Hyperfine interaction parameters and ground-state wavefunctions of vanadyl ion complexes

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Abstract. Using crystal field approach a theoretical estimate of the ground-state wavefunctions of vanadyl ion doped in various crystals have been made using ESR data and is found to be d_{xy} in our coordinate system with slight admixture of the excited states $d_{x^2-y^2}$, d_{xz} and d_{yz}. The hyperfine interaction parameter P and Fermi contact coupling parameter K have also been estimated for these vanadyl-doped crystals. Results agree with similar studies made earlier.

Keywords. Hyperfine interaction parameters; ground-state wavefunctions; vanadyl ion; crystal field approach; electron spin resonance.

I. Introduction

Electron spin resonance (ESR) is useful to study the properties of various materials containing paramagnetic impurities such as transition metal ions. The spin Hamiltonian parameters give information about the internal structure of its environment. One of these is the vanadyl ion VO^{2+}. Since tetravalent vanadium exists as a stable vanadyl a number of workers (Rao *et al* 1968; Manoharan and Rogers 1968; Flowers *et al* 1973; Jain and Srinivasan 1977; Jain 1979) have studied these ion-doped lattices. The chemistry of this ion has been reviewed by Selbin (1965, 1966). This ion is formulated as having V^{4+} ion with electronic structure $[Ar]^{18}$ $3d^1$ and a closed shell oxide, O^{2-}, ion and VO^{2+} contains a single unpaired d electron attached to the V^{4+} ion. Its configuration would be similar to the d^1 configuration Ti^{3+} or the conjugate configuration ions, such as Cu^{2+}.

The knowledge of ground-state wavefunction of such a paramagnetic ion doped in crystal is useful to study the ESR parameters g and A and to evaluate the dipolar hyperfine coupling constant P and the Fermi contact parameter K. K is related to the unpaired electron density at the vanadium nucleus and describes the isotropic hyperfine interaction. K is very sensitive to small deformations of the electron orbitals of the vanadium ion resulting in changes in spin polarization of inner s-shells caused by the unpaired electron.

It was, therefore, considered worthwhile to study the ground-state wavefunction of VO^{2+} and calculate the P and K values using crystal field approach. The K values obtained agree with the corresponding calculated values using molecular orbital theory. Further, the optical absorption spectra of these complexes support our calculations for the ground state of vanadyl-doped crystal.

P.—5

2. Theory and calculations

In vanadyl ion (Kohin 1979) the V-O bond has considerable covalent character and a
better description involves a $(V \equiv O)^{3+}$ closed shell molecular core having a
substantial covalent triple bond character. To this is added the single unpaired
d electron. This d orbital (one of the orbitally degenerate $Y_2^{\pm 2}$ or d_{xy}, $d_{x^2-y^2}$ orbitals)
is centred on the vanadium ion and lies in the plane perpendicular to the V-O
bond. With this picture of the molecular structure for the axially symmetric ion,
three of the five atomic d orbitals participate in the formation of the triple bond.
The lowest energy d_{z^2} orbital when suitably hybridized by inclusion of $4s$ orbital
forms of σ-bond with the oxygen p_z orbital, while the doubly degenerate d_{xz} and
d_{yz} orbitals form π bonds with the p_x and p_y oxygen orbitals. In general one very
short V-O bond preserves the identity of the VO^{2+} ion. The bonding to the
oxygen atom along the z-axis affects (McGarvey 1966) only the value of $g_\perp$ $g_\parallel$
being affected only by bonding with ligands in the xy plane with x and y-axes
coinciding with V-ligand bonds. Further, the spin-orbit interaction on the ligand
atoms in the xy plane can affect the spin-Hamiltonian but not any interaction on
the oxygen atom.

When the VO^{2+} ion is embedded in a crystal lattice, it is subjected to the crystalline
field due to surrounding ligands. In such vanadyl-doped crystals the crystal field is of
octahedral symmetry with tetragonal distortion and a small perturbation lowering
the symmetry. In the present calculations we have neglected small perturbation.
Thus the crystalline field is assumed to be basically of octahedral symmetry with
tetragonal distortion, where the tetragonal crystal field is assumed to be larger than
the magnitude of the Zeeman splitting.

In a octahedral field with a tetragonal distortion, the equivalent Hamiltonian
operator is (Abragam and Bleaney 1970)

$$H_{CF} = B_4 (O_4^0 + 5O_4^4) + B_2^0 O_2^0 + B_4^0 O_4^0. \tag{1}$$

where the B_4 is magnitude of the octahedral field and the last two terms represent the
tetragonal distortion of second and fourth degree in the potential, respectively. For
d^1 configuration in octahedral symmetry B_4 is a positive (Abragam and Bleaney
1970) quantity, and B_2^0 and B_4^0 are negative (Wertz and Bolton 1972; Poole and
Farach 1972) for a compression along the z axis which is applicable in the present
case. The splitting of the five levels due to these fields for the D state electron is
shown in figure 1.

