CHAPTER-V

EPR AND OPTICAL ABSORPTION
OF VANADYL DOPED MIXED
TUTTON SALT
Abstract

This chapter presents the results of optical absorption and EPR studies in a mixed, Tutton salt doped with vanadyl ions. The results of both the studies have been further correlated to estimate the various molecular orbital and other parameters involving the doped vanadyl ion and the surrounding host lattice.

5.1 Introduction
Vanadium occurs in many natural systems [1] and the V\(^{51}\) nucleus, approximately 100% abundant, has a large nuclear magnetic moment and a nuclear spin of \(7/2\). The electron paramagnetic resonance is ideally suited to identify vanadium through its characteristic eight line spectrum. The 4+ oxidation state of vanadium almost exclusively exists in the VO\(^{2+}\) (Vanadyl) ion. The magnetic susceptibility data on various vanadyl complexes [2, 3] indicate that the magnetic moment is close to the spin only value for a single unpaired electron. The vanadyl ion has consequently been used as an EPR probe in a variety of systems to study phenomena ranging from phase transition to dynamics and structure of complex biological systems [1, 4].

The 4+ state of vanadium has a single d – electron. So, as per Chapter 3, it requires a non-cubic crystalline field for EPR to be observed and this requirement is fulfilled by vanadyl complexes. The chemistry and bonding of vanadyl complexes has been studied quite in detail by Selbin [3] and spectral properties of many vanadyl complexes have been discussed by him & Boucher et al [3, 5].
The EPR results of vanadyl ions in alkali halides has been reported in the last Chapter. For these systems too, the net crystalline electric field on the VO$^{2+}$ site was non-cubic.

The Tutton salts are, further, a group of isomorphous compounds with monoclinic symmetry. In these salts vanadyl ions, when doped, are likely to occupy the divalent cation sites, which have a surrounding of distorted octahedron of water groups. The field at the divalent cation site of Tutton salt is thus inherently non-cubic and is likely to be further distorted due to the effect of V=O bond itself, thus fulfilling the requirement for observing the EPR of doped vanadyl ions.

The pioneering studies of Borcherts and Kikuchi [6] on VO$^{2+}$ in Zn(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O Tutton salt, proposed the substitution of VO$^{2+}$ in the place of divalent metal cation and the formation of vanadyl sulphate pentahydrate complex. Further V=O was found to have three possible orientations with relative populations 20:5:1. The EPR studies of VO$^{2+}$ in CoK$_2$(SO$_4$)$_2$.6H$_2$O host lattice [7] have revealed only two nearly equal populous orientations with very different linewidths. In a later work of Upreti & Saraswat [8], VO$^{2+}$ ions have further been studied through EPR in
Co(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O abbreviated as CASH, Fe(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O [FASH], Ni(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O [NASH] and NiK$_2$(SO$_4$)$_2$.6H$_2$O [NKSH]. For CASH and FASH hosts, two V=O complexes showing EPR spectra in the ratio 5:3 are reported. However, no observable EPR spectra were observable for VO$^{2+}$ in NASH and NKSH hosts from room temperature down to 77K.

5.2 Relative occupancy of vanadyl ions at different orientations

In the work of Borcherts and Kikuchi [6] the formation of vanadyl sulphate penta hydrate complex has been reported. While considering the occupancy of B$^{2+}$ ion sites in ZASH by vanadyl ion, this appears quite untenable. The B$^{2+}$ ion sites are surrounded by six water groups, thus there is no scope of SO$_4$ entering the octahedral cage of H$_2$O groups. The only tenable situation, however, is that one of the six water groups is made to leave its normal site for an interstitial position in the lattice. The V=O would then point along such a vacant H$_2$O group site and in this process, a VO (H$_2$O)$_5$ complex would be formed.

Three types of water groups with oxygens as O(7), O(8) and O(9) may have to leave their normal sites on addition of vanadyl ions. It is known that the B$^{2+}$-O (7,8,9) distances are not all equal in a
Tutton salt. As per the crystal data reported in Chapter 2, B-O(7) and B-O(8) bonds are nearly equal and larger than the B-O(9) bonds, which are the shortest in a Tutton salt. Further, all the three oxygens O(7), O(8), O(9) and also their water groups are bonded in the lattice differently through respective hydrogen bondings. Which of the three possible V=O orientations will be more plausible in a Tutton salt and will obviously depend upon the bonding in the lattice of the oxygen O(7), O(8) or O(9) to be replaced. Now, as reported in the literature, B-O(9) is the shortest bond and the strongest. Accordingly, replacing the O(9) water groups by V=O bond would be the most different process and V=O alignment along this direction would be the rarest.

