EPR of VO^{2+} Doped $Cd_2ZrF_8 \cdot 6H_2O$ Single Crystals

Geetha Jayaram and V. G. Krishnan
Physics Department, Osmania University, Hyderabad – 500007, India

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X-band EPR measurements have been carried out on VO^{2+} doped single crystals of $Cd_2ZrF_8 \cdot 6H_2O$. The angular variation of the ^{19}F superhyperfine structure did show that the VO^{2+} ion occupies an interstitial site with C_{4v} symmetry.

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Introduction

The magnetic complex associated with VO^{2+} ions in $M^I{}_2M^{II}(SO_4)_2 \cdot 6H_2O$ Tutton salts is the vanadyl pentahydrate $[VO(H_2O)_5]$ complex. In these crystals V^{4+} substitutes M^{II} ions, an one water molecule of the $M^{II}(H_2O)_6$ octahedron is replaced by O^{2-}. Since VO^{2+} possesses strong directional properties it is interesting to give a complete description of the $M^{II}(H_2O)_6$ complex in the crystal. Conclusive evidence regarding the orientation of the complex in Tutton salts was provided only by an ENDOR study of VO^{2+} in $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$ [1]. The proton superhyperfine structure (SHFS) along certain orientations did show that the V^{4+} ion, substituting the Mg^{2+} ion, is lifted out of the equatorial plane containing the four water molecules. In $(NH_4)_3AlF_6$, VO^{2+} formed VOF_5^{3-} according to the observed Fluorine (^{19}F, $I=1/2$) SHFS [2].

Recently we undertook a series of studies in lattices where both interstitial and substitutional occupation sites were possible for transition metal impurities. In ethylenediammonium hexafluorozirconate, vanadyl ions were shown to occupy two types of interstitial sites with the help of the ^{14}N and ^{19}F SHFS [3], whereas VO^{2+} in 1,5-pentanediammonium hexafluorozirconate was found to occupy an interstitial site with the EPR spectra exhibiting a transition from isotropy to anisotropy between 353 K and 77 K [4]. In the case of Mn^{2+} doped $Cd_2ZrF_8 \cdot 6H_2O$, Mn^{2+} occupied the Zr^{4+} site [5]. This was unusual in view of the existence of an isomorphous $Mn_2ZrF_8 \cdot 6H_2O$ [6]. Here we report an EPR study of VO^{2+} doped $Cd_2ZrF_8 \cdot 6H_2O$.

Experimental

5 mm^3 sized single crystals were grown from an acidic solution containing CdF_2 and ZrF_4 in stoichiometric ratio in 40%. Hydrofluoric acid. The VO^{2+} impurity content in the solution was $<0.1\%$ and in the crystals <100 ppm. $Cd_2ZrF_8 \cdot 6H_2O$ monoclinic [7] with space group B2/b and unit cell dimensions $a=11.464$ Å, $b=13.732$ Å, $c=8.223$ Å and $\gamma=119.82°$ with $Z=4$.

In the CdF_4O_3 polyhedron the arrangement of atoms is pentagonal bipyramidal. The equatorial plane is formed by CdF_4O with two oxygens occupying the apical positions. The Cd-F distances vary between 2.295 Å and 2.483 Å. Eight fluorines form a distorted cube around the Zirconium ion. These can be divided into two sets of four fluorines with Zr-F distances in each set varying between 2.074 Å and 2.132 Å. Figure 1 (a) and (b) show the geometry around the Cd^{2+} and Zr^{4+} ions.

EPR spectra were recorded at room temperature on Varian E-12 and JEOL–RE-3X spectrometers operating in the X-band (9.42–9.46 GHz), employing 100 kHz magnetic field modulation.

Results

EPR spectra were recorded in two mutually perpendicular planes. In a general direction in the *ab** plane (*b** chosen perpendicular to *a*-axis), the spectrum was complicated due to a number of weak lines, presumably due to the interaction of the ^{51}V unpaired electron ($S=1/2$, $I=7/2$), with more than one equivalent as well as inequivalent fluorines. This would split the Vanadium hyperfine lines into smaller compo-

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Reprint requests to Dr. G. Jayaram.

