CHAPTER IV

EPR OF VO$^{2+}$ IN RbCl CRYSTALS
Abstract

EPR of VO\textsuperscript{2+} ions incorporated in single crystals of RbCl from room temperature to the liquid nitrogen temperature has been presented in this chapter. At LNT, the spectrum recorded is anisotropic, exhibiting both parallel and perpendicular components. However, at RT the observed spectrum is isotropic, suggesting fast reorientation of VO molecular ions.

The spin Hamiltonian parameters have been obtained for both the spectra in RbCl : VO\textsuperscript{2+} system and correlated with each other. Further, the line-widths of the room temperature spectra are found to obey a parabolic variation as proposed originally by Kivelson.
4.1 Introduction

It is known that when alkali halide crystals are doped with divalent impurities like Mn\textsuperscript{2+}, alkali ion vacancies are created to account for charge neutrality. The divalent ions could go in substitutionally or interstitially in the crystal or could also go in clusters or precipitates. The vacancy could be a nearby neighbour to the divalent ion or it could be far away from it. The EPR spectra reported elsewhere [1-3] clearly indicate the different ways in which the impurity ions go into the crystal.

EPR of VO\textsuperscript{2+} doped in NH\textsubscript{4}Cl single crystal was studied by Sastry and Venkateswarlu [4] and that in KNO\textsubscript{3} and CsNO\textsubscript{3} by Rao, Sastry and Venkateswarlu [5]. It has been found from these studies that the molecular ion VO\textsuperscript{2+} does not have a fixed orientation in these crystals and undergoes a fast readjustment at room temperature, while it shows the effects of hindered rotation at low temperatures. On the other hand, VO\textsuperscript{2+} is known to have preferred orientations in Tutton salts [6] and in rubidium and cesium alums [7]. Again, Rao, Sastry and Venkateswarlu [8] have further found from their EPR studies that the VO\textsuperscript{2+} ion has preferred orientation in the potassium and
ammonium aluminium alums & MAG alum. Pandey and Venkateswarlu [9] have reported distinct orientation of VO\(^{2+}\) in ammonium sulphate single crystals.

Bandyopadhayay [10] has reported EPR of vanadium glasses and interpreted the results to V\(^{4+}\) ion being complexed as a VO\(^{2+}\) ion within a tetragonally distorted octahedral sites. The interest of workers towards EPR studies in vanadyl doped samples continues even now. Deva Prasad Raju et al [11] have reported EPR of VO\(^{2+}\) ions in KZnCl\(_2\)SO\(_4\).3H\(_2\)O single crystals and have reported presence of more than three magnetic complexes which correspond to distinct sites of VO\(^{2+}\) ion. However, recent EPR studies of VO\(^{2+}\) in potassium thiourea bromide single crystals [12] report a single eight line spectrum attributed to VO\(^{2+}\) complexed with sulphur atoms.

The present work has been undertaken to get information about the VO\(^{2+}\) complex inside a simpler alkali halide crystal of RbCl and the results obtained have been compared with those available [13] for NaCl and KCl hosts. Finally, the applicability of Kivelson’s theory [14] of paramagnetic relaxation has also been examined for this system.
4.2 Experimental

VO\(^{2+}\) - doped rubidium chloride crystals were grown by slow evaporation of a saturated solution of rubidium chloride containing a known quantity (0.5 mole percent) of vanadyl chloride. The rubidium chloride host was of E. Merck, A.R. quality. Nice cubic crystals with shining faces appeared after about 15 days of evaporation. The lower temperature of the surroundings improved the growth rate and the size of the crystals.

The EPR measurements were carried out at X – band, 9.5 MHz frequency with a Varian E – line century series EPR spectrometer E-109 and a 9 inch rotating electromagnet using 100 KHz field modulation. The magnetic field was calibrated using DPPH as the field maker. The proton resonance monitoring with a fluxmeter helped to measure the magnetic field corresponding to the proton resonance and thus of all the EPR peaks in the observed spectrum. The spectra were recorded at room temperature and at –180\(^{0}\)C (liquid nitrogen temperature) with the help of a Varian variable temperature accessory.
4.3 The EPR in a d\textsuperscript{n} configuration

The unpaired d – electrons in iron-group transition metal ions render them paramagnetic. The Table 4.1 gives the number of d-electrons, spin arrangement of free ion and other details for the case of tetravalent vanadium and divalent manganese.

4.3.1 The d – orbitals of a free ion

For a d-electron the I- value is 2 and orbital degeneracy is 5. The nature of d-orbitals is already described in the last chapter. The degeneracy of d-electrons is partly lifted, when placed in a octahedral crystalline field. Thus obtained three-fold degenerate orbitals are assigned as t and the two-fold degenerate ones as e.

4.3.2 Effect of ligand field on energy levels

If a paramagnetic ion is placed substitutionally at a cation site in a crystal, it is surrounded by anions. These anions are called ligands. The number of ligands surrounding the central ion represents its coordination number. These ligands may be negative ions or at times neutral molecules with a permanent lone pair of electrons and do change the energy level scheme of the ion in question resulting in ligand-splitting of its d-orbitals.
The orbital degeneracy of d – orbitals is partly or fully removed by the crystal field. In a NaCl crystal doped with divalent manganese, the Cl⁻ ligands form nearly octahedral coordination about the divalent ion and provide the crystal field. The electrostatic field of the negative charges and at times its covalent bonding with the ligand orbitals affects the d-electrons of the metal ion. This causes the energy levels corresponding to \( d_{x^2} \) and \( d_{x^2-y^2} \) to be raised and those corresponding to \( d_{zy}, d_{yz} \) & \( d_{zx} \) to be lowered. The energy gap between these two types of orbitals is the ligand field splitting and is represented by \( \Delta \) or 10 Dq by convention. The Fig 3.2 shows the energy level scheme for this type of symmetry.