The observed 20:5:1 intensity for the EPR spectra of vanadyl ions in zinc ammonium sulphate hexahydrate Tutton salt accordingly suggests that the weakest spectrum should belong to the V=O bond along the B-O (9) orientation. The B-O(7) and B-O(8) bonds would subsequently correspond to other orientations of V=O. Out of two remaining orientations, the stronger would depend upon, which of O(7) or O(8) can be made to leave the normal site with better ease.

The observation of only two sites in VO$^{2+}$ : CASH with intensity ratio 1:1 further suggests that B-O(9) bond is strongest in
this host and cannot be broken. However, the other two bonds B-O(7) and B-O(8) being equally strongly breakable, attribute equal probability for the two orientations of V=O occupancy.

The results of EPR studies by Saraswat & Upreti [7] in the system VO$^{2+}$ - CKSH further suggest a quite strong B-O(9) bond and the remaining two B-O(7) and B-O(8) bonds to have bond-strengths in the reverse ratio of 5:3 and thus to be actually 3:5. The unique case of NASH and NKSH hosts suggests that all B-O bonds are quite strong in such salts and are not broken at all, with energy exchanges involved during substitution of V=O in Tutton salts.

5.3 Optical absorption data of vanadyl ions

The energy level pattern of VO$^{2+}$ in tetragonal environment has been shown in Fig. 3.4 of Chapter 3, with $b_2$ as the highest occupied level. The relevant portion of the set of energy levels of this figure is redrawn in Fig. 5.1 with $^2B_2$ as the lowest level and $^2E$, $^2B_1$ and $^2A_1$ as the higher vacant levels. The expected transitions with energy changes $E_1$, $E_2$ and $E_3$ are depicted here for the transitions $^2B_2 \rightarrow ^2E$, $^2B_2 \rightarrow ^2B_1$ and $^2B_2 \rightarrow ^2A_1$ respectively. Also shown in the figure are the characters of different $d$ – orbitals involved for these levels.
The earliest reported optical absorption spectra for vanadyl ions are due to Ballhausen & Gray [9]. These workers have reported spectra for the complex $\text{VO(H}_2\text{O)}_5^{2+}$ as two broad maxima at approximately 13,000 cm$^{-1}$ and 16,000 cm$^{-1}$ which correspond respectively to $b_2 \longrightarrow e_{\pi}^*$ and $b_2 \longrightarrow b_1^*$ electron transitions. These compare well with the results of other workers [10-15] about optical absorption of VO$^{2+}$ in a variety of hosts, including solvents, glasses and single crystals, as quoted in Table 5.1.

5.4 Experimental

VO$^{2+}$ - doped $(\text{NH}_4)_2\text{Mg}_{0.5}\text{Zn}_{0.5}(\text{SO}_4)_2.6\text{H}_2\text{O}$ crystals were grown by slow evaporation of a saturated solution in distilled water, containing $(\text{NH}_4)_2\text{SO}_4$, MgSO$_4$ and ZnSO$_4$ in the molar ratio 2:1:1. About 1% by weight of vanadyl sulphate was also added to the solution before the growth of crystals. In a typical growth process about 50 ml of saturated solution as above were kept for evaporation in a beaker at $10^0\text{C}$. Good crystals with shining faces appeared after about 15 days and majority of these had prismatic appearance.

As the EPR spectrum of a powdered sample itself furnishes sufficient information about the parameter $g_\parallel$, $g_\perp$, $A_\parallel$ & $A_\perp$, the present studies were devoted to the powdered samples. This avoided critical
alignment conditions. The spectra were recorded at RT using Varian E-line century series spectrometer E–109. The DPPH was used as the field marker and its magnetic field was calibrated with the help of Varian E–500 digital NMR gaussmeter.

The optical absorption spectra were recorded with the help of a Hitachi UV-Visible spectrometer in very thin slices of crystal samples.

5.5 **Effect of covalency on g and A parameters**

The relevant energy levels of V-O molecular complex are described by Fig. 5.1. The energy of transition from the level $^2B_2$ to $^2E$ is denoted by $E_1$, from the level $^2B_2$ to $^2B_1$ as $E_2$ and that from $^2B_2$ to $^2A_1$ as $E_3$.

