

## Study of Electron Paramagnetic Resonance and Optical Absorption of Vanadyl Doped Systems

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### ABSTRACT

The general theory of EPR of transition metal ions and complexes is outlined with a special reference to  $V^{4+}$  and  $Mn^{2+}$  ions. The energy of d-electrons in crystalline fields of various symmetries are briefly described. Basic features of spin-Hamiltonian formalism as a guide to interpreting EPR spectra are mentioned. The g-tensor in ions with  $S= 1/2$  has been described. The general feature, concerning hyperfine splitting from the metal nucleus are discussed. The theory of EPR spectra in liquids with a special reference to vanadyl molecular ion is also given. The original of optical absorption in vanadyl ion doped systems is also explained.

### INTRODUCTION

The unpaired d-electrons in iron group transition metal ions render them paramagnetic. The table-1 gives the number of electrons, spin-orbit constant, spin arrangement of free ion and the total spin in the case of tetravalent vanadium and divalent manganese (for comparison).

**Table-1**  
**Characteristics of some free ions of iron-group transition metals**

Ion	Configuration	Spin-orbit constant ( $cm^{-1}$ )	Spin-arrangement of free ion	Total spin S	Ground state	Nuclear spin I and abundance
$V^{4+}$	$3d^1$	154		$1/2$	${}^2D_{3/2}$	$\frac{7}{2}(v^{5'})99.3\%$
$Mn^{2+}$	$3d^5$	347		$5/2$	${}^5S_{5/2}$	$\frac{5}{2}(M_n^{2+})100\%$

### d-orbitals of a free ion

The degeneracy is partly lifted, when the d-electron is placed in a crystalline field. The three-fold degenerate orbitals are assigned as  $t_2$  and the two-fold degenerate ones as  $e_g$ .

### Effect of ligand field on energy levels

If a paramagnetic ion is placed substitutionally at a action site in a crystal, it is surrounded by axioms. These axioms are called ligands. The number of ligands surrounding the central ion is called the coordination number. These ligands which may be negative ions or at times neutral molecules with a permanent lone pair of electrons, change the energy level scheme resulting in ligand - field splitting of the d-orbital of the embedded paramagnetic ion.

Usually, the orbital degeneracy of the d-orbitals is partly or fully removed by the crystal field. In NaCl crystal doped with divalent manganese, the  $Cl^-$  ligands form nearly octahedral coordination about the

divalent ion. The electrostatic field of the negative charges and the covalent bonding with the ligand orbitals affect the d-electrons of the metal ion. This causes the energy levels corresponding to  $d_{z^2}$  and  $d_{x^2-y^2}$  to be raised and those corresponding to  $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$  to be lowered. The energy gap between these two types of orbitals is the ligand field splitting and is called  $\Delta$  or  $10 Dq$  by convention<sup>1</sup>.

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-2 gives the notations and transformation properties of atomic orbitals under crystalline fields of different symmetries. The onset of lower symmetry causes splitting of energy levels and even the ground state configuration gets modified. The EPR experiments thus easily reveal tetragonal or trigonal distortions in cubic systems.

**Table-2**  
**Transformation properties of atomic orbitals under crystalline fields of different symmetries**

Atomic orbitals	Octahedral $O_h$	Tetrahedral $T_d$	Square planar $D_{4h}$
S	$a_{1g}$	$a_1$	$a_{1g}$
px py pz	$t_{1u}$	$t_2$	$e_u$ $a_{2u}$ $b_{2g}$
dxy dxz dyz	$t_{2g}$	$t_2$	$e_g$
$dz^2$	$e_g$	$e$	$a_{1g}$
$d_{x^2-y^2}$			$b_{1g}$

The splitting of energy levels in the absence of magnetic field is governed by Kramer's theorem, 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 Kramers 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.

### Spin-orbit 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 from the surroundings by  $5s^25p^6$  electrons and are therefore less affected by the crystal field. Accordingly, in such cases, spin-orbit interaction is stronger than crystalline field interaction.

In general, there are therefore 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 latter interaction is stronger than the former. In the iron group (3d) transition elements the splitting of the order of  $20,000 \text{ cm}^{-1}$  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 behaviour of the ion in a magnetic field is modified.

