orbital mixing with 3d$_{xy}$ orbital of the vanadium. P is the dipolar interaction term between magnetic moments of the unpaired electron and the vanadium nucleus. One can calculate the dipolar interaction term by neglecting second-order effects and using the negative values for A_i [23, 24]:

$$P = \frac{7(A_{\parallel} - A_{\perp})}{6 + (3/2)(\lambda/\Delta_{\parallel})}. \tag{6}$$

Using (4) and (5) and eliminating v, we have an expression for β_2^2 as follows [20, 24]:

$$\beta_2^2 = -\frac{7}{6}\left(\frac{(A_{\parallel} - A_{\perp})}{P} + (g_e - g_{\parallel}) - \frac{5}{14}(g_e - g_{\perp})\right). \tag{7}$$

One can find the calculated molecular bonding coefficients in Table 2. β_2^2 is the covalency ratio of V=O bonds [3, 20, 24]. The value of β_1^2 is 0.5 or 1.0 indicating whether the bond is covalent or ionic in nature, respectively. However, if the value is neither of them, the bonding is moderately ionic and covalent. The parameters $(1-\beta_1^2)$ and $(1 - \gamma^2)$ show the covalency rates of the vanadium atom. The first parameter gives the effect of the σ-bonding with the equatorial ligands, while the second gives the effect of π-bonding with the vanadyl oxygen [3, 20]. In this work, γ^2 is less than β_1^2 for all sites in AHT:VO^{2+} complex indicating that in-plane σ-bonding is more ionic and out-of-plane π-bonding is moderately ionic in nature.

Figure 3 shows the powder EPR spectrum of the AHT:VO^{2+} single crystals and its computer simulation. We measured the g and A values of the powder spectrum. The results are as follows: $g_{\parallel} = 1.941$, $g_{\perp} = 1.986$, $A_{\parallel} = 192.1 \times 10^{-4}$ cm^{-1}, and $A_{\perp} = 72.86 \times 10^{-4}$ cm^{-1}. These results are reasonable and compatible with the single-crystal data.

Table 2: Theoretical and experimental molecular bonding coefficients and the principal values of **g** and **A** tensors of VO^{2+} ions observed in different powder complexes (A and P are in 10^{-4} cm^{-1}, $\Delta g = \pm 0.005$ and $\Delta A = \pm 5 \times 10^{-4}$ cm^{-1}, κ is the Fermi contact parameter).

Powder complex	$g_\parallel$	$g_\perp$	g_{iso}	$\|A_\parallel\|$	$\|A_\perp\|$	$\|A_{iso}\|$	κ	$\|P\|$	β_1^2	β_2^2	γ^2	$1-\beta_1^2$	$1-\gamma^2$	Ref.
AHT[a]	1.941	1.986	1.971	189.2	76.86	114.3	0.84	131.1	0.70	1.00	0.48	0.30	0.52	This work
AHT[b]	1.944	1.980	1.968	188.6	80.94	116.8	0.95	125.2	0.67	1.00	0.66	0.33	0.33	This work
DADT	1.940	1.990	1.973	189.0	70.50	110.0	0.84	121.0	0.76	0.99	0.71	0.24	0.29	[5]
DST	1.922	1.984	1.963	183.0	70.70	108.1	0.81	–	–	0.96	–	–	–	[10]

[a]Experimental, [b]Theoretical.

