

EPR investigation of ^{14}N and ^{19}F superhyperfine interaction in VO^{2+} -doped ethylenediammonium hexafluozirconate single crystals

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(Received 28 April 1993)

X-band electron-paramagnetic-resonance measurements have been carried out on VO^{2+} -doped single crystals of $[\text{NH}_3(\text{CH}_2)\text{NH}_3]\text{ZrF}_6$ at room temperature. Superhyperfine structure due to ^{14}N and ^{19}F has been observed in abundance in the spectra recorded at all orientations. There are two occupation sites for VO^{2+} , both interstitial, in the triclinic cell.

INTRODUCTION

Since the report by Borcherts and Kikuchi,¹ electron-paramagnetic-resonance (EPR) studies on VO^{2+} in Tutton salts have formed the basis of subsequent investigations. Recent studies²⁻⁷ on ammonium Tutton salts (with Zn, Mg, Cd, Fe, and Co as the divalent ions) have specifically been carried out to show the significance of the ligand (proton) hyperfine structure observed in these crystals at certain orientations. Deuterations of $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ were carried out to establish the origin of the superhyperfine structure. Misra and Sun² went a step further to suggest that an electron-nuclear double resonance (ENDOR) study on $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ be carried out to put their conclusion on firm footing. They had apparently overlooked a proton ENDOR study on $[\text{VO}(\text{H}_2\text{O})_5]$ in $(\text{NH}_4)_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ reported by Atherton and Shackleton⁸ in 1980. Their study had resulted in a complete understanding of the origin of proton superhyperfine structure (SHFS). They had also identified the displacement of vanadium by 0.2 Å from the position originally occupied by a Mg^{2+} ion. Such a shift would make the equatorial arrangement of ligand somewhat pyramidal. This lowering of symmetry would lead to a reduction of the overlap between the 3d orbitals and the ligand orbitals. In fact, Kasthuriengan and Rajan⁹ in their study on $\text{K}_2\text{Mg}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{K}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ have clearly shown in their spectra that in a particular direction for the protonated and deuterated crystals, the proton SHFS disappeared in the deuterated crystals. ^{19}F SHFS was observed first for VO^{2+} -doped $(\text{NH}_4)_3\text{AlF}_6$ single crystals by Manoharan and Rogers.¹⁰

We have embarked on an EPR study of transition-metal ions (VO^{2+} , Mn^{2+} , Cu^{2+} , Cr^{3+} , Fe^{3+} , and MoO^{3+}), in a variety of fluometallate (IV) crystals with a view to accommodate the transition-metal ions in suitable interstitial sites, or in the tetravalent-ion sites. Such a variety of occupational sites, if made available, would have to be distinguished by the SHFS that could be observed at different orientations. This unconventional aspect has, hitherto, been neglected in the variety of studies reported.

EXPERIMENT AND CRYSTAL STRUCTURE

Single crystals of 3 mm³ and larger sizes are grown at room temperature from an aqueous solution containing ethylenediammonium fluoride (enH_2F_2) and ZrF_4 in 1:1 ratio. The solution is maintained at $\text{pH} < 2$. VO^{2+} impurity is less than 0.1% in the crystal. $(\text{enH}_2)\text{ZrF}_6$ and $\text{C}_2\text{N}_2\text{H}_{10}\text{ZrF}_6$, crystallize in the triclinic class¹¹ with space group $P\bar{1}$, $a = 649.1$ pm, $b = 749.3$ pm, $c = 885.6$ pm, $\alpha = 103.18$, $\beta = 107.72$, and $\gamma = 99.9$ with $Z = 2$. The crystal structure consists of two $[\text{NH}_3(\text{CH}_2)_2\text{NH}_3]^{2+}$ and $(\text{Zr}_2\text{F}_{12})^{4-}$ groups. Zr atoms are in a pentagonal bipyramidal coordination with two bridging fluorine atoms.