### 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<sup>2</sup> is such as to make

$$\lambda(r) \frac{\ell \cdot \underline{s}}{r_{ij}} < v < \frac{e^2}{r_{ij}}$$

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

$$V = V(R) + V_0$$

where V(R) spans the totally symmetric a<sub>1g</sub> representation in the group. C<sub>h</sub> and V<sub>0</sub> represents the cubic symmetry as

$$V_0 = x^4 + y^4 + z^4 - \frac{3}{5}r^4$$

If, however, the symmetry is lower, low symmetry terms are also seen in V<sub>0</sub>.

Apart from three competitive terms mentioned, there are other terms too in the Hamiltonian of a transition metal ion. These are mentioned in Table-3 in near decreasing order of energy.<sup>15</sup> To interpret the results of EPR one has to consider the various significant terms of this table.

This levels more than 10<sup>3</sup> cm<sup>-1</sup> above the ground level, may be ignored at room temperature, as they 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-Saunders coupling.

For a general 3d-ion configuration, 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> 3d<sup>n</sup>, the first five sub-level with the configuration 1s<sup>2</sup> 2s<sup>2</sup> 2p<sup>6</sup> 3s<sup>2</sup> 3p<sup>6</sup> provide a diamagnetic closed shell with L = S = 0. Thus for Mn<sup>2+</sup> with n = 5, the ground state has L = 0 and S = S/2 and for V<sup>4+</sup> with n = 1. The ground state corresponds to L = 2 and S = 1/2.

**Table-3**  
**Different terms in the Hamiltonian for iron group transition metals**

Sub-Hamiltonian	Symbol	Magnitude of Energy (cm <sup>-1</sup> )	Energy Expression
Free ion energy	fd <sub>1</sub>	10 <sup>5</sup>	$\sum_k \left( \frac{pk^2}{2m} - \frac{Ze^2}{r_k} \right) + \frac{S}{j < k} \frac{e^2}{r_{jk}}$
Crystal field	fd <sub>2</sub>	10 <sup>4</sup>	V(r)
Spin-orbit interaction	fd <sub>3</sub>	10 <sup>2</sup>	λ <u>L.S</u>
Zeeman term	fd <sub>4</sub>	1	β1±( <u>L</u> + 2 <u>S</u> )
Spin-spin interaction	fd <sub>5</sub>	1	W <sub>ss</sub>
Interaction with nuclear field	fd <sub>6</sub>	10 <sup>-2</sup>	W <sub>hf</sub>
Interaction with external magnetic field	fd <sub>7</sub>	10 <sup>-3</sup>	r β <sub>N</sub> <u>H.I</u>

A general ground state for a transition metal ion is (2L+1) (2S+1) 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

$$fd = g \beta \underline{H} \cdot \underline{S}'$$

is used to determine the energy perturbation in an applied d.c. magnetic field H of an EPR experiment.

This concept of spin-Hamiltonian is due to Abragam and Pryce<sup>2</sup>. The  $10 >$  with  $l = 0$  or bital contains a single electron in the ground state of the paramagnetic complex. Neglecting the spin-orbit coupling, this may be represented by  $10, \frac{1}{2} >$ ,  $10, -\frac{1}{2} >$ . The perturbation due to spin orbit coupling changes these states and the perturbed forms are :-

$$10, \frac{1}{2} > + c |1, -\frac{1}{2} > \equiv | \frac{1}{2} >$$

$$10, -\frac{1}{2} > + d | -1, \frac{1}{2} > \equiv | -\frac{1}{2} >$$

In the absence of a magnetic field, the states  $1\frac{1}{2} >$  and  $1-\frac{1}{2} >$  are degenerate and form a Kramers' doublet. The application of magnetic field  $H_z$  in the direction of  $z$  - axis causes a perturbation  $\beta H_z(L_z + 2S_z)$ . The matrix elements of this perturbation and the state  $1\pm \frac{1}{2} >$  determine the energy separation between the resulting pair of levels. Consequently, the observed splitting is just what one expects on completely ignoring the orbital angular momentum, but on replacing its effect by an anisotropic coupling between the electron spin and the static magnetic field.

If  $S_x$ ,  $S_y$  and  $S_z$  are the components of fictitious spin  $S'$  and  $1+ >$  and  $1- >$  are the eigenfunction of  $S_z$  with eigenvalues  $+\frac{1}{2}$  and  $-\frac{1}{2}$ , given as

$$S_z 1+ > = \frac{1}{2} 1+ >$$

$$S_z 1- > = -\frac{1}{2} 1- >$$

The g-tensor may be derived by constructing the matrix of  $\underline{L} + g\underline{S}$  for the states  $1+ >$  &  $1- >$ .

