EPR Studies of VO\(^{2+}\) in Ba(ClO\(_4\))\(_2\) \cdot 3H\(_2\)O Single Crystals

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The results of an electron paramagnetic resonance (EPR) study of vanadyl ion VO\(^{2+}\) doped in single crystals of Ba(ClO\(_4\))\(_2\) \cdot 3H\(_2\)O are reported. The spectra indicated the presence of two substitutional and interstitial sites depending on the orientation. The spin-Hamiltonian parameters were determined from single crystal and powder EPR data. These parameters were found to be axial symmetric for the powder sample, whereas they showed deviations from axial symmetry for the single crystal.

1. Introduction

EPR studies of transition metal complexes give valuable information about the bonding of the central metal ion with the ligands. The bonding parameter is obtained from the spin-Hamiltonian constants which describe the resonance spectra. Since the vanadyl ion EPR spectrum is very sensitive to the crystalline-field environment, it has been the subject of a number of studies in crystals, some of which are alkaline earth formates [1–5], tutton salts [6–12], oxalates [13,14] and citrates [15,16]. The metal ion is usually surrounded by a distorted octahedron of oxygen ligands. However, the behaviour of unpaired electron in vanadyl complexes is dominated by the strong V = O bond. As a result, most of the complexes posses a square pyramid symmetry and the g and A tensors are found to be axially symmetric. It is, therefore, interesting to study the local symmetry and the bonding of the vanadyl complex by correlating EPR and optical results. In this paper, EPR studies have been carried out on VO\(^{2+}\) doped in single crystal of Ba(ClO\(_4\))\(_2\) \cdot 3H\(_2\)O (BPTH).

2. Crystal Structure

The crystal structure of BPTH is hexagonal bi-molecular with unit cell dimensions \(a = 0.72944\) nm and \(c = 0.96744\) nm. Two possible space groups, \(P6_3\) and \(P3_1m\), have been suggested in an X-ray crystallographic study [17]. It was found that the Ba atom is surrounded icosahedrally by six water and six perchlorate oxygen atoms. The \(C_{3v}\) symmetry of the ClO\(_4\) tetrahedron is along the c-axis of the crystal. The position of the protons is proposed to be between the water oxygen and the perchlorate oxygen. There are three protons near three oxygens in the base of each perchlorate tetrahedron. The proton positions have not been determined. The centro-symmetric structure differs from the non-centrosymmetric one only in a slight displacement of the ClO\(_4\) tetrahedron along the c-axis accommodating in the mirror plane.

3. Experimental Details

Commercial BPTH was from Aldrich. Single crystals were grown at room temperature from a saturated aqueous solution of BPTH to which a small amount of V\(_2\)O\(_5\) was added as impurity. When heavily doped, the crystals were dark grey and shapeless. EPR spectra were recorded on an X-band (~9.2 GHz) EPR spectrometer (Varian model E-109C) with 100 kHz field modulation. The crystals were mounted on a single circle goniometer which can be fitted with the EPR rectangular cavity operating in TE102 mode. The spectra were recorded as functions of the orientation of the magnetic field at intervals of 20° in the three mutually perpendicular planes \(bc\), \(a^*b\) and \(ca^*\) defined as morphologically shown in Figure 1. The microwave resonance frequency was determined by using a standard field marker (DPPH, \(g = 2.0036\)). EPR spectra of a powdered sample (crystal crushed to a fine powder) were recorded at room temperature (RT) and liquid nitrogen temperature (LNT).

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4. Results and Discussion

The EPR spectra of VO$_{2}^{+}$ doped in BPTH single crystals for three typical orientations are shown in Figure 2. For an arbitrary orientation of the magnetic field $B$, four sets of typical VO$_{2}^{+}$ spectra with two sets of strong intensity (in Fig. 2 b indicated with I and II) and two sets of much weaker intensity (in Fig. 2 a, c indicated with III and IV), characterised by eight VO$_{2}^{+}$ allowed hyperfine (hf) lines each were observed. Their intensities are found to be equal. Angular variation of the field positions of the hf lines corresponding to two sets of strong intensity are shown for the different orientations of $B$ about the axes $a^*$, $b$ and $c$ in Fig. 3, where $a^*$ refers to the direction perpendicular to the $bc$ plane. The analysis has been carried out only for the two strong groups (I, II), since the weak lines were quite difficult to follow.

