EPR Investigation of VO^{2+} Ion in $[C(NH_2)_3]_3AlF_6$ Single Crystals

T. Lakshmi Kasturi, Geetha Jayaram, and V. G. Krishnan
Physics Department, Osmania University, Hyderabad-500 007, India

Z. Naturforsch. **51a**, 1067–1072 (1996); received June 28, 1996

X-band EPR spectra have been recorded at room temperature for VO^{2+} impurity in single crystals of tris-Guanadiniumhexafluoroaluminate, $[C(NH_2)_3]_3AlF_6$. ^{19}F super hyperfine structure has been observed on the ^{51}V hyperfine lines. VO^{2+} replaces Al^{3+} to form an effective VOF_5 complex. There are three possible V–O bond orientations in the AlF_6 octahedron but with differing occupancy factors. Bonding parameters have been evaluated.

Introduction

The simple electron paramagnetic resonance (EPR) spectrum of VO^{2+} ion ($S = 1/2$, $I = 7/2$) has made it a prominent impurity ion for the characterization of structural features of Tuttons salts, Alums, Langebenites, oxalates as well as nonhydrated sulphates [1, 2]. Since the report by Borcherts and Kikuchi [3], EPR studies on VO^{2+} in Tutton salts have formed the basis of the majority of subsequent investigations. Recent reports [4] on Ammonium Tutton salts (with Zn, Mg, Cd, Fe, Co as divalent ions) have specifically stressed on the significance of the proton hyperfine structure observed at certain orientations. One important conclusion drawn from the ENDOR study [5] of VO^{2+} doped $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ is the lifting of V^{4+}, by 0.2 Å from the position originally occupies by Mg^{2+}, above the plane of the four equatorial water molecules. This makes the arrangement of atoms pyramidal. This lowering of symmetry reduces the overlap between the 3d-orbitals and ligand orbitals.

^{19}F superhyperfine structure (SHFS) we first reported for VO^{2+} doped $(NH_4)_3AlF_6$ single crystals [6]. From the angular variation study the authors have concluded that the SHFS is observed not only from the four equatorial fluorines but also from the axially located fifth fluorine. They have also reported large in-plane ^{19}F SHF splitting of 41 G on each of the eight perpendicular ^{51}V hf lines. This would give rise to a total of more than forty SHF lines occupying more than 1,000 G of the central part of the spectrum preventing the identification of the individual hf lines. Considering the $A_\perp$ hf value of 69.9 G, a large overlap should occur. This would make quantitative estimates very difficult.

We have carried out studies on a series of VO^{2+} doped tetra-penta- as well as hexa-fluoaluminates. Recently we reported ^{19}F SHFS in $Cd_2ZrF_8 \cdot 6H_2O$ [7], ^{14}N, ^{19}F in $[H_3N(CH_2)_2NH_3]ZrF_6$ [8], ^{19}F in $[H_3N(CH_2)_3NH_3]ZrF_6$ [9] and ^{19}F in $[C_6H_{14}N]_3AlF_6$ [10]. Here we report the study in VO^{2+} doped tris(guanidinium) hexafluoro aluminate (TGHFA) single crystals.

Experimental and Crystal Structure

Single crystals of 5 mm^3 size are grown easily from aqueous solution containing $[C(NH_2)_3]F$ in excess and AlF_3 by slow evaporation at room temperature. $VOSO_4 \cdot 5H_2O$ is used to introduce the impurity in the solution. The crystals are found to grow with the morphology of $Pb(NO_3)_2$ with a prominent [111] face. EPR spectra are recorded on a Varian E-12 spectrometer operating at X-band frequencies (9.07–9.51 GHz) with 100 kHz magnetic field modulation.

Tris-guanidiniumfluoaluminate with the molecular formula $[C(NH_2)_3]_3AlF_6$ crystallizes in the cubic class with the space group P a 3, with $a = 13.93$ Å and eight molecules per unit cell [11]. Six fluorines from a regular octahedron around Al^{3+} ion. MF_6^{3-} anions are arranged as Na^+ and Cl^- in NaCl lattice. Guanidinium cations are distributed on 24-fold general positions.