The ligands often cause distortion of the atomic orbitals of the paramagnetic ion, so that very few complexes in the solid state actually possess regular symmetry like \( O_h \). The Table 4.2 gives the transformation properties of atomic orbitals under crystalline fields of different symmetries. The onset of lower symmetry causes splitting of energy levels and at times even the ground state configuration gets modified. The EPR experiments easily reveal the tetragonal or trigonal distortions in cubic systems.
The splitting of energy levels in the absence of magnetic field is governed by Kramer’s theorem [15] which states that for a system containing an odd number of electrons, at least two fold degeneracy must remain in the absence of magnetic field. Such pairs of states called the Kramer’s doublets are time conjugate, one being obtainable from the other by time – reversal and are thus not split by an electrostatic perturbation, which is even under time reversal.

4.3.3 Spin – orbit Vs. Crystal – field interaction

In crystal systems doped with first transition group elements, the outermost 3d electrons are exposed to the surroundings. The interaction with the crystalline field is therefore quite strong, and in many situations stronger than the spin – orbit interaction. On the other hand, in the case of rare earth ions, the 4f electrons are shielded form the surroundings by \(5s^2 \ 5p^6\) electrons and therefore less affected by the crystal field. Accordingly, in such cases, spin- orbit interaction is stronger than the crystalline field interaction.

In general, there are two interactions, which vie with each other, one the spin-orbit coupling and other the interaction of crystalline field with the orbital motion. The spatial degeneracy is partly lifted when the crystalline field interaction is stronger than the
spin orbit coupling interaction. In the iron group 3d transition elements thus obtained splittings are of the order of 20,000 cm\(^{-1}\) and are easily observable.

However, depending upon its strength, the spin – orbit coupling causes a little of the orbital magnetic moment to be admixed with the spin, so that the behavior of the ion in a magnetic field is modified.

### 4.3.4 Spin – Hamiltonian

The magnetic properties of an ionic complex in a crystal field are intimately connected with the energy levels of the ion. For complexes of the first transition group, the magnitude of the potential \( V \) provided by the ligands is such, as to make

\[
\lambda(r) l.s < V < \frac{e^2}{r_{ij}}
\]

For octahedral symmetry complexes, the \( V \) as above can be expressed as

\[
V = V(R) + V_o
\]

where \( V(R) \) spans the totally symmetric \( a_{1g} \) representation in the group \( O_h \) and \( V_o \) represent the cubic symmetry as

\[
V_o = x^4 + y^4 + z^4 - \frac{3}{5} r^4
\]
If, however, the symmetry is lower, low symmetry terms are also seen in $V_o$.

Apart from the three competitive terms mentioned, there are other terms too in the Hamiltonian of a transition metal ion. These are mentioned in Table 4.3 in approximately decreasing order of energy. To interpret the results of EPR effectively one has to consider the various such significant terms in the Hamiltonian.

The levels more than $10^3$ cm$^{-1}$ above the ground level, may be ignored at room temperature, as these are insufficiently populated to contribute to any absorption spectrum. Thus one is left with the lowest lying levels, characterized by orbital and spin quantum numbers $L$ and $S$ described by Russell–Sauders coupling.

For a general 3d – ion configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^n$, the first five sub-levels with the configuration $1s^2 2s^2 2p^6 3s^2 3p^6$ provide a diamagnetic shell with $L = S = 0$. Thus for Mn$^{2+}$ with $n= 5$, the ground state has $L = 0$ and $S = 5/2$ and for V$^{4+}$ with $n = 1$ ground state corresponds to $L = 2$ and $S = \frac{1}{2}$.

A general ground state for a transition metal ion is $(2L+1) (2S+1)$ - fold degenerate. However, the crystal field lifts this degeneracy fully or partly and the system is described by a real (or
fictitious) spin S and the concept of spin – Hamiltonian with $\mathbf{H} = \beta_o \mathbf{H}$. $\mathbf{S}^\prime$ is used to determine the energy perturbation in an applied d. c. magnetic field $\mathbf{H}$ of an EPR experiment.

This concept of spin Hamiltonian is due to Abragam and Pryce [16]. The orbital $|0\rangle$ with $l = 0$ contains a single electron in the ground state of the paramagnetic complex. Neglecting the spin-orbit coupling, this may be represented by $|0, +\frac{1}{2}\rangle, |0, -\frac{1}{2}\rangle$. The perturbation due to spin-orbit coupling changes these states and the perturbed forms are:

$$|0, +\frac{1}{2}\rangle + c |1, -\frac{1}{2}\rangle \equiv |+\frac{1}{2}\rangle$$

$$|0, -\frac{1}{2}\rangle + d |1, +\frac{1}{2}\rangle \equiv |-\frac{1}{2}\rangle$$

In the absence of a magnetic field, the states $|+\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ are degenerate and form a Kramer’s doublet. The application of magnetic field $\mathbf{H}$ in the direction of $z$-axis however causes a perturbation $\beta_o H_z (L_z + 2S_z)$.