EPR spectra are recorded on a conventional X-band spectrometer (JEOL-3X) with 100 kHz magnetic-field modulation.

RESULTS AND DISCUSSION

EPR spectra are recorded at room temperature in three mutually perpendicular planes. Figure 1 shows the crystal morphology along with (i) the choice of X^* , Y^* , and C^* axes; (ii), the directions of the $\text{V}=\text{O}$ bond orientations. This procedure is adapted keeping in view the absence of at least a twofold symmetry axis as in the case of a monoclinic crystal. In plane I, two sets of eight lines, evidently due to the hyperfine interactions of ^{51}V ($I = 7/2$), are recorded. Their intensities are found to be in the ratio 10:1.

The angular variation of the spectra indicated that the g and ^{51}V hyperfine (A) tensors are nearly cylindrical with common principal axes. The large vanadium hyperfine splitting necessitates the use of a resonance formula with the second-order corrections,^{12,13}

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

where

$$g^2 A^2 = g_{\parallel}^2 A_{\parallel}^2 \cos^2\theta + g_{\perp}^2 A_{\perp}^2 \sin^2\theta, \quad (2)$$

$$g^2 = g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta. \quad (3)$$

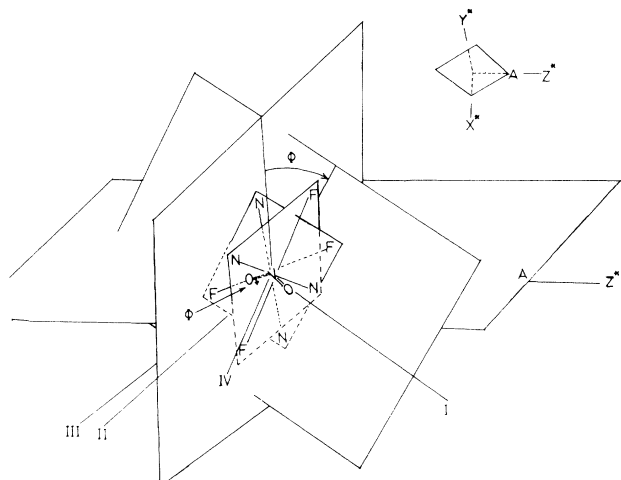


FIG. 1. Crystal morphology, choice of X^* , Y^* , and Z^* axes and the directions of $V=O$ bond orientations.

θ is the angle between the static field H_{m_I} and the molecular axis, m_I the magnetic quantum number of ^{51}V spin and $H_0 = h\nu/g\beta$ the microwave energy expressed in Gauss.

The hyperfine splittings are determined from a pair of lines, m_I and $-m_I$, using the relation

$$A = (H_{m_I} - H_{-m_I}) / 2m_I. \quad (4)$$

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

$$\left(\frac{7}{2}\right) A_{\perp}^2 (A_{\parallel}^2 + A^2) / 4A^2 H_0, \quad (5)$$

which is maximum for the direction perpendicular to the unique axis, and of the order of 10 G or less. Since $A_{\parallel} \approx 3A_{\perp}$, such a correction is only significant for g_{\perp} in X-band experiments.

Because of the appearance of ligand hyperfine structure at all orientations, 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 axes in the equatorial plane bisecting the $F-V-N$ and $N-V-F$ bond angles. This represents an interstitial location in the lattice. The substitutional Zr site is surrounded by seven fluorines in a low-symmetry pentagonal bipyramidal arrangement. Such an arrangement of seven fluorines, where two fluorines are involved in bridging between (ZrF_7) units, would not give rise to a symmetrical and regular SHFS in any plane, as was observed.