Results and Discussion

EPR spectra are recorded in three different planes, i.e. i) (111) plane, ii) a plane perpendicular to the (111)

Reprint requests to Dr. G. Jayaram.

0932-0784 / 96 / 1000-1067 $ 06.00 © – Verlag der Zeitschrift für Naturforschung, D-72072 Tübingen

plane with [111] direction in the H-plane for angles varying between + 90° to − 90° with the magnetic field direction, and iii) (001) plane.

In the (111) plane, the spectrum in a general direction shows a large number of narrowly spaced lines. Angular variation shows only a movement of these lines among themselves, accompanied by variation in spacing as well as their intensities within one group. These line are identified as superhyperfine (SHF) lines resulting from the interaction of ^{19}F nuclei ($I = 1/2$) with the ^{51}V unpaired electron. For no orientation of H in this plane are we able to observe the eight ^{51}V ($I = 7/2$) hyperfine lines. Hence there are no V−O bond directions in the (111) plane. From Fig. 1, the spectrum recorded in the (111) plane, one can conclude that there are some V−O bond orientations within the AlF_6 octahedron that lie in the plane perpendicular to the (111) plane. In Fig. 1 one can also see three groups of ^{19}F SHFS, in place of the expected eight sets, indicating that there is considerable overlap among the SHF lines of neighbouring hf lines.

Figure 2a shows the spectrum recorded for the [111] axis making an angle of 40° with the magnetic field. We can see three distinct types of ^{51}V hf lines identified by the number of SHFS components as well as their intensities. In the low field we can see the hf lines without any SHF splitting (set I). The central part of the spectrum has an arrangement of SHF components (set II) that is similar to that seen in Figure 1. In the high field region we see at high instrument gain a ten components pattern. When [111] is oriented to make 70° with the H − direction, we see the extremum of ^{51}V hf lines, indicating that the magnetic field is along the V−O bond for set II (Figure 2b).

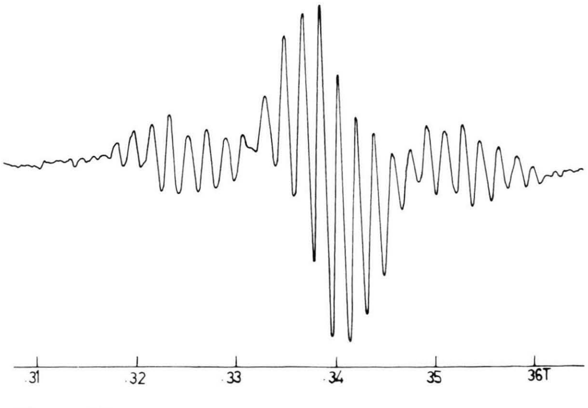

Fig. 1. EPR spectrum in the (111) plane.

In the (010) plane, the EPR spectrum recorded for H along the V−O bond for set II is shown in Figure 3a. As has been seen in Fig. 2a, there is no SHFS on the hf lines for set II. Rotation by 40° from the V−O bond direction shows a splitting on the hf lines of sets I, II and III (Figure 3b). Set I with five components shows the interaction of four equatorial fluorines with the unpaired electron of ^{51}V. The ten components structure seen for set II is due to the further splitting of each of the five lines due to interaction with the fifth axial fluorine bonded in the position opposite the V−O bond.

Some of the observations that make the study interesting are i) no ^{51}V hyperfine lines are seen in the entire (111) plane, ii) absence of ^{19}F SHFS on the hf lines for H oriented along the V−O bond, iii) a ten line SHFS observed for an orientation of H that is intermediate to a direction along and perpendicular to the V−O bond, as seen in Figs. 2a and 3b.

During our EPR investigation of Cr^{3+} ion replacing Al^{3+} in the AlF_6 octahedron [12] we have found from the angular study of the ^{53}Cr fine structure-lines that the [111] axis of the octahedron is rotated by 88° with respect to the crystallographic *c*-axis. Therefore the three possible V−O bond orientations in the two AlF_6 octahedra are such that i) the projection of these on the (111) plane almost wipes out the ^{51}V hf structure, and ii) the projection of these bonds are distributed on the (111) plane accompanied by additional splitting due to the ^{19}F ligands. Hence an overall cancellation of the intensities of the SHF and the hf lines occurs due to their being widely distributed in the (111) plane. For higher instrument gain the spectrum shows a number of sets of weak ^{41}V hf lines split into ^{19}F components, thus supporting the reasoning.