The VO$_{2}^{+}$ ion has the electronic configuration (Ar$^{18}$) 3d$^{1}$. The EPR spectra of vanadyl complexes can be satisfactorily explained in terms of an unpaired electron ($S = 1/2$) interacting with a vanadium nucleus ($^{51}$V, 99.8% abundant, $I = 7/2$). The spectrum can be described in terms of a spin-Hamiltonian of the form

$$\mathcal{H} = \beta \mathbf{B} \cdot \mathbf{g} S + S \cdot \mathbf{A} I,$$

where the first and the second terms describe the electron Zeeman and nuclear hyperfine interactions, respectively. The spin-Hamiltonian parameters have their usual meaning. Additional terms, including quadrupole coupling, zero field splitting and nuclear Zeeman interactions, are sufficiently small to be neglected.

The $g^2$ and $A^2$ matrices corresponding to I, II complexes were diagonalized using standard procedures. The eigenvalues were found by calculating the second order perturbation term, and the eigenvectors were obtained in the $a^*$, $c$ and $b$ coordinate system. The $K$ values were evaluated by the use of a least squares fitting procedure [18–20], applicable to noncoincident principal axes of the $g^2$ and $A^2$ tensors. The values obtained from single crystals for VO$_{2}^{+}$ ions I and II and powder data at RT and at LNT are listed in Table 1. Although the powder spectra at RT and LNT have given almost the same EPR parameters, the powder spectrum shows axial symmetry as shown in Figure 4. The single crystal does not show axial symmetry due to low symmetry. It is obvious from the characteristics of the EPR spectrum of the polycrystalline sample that all the sites are chemically equivalent at RT and at LNT. BPTH contains two molecules in the unit cell. The variation of line positions of I and II ions indicates that these are two substitutional sites being chemically equivalent but magnetically inequivalent. It also showed that the morphologically chosen axes coincide with the crystallographic axes. When the magnetic field lies along all of the axes and in the $a^*b$ plane, the two sites become equivalent. Therefore the $a^*b$ plane is the intersection plane of two sites indicating the presence of a mirror plane. This strongly sup-

<table>
<thead>
<tr>
<th>Complex</th>
<th>Principal values (hf in units of $10^{-4}$ cm$^{-1}$)</th>
<th>Direction cosines</th>
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<tbody>
<tr>
<td></td>
<td>$g_{xx}$, $g_{yy}$, $g_{zz}$</td>
<td>$a^*$, $c$, $b$</td>
</tr>
<tr>
<td>I</td>
<td>$1.993 \pm 0.001$, $1.987 \pm 0.001$, $1.937 \pm 0.001$</td>
<td>$0.460$, $-0.882$, $-0.095$</td>
</tr>
<tr>
<td>II</td>
<td>$1.992 \pm 0.001$, $1.987 \pm 0.001$, $1.937 \pm 0.001$</td>
<td>$0.460$, $-0.882$, $-0.095$</td>
</tr>
<tr>
<td>Powder</td>
<td>$1.992 \pm 0.001$, $1.937 \pm 0.001$</td>
<td>$0.460$, $-0.882$, $-0.095$</td>
</tr>
<tr>
<td>at RT</td>
<td>$1.992 \pm 0.001$, $1.937 \pm 0.001$</td>
<td>$0.460$, $-0.882$, $-0.095$</td>
</tr>
<tr>
<td>at LNT</td>
<td>$1.992 \pm 0.001$, $1.937 \pm 0.001$</td>
<td>$0.460$, $-0.882$, $-0.095$</td>
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Fig. 2. The EPR spectra at RT of VO$_2^{2+}$ doped in BPTH crystal for a) $B$ in the direction of the $b$ axis, b) $B$ at an angle of 20° with the $b$ axis in the $bc$ plane, c) $B$ at an angle of 160° with the $a^*$ axis in the $a^*b$ plane.
ports the space group is $P6_3/m$. On the other hand, the weak lines (III, IV) were attributed to interstitial sites and found to be orientation dependent. The interstitial site was observed to be isotropic in the study of VO$^{2+}$ doped Barium formate [1], whereas it is found to be anisotropic in this study.