Kivelson and Lee [12] have described how the overlapping of ligand orbitals leads to the modification of $g$ and $A$ – tensor components for VO$^{2+}$ ion complex with tetragonal symmetry. This leads to –

\[
\begin{align*}
g_{||} &= g_e \left[ 1 - \frac{4\alpha^2 \beta^2}{E_2} \right] \\
g_{\perp} &= g_e \left[ 1 - \frac{\lambda \gamma^2 \beta^2}{E_1} \right]
\end{align*}
\]
\[ A_\parallel = -P \left\{ \beta^2 \left( \frac{4}{7} + K \right) + \Delta g_\parallel + \frac{3}{7} \Delta g_\perp \right\} \]

and \[ A_\perp = +P \left\{ \beta^2 \left( \frac{2}{7} - K \right) - \frac{11}{14} \Delta g_\perp \right\} \]

Here, \( g_e \) is free electron \( g \) – value of 2.0023

\( \lambda \) is spin – orbit coupling constant

\( \beta^2 \) is measure of plane \( \pi \) – bonding of vanadium with the equatorial ligands and usually taken to be 1, as occupied highest level (\( d_{xy} \)) is assumed strictly non – bonding.

\( K \) is isotropic Fermi contact interaction

\( \parallel \) is \( (g_e - g_\parallel) \)

\( \Delta g_\parallel \) is \( (g_e - g_\parallel) \)

\( P \) is \( 2\beta_0\beta_N\gamma_0 \left\langle d_{xy} \left| \frac{1}{r^3} \right| d_{xy} \right\rangle \),

with \( \beta_0 \) as Bohr magneton

\( \beta_N \) as nuclear magneton and

\( \gamma_0 \) as nuclear gyro – magnetic ratio

Taking \( \beta^2 \) as 1, we obtain the above equations in the form –

\[ g_\parallel = g_e \left( 1 - \frac{4\lambda\alpha^2}{E_2} \right) \]

\[ g_\perp = g_e \left( 1 - \frac{\lambda\gamma^2}{E_1} \right) \]
A_\parallel = - P \left\{ \frac{4}{7} + K + \frac{3}{7} \Delta g_\parallel \right\} \\
A_\perp = P \left\{ \frac{2}{7} - K - \frac{11}{14} \Delta g_\perp \right\}

It must be remarked here that the expressions \((1-\gamma^2)\) and \((1-\alpha^2)\) represent the degree of covalencies. The covalency increases as the values of \((1-\gamma^2)\) and \((1-\alpha^2)\) increase. The former gives an indication of the influence of the \(\pi\)-bonding between the \(V^{4+}\) ion and the vanadyl oxygen; while the latter indicates the influence on \(\sigma\) – bonding by equatorial ligands.

5.6 Results and Discussion

The results obtained from the EPR and optical absorption studies in the mixed system of \((NH_4)_2Mg_{0.5}Zn_{0.5}(SO_4)_{2.6}H_2O\) are discussed forthwith under different headings.

5.6.1 EPR Studies

Fig. 5.2 has shown the EPR spectrum of \(VO^{2+}\) - doped mixed Tutton salt system as above, in the powdered polycrystalline phase. The spectrum clearly exhibits the characteristics of powered sample as mentioned in Chapter 4. Both upper and lower contours are not simultaneously seen in the first derivative absorption spectrum of
Fig. 5.2. The turning points of both parallel and perpendicular spectra are well defined. Now, using the positions of these turning points for the eight hyperfine lines and field expressions for such transitions as given in Chapter 4, $g_\parallel$, $g_\perp$, $A_\parallel$ & $A_\perp$ have been evaluated as

$$g_\parallel = 1.932 \pm 0.002$$
$$g_\perp = 1.979 \pm 0.002$$
$$|A_\parallel| = 201.9 \pm 3.0 \text{ gauss}$$
$$|A_\perp| = 78.7 \pm 3.0 \text{ gauss}$$

Now, for an EPR centre with a $g$ – value of $\approx 2$, the value of 1 Gauss is equivalent to $0.9 \times 10^{-4} \text{ cm}^{-1}$. Thus in energy units,

$$A_\parallel = (181.7 \pm 2.8) \times 10^{-4} \text{ cm}^{-1}$$
$$A_\perp = (70.8 \pm 2.8) \times 10^{-4} \text{ cm}^{-1}$$

The signs of $A_\parallel$ and $A_\perp$ have however been found to be negative as per section 5.6.3.1.