The lowest state d_{xy} mixes with $d_{x^2-y^2}$, d_{xz} and d_{yz} states due to spin-orbit
coupling. The spin-orbit coupling matrix (Poole and Farach 1972) is of the form

$$\langle \psi_i | \lambda \ \mathbf{L. S.} | \psi_j \rangle.$$

Applying the first order perturbation theory it is found that the ground state is of
the following form:

$$| \pm \rangle = \pm C_1 | \pm 2, \pm \tfrac{1}{2} \rangle \mp C_2 | \mp 2, \pm \tfrac{1}{2} \rangle \pm C_3 | \mp 1, \mp \tfrac{1}{2} \rangle, \tag{2}$$
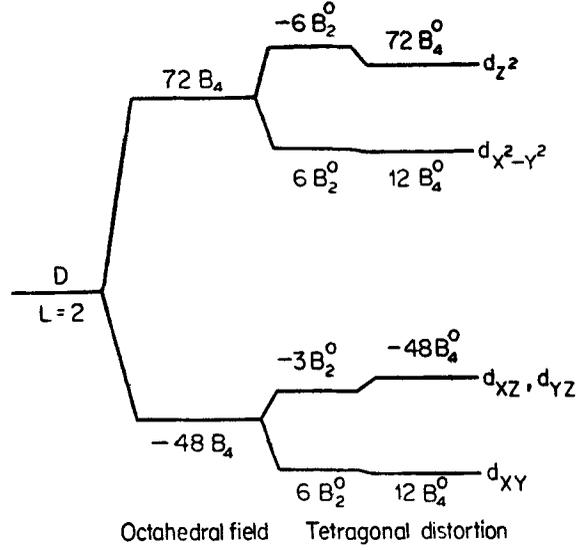
Figure 1. Schematic representation of energy levels of the configuration d^1 as split by octahedral field and by tetragonal distortion.

where the coefficients C_1, C_2 and C_3 give information about the admixture of these states. It is appropriate to relate C_1, C_2 and C_3 with the g factor. This is done by assuming the identity (Poole and Farach 1972)

$$\beta\ \textbf{H}.\ (\textbf{L} + 2\ \textbf{S}) = \beta\ \textbf{H}.\vec{\tilde{g}}.\ \tilde{\textbf{S}}, \tag{3}$$

where $\tilde{\textbf{S}}$ is the effective spin and $\textbf{S}$ is the actual spin. This is equivalent to

$$i\ (L_x+2S_x) + j\ (L_y+2S_y) + k\ (L_z+2S_z) = g_\perp\ (\tilde{S}_x\ i + \tilde{S}_y\ j) + g_\parallel\ \tilde{S}_z\ k. \tag{4}$$

The matrices of the left and right side components are compared to determine the quantities $g_\perp$ and $g_\parallel$. The effective spin ground state eigenfunctions $|\ \pm\ \rangle$ given in (2) are used and we obtain

$$g_\parallel = 2(3C_1^2 - C_2^2 - 2C_3^2), \tag{5}$$

and $\qquad g_\perp = 4C_1(C_2 - C_3). \tag{6}$

Further the normalization of the eignfunctions $|\ \pm\ \rangle$ give

$$C_1^2 + C_2^2 + C_3^2 = 1 \tag{7}$$

With experimental values of $g_\parallel$ and $g_\perp$ solution of (5), (6) and (7) for C_1, C_2 and C_3 will define the ground-state wavefunction of the system as given in (2).

Using these wavefunctions the hyperfine structure constants can be obtained (McGarvey 1966; Abragam and Bleaney 1970), as

$$A_{\parallel} = P[g_{\parallel} - (K + 15/7)(1 - 2C_3^2) - (3/7)(1 + 4C_2C_3)], \tag{8}$$

and

$$A_{\perp} = P[(11/14)g_{\perp} - 2C_1C_2(K + 9/7)]. \tag{9}$$

Substituting computed values for the coefficients and experimental values of $g_{\parallel}$, $g_{\perp}$, $A_{\parallel}$ and $A_{\perp}$ as given in table 1 we can solve (8) and (9) for P and K. These values are given in table 2. In evaluating the values for P and K we have taken $A_{\parallel}/A_{\perp}$ to be positive with both $A_{\parallel}$ and $A_{\perp}$ to be negative (Kasi Viswanath 1977). Values obtained for P and K by taking $A_{\parallel}/A_{\perp} < 0$ do not agree with those obtained by the molecular orbital theory, and therefore these values are not given for $A_{\parallel}/A_{\perp} < 0$. Appreciable values for P and K account for the partial unpairing or polarization of the inner s electrons as a result of an interaction with the unpaired d electrons.

3. Discussion

In the crystals discussed here vanadium ion has generally been located at the centre of an octahedron of ligands which hold the vanadyl in a fixed direction. Therefore, the crystal field considered here is octahedral with small tetragonal distortion. The ground-state wavefunctions calculated are given in table 2. In our coordinate system (Selbin *et al* 1967) these wavefunctions are of the d_{xy} type with a slight admixture of the excited states d_{xz}, d_{yz} and $d_{x^2-y^2}$. Since unpaired s-electron contributes considerably to the hyperfine structure splitting by virtue of core polarization parameter, K, a small amount of admixture may be necessary to explain the splitting. The contribution of the unpaired s-electron is taken phenomenologically as $PKS \cdot I$. For transition ions K is positive. P also varies from crystal to crystal. Van Wieringen (1955) had shown that there is a regular variation of P with covalency. The more ionic the crystal, the larger will be the splitting and hence larger P.