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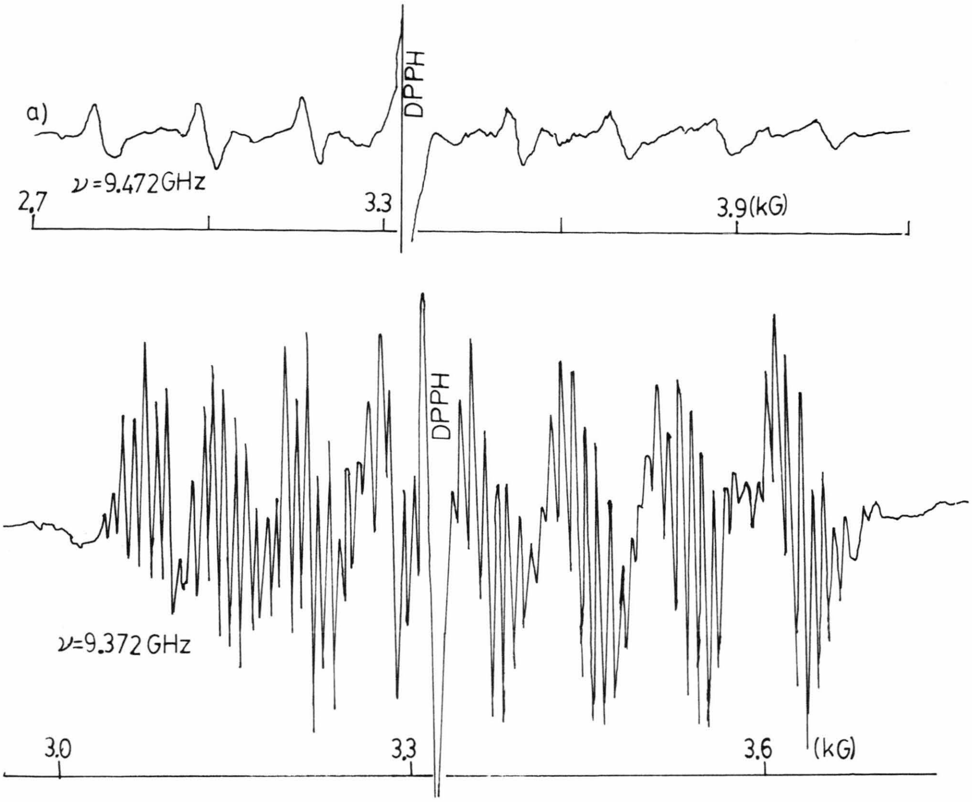

Fig. 1. a) CdF_4O_3 polyhedron and b) ZrF_8 polyhedron in $Cd_2ZrF_8 \cdot 6H_2O$.

nents. Angular variation showed that the eight hf lines had their maximum separation on either side of the α-axis making an angle of $(16+2)^\circ$. However, these hyperfine lines were broad, $\Delta H_{pp} = 25-35$ G (Figure 2 (a)). A slight rotation from these directions resulted in the splitting of the 8 hyperfine lines into a large number of weak lines which could not be followed in the angular variation. This feature was seen throughout the *ab** plane. The large linewidth could be attributed to unresolved ^{19}F SHFS.

In the *b*c* plane the spectrum consisted of eight closely spaced vanadium hyperfine lines, each of which was split into ten components. A rotational study in this plane showed no measurable angular variation of the hf lines, a feature typical of axial symmetry at the VO^{2+} sites. The only change seen throughout this plane was in the positions of the superhyperfine components. There was considerable overlap among these lines for the low field ^{51}V hf lines. Figure 2(b) shows a typical well resolved spectrum in the *b*c* plane.

The spin-Hamiltonian used to describe the spectrum is given by

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

The magnetic field positions of the Vanadium hf lines along the z-axis are calculated by the following general formula for rhombic symmetry:

$$H_z(m_I) = H_z^0 - A_z m_I - [(A_x^2 + A_y^2)/4 H_z^0][I(I+1) - m_I^2].$$

For the case of axial symmetry we have

$$A_z = A; \quad A_x = A_y = B; \quad g_z = g_\parallel; \quad g_x = g_y = g_\perp,$$

The expression describing the line positions along a perpendicular direction is obtained by a cyclic permutation of the subscripts of the above equation. The evaluated parameters are given in Table 1 along with other reported values.