The spin-Hamiltonian is accordingly written as

$$\begin{aligned} \text{fd} &= \beta \underline{H}, g, \underline{S} \\ &= \beta \{g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)\} \end{aligned}$$

It is 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.

### Applications of spin-Hamiltonian

Let us consider the case of  $V^{4+}$  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 quite valid for a crystalline complex of  $V^{4+}$ , as  $fd_2$  (crystal field) is stronger than  $fd_3$  (spin-orbit interaction) and the free ion spin-orbit coupling is completely broken.

For a  $d^1$  system, the shell is less than half filled and therefore  $g$  is positive. In the absence of applied magnetic field, the lower t level of a  $d^1$  system is split into three Kramers' doublets, because of either crystalline field or spin-orbit coupling or both. This application of d.c. magnetic field at this stage amounts to introducing a perturbation  $fd_4$  equivalent to

$$fd_4 = \underline{H}, (\underline{L} + 2\underline{S})$$

This interaction which is linear in  $\underline{H}$  lifts the Kramers' degeneracy completely. In a paramagnetic resonance experiment with normal d.c. magnetic fields, only the lowest doublet is this effective and one absorption peak results. However, due to hyperfine interaction with the nucleus, each of the two levels is further split into  $(2I + 1)$  levels, where  $I$  is the spin of the metal ion nucleus. In the case of  $V^{4+}$  with  $I = 7/2$ , this results in an eight line hyperfine spectrum.

### Hyperfine structure

Hyperfine interactions are mainly 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<sup>4</sup> is also significant. The octets in the EPR of vanadyl ion and the 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  $\underline{\mu}_i$  and  $\underline{\mu}_j$  separated by  $r_{ij}$  is

$$V_{ij} = \frac{\underline{\mu}_i \cdot \underline{\mu}_j}{r_{ij}^3} - \frac{3(\underline{\mu}_i \cdot \underline{r}_{ij})(\underline{\mu}_j \cdot \underline{r}_{ij})}{r_{ij}^5}$$

The above expression for  $V_{ij}$  is treated as an operator and summed up for all neighbours (j) for 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  $\underline{S}$  and as per terminology of Abragam et al.<sup>2</sup>, the overall electron-nuclear interaction energy is described as

$$W_{hf} = 2r\beta\beta_N \left[ \frac{3(\underline{S} \cdot \underline{r})(\underline{I} \cdot \underline{r})}{r^5} - \frac{(\underline{S} \cdot \underline{I})}{r^3} + \left\{ \frac{\underline{L} \cdot \underline{I}}{r^3} + \frac{4\pi}{3} \delta(r)(\underline{S} \cdot \underline{I}) \right\} \right]$$

where  $r$  is nuclear gyro-magnetic ratio,  $\beta$  is Bohr magneton and  $\beta_N$  nuclear magneton.

The first two terms in the 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 and the last term is the Fermi contact interaction.

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

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

When  $A_x$ ,  $A_y$  and  $A_z$  are the principal values of hyperfine tensor  $\underline{A}$ . If  $\underline{A}$  is isotropic, one has

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

To complete the list of interactions as per Table-3, it must be emphasized that the term  $W_{SS}$  is significant when we have a system with a large number of interacting spins and the term  ${}^1b_N \underline{H} \cdot \underline{I}$  describes the direct interaction of nuclear spin with the external d.c. magnetic field.

### EPR of centres in liquid-like samples

The paramagnetic complexes in liquid solutions can be considered as microcrystals tumbling 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 the molecule the spin-Hamiltonian can now be written as<sup>5,6</sup>

$$fd = \beta [g_{||} H_r S_r + g_{\perp} (H_p S_p + H_q S_q)] + A_{||} I_r S_r + A_{\perp} (I_p S_p + I_q S_q)$$

This can be transformed to the laboratory coordinate system by using the transformation equation as

$$\begin{aligned} H_r &= H \cos \theta \\ S_r &= S_z \cos \theta + S_x \sin \theta \cos \phi + S_y \sin \theta \sin \phi \\ &= S_z \cos A + \frac{1}{2} [S_+ e^{-i\phi} + S_- e^{i\phi}] \sin \theta \end{aligned}$$