No ^{19}F SHFS in the hf lines for H oriented along the V−O bond would mean that i) the hf splitting is less than the line width of the individual components. In $VO^{2+}:(NH_4)_3AlF_6$ [6] the ^{19}F SHFS is observed for H away from the V−O bond. It is unrealistic to expect a resolution of $^{19}F_{axial}$ SHFS since it is definitely less than 2G. ii) Large anisotropy in the splitting, varying from a maximum of 27G to a minimum of 5G, corresponding to H along the F−V−F bond direction and the F−V−O bond direction, respectively. Such a large anisotropy, as well as the smearing of the SHFS lines, has been reported earlier for $VO^{2+}:Cd_2ZrF_8 \cdot 6H_2O$ [7], where the V−O bond is oriented perpendicular to the plane formed by the four fluorines to form a planar VOF_5 species.

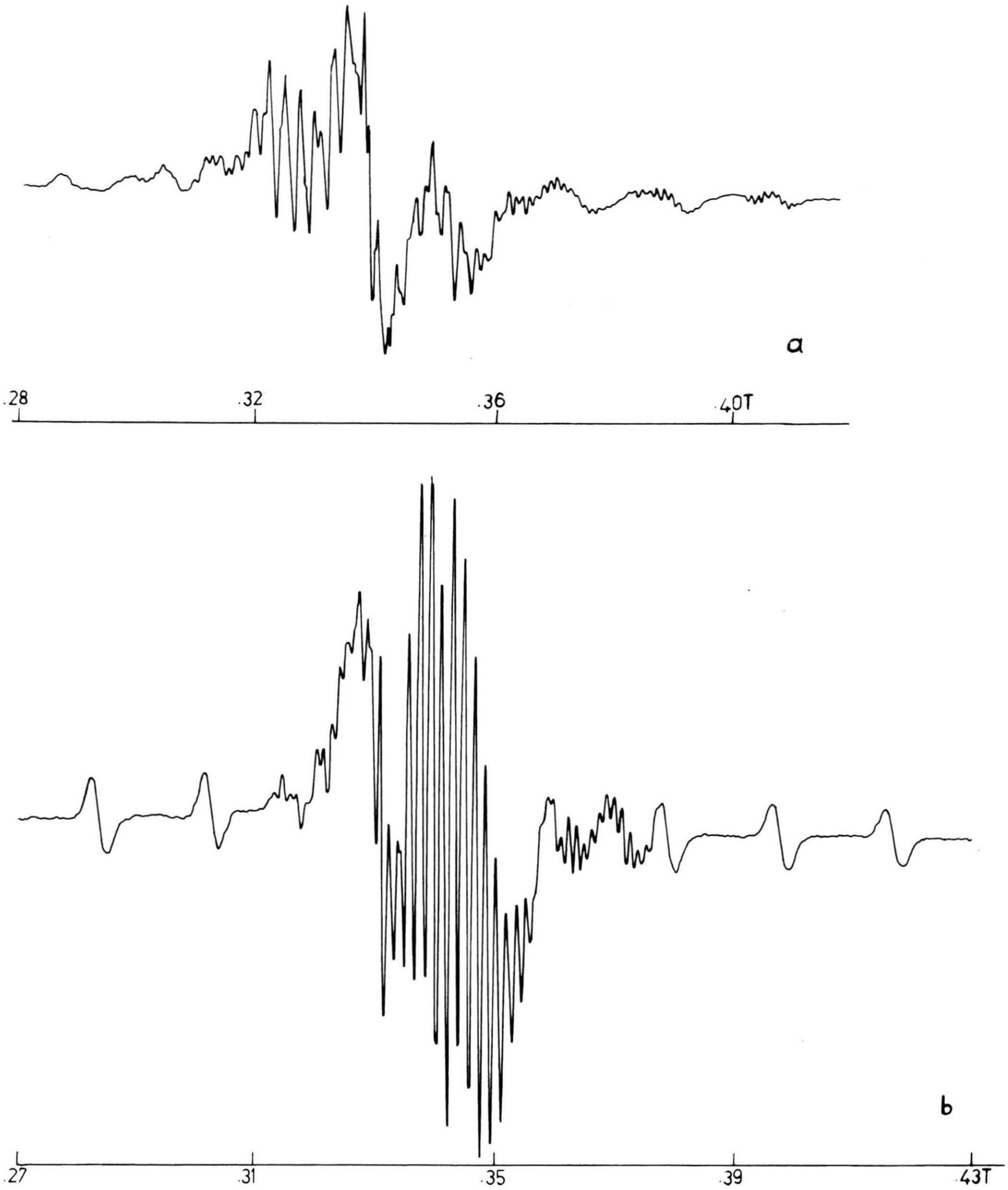

Fig. 2. (a) Spectrum with the [111] direction making 40° with H. (b) Spectrum in a plane perpendicular to the (111) plane and the [111] direction making 70° with H.

The spectra could be analysed using an axial spin-Hamiltonian

$$\mathcal{H} = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) .$$

The angular variation of the spectra indicated that the g and ^{51}V hyperfine tensors are nearly cylindrical with common principal axes. The large vanadium hyperfine splitting necessitates the use of a resonance formula with second-order corrections

$$H = H_{m_I} - A m_I + A_{\perp}^2 (A_{\parallel}^2 + A^2) \cdot [I(I+1) - m_I^2]/4 A^2 H_0 , \qquad (1)$$