If $S_x$, $S_y$ and $S_z$ are the components of fictitious spin $S^\prime$ and $|+\rangle$ and $|->$ are the eigenvalues of $S_z$ with eigenfunctions $+\frac{1}{2}$ and $-\frac{1}{2}$, given as

$$S_z |+\rangle = +\frac{1}{2} |+\rangle$$

$$S_z |->\rangle = -\frac{1}{2} |->\rangle,$$
The $g$ – tensor may be derived by constructing the matrix of $L + g_\epsilon S$ for the states $|+\rangle$ and $|-\rangle$.

The spin – Hamiltonian is accordingly written as

$$H = \beta_0 \mathbf{H}. \mathbf{g}. \mathbf{S}$$

$$= \beta_0 \{ g_{||} H_z + g_{\perp} (H_x S_x + H_y S_y) \}.$$ 

It is however to be seen that the $Z$ – axis of $g$ – tensor coincides with the symmetry axis of the system.

The Hamiltonian as above is called the spin – Hamiltonian and it operates on wave functions expressed in terms of spin variables only.

4.4 Application of spin – Hamiltonian for $d^1$ ion

Let us consider the case of vanadyl ion with a single 3d electron. The ground state of such an ion is a D state. By spin – orbit coupling this splits into $^2D_{3/2}$ and $^2D_{5/2}$, the former being lower in energy. Such a classification is, however, not quite valid for a crystalline complex of $V^{4+}$, where $H_2$ (crystal field interaction) is stronger than $H_3$ (spin – orbit interaction) resulting in complete breakdown of spin – orbit coupling.

For a $d^1$ system, the shell is less than half filled and therefore the spin orbit coupling parameter is positive. In the absence of
applied magnetic field, the lower level of a d\textsuperscript{1} system is split into three Kramer’s levels, because of either crystalline field or spin – orbit coupling or both. The application of d.c. magnetic field at this stage amounts to introducing a perturbation $H_4$ equivalent to

$$H_4 = \beta_0 H. (L+2S)$$

This interaction which is linear in $H$, lifts the Kramer’s degeneracy completely. In a paramagnetic resonance experiment with normal d.c. magnetic field, only the lowest doublet is thus effective and only one absorption peak results. Such a situation is shown in Fig. 4.1 for a crystalline field of rhombic symmetry. However, due to hyperfine interaction with the nucleus, each of the two levels in further split into $(2I+1)$ levels, where $I$ is the spin of the metal ion nucleus. In the case of V\textsuperscript{4+} with $I = 7/2$, this results in an eight line hyperfine spectrum.

4.4.1 Hyperfine Structure

Hyperfine interactions are mainly the magnetic dipole interactions between the electronic magnetic moment and nuclear magnetic moment of the paramagnetic ion. In the case of s – electrons or in systems with effective spin zero, the Fermi contact term, is however, also significant. The octets in the EPR of vanadyl ion and
sextets in the EPR of divalent manganese are the result of hyperfine interaction involving energy $W_{hf}$.

The classical expression for the potential energy $V_{ij}$ of interaction between the magnetic dipoles of moments $\mu_i$ and $\mu_j$ separated by $r_{ij}$ is

$$V_{ij} = \frac{i \cdot \mu_j}{r_{ij}^3} - \frac{3(i \cdot r_{ij}) \cdot (\mu_j \cdot r_{ij})}{r_{ij}^5}$$

The above expression for $V_{ij}$ is treated as an operator and summed up for all neighbours $j$ for any spin $i$, yields the dipole – dipole interaction term in the Hamiltonian.

In the spin – Hamiltonian approach, one attempts to relate the magnetic moment to the spin operator $S$ and as per terminology of Abragam and Pryce [16], the overall electron-nuclear interaction energy is described as –

$$W_{hf} = 2\gamma \beta_0 \beta_n \left\{ \frac{3(S.r)(I.r)}{r^5} - \frac{(S.I)}{r^3} + \frac{L.I}{r^3} + \frac{4\pi}{3} \delta(r)(S.I) \right\}$$

where $\gamma$ is nuclear gyro-magnetic ratio, $\beta_0$ is the Bohr magneton and $\beta_n$ the nuclear magneton.
The first two terms in the above expression correspond to the dipole-dipole interaction between the electronic and nuclear magnetic moments. The third term is the contribution from orbital motion of electron & the last term is the Fermi contact interaction.

Now considering the expectation value of $W_{hf}$ for all space ($r$), we have:

$$H_{hf} = A_z I_z S_z + A_x I_x S_x + A_y I_y S_y$$

where $A_x$, $A_y$ and $A_z$ are the principal values of hyperfine tensor $A$. If $A$ is axial, one has-

$$H_{hf} = A_\parallel I_z S_z + A_\perp (I_x S_x + I_y S_y)$$

To complete the list of interactions as per Table 4.3 it must be emphasized that the spin interaction term $W_{ss}$ is significant when we have a system with a large number of interacting spins and the term $\gamma$ describes the direct interaction of nuclear spin with the external d.c. magnetic field.