From the angular variation of the spectra in the VOF_4 plane, A_{max} $(^{19}F_{eq})$ and A_{min} $(^{19}F_{eq})$ are calcu-

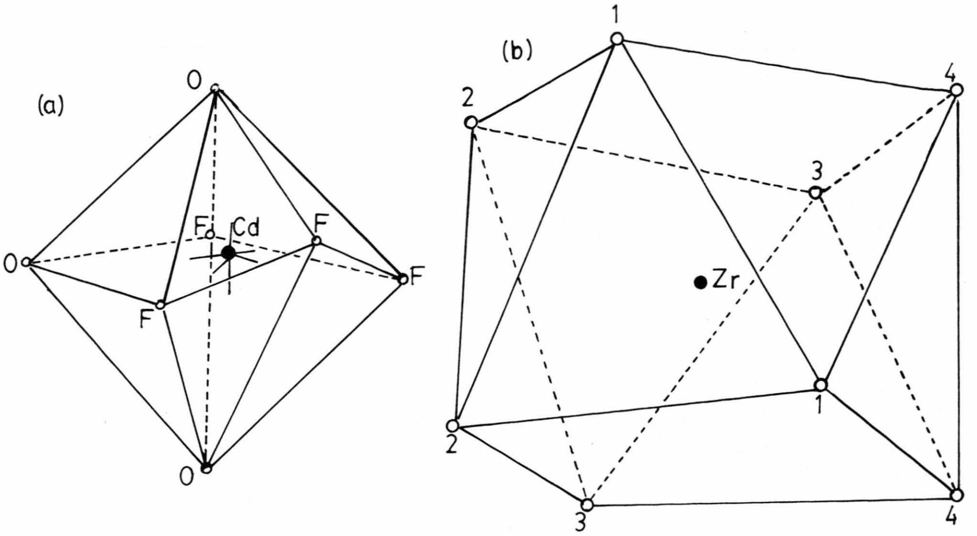

Fig. 2. EPR spectrum a) in the ab^* plane for H oriented at +18° with respect to a-axis and b) in the b^*c plane.

Table 1. Spin-Hamiltonian parameters of VO^{2+} ions in some lattices.

System	$g_{\parallel}$	$g_{\perp}$	A^*	B^*	A_{max}^* (^{19}F)	A_{min}^* (^{19}F)	Ref.
$Cd_2ZrF_8 \cdot 6H_2O$	1.935	1.981	185	76.4	17.1	8.3	This work
$[H_3N(CH_2)_2NH_3] \cdot ZrF_6$	1.956	1.997	179	68	9.5	5.0	[3]
$(NH_4)_3AlF_6$	1.937	1.977	178	64	34.7	13.4	[2]
$(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$	1.933	1.981	183	71.4	–	–	[12]
$(NH_4)_2InCl_5 \cdot H_2O$	1.945	1.985	173	63.8	–	–	[8]
$(NH_4)_2SbCl_5$	1.948	1.979	169	62.8	–	–	[11]
$(NH_4)_2Zn_2(SO_4)_3$	1.934	1.979	183	72.5	–	–	[8]
$NH_4Al(SO_4)_2 \cdot 12H_2O$	1.933	1.981	183	71.4	–	–	[8]

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

lated and given in Table 1 along with corresponding values for VO^{2+} in $[H_3N(CH_2)NH_3]ZrF_6$ and $(NH_4)_3AlF_6$.

Discussion

In earlier studies the vanadyl ion was found to accupy sites where a) the V-O bond replaces an M-O bond as in Tutton salts and langebenites [8], hexaurea AlX_3 ($X = ClO_4$, Cl, Br, I) [9, 10], and b) the V-O bond in oriented perpendicular to the plane containing the MX_4 ion (X = Cl, Br) as in $(NH_4)_2SbCl_5$ [11]. From the structure of $Cd_2ZrF_8 \cdot 6H_2O$, four fluorines and one oxygen surround the Cd^{2+} ion forming the equatorial plane (Figure 1 (a)). The Cd atom is lifted above this plane by 0.3 Å. The F-Cd-F bond angles deviate considerably from orthogonality, viz., 62.3°, 80.5° and 64.1°. These features prevent the four fluorines from being equivalent for any orientation of the external magnetic field. Hence the V-O bond orienting itself along a Cd-O bond does not explain the above observation.