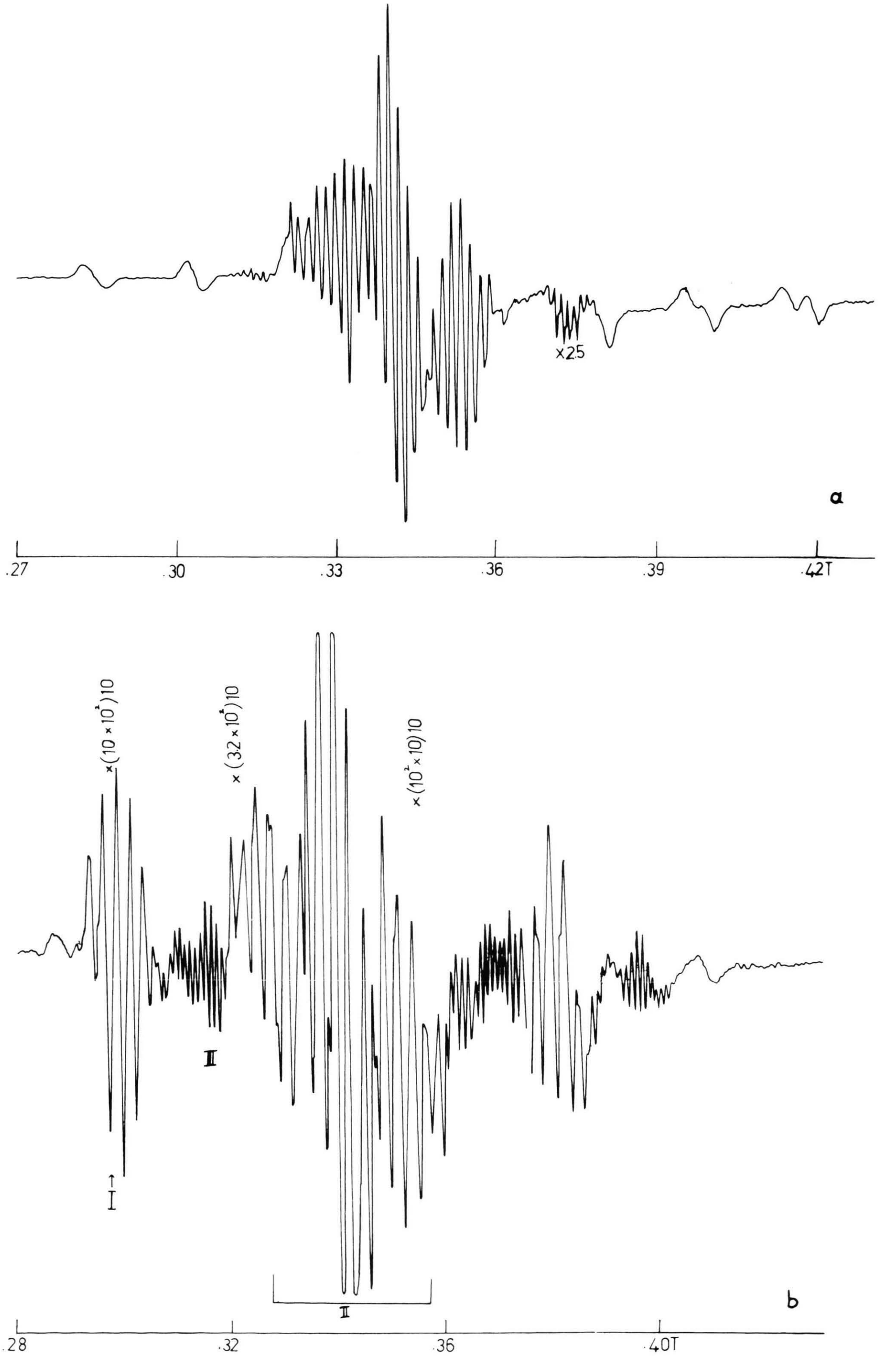

Fig. 3. (a) Spectrum along the V–O bond for set II. (b) Spectrum 40° away from the V–O bond.

Table 1. The spin-Hamiltonian parameters for VO^{2+} in some lattices.

Lattice	Complex	$g_{\|}$	$g_{|}$	$A_{\|}$ *	$A_{|}$ *	Ref.
TGHFA	VOF_5	1.939	1.983	182	72	This work
TCHAHFA	VOF_4	1.937	1.979	176.3	67.3	[10]
$penH_2ZrF_6$	VON_2F_2	1.931	1.982	182	68.3	[9]
enH_2ZrF_6	VON_2F_2	1.956	1.997	175.8	65.8	[8]
$Cd_2ZrF_8 \cdot 6H_2O$	VOF_4	1.935	1.981	185	76.4	[7]
$(NH_4)_3AlF_6$	VOF_5	1.937	1.977	178.5	64	[6]
Glycine	VON_2O_2	1.942	1.986	155.8	85.3	[4]
L-alanine	VON_2O_2	1.955	2.006	170.6	57.1 66.5	[4]
Dimethyl alanine	VON_2O_2	1.925	1.994	182.3	77.2 58.6	[4]
	VON_2O_2	1.939	1.991	181	46.5 81.8	[4]
Tutton salt	$VO(H_2O)_5$	1.931	1.979	182	72	[5]

* in units of 10^{-4} cm^{-1}.

where

$$g^2 A^2 = g_\perp^2 A_\|^2 \cos^2\theta + g_\perp^2 A_\perp^2 \sin^2\theta\,, \tag{2}$$

$$g^2 = g_\|^2 \cos^2\theta + g_\perp^2 \sin^2\theta\,. \tag{3}$$

θ is the angle between the static field H_{m_I} and the molecular axis.

The hyperfine splittings are determined from the lines m_I and m_{-I}, using the relation

$$A = (H_{m_I} - H_{m_{-I}})/2m_I\,. \tag{4}$$

In the above equation there is no second order term. The g value is obtained from the outermost hf pair. $+7/2$ and $-7/2$, to minimise the second order effects. The shift from the centre field $(H_{7/2} + H_{-7/2})/2$ is given by

$$(7/2)\,A_\perp^2 (A_\|^2 + A^2)/4A^2 H_0\,,$$

which is maximum for the direction perpendicular to the unique axis (V–O bond direction), and of the order 10 G or less. Since $A_\| = 3A_\perp$, such a correction is only significant for $g_\perp$ in X-band experiments.

Due to the observation of ligand hyperfine structure it is necessary to define a suitable coordinate system. The Zeeman and ^{51}V hyperfine structure are considered to originate at the Vanadium nucleus. The z-axis is chosen along the V–O bond, and the x- and y-axis in the equatorial plane along the F–V–F bond.