4.5 **EPR parameters in general**

A vanadyl ion usually occurs as an octahedral complex with the surrounding ligands. The formation of molecular orbitals leading to a unpaired electron in $b_2$ – state is already explained in Chapter 3 and the arrangement is equivalent to a $d^1$ system.
A general spin–Hamiltonian [17] is however described as:

\[ \mathbf{H} = \mathbf{H}_o g_z S_z \mathbf{H}_z + \frac{1}{2} (g_x S_x + g_y S_y) + D \left[ S_z^2 - S (S+1)/3 \right] + E \left( S_x^2 - S_y^2 \right) + A_z I_z S_z + A_x I_x S_x + A_y I_y S_y \]

As described earlier, the d^1 electron system of VO^{2+} has an effective spin \( \frac{1}{2} \). Thus, fine structure involving D and E vanishes. If VO^{2+} has near tetragonal surroundings, then tensors \( g \) and \( A \) are axial and we have

\[ \mathbf{H} = \mathbf{H}_o g || S_z \mathbf{H}_z + \frac{1}{2} (g_x S_x + g_y S_y) + A || I_z S_z + A || (I_x S_x + I_y S_y) \]

### 4.5.1 EPR of VO^{2+} ion

The Hamiltonian leads to the following magnetic field resonance values for the hyperfine structure components in the EPR spectrum of VO^{2+}:

\[ \mathbf{H} = \mathbf{H}_o - \frac{K m_I}{g \beta} - \frac{A^2 (A^2 + K^2)}{4H_o g^2 \beta^2 K^2} [I(I+1) - m_I^2] \]

\[ - \frac{(A^2 - A^2) g^2 g_{\parallel}^2}{2H_o g^2 \beta^2 K^2} \sin^2 \theta \cos^2 \theta m_I^2 \]

where \( \mathbf{H}_o = \frac{\hbar}{g \beta} \),

\[ g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \]

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\[ K^2 g^2 = A_{\parallel}^2 g_{\parallel}^2 \cos^2 \theta + A_{\perp}^2 g_{\perp}^2 \sin^2 \theta, \]

\( \theta \) being the angle between the crystalline or molecular field z-axis and the direction of magnetic field H.

When the system under consideration has all possible orientations of VO molecule, as in a glassy sample, the resonance lines are, in general, distributed for each \( m_I \) value between two extreme positions, which are characteristic of parallel and perpendicular configurations. By the analysis of lineshapes of such a spectrum, it is however possible to evaluate the components of \( g (g_{\parallel} & g_{\perp}) \) and \( A (A_{\parallel} & A_{\perp}) \).

### 4.6 Paramagnetic centres in liquid-like samples

The paramagnetic complexes in liquid solutions can be considered as microcrystals jumbling in a random way, as they are jostled by the molecular motions of the solvent liquid. The immediate environment of the paramagnetic ion in these microcrystals can be as high as cubic with strong possibility of an axial component. In a coordinate system \((p, q, r)\) fixed in molecule the spin–Hamiltonian can now be written as \([17, 18]\)

\[
H = \beta_o \left\{ g_{\parallel} H_r S_r + g_{\perp} (H_p S_p + H_q S_q) \right\} \\
+ A_{\parallel} I_r S_r + A_{\perp} (I_p S_p + I_q S_q)
\]
This can be transformed to the laboratory coordinate system by using the transformation equations as:

\[ H_r = H \cos \theta \]
\[ S_r = S_z \cos \theta - S_x \sin \theta \cos \Phi + S_y \sin \theta \sin \Phi \]
\[ = S_z \cos \theta + \frac{1}{2} [S_+ e^{-i\Phi} + S_- e^{+i\Phi}] \sin \theta \]

and similarly for other components of \( \mathbf{H} \) and \( \mathbf{S} \) when we obtain [17, 18].

\[ \mathbf{H} = g_0 \beta \mathbf{S}_z + a \mathbf{I} \mathbf{S} + \left( \frac{1}{3} \right) (\Delta g_0 \beta_0 H + b I_z) (3\cos^2 \theta - 1)S_z \]
\[ + \frac{b}{2} \sin \theta \cos \theta \left( I_+ e^{-i\Phi} + I_- e^{+i\Phi} \right)S_z \]
\[ + \frac{1}{2} (\Delta g \beta_0 H + b I_z) \sin \theta \cos \theta \left( S_+ e^{-i\Phi} + S_- e^{+i\Phi} \right) \]
\[ + \frac{b}{4} \sin^2 \theta \left( I_+ S_+ e^{-2i\Phi} + I_- S_- e^{+2i\Phi} \right) \]
\[ - \frac{b}{12} (3\cos^2 \theta - 1)(I_+ S_+ + I_- S_-) \]

where \( g = 1/3 (g_\| + 2g_\perp) \), \( \Delta g = g_\| - g_\perp \)
\( a = 1/3 (A_\| + 2A_\perp) \), \( b = A_\| - A_\perp \)

While \( I_\pm \) and \( S_\pm \) are the usual raising and lowering operators, operating on nuclear and electronic spin states respectively.

As the molecule trembles, \( \theta \) and \( \Phi \) are time dependant and the above Hamiltonian can be written as

\[ \mathbf{H} = \mathbf{H}_0 + \mathbf{H}(t) \]
where $H_0$ is time independent and isotropic, given by first two terms in the general expression for $H$ above and $H(t)$ contains rest of the terms and is time dependent due to random time dependence of $\theta$ and $\Phi$. If the random motion is extremely rapid which means that $\hbar$ times the motional frequency exceeds the interaction energy in question, the time dependent terms average out and have little effect. This is the limiting case of situation. In general, however, the time dependent terms lead to important effects. Mc Connell [18] has shown that the anisotropies in $g$ and $A$ terms, which are averaged out to zero due to rapid tumbling motion of the molecule, $\langle H(t) \rangle = 0$, do contribute to the line widths of the isotropic spectrum, given by the Hamiltonian $H_0$. These linewidths are predicted to follow a formula

$$\Delta \nu \approx \frac{\zeta_c}{\Delta \nu_{\beta} H + b \hbar}{H^2}/h$$

where $\zeta_c$ is the correlation time, describing the random motion of the molecule.