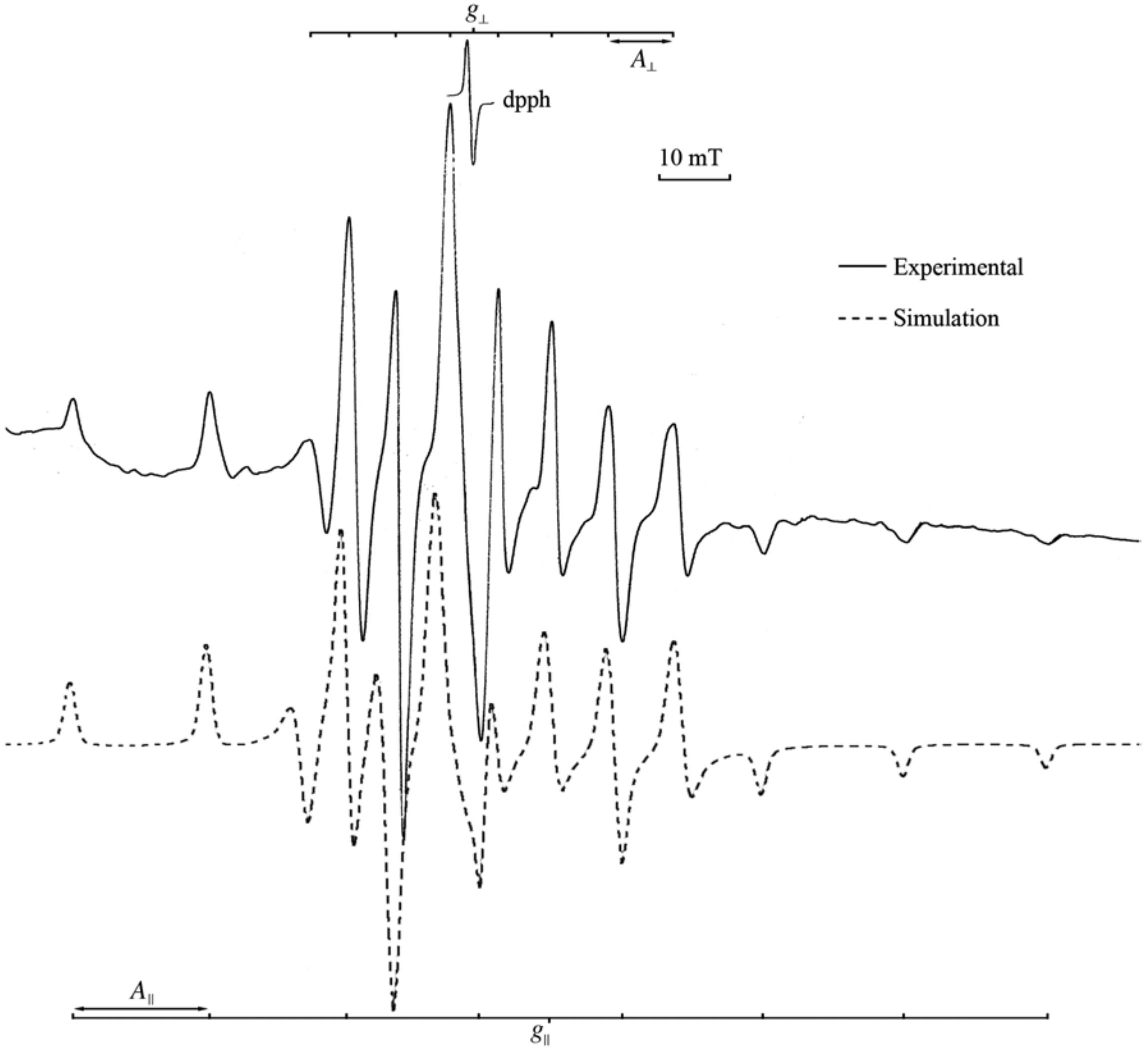

Figure 3: Experimental and simulated EPR spectrum of AHT:VO^{2+} powder sample at room temperature.

One can calculate the octahedral field parameter (Dq) and the tetragonal field parameters (Ds and Dt) by fitting the theoretical results of optical absorption and EPR spectra to the experimental results [8]:

$$\Delta_\perp = {}^2B_{2g} \rightarrow {}^2E_g = -3\,\mathrm{Ds} + 5\,\mathrm{Dt}, \tag{8}$$

$$\Delta_\parallel = {}^2B_{2g} \rightarrow {}^2B_{1g} = 10\,\mathrm{Dq}, \tag{9}$$

$$\Delta = {}^2B_{1g} \rightarrow {}^2A_{1g} = 10\,\mathrm{Dq} - 4\,\mathrm{Ds} - 5\,\mathrm{Dt}. \tag{10}$$

We used the theoretical formulas to calculate the tetragonal field parameters as described in [25, 26].

The calculated values for the parameters are Dq = 1662, Ds = –1974.5, and Dt = 977.6 cm^{-1}. Hence, the theoretical optical absorption energies are $\Delta_\perp = 10\,811$, $\Delta_\parallel = 16\,620$, and $\Delta = 19\,630$ cm^{-1}.

From perturbation theory, one can derive the equations for the theoretical values of the spin Hamiltonian parameters for $3d^1$ ions in tetragonal symmetry as [27, 28]:

$$g_\parallel = g_e - \frac{8k\zeta}{\Delta_\parallel} - \frac{(k+g_e)\zeta^2}{\Delta_\perp^2} - \frac{4k\zeta^2}{\Delta_\perp \Delta_\parallel}, \tag{11}$$

$$g_\perp = g_e - \frac{2k\zeta}{\Delta_\perp} + \frac{(k-g_e)\zeta^2}{\Delta_\perp^2} - \frac{2g_e\zeta^2}{\Delta_\parallel^2}, \tag{12}$$

where k is the orbital reduction factor, and ζ is the spin-orbital coupling parameter. We have $\zeta \approx k\zeta_0$, where $\zeta_0 \approx 248$ cm^{-1} for a free V^{4+} ion [1]. After calculating the g factors theoretically, one can use (4) and (5) to find theoretical A values. Here, again we have $P \approx kP_0$, where $P_0 \approx 172 \times 10^{-4}$ cm^{-1} for a free V^{4+} ion [29]. Taking $\beta_2^2 = 1$ [8] and adjusting the parameters $\kappa \approx 0.95$ and $k \approx 0.69$, we found the theoretical values for the AHT:VO^{2+} powder sample. One can find both experimental and theoretical results in Table 2.

4 Conclusion

We studied the EPR spectra of the vanadyl ions in AHT single crystal. The angular variation in g^2 values in the EPR spectra shows that VO^{2+} ions form four magnetically non-equivalent sites in the unit cell of AHT complex. The paramagnetic centre (VO^{2+}) exhibits axial symmetry in the complex. An octahedral complex with a tetragonal compression shows the relation between the g and A values as follows [1]: $g_\parallel < g_\perp < g_e$ and $|A_\parallel| > |A_\perp|$. Since our results suit the case, we can conclude that the paramagnetic centre in AHT single crystal is tetragonally compressed.

Molecular orbital bonding coefficients indicate the bonding nature of the paramagnetic centre with its environment. One can infer from Table 2 that the in-plane σ-bonding of the vanadium ion with the equatorial ligands is 30 % covalent and out-of-plane π-bonding of the vanadium with the oxide is 52 % covalent in the powder sample.

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