The spin-Hamiltonian parameters evaluated are,

$$g_\| = 1.939 \pm 0.002\,,$$
$$g_\perp = 1.979 \pm 0.002\,,$$
$$A_\|(^{51}V) = 182 \times 10^{-4}\ \text{cm}^{-1}\,,$$
$$A_\perp(^{51}V) = 72 \times 10^{-4}\ \text{cm}^{-1}\,,$$
$$A_\|(^{19}F_{eq}) = 25.2 \times 10^{-4}\ \text{cm}^{-1}\,,$$
$$A_\perp(^{19}F_{eq}) = 11.2 \times 10^{-4}\ \text{cm}^{-1}\,,$$
$$A_\|(^{19}F_{ax}) = 4.7 \times 10^{-4}\ \text{cm}^{-1}\,,$$
$$A_\perp(^{19}F_{ax}) < 2 + 10^{-4}\ \text{cm}^{-1}\,.$$

The spin-Hamiltonian parameters for VO^{2+} in some lattices are presented in Table 1.

The ground state wave function for the d^1 ion is represented as a linear combination of $|x^2 - y^2>$ and $|z^2>$ states. The effect of covalency is given indirectly by the modified value of the spin-orbit parameter λ and the $\langle r^{-3}\rangle$ value. The g tensor anisotropy is the consequence of some orbital angular momentum contribution introduced into the ground state by the spin-orbit interaction. Hence such anisotropy is affected by the symmetry of the overall charge distribution.

On the other hand, the hyperfine coupling is a magnetic interaction between the metal nucleus and the unpaired spin distribution. It's anisotropy is primarily determined by the symmetry of the unpaired electron molecular orbital. The effective spin-orbit coupling for the system investigated can be estimated from the g value expression [13]

$$g_\| = g_e - (8\alpha^2 \lambda/\Delta_{xy})\,. \tag{5}$$

Assuming that the ground state is predominantly $|x^2 - y^2\rangle$, α is evaluated by substituting $\lambda = 170$ cm^{-1} and $\Delta E = 18{,}200$ cm^{-1} [6] for the $|x^2 - y^2\rangle \leftrightarrow |xy\rangle$ transition.

The observation of well resolved SHFS indicates a certain amount of metal-ligand delocalisation. Analysis of this SHFS can lead to an estimate of the extent of delocalisation and a description of the molecular orbital containing the unpaired electron. The ^{19}F tensors are usually axially symmetric about the V–F bond. The coupling constant can be expressed as

$$A_\| = A_y\,, \quad A_\perp = (A_x + A_z)/2\,. \tag{6}$$

These coupling constants can be resolved into isotropic and anisotropic (dipolar) parts according to the equations

$$A_\| = K + 2T\,, \quad A_\perp = K - T\,, \tag{7}$$

where K is the isotropic and T the dipolar part. The isotropic part is due to contact interaction in which the unpaired electron has a finite probability density at the nucleus. Large contact interactions are expected only if the molecular orbitals containing the unpaired electron have some 's' character. The dipolar part arises from the through-space effect as well as *p*-orbital contribution to the molecular orbital. Assuming that only the 2*s* and 2*p* orbitals of fluorine participate in bonding with the ^{51}V ion, isotropic and dipolar coupling constants can be expressed as

$$K(\mathrm{cm}^{-1}) = \delta^2 (8\pi g_e g_N \beta_e \beta_N)[|\Psi_{2s}(0)|^2]/3hc\,, \qquad (8)$$

$$T(\mathrm{cm}^{-1}) = \gamma^2 (2 g_e g_N \beta_e \beta_N)(\langle r^{-3}\rangle_{2p})/5hc + (\alpha^2 g_e g_N \beta_e \beta_N / R^3 hc)\,. \qquad (9)$$