The linewidths $\Delta \beta$ of different $m_I$ hyperfine lines can thus be found to obey the relation [19].

$$\Delta \beta = a_1 + a_2 m_I + a_3 m_I^2$$

Rogers and Pake [20] first observed such linewidth variations in their study of EPR of VO$^{2+}$ complexes in solutions. Such effects
have further been seen by different workers [21-23] in glassy samples.

4.7 Results and Discussion

The room temperature EPR spectra for RbCl : VO$^{2+}$ furnish an isotropic angular independent octet. The corresponding spectrum termed as I, is shown in Fig. 4.2. As the temperature is lowered, the linewidths of hyperfine lines are found to increase leading to overall broadening of the spectrum I and its complete disappearance around –150°C. A new spectrum II, however, appears at the liquid nitrogen temperature. This new spectrum contains both parallel and perpendicular components. Fig.4.3 shows such a spectrum II for RbCl : VO$^{2+}$ with H perpendicular to a cubic face of the crystal. In this spectrum, the parallel component with greater spread is labeled as “a” while the perpendicular component as “b”.

At the liquid nitrogen temperature of measurement, it was not practicable to study the angular variation of EPR spectrum precisely. The LNT spectrum nevertheless appeared to exhibit a general identical appearance for different orientations of H. Finally, the change of EPR spectrum on cooling from type I to type II is found to be reversible; the type II spectrum changing to type I on heating.
The nature of isotropic spectrum I is similar to that reported by Rao et al [5] in the case of KNO$_3$ : VO$^{2+}$ and CsNO$_3$ : VO$^{2+}$ at room temperature and that reported by O’ Reilly [24] for vanadyl entioporphyrin I (VEPI) in benzene solution. This is also similar to eight line EPR spectrum reported for VO$^{2+}$ in Mg(ClO$_4$)$_2$. 6H$_2$O[21] and in calcium oxalate monohydrate [25].

On the other hand, the spectrum II is similar to that obtained for VO$^{2+}$ in KNO$_3$, CsNO$_3$ and NH$_4$Cl hosts [4,5] at LNT. Further, this spectrum resembles to that obtained by Hochstrasser [25] at room temperature itself for VO$^{2+}$ in amorphous glass and that obtained by O’ Reilly [24] for VEPI dissolved in highly viscous petroleum oil.

4.7.1 Spectrum I

The present spectrum I for VO$^{2+}$ in RbCl is isotropic and independent of crystal orientation with respect to the applied d.c. magnetic field. This indicates that vanadyl molecules have no preferred orientation at room temperature in RbCl host.

The origin of spectrum I is most likely due to fastly tumbling V-O bonds and RbCl appears to behave like a liquid for vanadyl ion. This results in averaging out of anisotropies of g and A tensors. The expression for the resonance magnetic field H for a hyperfine
transition ($m_I$<-->$m_I$) corresponding to a component of nuclear spin can be obtained from Eq. 4.1, by putting $A_{||} = A_{\perp} = A_0$ and $g_{||} = g_{\perp} = g_o$ as

$$H (m_I) = H_o - (A_0 m_I / g_0 \beta) - \left( \frac{1}{2H_o} \right) (A_0 / g_0 \beta_o)^2 [I(I+1) - m_I^2] \quad (4.2)$$

The calculation using the field expressions for eight hyperfine ($m_I$) lines as per above Eq.(4.2), yields the values of $g_o$ and $A_0$ for the spectrum I, as –

$$g_o = 1.967 \pm 0.001$$

$$A_0 = (107.2 \pm 1.0) \times 10^{-4} \text{ cm}^{-1}$$

To facilitate the calculations, the expression involving $A_0^2$ in Eq.(4.2) was first evaluated using the approximate values of $g_o$ and $A_0$, the second iteration then gave the better results as obtained.

Table 4.4 gives the relative values of $g_o$ and $A_0$ for VO$^{2+}$ in NaCl, KCl and RbCl hosts. The g-shifts are also indicated alongwith. Both the parameters $g_o$ and $A_0$ have been found to vary in a regular fashion as the host is varied in the series NaCl, KCl and RbCl. The variation in $g_o$ indeed seems to follow the variation in the crystalline field at the alkali cation site, as explained forthwith.
The g-value for a non-interacting orbital singlet is expected to be 2.0023. However, when the ion, in question, is acted upon by a crystalline field, its g-value reflects contributions from non L=0 states through spin-orbit coupling and the effective g is given as [17]

\[ g_i = 2.0023 - C_i \frac{\lambda}{4} \]  

Here C_i are appropriate constants for different components g_x, g_y and g_z of g and \( \Delta E \) is the separation of upper non L=0 excited state of the ion under consideration.

For Mn^{2+}, \( \Delta E \) corresponds to the energy separation of \(^4\text{P}\) from the ground state \(^6\text{S}\) and for VO^{2+} it is obviously the separation of excited \( e_{\pi^*} \) state from the non-bonding state \( b_2 \).