### 5.6.2 Optical studies

The optical absorption spectrum in the UV-Visible range for the system \((\text{NH}_4)_2\text{Mg}_{0.5}\text{Zn}_{0.5}\text{(SO}_4)_{2.6}\text{H}_2\text{O} : \text{VO}^{2+}\) is given in Fig. 5.3. Two prominent bands at 12,530 cm$^{-1}$ and 15,870 cm$^{-1}$ have been observed and these correspond to the energy differences $E_1$ and $E_2$ respectively of Fig. 5.1.
5.6.3 Correlation of Optical Absorption & EPR results

The turning points with only one side (up/down) contours indicate the positions of parallel components of the most populated Mg/Zn sites in the mixed Tutton salt. The perpendicular components however present both up and down contours. The components of $g$ and $A$ tensors calculated from the turning point positions, thus represent the behaviour of such a type of site for VO$^{2+}$.

So far optical absorption spectrum is concerned only two broad bands have been observed. This indicates that the crystalline environment of VO$^{2+}$ in both Mg$^{2+}$ & Zn$^{2+}$ types of octahedral of water groups are nearly identical and the observed bands are due to overlap of such pairs of bands of VO$^{2+}$ spectra.

5.6.3.1 Calculation of Molecular Orbital Parameters

The following gives evaluation of various molecular orbital parameters for the most prominently occupied site for VO$^{2+}$ in the mixed Tutton salt host.

We have, $g_\parallel = 1.932$

$g_\perp = 1.979$

$E_1 = 12530 \text{ cm}^{-1}$

$E_2 = 15870 \text{ cm}^{-1}$
Using the formulae of Sec. 5.5, we have

\[ g_\| = 1.932 = 2.0023 \left(1 - \frac{4\lambda \alpha^2}{15870}\right) \]

and

\[ g_{\perp} = 1.979 = 2.0023 \left(1 - \frac{\lambda \gamma^2}{12530}\right) \]

Now assuming \( \lambda = 249 \text{ cm}^{-1} \), as per Muncaster & Parke [16], the above two equations yield

\[ 1.932 = 2.0023 \left(1 - \frac{(4)(249)\alpha^2}{15870}\right) \]

\[ 1.979 = 2.0023 \left(1 - \frac{249\gamma^2}{12530}\right) \]

On solving the two equations one obtains –

\[ \alpha^2 = 0.5594 \text{ , } \alpha = 0.748 \text{ and } (1-\alpha^2) = 0.44 \]

\[ \gamma^2 = 0.5855 \text{ , } \gamma = 0.765 \text{ and } (1-\gamma^2) = 0.41 \]

As mentioned, \( (1-\alpha^2) = 0.44 \) gives the degree of covalency of \( \sigma - \) bonding between \( V^{4+} \) and oxygen’s of \( \text{H}_2\text{O} \) groups and \( (1-\gamma^2) = 0.41 \) gives the degree of covalency of \( \pi - \) bonding between \( V^{4+} \) and vanadyl oxygen.

Again, using the expression for \( A_\| \) as
\[ A_\parallel = -P \left( \frac{4}{7} + K + \frac{3}{7} \Delta g_{\parallel} + \frac{3}{7} \Delta g_{\perp} \right) \]

and the values \( |A_\parallel| = 180.2 \text{ cm}^{-1}, \Delta g_{\parallel} = 0.0703 \) and \( \Delta g_{\perp} = 0.0233 \) one gets

\[-181.7 \times 10^{-4} = -P [K + 0.6517] \]  ----  (A)

The expression for \( A_\perp \) is

\[ A_\perp = +P \left( \frac{2}{7} - K - \frac{11}{14} \Delta g_{\perp} \right) \]

Substituting, the known values of \( |A_\perp| \) (Sec. 5.6.1) and \( \Delta g_{\perp} \), this gives

\[-70.8 \times 10^{-4} = P [-K + 0.2674] \]  ----  (B)

Dividing Eq. (A) by Eq. (B), we obtain

\[
\frac{181.7}{70.8} = \frac{-K - 0.6517}{-K + 0.2674}
\]

or \( K = 0.8571 \)