In these expressions, δ and γ are the molecular orbital (MO) co-efficients of the fluorine 2s and 2*p* orbitals, respectively. The second term of the expression for T is the direct dipole-dipole term in which α^2 is the unpaired electron density on the Vanadium ion and R is the distance between Vanadium and Fluorine. The MO co-efficients δ and γ can be calculated from the equations above, using the observed values of K and T along with the values of R. $|\psi(0)|^2_{2s}$ is taken from a Hartree-Fock calculation [14], and $\langle r^{-3}\rangle_{2p}$ is determined from the EPR investigation of atomic fluorine [15]. Table 2 lists the molecular bonding parameters for TCHAHFA and some other systems, where the following values have been used for their evaluation:

$$|\varphi(0)_{2s}|^2 = 11.374 \text{ (a. u)}\,,$$
$$\langle r^{-3}\rangle_{2p} = 7.545 \text{ (a. u)}\,, \quad R(\text{V}-\text{F}) = 1.98\ \text{Å}\,.$$

Table 2. Molecular bonding parameters.

System	K *	T *	γ^2	δ^2
TGHFA	15.9	4.7	0.021	0.112
TCHAHFA	8	3	0.021	0.041
enZF	6.5	1.5	0.033	0.013
penZF	7.7	2.1	0.036	0.015

* in units of 10^{-4} cm^{-1}.

The values of δ^2 and γ^2 indicate that the delocalization of the unpaired electron from the Vanadium to the Fluorine ligand is greater for TGHFA than for VO^{2+} in CdZrF · 6HO [7], enZF [8], penZF [9] and TCHAHFA [10].

Conclusions

From the EPR studies on VO^{2+} doped TGHFA, VO^{2+} is found to enter the lattice substituting Al^{3+}. It is seen that there are three V–O bond orientations in each of the two AlF_6 octahedra with different occupancy factors. The considerable misalignment of the AlF_6 octahedra is reflected in the smearing out of the ^{51}V hf and ^{19}F SHFS in the (111) plane. The g and ^{51}V hf tensors are nearly cylindrical with common principal axes. The ^{51}V hyperfine splitting is large and shows marked anisotropy. The g tensor anisotropy is also large. The SHFS of the equatorial fluorines observed indicates a larger metal-ligand delocalization than what was seen in tris(cyclohexylammonium) hexafluoaluminate [10]. The interaction with the axial fluorine is also estimated. The bonding parameters have been evaluated using the observed ^{19}F ligand hyperfine values.

Acknowledgements

The authors thank Prof. S. V. Suryanarayana for constant encouragement and Dr. T. K. Gundu Rao, R.S.I.C., I.I.T., Bombay, for extending the EPR spectrometer facility. The authors TLK and GJ thank the Department of Science and Technology for financial support.

[1] R. P. Kohin, Magn. Reson. Rev. **5,** 75 (1979).
[2] S. K. Misra and T. Sun, Phys. Rev. **44 B,** 10333 (1991).
[3] R. H. Borcherts and C. Kikuchi, J. Chem. Phys. **40,** 2270 (1964).
[4] S. K. Misra and C. Wang, Physica **B 168,** 170 (1991).
[5] N. M. Atherton and D. Shackleton, Mol. Phys. **39,** 1471 (1980).
[6] P. T. Manoharan and M. T. Rogers, J. Chem. Phys. **49,** 3912 (1968).
[7] G. Jayaram and V. G. Krishnan, Z. Naturforsch. **50 a,** 953 (1995).
[8] G. Jayaram and V. G. Krishnan, Phys. Rev. **49 B,** 271 (1994).
[9] T. L. Kasturi, G. Jayaram, and V. G. Krishnan, Phys. Rev. **B.** In press.
[10] T. L. Kasturi, G. Jayaram, and V. G. Krishnan, J. Phys. (Condensed Matter). In press.
[11] P. Bukovec, Monat. Chem. **114,** 277 (1983).
[12] T. L. Kasturi, G. Jayaram, and V. G. Krishnan, Phys. Rev. **B.** In press.
[13] B. R. McGarvey, in Transition Metal Chemistry, Ed. R. L. Carlin, Marcel Dekker, New York 1966, Vol. 3.
[14] A. J. Freeman and R. B. Frenkel, Hyperfine Interactions, Academic Press, New York 1967.
[15] J. A. McMillan and T. Halpern, Hyperfine Interactions: Tables of isotropic and anisotropic parameters for hydrogen to bismuth, Argonne National Laboratory, Rep. No. ANL 7784, 1971.