The g-shift \( (g - 2.0023) \) is negative for a paramagnetic ion with less than half filled shell, wherein \( \lambda \) is positive. The shift is however, positive for more than half filled shell with \( \lambda \) being negative.

The \( \Delta E \) would obviously depend upon the strength of the crystalline field, acting on the ion. Now, the cubic lattice parameter ‘d’ increases in the series NaCl, KCl and RbCl (Table 4.5). The \( \Delta E \) value would therefore be largest for NaCl and the least for RbCl. The
variation observed in $g_o$ for VO$^{2+}$ in different alkali chloride hosts is thus qualitatively explained as per Eq. (4.3).

### 4.7.2 Spectrum II

With the lowering of temperature, the line widths of the hyperfine lines of spectrum I increased, resulting in total broadening of the spectrum at about $-100^\circ C$. However, on further cooling the sample to LNT, a two octet spectrum II had appeared. This spectrum consisted of eight hyperfine lines, marked “a”, of parallel configuration with H parallel to V=O molecular axis and another eight hyperfine lines, marked “b”, of perpendicular configuration with H perpendicular to molecular axis.

The group “a” of hyperfine lines of Spectrum II (Fig.4.3) does not possess the usual first derivative appearance of an absorption peak, to show up both positive and negative portions. In such hyperfine lines only positive contours are seen. This shows that the absorption in the group “a” of lines is not due only to single peaks, but represents continuous absorption build up, probably due to various angular parts alongwith different hyperfine lines. Such line shapes are representative of powder spectra and were extensively investigated by Poole, Jr. and Farach [26] and also by
Taylor et al [27] through computer simulation. These workers have shown that the computer simulated spectra of powder samples show peak positions corresponding to the so called turning points in the angular dependence of the single crystal resonance fields.

Thus, the spectrum “a” of VO$^{2+}$ in RbCl at LNT corresponds to the Z-axis ($\theta=0$) spectrum, also called the $\parallel$ spectrum and the spectrum “b” corresponds to the $X/Y-\text{axis}$ ($\theta=90^\circ$) spectrum, also called the $\perp$ spectrum.

Both the sets of eight hyperfine lines “a” and “b” were suitably fitted to Eq.(4.1) and $A_\parallel$, $A_\perp$, $g_\parallel$ and $g_\perp$ were found. There values are given in Table 4.6 alongwith $A_o$ and $g_o$ calculated earlier for spectrum I.

Mc Connell [18] and O’ Reilly [24] had obtained relations which relate $g_o$ and $A_o$ for a fastly reorienting vanadyl ion with its $g_\parallel$, $g_\perp$ and $A_\parallel$, $A_\perp$. These are given as –

$$g_o = \frac{g_\parallel + 2g_\perp}{3}$$

$$A_o = \frac{A_\parallel + 2A_\perp}{3} \quad ---- \quad (4.4)$$
It is seen that the values of different parameters obtained presently obey Eq. (4.4) reasonably well.

4.7.3 Origin of Spectrum II

The disappearance of spectrum I, on cooling and appearance of different spectrum II at LNT is seen for VO\(^{2+}\) in a number of hosts viz. NH\(_4\)Cl [4], KNO\(_3\) & CsNO\(_3\) [5] and potassium thio urea bromide crystals [12]. In all these cases, the disappearance of spectrum I on cooling has been attributed to increased line widths. The reappearance of spectrum like II has further been attributed to some sort of structural phase transition in corresponding hosts. But, so far present host RbCl is concerned, no phase transitions are attributable in it near LNT. Accordingly, a new model has been proposed to understand increased clamping of V=O molecules at LNT in RbCl host, to lead to the origin of spectrum II.

4.7.3.1 New Model for Spectrum II

A VO\(^{2+}\) ion would substitute the Rb\(^+\) sites in RbCl lattice. This would lead to creation of a cation vacancy which could be at any of the twelve nn (101) type or at six nnn (001) type positions, leading to many (eighteen) different possible positions of vacancy with respect
to VO$^{2+}$ ion. Accordingly, a V-O bond is likely to have minimum energy position with its alignment along any of possible orientations.

It may be repeated that at room temperature we have all possible tumbling orientation of V=O, initiated due to quick jumps among many different equivalent locations and thus eight line isotropic spectrum I is observed. However, some broadening of lines in this spectrum is due to incomplete averaging of g and A anisotropies.

A V=O bond thus appears to make movements, while trapped along different 3-dimensional potential wells, as above. At room temperature, the V=O bonds probably possess sufficiently large energy to overcome such potential wells, quite easily to execute very fast tumbling motion. Therefore, anisotropic effects are averaged out effectively and only the isotropic spectrum I is observed.

On lowering the temperature, the effects of potential wells starts becoming decisive, widths of the individual lines in spectrum I increase sharply, resulting in their apparent disappearance. As the temperature of the sample is reduced from RT downwards, the role of potential wells on V=O alignments becomes assertive; the V=O
bonds instead of revolving freely in space, are restricted to execute angular oscillations about minimum energy orientations as above.

At LNT, the V=O molecules with much reduced energy would occupy positions close to above eighteen orientations in the 3-d space and these positions would not be interchangeable. Thus, so far V=O bonds are concerned, the RbCl : VO$^{2+}$ system now behaves roughly as a powdered sample with varied rigid orientations of V=O bond. Accordingly one observes in it both “a” type (parallel) and “b” type (perpendicular) EPR spectra.