In the $a^*b$ plane, the lines indicated with I and II show maximum separation, while the lines indicated with III and IV show minimum separation. When the magnetic field is in the $a^*b$ plane, the spectrum shows a maximum at an angle of 60° with $a^*$ axis, and it shows minimum at 160°. The obtained values for these two oriented spectra almost equal the $A_{//}$ and $A_{\perp}$ values of the powder spectrum given in Table 1. These two special orientations correspond to a magnetic field almost parallel and perpendicular to the $V=O$ bonding of two sites.

Barium is surrounded icosahedrally by six water and six perchlorate oxygen atoms. It is most probable that the VO$^{2+}$ ions also have a similar environment of the substitutional sites. Thus the wavefunctions and expression for the spin-Hamiltonian parameters in the present case will be the same as those for the VO(H$_2$O)$_5^{2+}$. The spin-Hamiltonian parameters for VO(H$_2$O)$_5^{2+}$ are given in [21–24]:

$A_{//} = P \left[ -k - \frac{4}{7} \beta^2 - (g_e - g_\|) - \frac{3}{7} (g_e - g_\perp) \right]$, (2)

$A_{\perp} = P \left[ -k + \frac{2}{7} \beta^2 - \frac{11}{14} (g_e - g_\perp) \right]$. 
Fig. 4. The EPR spectrum of a powder sample of the VO$^{2+}$ doped in BPTH, a) at RT and b) at LNT.
where \( P \) is the parameter which is a measure of the radial distribution of the unpaired electron wavefunctions. \( P = 2.0023 g_N \beta_N ^2 \langle r^3 \rangle \), \( k \) is the Fermi contact parameter which is related to the unpaired electron density at the vanadium nucleus, and \( \beta_2 \) is the molecular orbital coefficient indicating the extent of overlap of the vanadium orbitals with ligand orbitals. As the ground state of the \( \text{VO}(\text{H}_2\text{O})^2^+ \) complex is a non-bonding orbital, one should expect a value of unity for \( \beta_2 \). The deviation from unity indicates the overlap of ligand orbitals. If \( \beta_2 \) is taken as unity [24], it is possible to make rough estimations of \( P \) and \( k \). Substituting the values of \( g //, g _\perp, A //, A _\perp \) evaluated from the powder EPR spectrum in the above equations, one gets \( P = -127 \times 10^{-4} \) cm\(^{-1}\) and \( k = 0.85 \). The values of \( P \) and \( k \) are close to the values observed for \( \text{VO}^2^+ \) in \( \text{Cd}(	ext{COO})_2\_3\text{H}_2\text{O} \) [13], \( \text{Cd}((\text{NH}_4)_2\text{SO}_4\_6\text{H}_2\text{O} [25] and (\text{NH}_4)_2\text{Mg}(\text{SO}_4\_6\text{H}_2\text{O} [7], where the ion is surrounded by oxygen or water molecules in which the covalency effect is small. In addition to this, the principal values of the \( g \) and \( A \) tensors of \( \text{VO}^2^+ \) in BPTH are approximately in the same order as in previous studies on various lattices [7, 9, 13, 14, 25]. The deviations of the spin-Hamiltonian parameters from the axial symmetry in Table 1 indicate that in BPTH the ligand field symmetry of oxygens around \( \text{VO}^2^+ \) is lower than axial.

6. Concluding Remarks

- \( \text{VO}^2^+ \) enters the BPTH lattice, both substitutionally and interstitially. The substitutional incorporation is much more favourable than the interstitial one, and both are orientation dependent.
- There is no detail information about BPTH crystal. The EPR results support the \( P6_3/m \) space group among \( P6_3 \) and \( P6_3/m \), both of which are suggested by X-ray study for the BPTH crystal.
- Heavy doping affects the crystallisation.
- The powder spectra show axial symmetry but the crystal data show deviation from axial symmetry.
- The large value of \( k \) indicates a large contribution to the hyperfine constant by the unpaired S-electron and probably also a contribution from spin polarisation.