We consider two possible orientations of the V-O bond with reference to the distorted cube of eight fluorines around the Zr^{4+} ion: The V-O bond 1) replaces any of the Zr-F bonds, 2) is in a position intermediate to any two Zr-F bonds, resulting in three distinct mutually perpendicular orientations. In the first case, if the shortest pair of Zr-F bonds are replaced, then the probability of replacing the remaining three pairs of Zr-F bonds would decrease with increasing bond lengths, as observed in $(NH_4)_2Zn(SO_4)_2 \cdot 6H_2O$ [12]. One would then expect four sets of eight hf lines with varying intensities. The second possibility would result in three sets of eight lines along a general direction. But when the magnetic field is along one of the three V-O bond orientations, the spectrum would consist of one set of eight lines with maximum separation and a second set with minimum separation and twice the intensity. This is due to one V-O bond oriented parallel and two V-O bonds oriented perpendicular to the magnetic field. The observed spectra did not correspond to either of the above two possibilities.

The ten SHFS lines could be considered as two sets of five lines due to two independent sets of four fluorines. The V^{4+} ion occupies an interstitial position in the plane formed by either set of four fluorines within the distorted ZrF_8 cube (Figure 1(b)). The V-O bond is oriented perpendicular to the plane and makes an angle of +18° with the *a*-axis. When the magnetic field is along the V-O bond of one of the VOF_4 complexes, the SHFS on each of the ^{51}V hf lines is smeared and appears only as a broadening. This is due to the two fluorine planes being relatively twisted to each other by about 40°. Figure 3 shows the orientation of the V-O bonds as well as the twisting of the fluorine planes. It is not unusual for the V-O bond to bring about small twists or tilts of the VOF_4 complexes [13].

From the comparison of the parameters for ^{19}F in VO^{2+} doped $Cd_2ZrF_8 \cdot 6H_2O$ and $(NH_4)_3AlF_6$ one can say that the arrangement of the four fluorines around V^{4+} ion is nearly the same in both the systems. Thus there is a fairly tight in-plane σ-bond. The super hyperfine splitting would have been larger in the former lattice if the V^{4+} ion had replaced the Zr^{4+} ion, because the Zr-F bond distances are rather short (2.074–2.132 Å).

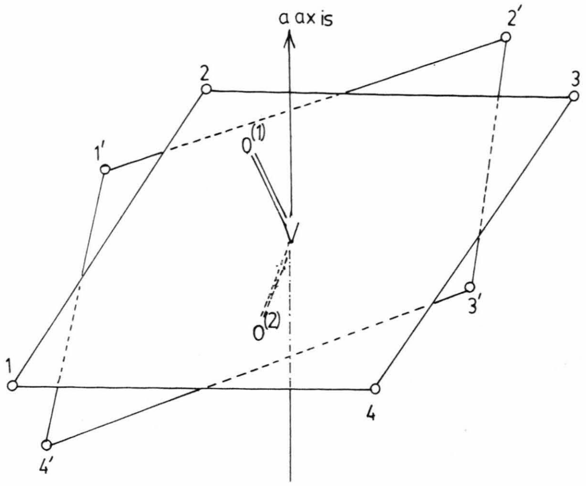

Fig. 3. Orientation of the V-O bond and relationship between the two VOF_4 complexes.

For single crystals of $Cd_2ZrF_8 \cdot 6H_2O$ it can thus be concluded that the paramagnetic VO^{2+} impurity prefer to occupy the unusual interstitial site surrounded by four fluorines rather than the substitutional Cd^{2+} or Zr^{4+} sites. This is in agreement with the general observation that the V-O bond prefers a square planar arrangement of the ligands that results in a C_{4v} site symmetry.

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