4.7.4 Line width studies

The nature of various hyperfine lines with regard to line-width variation is similar to what has been reported earlier in the case of NH$_4$Cl [4], KNO$_3$ and CsNO$_3$ hosts [5]. Thus, it was interesting to see the applicability of Kivelson’s theory [14] of paramagnetic relaxation in liquids to the present RbCl crystal system. According to this theory the line-width of a hyperfine component [19] is given by –

$$\Delta B = \pi \sqrt{3} \left( a_1 + a_2 m_1 + a_3 m_1^2 \right)$$

where the factors $a_1$, $a_2$ and $a_3$ depend on the anisotropic $g$ factor, anisotropic hyperfine interaction, the correlation time $\zeta_c$ (describing
the rapid motion of the paramagnetic complex) and the resonance frequency.

The experimental line widths of different hyperfine components at room temperature in the present spectrum I, were obtained by using the relation

\[
\text{derivative height} \times (\text{line-width})^2 = \text{constant} \quad \text{---- (4.6)}
\]
given by Rogers and Pake [20]. Here, it is assumed that the population difference between different \( m_I \) levels of the system is negligible.

The line-width and derivative height of one hyperfine component \( +\frac{1}{2} \rightarrow -\frac{1}{2} \) in the observed spectrum I (Fig. 4.2) was measured directly. Then, using the observed derivative heights, the line-widths of the other hyperfine transitions were calculated through the relation of Eq. (4.6) above. Thus obtained values of \( \Delta B \) for the line-widths of the various hyperfine components are given in Table 4.7. The constants \( a_1, a_2 \) and \( a_3 \) were then calculated by fitting the experimental data to the required equation (4.5) and the values obtained are given in Table 4.8. Fig. 4.4 shows the parabolic plot for variation of \( \Delta B \) with \( m_I \) values and this lies close to the experimental data.
The $a_1$, $a_2$ and $a_3$ values available for vanadyl ion in RbBr and RbI hosts [28] are also given in Table 4.8. It may be mentioned that no proper data for $a_1$, $a_2$ and $a_3$ constants are available for VO$^{2+}$ doped NaCl and KCl systems.

It is seen that $a_1$ parameter is positive and increases monotonously in the series of hosts RbCl, RbBr and RbI. The $a_2$ parameter is however negative for all the hosts. It varies very slightly form RbCl to RbBr, but changes abruptly form RbBr to RbI. The parameter $a_3$ is positive for all the hosts and decreases in the series of hosts RbCl, RbBr and RbI.

Using the expression of Rogers and Pake [20], the correlation time $\tau_c$ has been calculated and is found to be $0.70 \times 10^{-11}$ sec. This value is close to the value of $\tau_c$ estimated by Kivelson [14] for a vanadyl complex in benzene solution to be $6 \times 10^{-11}$ sec. The same order of $\tau_c$ in both RbCl and benzene hosts, supports the assumption that vanadyl ion exhibits liquid-like behavior in RbCl lattice at room temperature.
4.8 References


13. Pawan Kumar, Private Communication.


Table 4.1

Characteristics of some free ions of ion – group transition metals

<table>
<thead>
<tr>
<th>Ion</th>
<th>Configuration</th>
<th>Spin-orbit constant $\lambda$ (cm$^{-1}$)</th>
<th>Spin – arrangement of free ion</th>
<th>Total spin $S$</th>
<th>Ground state</th>
<th>Nuclear Spin I and abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{4+}$</td>
<td>3d$^1$</td>
<td>154</td>
<td></td>
<td>1/2</td>
<td>$^2D_{3/2}$</td>
<td>7/2($V^{5+}$) 99.8%</td>
</tr>
<tr>
<td>$Mn^{2+}$</td>
<td>3d$^5$</td>
<td>347</td>
<td></td>
<td>5/2</td>
<td>$^6S_{5/2}$</td>
<td>5/2 ($Mn^{2+}$) 100%</td>
</tr>
</tbody>
</table>
Table 4.2

Transformation properties of atomic orbitals under crystalline fields of different symmetries.

<table>
<thead>
<tr>
<th>Atomic Orbitals</th>
<th>Octahedral $O_h$</th>
<th>Tetrahedral $T_d$</th>
<th>Square planar $D_{4h}$</th>
<th>Square pyramidal $C_{4v}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S$</td>
<td>$a_{1g}$</td>
<td>$a_1$</td>
<td>$a_{1g}$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>$p_x$</td>
<td></td>
<td></td>
<td>$e_u$</td>
<td>$e$</td>
</tr>
<tr>
<td>$p_y$</td>
<td>$t_{1u}$</td>
<td></td>
<td>$t_2$</td>
<td></td>
</tr>
<tr>
<td>$p_z$</td>
<td></td>
<td></td>
<td>$a_{2u}$</td>
<td>$a_2$</td>
</tr>
<tr>
<td>$d_{xy}$</td>
<td></td>
<td></td>
<td>$b_{2g}$</td>
<td>$b_2$</td>
</tr>
<tr>
<td>$d_{xz}$</td>
<td>$t_{2g}$</td>
<td>$t_2$</td>
<td>$e_g$</td>
<td>$e$</td>
</tr>
<tr>
<td>$d_{yz}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$d_z^2$</td>
<td>$e_g$</td>
<td>$E$</td>
<td>$a_{1g}$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>$d_x^2 - y^2$</td>
<td></td>
<td></td>
<td>$b_{1g}$</td>
<td>$b_1$</td>
</tr>
</tbody>
</table>
Table 4.3