Now from Eq. (A)

\[ +181.7 = P [1.5088] \]

or \( P = 120.4 \times 10^{-4} \text{ cm}^{-1} \)

Subsequently, \( PK = 103.1 \times 10^{-4} \text{ cm}^{-1} \)

The \( A_\parallel \) and \( A_\perp \) can be broken into their dipolar portion and Fermi contact contributions \((-PK)\) as

\[ A_\parallel = A'_\parallel - PK \]
giving \[ g = -78.6 \times 10^{-4} \text{ cm}^{-1} \]

Further, as \[ A = A - PK \]

one obtains \[ A = + 32.3 \times 10^{-4} \text{ cm}^{-1} \]

5.7 Conclusions

5.7.1 Comparison of spin – Hamiltonian & MO parameters

Table 5.2 gives the spin – Hamiltonian & molecular orbital parameters for VO\(^{2+}\) in the present mixed system and also in some other crystal lattices for comparison[13,17-19].

It is seen that both g and A terms possess three unique principal values for all these systems. Further, barring the case of KMgClSO\(_4\).3H\(_2\)O host the g and A tensors in general possess near tetragonal symmetry.

5.7.2 Fermi – contact parameter K

The Fermi – contact parameter K for the above systems has been found to range between 0.72 and 0.86. It is related to unpaired electron density at the vanadium nucleus and is due to s – character of the magnetic spin of the vanadium. The s – character results basically from the partial unpairing or polarization of the inner electrons as a result of interaction with unpaired d – electrons. The quite large value of 0.86 for K in the mixed Tutton salt doped with VO\(^{2+}\), indicates
that there is a large contribution to hyperfine coupling constant due to unpaired s – electron, probably through spin polarization.

5.7.3 The value of P

The value of P which represents dipole – dipole interaction of electronic and nuclear moments has been found to be $120.4 \times 10^{-4} \text{ cm}^{-1}$ for VO$^{2+}$ in the mixed Tutton salt. The standard value of P for a free VO$^{2+}$ ion is however $160 \times 10^{-4} \text{ cm}^{-1}$ [13]. The observed value of P for VO$^{2+}$ in the mixed Tutton salt is thus considerably reduced up to 75% of the ideal value. This indicates a significant amount of covalent bonding in the VO complexes doped in the mixed Tutton salt.

5.7.4 Covalency parameters

As per Table 5.2, the covalency parameters $\alpha$ and $\gamma$ show large variation from one system to another [13, 17-19]. However, $\alpha$ and $\gamma$ values in different systems cannot be compared due to their dependence on $\lambda$, the spin – orbit coupling parameter. We assumed $\lambda$ to be $249 \text{ cm}^{-1}$ in congruence with Khasa et al [14] and Mancaster & Parke [16]. However, Kivelson & Lee [12] and Dev Prasad Raju et al [13] assumed this to be $170 \text{ cm}^{-1}$ only.
5.7.5 Values of dipolar terms, hyperfine parameters, PK & $\Delta g_{||} / \Delta g_{\perp}$

Table 5.3 gives values of dipolar portion in hyperfine interaction parameters $\parallel$ and $\perp$, Fermi contact contribution PK and $\Delta g_{||} / \Delta g_{\perp}$ for some VO$^{2+}$-doped systems [14, 15, 20, 21]. The dipolar terms $\parallel$ and $\perp$ are about the same for all the systems reported, except the case of LiPbBTe: 9 Mol % V$_2$O$_5$, wherein these are quite lower. The PK values range between 87.0 x $10^{-4}$ cm$^{-1}$ to 105.83 x $10^{-4}$ cm$^{-1}$ for these systems.

The $\Delta g_{||} / \Delta g_{\perp}$ values further show a large variation to be between 1.256 & 3.017 for different systems of Table 5.3. The theoretical value of $\Delta g_{||} / \Delta g_{\perp}$ is 1 of a regular octahedral system. The deviation of this ratio $(\Delta g_{||} / \Delta g_{\perp})$ from 1 indicates departures from the regular octahedral coordination of VO$^{2+}$. The ratio is the maximum for VO$^{2+}$ in the present mixed Tutton salt host and indicates that among the systems mentioned in Table 5.3, the present one has the extreme tetragonal distortion of electric field at the vanadium site.
5.8 References