We follow the treatment of Verbeek and Cornaz.¹⁴ When the applied field is parallel to $V=O$ axis of (VON_2F_2) species, ($\theta=0^\circ$ and $\phi=90^\circ$), all four equatorial ligands, viz., two nitrogens and two fluorines, are

equivalent. As a result, each vanadium hyperfine line is split into seven components. These splittings are designated $^L A_z$, where L represents ^{19}F and ^{14}N . When the field is parallel to the $F-V-N$ bond in the equatorial plane, i.e., $\theta=90^\circ$ and $\phi=0^\circ$, the two fluorines will give rise to a triplet SHFS for each of the eight hyperfine lines. With the field is parallel to the $N-V-N$ bond, i.e., $\theta=90^\circ$ and $\phi=90^\circ$, the two nitrogens give a quintet SHFS. Since one of the splittings is much larger than the other, each vanadium line is expected to split into 15 components. If the linewidth of the nitrogen SHFS is greater than the splitting due to ^{19}F SHFS, the latter is not resolved.

All the features hitherto described and discussed are, indeed, observed in the angular variation study. For the directions indicated by I–IV in Fig. 1, the corresponding spectra are shown in Figs. 2(a)–2(d). These directions correspond to (i) $H \parallel$ to the $V=O$ bond orientation of the dominant species; (ii) $H \perp$ to the above direction; (iii) $H \parallel$ to the $V=O$ bond direction of the weak species whose projection falls in the Z^*X^* plane (Θ in Fig. 1 being the angle made by the $V=O$ bond with the direction III); (iv) H making an angle of 50° with each of the $V=O$ bond

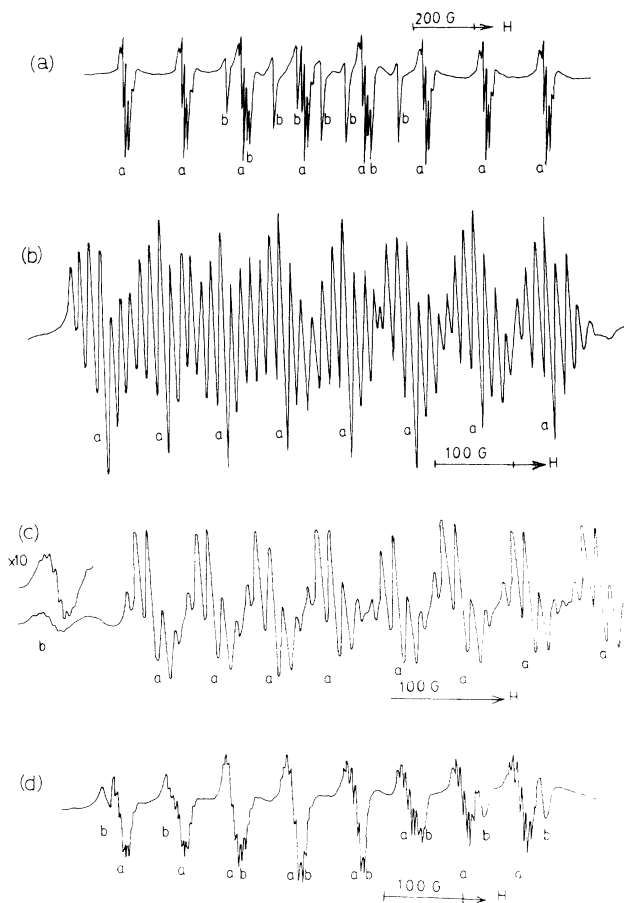


FIG. 2. EPR spectra for (a) $H \parallel$ to $V=O$ bond orientation of the dominant species (b) $H \perp$ to $V=O$ bond orientation for the dominant species (c) $H \parallel$ to $V=O$ bond orientation of the weak species, (d) H making an angle $\sim 50^\circ$ with each of the $V=O$ bond orientations.

orientations. This direction represents the crossover of the hyperfine lines due to the two possible orientations.

Figure 3 shows the molecular arrangement around the interstitial VO^{2+} site in the unit cell of ethylenediammonium hexafluorozirconate.

From the angular variation study, it is found that a slight misalignment of the g and A tensors may be present. This is less than 10° , the error in measurement being $\sim 3^\circ$.