Different terms in the Hamiltonian for iron – group transition metal ions

<table>
<thead>
<tr>
<th>Sub-Hamiltonian</th>
<th>Symbol</th>
<th>Magnitude of Energy (cm(^{-1}))</th>
<th>Energy Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free ion energy</td>
<td>(H_1)</td>
<td>(10^5)</td>
<td>(\sum_k \left( \frac{p_k^2}{2m} - \frac{Ze^2}{r_k} \right) + \sum_{j&lt;k} \frac{e^2}{r_{jk}})</td>
</tr>
<tr>
<td>Crystal field</td>
<td>(H_2)</td>
<td>(10^4)</td>
<td>(V(r))</td>
</tr>
<tr>
<td>Spin-orbit interaction</td>
<td>(H_3)</td>
<td>(10^2)</td>
<td>(\lambda L.S)</td>
</tr>
<tr>
<td>Zeeman Term</td>
<td>(H_4)</td>
<td>1</td>
<td>(\beta_n H. (L + 2S))</td>
</tr>
<tr>
<td>Spin – spin interaction</td>
<td>(H_5)</td>
<td>1</td>
<td>(W_{ss})</td>
</tr>
<tr>
<td>Interaction with nuclear field</td>
<td>(H_6)</td>
<td>(10^{-2})</td>
<td>(W_{hf})</td>
</tr>
<tr>
<td>Interaction with external magnetic field</td>
<td>(H_7)</td>
<td>(10^{-3})</td>
<td>(r\beta_N H.I.)</td>
</tr>
</tbody>
</table>
Table 4.4

$g$ – and $A$ – parameters for spectrum I of VO$^{2+}$ in alkali chloride hosts.

<table>
<thead>
<tr>
<th>Host</th>
<th>$g_o$ – parameter</th>
<th>$A_o$ – parameter ($\times 10^{-4}$ cm$^{-1}$)</th>
<th>g-shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl [13]</td>
<td>1.971±0.001</td>
<td>104.0±1.0</td>
<td>- 0.031</td>
</tr>
<tr>
<td>KCl [13]</td>
<td>1.969±0.002</td>
<td>106.8±1.5</td>
<td>- 0.033</td>
</tr>
<tr>
<td>RbCl (This work)</td>
<td>1.967±0.001</td>
<td>107.2±1.0</td>
<td>- 0.035</td>
</tr>
</tbody>
</table>
Table 4.5

Lattice parameter $d'$ for alkali chloride crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Lattice parameter $d'$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>5.62</td>
</tr>
<tr>
<td>KCl</td>
<td>6.28</td>
</tr>
<tr>
<td>RbCl</td>
<td>6.49</td>
</tr>
</tbody>
</table>
Table 4.6

g – and A – parameters of VO$^{2+}$ in RbCl single crystal

<table>
<thead>
<tr>
<th>Spectrum Type</th>
<th>g – parameters</th>
<th>A – parameter (x10$^{-4}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$g_o = 1.967 \pm 0.001$</td>
<td>$A_o = 107.2 \pm 1.0$</td>
</tr>
<tr>
<td>I</td>
<td>$g_\parallel = 1.938 \pm 0.002$</td>
<td>$A_\parallel = 189.2 \pm 2.0$</td>
</tr>
<tr>
<td></td>
<td>$g_\perp = 1.969 \pm 0.002$</td>
<td>$A_\perp = 64.2 \pm 2.0$</td>
</tr>
</tbody>
</table>
Table 4.7

Experimental $\Delta B$ values for different hyperfine transitions in spectrum I of VO$^{2+}$ : RbCl system.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>$m_f$ for transition</th>
<th>$\Delta B$ (Gauss)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>+7/2</td>
<td>24.8</td>
</tr>
<tr>
<td>2</td>
<td>+5/2</td>
<td>20.8</td>
</tr>
<tr>
<td>3</td>
<td>+3/2</td>
<td>18.5</td>
</tr>
<tr>
<td>4</td>
<td>+1/2</td>
<td>18.3</td>
</tr>
<tr>
<td>5</td>
<td>-1/2</td>
<td>21.1</td>
</tr>
<tr>
<td>6</td>
<td>-3/2</td>
<td>24.6</td>
</tr>
<tr>
<td>7</td>
<td>-5/2</td>
<td>29.6</td>
</tr>
<tr>
<td>8</td>
<td>-7/2</td>
<td>35.7</td>
</tr>
</tbody>
</table>
Table 4.8

Values of the coefficients $a_1$, $a_2$ and $a_3$

<table>
<thead>
<tr>
<th>Host</th>
<th>$a_1$(mT)</th>
<th>$a_2$(mT)</th>
<th>$a_3$(mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RbCl</td>
<td>0.363</td>
<td>-0.033</td>
<td>+0.0163</td>
</tr>
<tr>
<td>RbBr</td>
<td>0.286</td>
<td>-0.035</td>
<td>+0.0139</td>
</tr>
<tr>
<td>RbI</td>
<td>0.217</td>
<td>-0.018</td>
<td>+0.0088</td>
</tr>
</tbody>
</table>