Table 5.1

Observed optical absorption peaks for different vanadyl systems

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>Electronic transitions (cm$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$b_2 \rightarrow e_\pi^*$</td>
<td>$b_2 \rightarrow b_1^*$</td>
</tr>
<tr>
<td>1</td>
<td>VO$^{+2}$ : GeO$_2$</td>
<td>13,300</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>VO$^{+2}$ : PTB single crystal</td>
<td>12,495</td>
<td>16,415</td>
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<tr>
<td>3</td>
<td>VO(Ac)$_2$ in CHCl$_3$</td>
<td>14,800</td>
<td>16,800</td>
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<td>4</td>
<td>VO(Ac)$_2$ in THF</td>
<td>13,700</td>
<td>16,900</td>
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<td>5</td>
<td>VO$^{+2}$ : PZCST single crystal</td>
<td>14,405</td>
<td>16,497</td>
</tr>
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<td>6</td>
<td>VO$^{+2}$ : KCl.K$_2$O.B$_2$O$_3$ glass</td>
<td>12,642</td>
<td>17,794</td>
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<tr>
<td>7</td>
<td>VO$^{+2}$ : KBr.K$_2$O.B$_2$O$_3$ glass</td>
<td>12,876</td>
<td>18,182</td>
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<tr>
<td>8</td>
<td>LiPbBTe : 9Mol %V$_2$O$_5$</td>
<td>11,320</td>
<td>-</td>
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<tr>
<td>9</td>
<td>Mg,Zn mixed ammonium Tutton salt</td>
<td>12,530</td>
<td>15,870</td>
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This work
Table 5.2

The spin-Hamiltonian and molecular orbital parameters for VO$^{2+}$ ions in some crystalline lattices for comparison

<table>
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<tr>
<th>Sl. No.</th>
<th>Host crystal</th>
<th>g- values</th>
<th>A –values ($10^{-4}$ cm$^{-1}$)</th>
<th>Molecular orbital coefficients (P in $10^{-4}$ cm$^{-1}$)</th>
<th>Ref.</th>
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<td>Site – I</td>
<td>Site – II</td>
<td>Site – I</td>
<td>Site – II</td>
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<td>KZnClSO$_4$.3H$_2$O</td>
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<td>$A_x = 52$</td>
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<td>$g_y = 1.972$</td>
<td>$g_y = 1.983$</td>
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<td>$g_z = 1.920$</td>
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<td>$A_z = 192$</td>
<td>$A_z = 182$</td>
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<td>Mg, Zn mixed ammonium Tutton salt</td>
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<td></td>
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<td>$g_{\perp} = 1.979$</td>
<td></td>
<td>$A_{\perp} = 70.8$</td>
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Table 5.3

$\Delta g_{\parallel}$, $\Delta g_{\perp}$, PK and $\frac{\Delta g_{\parallel}}{\Delta g_{\perp}}$ of VO$^{2+}$ in different systems at RT.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>System</th>
<th>$\parallel$ (10$^{-4}$ cm$^{-1}$)</th>
<th>$\perp$ (10$^{-4}$ cm$^{-1}$)</th>
<th>PK (10$^{-4}$ cm$^{-1}$)</th>
<th>$\frac{\parallel}{\perp}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 x KCl. (0.3-x)K$_2$O.0.7B$_2$O$_3$</td>
<td>-75.9</td>
<td>+30.1</td>
<td>91.60</td>
<td>2.0027</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>LiPbBTe;9Mol%V$_2$O$_5$</td>
<td>-62.0</td>
<td>+42.0</td>
<td>96.90</td>
<td>1.256</td>
<td>15</td>
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<tr>
<td>3</td>
<td>3.5PbO.B$_2$O$_3$.3V$_2$O$_5$</td>
<td>-75.8</td>
<td>+26.8</td>
<td>105.83</td>
<td>1.3204</td>
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<tr>
<td>4</td>
<td>2BaO.3B$_2$O$_3$.5mol%V$_2$O$_5$</td>
<td>-78.4</td>
<td>+29.3</td>
<td>87.0</td>
<td>1.88</td>
<td>21</td>
</tr>
<tr>
<td>5</td>
<td>Mg, Zn mixed ammonium Tutton salt</td>
<td>-78.6</td>
<td>+32.3</td>
<td>103.1</td>
<td>3.017</td>
<td>This work</td>
</tr>
</tbody>
</table>

This work