Table 1. Experimental values of g and A for vanadyl-doped crystals.

Crystal lattice	g value		A value in units of 10^{-4} cm^{-1}		Reference
	$g_{\parallel}$	$g_{\perp}[=\frac{1}{2}(g_x + g_y)]$	$A_{\parallel}$	$A_{\perp}[=\frac{1}{2}(A_x + A_y)]$	
$Cs_2Zn(SO_4)_2.6H_2O$	1·936	1·984	181	70·8	Jain and Srinivasan (1977)
$NH_4Al(SO_4)_2.12H_2O$	1·940	1·978	176	67·0	Rao *et al* (1968)
$(NH_4)_2SeO_4$	1·920	1·987	188	75·48	Jain (1979)
$(NH_4)_2SbCl_5$	1·948	1·979	168·8	62·8	Flowers *et al* (1973)
$(NH_4)_3AlF_6$	1·937	1·977	178	64·0	Manoharan and Rogers 1968

Table 2. Ground-state wavefunctions and the calculated values of P and K for vanadyl-doped crystals.

Crystal lattice	Ground-state wave function	$\lvert P \rvert$ in 10^{-4} cm^{-1}	K
$Cs_2Zn\,(SO_4)_2.6H_2O$	$\pm \dfrac{1}{\sqrt{2}}(\lvert \pm 2, \pm \tfrac{1}{2} \rangle - \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\mp 0.0056\,(\lvert \pm 2, \pm \tfrac{1}{2} \rangle + \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\pm 0.0054\,\lvert \mp 1, \mp \tfrac{1}{2} \rangle$	120.54	0.86
$NH_4Al\,(SO_4)_2.12H_2O$	$\pm \dfrac{1}{\sqrt{2}}(\lvert \pm 2, \pm \tfrac{1}{2} \rangle - \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\mp 0.0052\,(\lvert \pm 2, \pm \tfrac{1}{2} \rangle + \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\pm 0.0076\,\lvert \mp 1, \mp \tfrac{1}{2} \rangle$	119.84	0.83
$(NH_4)_2SeO_4$	$\pm \dfrac{1}{\sqrt{2}}(\lvert \pm 2, \pm \tfrac{1}{2} \rangle - \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\mp 0.0070\,(\lvert \pm 2, \pm \tfrac{1}{2} \rangle + \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\pm 0.0043\,\lvert \mp 1, \mp \tfrac{1}{2} \rangle$	120.60	0.90
$(NH_4)_2SbCl_5$	$\pm \dfrac{1}{\sqrt{2}}(\lvert \pm 2, \pm \tfrac{1}{2} \rangle - \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\mp 0.0045\,(\lvert \pm 2, \pm \tfrac{1}{2} \rangle + \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\pm 0.0071\,\lvert \mp 1, \mp \tfrac{1}{2} \rangle$	117.49	0.80
$(NH_4)_3AlF_6$	$\pm \dfrac{1}{\sqrt{2}}(\lvert \pm 2, \pm \tfrac{1}{2} \rangle - \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\mp 0.0054\,(\lvert \pm 2, \pm \tfrac{1}{2} \rangle + \lvert \mp 2, \pm \tfrac{1}{2} \rangle)$ $\pm 0.0079\,\lvert \mp 1, \mp \tfrac{1}{2} \rangle$	124.94	0.78

Table 3. Optical data for vanadyl-doped crystals.

Host lattice	Wave numbers for transitions $d_{xy} \to d_{xz}$ and d_{yz} in cm^{-1}	Wave numbers for transitions $d_{xy} \to d_{x^2-y^2}$ in cm^{-1}	Calculated value of K using molecular orbital theory	Reference
$Cs_2Zn(SO_4)_2.6H_2O$	13.365	16.390	0.88	Lakshman Rao and Purandar (1980)
$NH_4Al(SO_4)_2.12H_2O$	13.000	15.700	–	Rao *et al* (1968)
$(NH_4)_2SeO_4$	13.333	16.129	0.90	Jain (1979)
$(NH_4)_2SbCl_5$	11.750	13.500	–	Flowers *et al* (1973)
$(NH_4)_3AlF_6$	14.100	18.200	0.85	Manoharan and Rogers (1968)

Various experiments on optical absorption spectra of VO^{2+}-doped crystals show broad bands (see table 3) at such values of wavenumbers which correspond to the *d-d* transition in vanadyl. The corresponding transition are $d_{xy} \to d_{x^2-y^2}$ and $d_{xy} \to d_{xz}$ and d_{yz}. These bands support our argument that d_{xy} is the ground state in our coordinate system.

Calculations based on the molecular orbital theory (Kohin 1979) for vanadyl-doped crystals give the values (table 3) of Fermi contact coupling parameter which closely agree with the corresponding values obtained by the present calculations.

Acknowledgements

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