The spin-Hamiltonian parameters evaluated are

$$g_{\parallel} = 1.956 + 0.002, \quad g_{\perp} = 1.997 + 0.002,$$

$$^{51}\text{V} A_{\parallel} = 175.8 \times 10^{-4} \text{ cm}^{-1}, \quad ^{51}\text{V} A_{\perp} = 65.8 \times 10^{-4} \text{ cm}^{-1},$$

$$^{14}\text{N} A_{\parallel} = 15.1 \times 10^{-4} \text{ cm}^{-1}, \quad ^{14}\text{N} A_{\perp} = 10.7 \times 10^{-4} \text{ cm}^{-1},$$

$$^{19}\text{F} A_{\parallel} = 9.5 \times 10^{-4} \text{ cm}^{-1}, \quad ^{19}\text{F} A_{\perp} = 5.0 \times 10^{-4} \text{ cm}^{-1}.$$

The ground-state function of a d^1 system is represented by a combination of $|x^2-y^2\rangle$ and $|z^2\rangle$ states. Effect of covalency will be given indirectly by the modified value of the spin-orbit parameter λ and the $\langle r^{-3} \rangle$ parameters. The result of such calculations strongly depend on the choice of the above parameters. The g -tensor anisotropy is the consequence of some orbital angular momentum introduced into the ground state by the spin-orbit interaction. Therefore, 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 only. Its 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,¹⁵

$$g_{\parallel} = g_e - (8a^2\lambda/\Delta_{xy}). \quad (6)$$

Assuming that the ground state is predominantly $|x^2-y^2\rangle$ and, therefore, choosing $a=0.997$, λ is varied till the calculated energy value of $|x^2-y^2\rangle - |xy\rangle$ is $18.2 \times 10^3 \text{ cm}^{-1}$. This is the only possible fitting on the

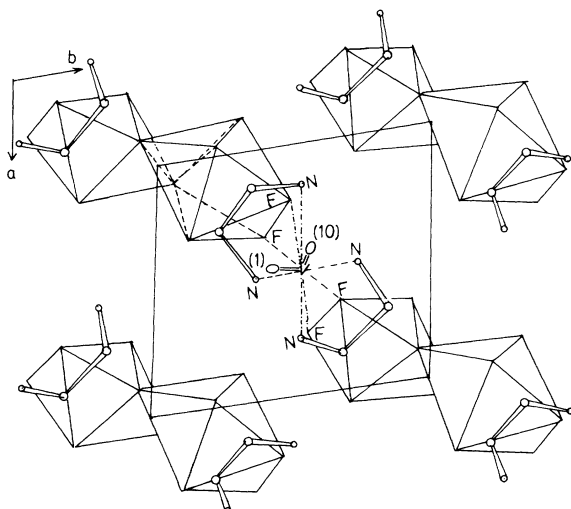


FIG. 3. Molecular arrangement around the interstitial VO^{2+} site in the unit cell of ethylenediammonium hexafluorozirconate.

basis of EPR results as well as the general observation of absorption in the visible region of the optical-absorption spectrum.¹⁰ Lower values for λ would imply a greater degree of covalency, which is not expected in an environment of fluorine and nitrogen. Hence, the above energy separation represents a reasonable choice. The possible ordering of the energy levels is, $|x^2-y^2\rangle < |xz\rangle < |yz\rangle < |z^2\rangle < |xy\rangle$.