And similarly for other components of  $\underline{H}$  and  $\underline{S}$  when we obtain<sup>5,6</sup>s

$$\begin{aligned} fd &= g\beta H S_z + a \underline{I} \cdot \underline{S} + \left( \frac{1}{3} \right) (\Delta g \beta H + b I_z) (3 \cos^2 \theta - 1) S_z \\ &\quad + \left( \frac{b}{2} \right) \sin \theta \cos \theta (I_+ e^{-i\phi} + I_- e^{i\phi}) S_z \end{aligned}$$

$$\begin{aligned}
 & + \frac{1}{2}(\Delta g \beta H + b I_3) \sin \theta \cos \theta (S_+ e^{i\phi} + S_- e^{-i\phi}) \\
 & + \left(\frac{b}{4}\right) \sin^2 \theta (I_+ S_+ e^{-2i\phi} + I_- S_- e^{+2i\phi}) \\
 & - \left(\frac{b}{12}\right) (3 \cos^2 \theta - 1) (I_+ S_- + I_- S_+)
 \end{aligned}$$

Where  $g = \frac{1}{3}(g_{\parallel} + 2g_{\perp})$ ,  $\Delta g = g_{\parallel} - g_{\perp}$

$$a = \frac{1}{3}(A_{\parallel} + 2A_{\perp}), \quad b = A_{\parallel} - A_{\perp}$$

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

As the molecule tumbles, ..... is time dependent and the above Hamiltonian can be written as  $fd = fd_0 + fd(t)$

Where  $fd_0$  is time independent and isotropic, given by first few terms in the general expression for  $fd$  above and  $fd(t)$  contains rest of the terms and is time dependent due to random time dependence of  $\theta$ . If the random motion is extremely rapid which means that  $h$  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<sup>6</sup> has shown that the anisotropies in  $g$  and  $A$  terms, which are averaged out to zero due to rapid tumbling motion of the molecule,  $\langle fd(t) \rangle = 0$ , do contribute to the line widths of the isotropic spectrum given by the Hamiltonian  $fd_0$ , these linewidths are predicted to follow a formula :

$$\Delta \nu \cong \frac{T_c (\Delta g \beta H + b m_I)^2}{\hbar^2}$$

Where  $T_c$  is the correlation time, describing the tumbling motion of the molecule. The line widths  $\Delta \beta$  of different  $m_I$  hyperfine lines can thus be found to ..... the relation<sup>7</sup>.

$$\Delta \beta = \alpha + \beta m_I + r m_I^2$$

Rogers and Pake<sup>8</sup> first observed such line width variations in their study of EPR .....  $Vo^{2+}$  complexes in solutions.

Such effects have further been seen by different workers<sup>9-11</sup> in glassy samples.

### Optical absorption studies

The ground state term for  $Vo^{2+}$  is  $^2D$ . In an octahedral symmetry, the electron occupies  $t_{2g}$  orbital and gives rise to  $^2T_{2g}$  ground state. On excitation, the d-electron occupies  $e_g$  orbital and gives rise to  $^2E_g$  state. Thus, only single transition  $^2T_{2g} \rightarrow ^2E_g$  and corresponding single band is expected for  $Vo^{2+}$  ions in an octahedron symmetry. However, due to non-symmetrical alignment of  $V=0$  band,  $Vo^{2+}$  site symmetry lowers to tetragonal or rhombic. In a tetragonal symmetry described by  $D_{4h}$  point group, as per Table-2, the lower  $^2T_{2g}$  level splits into  $^2B_{2g}$  and  $^2E_g$  levels. The upper level  $^2E_g$  splits into  $^2B_{1g}$  and  $^2A_{1g}$  levels. Therefore one can expect three bands corresponding to  $^2B_{2g} \rightarrow ^2E_g$ ,  $^2B_{2g} \rightarrow ^2B_{1g}$  and  $^2B_{2g} \rightarrow ^2A_{1g}$  in the regions  $10000-11400 \text{ cm}^{-1}$ ,  $14000-17000 \text{ cm}^{-1}$  and  $23000-26700 \text{ cm}^{-1}$  respectively.<sup>12,13</sup> The bands  $^2B_{2g} \rightarrow ^2E_g$  and  $^2B_{2g} \rightarrow ^2A_{1g}$  have been observed in glassy samples recently. The  $^2B_{2g} \rightarrow ^2B_{1g}$  band is quite weak in this sample. However, all the three expected bands have been observed in the  $1.0^{2+}$ , doped  $KZnClSO_4 \cdot 3H_2O$  single crystals.<sup>15</sup>

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