The observation of well-resolved ligand hyperfine structure is an indication of some amount of metal-ligand delocalization. An analysis of this hyperfine interaction can lead to an estimation of the extent of delocalization and a description of the molecular orbital containing the unpaired electron. The ^{14}N and ^{19}F hyperfine tensors are usually axially symmetric about the V—F and V—N bonds. This appears to be the case for the system under investigation, too. Taking the ligand hf tensor as axial, the coupling constant can be expressed in the following equations for N and F:

$$^{\text{N}} A_{\parallel} = ^{\text{N}} A_y, \quad ^{\text{N}} A_{\perp} = (^{\text{N}} A_x + ^{\text{N}} A_z)/2, \quad (7)$$

$$^{\text{F}} A_{\parallel} = ^{\text{F}} A_y, \quad ^{\text{F}} A_{\perp} = (^{\text{F}} A_x + ^{\text{F}} A_z)/2. \quad (8)$$

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

$$A_{\parallel} = K + 2T, \quad A_{\perp} = K - T, \quad (9)$$

where K is the isotropic part and T is the dipolar part. The isotropic part results from contact interaction in which the unpaired electron has a finite density at the nucleus. Large contact interactions are expected only if the molecular orbital containing the unpaired electron has some s character. The dipolar part arises from the through-space effects and p -orbital contributions to the molecular orbital. Assuming that only the $2s$ and $2p$ orbitals ($2p$ is directed along the V—N and V—F bonds) of nitrogen and fluorine participate in bonding with the vanadium ion, isotropic and dipolar coupling constants can be expressed as

$$K(\text{cm}^{-1}) = \delta^2(8\pi g_e g_N \beta_e \beta_N) [|\Psi_{2s}(\text{O})|^2] / 3hc, \quad (10)$$

$$T(\text{cm}^{-1}) = \gamma^2(2g_e g_N \beta_e \beta_N) (\langle r^{-3} \rangle_{2p}) / 5hc \\ + (\alpha^2 g_e g_N \beta_e \beta_N / R^3 hc). \quad (11)$$

In these expressions, δ and γ are the molecular-orbital (MO) coefficients of the nitrogen and fluorine $2s$ and $2p$ orbitals, respectively. The second term of the equation for T is the direct dipole-dipole term in which $\alpha^2(0.994)$ is the unpaired electron density on the vanadium ion and R is the distance between the vanadium ion and nitrogen as well as fluorine. The MO coefficients δ and γ can be calculated from the equations above, using the observed values of K and T along with values of R taken from the crystal structure data. $|\Psi_{2s}(\text{O})|^2$ is taken from a Hartree-Fock calculation¹⁶ and $\langle r^{-3} \rangle_{2p}$ determined from the EPR study of atomic nitrogen and fluorine.¹⁷ The values used are¹⁶

	$ \Psi_{2s}(\text{O}) ^2$ (a.u.)	$\langle r^{-3} \rangle_{2p}$ (a.u.)
^{14}N	4.812	3.02025
^{19}F	11.374	7.5451

$R(\text{V—N and V—F})=2.02 \text{ \AA}$

The values of N_K , N_T , F_K , F_T , ϵ^2 , and γ^2 are

$$N_K(10^{-4} \text{ cm}^{-1})=12.3, \quad F_K(10^{-4} \text{ cm}^{-1})=6.5,$$

$$N_T(10^{-4} \text{ cm}^{-1})=1.42, \quad F_T(10^{-4} \text{ cm}^{-1})=1.5,$$

$$\delta^2=0.068, \quad \delta^2=0.033,$$

$$\gamma^2=0.024, \quad \gamma^2=0.013.$$

The values of δ^2 and γ^2 indicate that there is a small but significant delocalization of the unpaired electron from the vanadium ion to the nitrogen and fluorine ligands.

CONCLUSION

EPR studies on VO^{2+} -doped ethylenediammonium hexafluozirconate single crystals have revealed the presence of an abundance of nitrogen and fluorine superhyperfine structure at all orientations. There are two interstitial occupational sites for the VO^{2+} ion with an occupancy ratio to 10:1.

ACKNOWLEDGMENTS

We thank Professor K. Rama Reddy for constant encouragement. We also thank Mr. K. Balarama Murty and Mr. N. Saratchandran for providing us with high-purity zirconium oxide. We are indebted to C. I. L. University of Hyderabad, for the use of their EPR spectrometer facilities.

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