



# EPR and optical absorption studies of vanadyl impurity in zinc potassium phosphate hexahydrate single crystal

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## ABSTRACT

Electron paramagnetic resonance (EPR) study of VO<sup>2+</sup> doped zinc potassium phosphate hexahydrate single crystal is carried out. The angular variation of the spectra is studied in the three crystallographic planes. The principal value of spin Hamiltonian parameters  $g$  and  $A$  and the direction cosines which principal axes make with the crystallographic axes are determined. The observed values are site I:  $g_{\parallel} = 1.9664 \pm 0.0002$ ,  $g_{\perp} = 1.9973 \pm 0.0002$ ,  $A_{\parallel} = 150 \pm 2 \times 10^{-4}$ ,  $A_{\perp} = 60 \pm 2 \times 10^{-4} \text{ cm}^{-1}$ ; site II:  $g_{\parallel} = 1.9276 \pm 0.0002$ ,  $g_{\perp} = 1.9921 \pm 0.0002$ ,  $A_{\parallel} = 155 \pm 2 \times 10^{-4}$  and  $A_{\perp} = 62 \pm 2 \times 10^{-4} \text{ cm}^{-1}$ . By comparison of direction cosines of  $g$  from EPR with the direction cosines of different bonds obtained from crystal structure data it is ascertained that the VO<sup>2+</sup> ion occupies Zn<sup>2+</sup> substitutional sites. The optical absorption study of the crystal at room temperature is also carried out. The bands observed in the optical absorption spectrum are attributed to d–d transitions. The EPR results together with the optical data are employed to estimate the molecular orbital (MO) coefficients. These MO coefficients (also called bonding coefficients) are further used to discuss the nature of bonding of VO<sup>2+</sup> ion with different ligands in the crystal.

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## 1. Introduction

Electron paramagnetic resonance (EPR) spectroscopy is extremely sensitive to the unpaired electron environment when magnetic nuclei are present in atoms of organic or inorganic molecules. The EPR studies of paramagnetic ion doped in diamagnetic host yield important information about the magnetic properties of matter, chemical bonding, dynamic interactions of spins with lattice, nuclear moments, the possibility of nuclear alignment and orientational properties of the host lattice [1–3].

Vanadium is one of the transition group elements that have been studied with EPR spectroscopy in divalent, trivalent and tetravalent states. The tetravalent state, V<sup>4+</sup> exists as VO<sup>2+</sup> ion with a single unpaired d-electron. The 3d<sup>1</sup> configuration of vanadyl ion allows electron paramagnetic resonance to be observed at ambient temperatures [4–6]. The behavior of unpaired electron in vanadyl complex is dictated by the strong V=O bonding and most of the complexes possess C<sub>4v</sub> symmetry. EPR studies of VO<sup>2+</sup> ion in a variety of host lattices have been reported [7–14]. These studies may be classified into two categories depending upon the nature of ligands present in the host lattice. If the lattice has water or sulfate ions as ligands, VO<sup>2+</sup> ion has fixed orientation and in other lattices it has preferential orientations. Literature survey

shows that most of the results are explained by considering the substitutional site for VO<sup>2+</sup> impurity. However, in a recent work [15], both substitutional and interstitial sites for VO<sup>2+</sup> impurity are reported. Therefore, interest is developed to ensure the location of the impurity ion and nature of bonding in zinc potassium phosphate hexahydrate (ZPPH) single crystal.

ZPPH is analogous to bio-mineral, struvite (MgNH<sub>4</sub>PO<sub>4</sub>·6H<sub>2</sub>O), a constituent of renal and vesical calculi. Various physical and chemical properties of these crystals are described by mineralogists, chemists and physicians due to their biomedical importance [16]. In this paper, we report the EPR and optical absorption studies of VO<sup>2+</sup> ion in ZPPH single crystal and deduce the spin Hamiltonian and molecular orbital (MO) coefficients. These MO coefficients are further used to discuss the nature of bonding of VO<sup>2+</sup> ion with different ligands in the crystal. EPR and optical study of VO<sup>2+</sup>:ZPPH has been done earlier by Ravikumar et al. [17]. They observed only one substitutional site in EPR and three bands in optical absorption while in our study we observed two substitutional sites in EPR and four bands in optical absorption.

## 2. Crystal structure

ZPPH [ZnKPO<sub>4</sub>·6H<sub>2</sub>O] single crystals are orthorhombic and belong to space group Pmn2<sub>1</sub>. The unit cell dimensions are  $a = 5.964$ ,  $b = 5.808$  and  $c = 12.495 \text{ \AA}$  with two molecules per unit cell [16,18]. The structure consists of PO<sub>4</sub> tetrahedra and the

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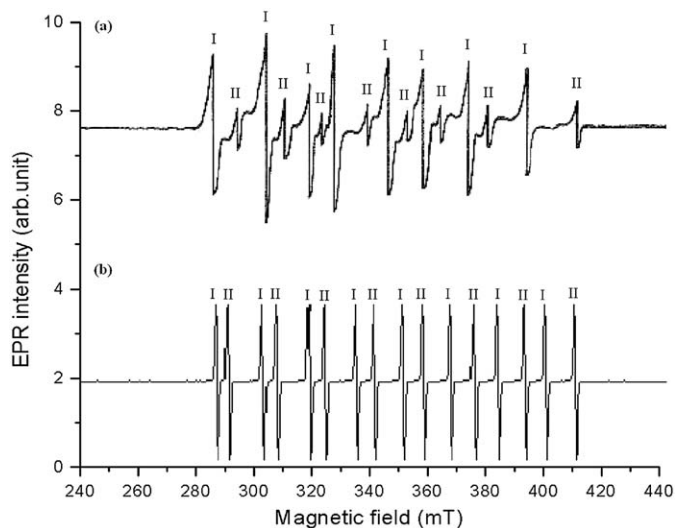
metal ion surrounded by six water molecules in a very distorted octahedral configuration.

### 3. Experimental

Single crystals of ZPPH were grown at room temperature by slow evaporation of equimolar aqueous solutions of potassium dihydrogen phosphate and zinc sulphate. Vanadyl sulfate solution of 0.2% was added as paramagnetic impurity. Good single crystals of  $\text{VO}^{2+}$  doped ZPPH with well-defined faces were obtained in about 20 days. The EPR spectra were recorded using Varian X-band EPR spectrometer (9.5 GHz) at room temperature. Single crystals were mounted at the end of goniometer device with the help of quick fix (adhesive) along the three mutually perpendicular axes **a**, **b** and **c** and the spectra were recorded at every  $10^\circ$  rotations. The magnetic field was measured with the help of Varian flux meter using proton probe and Hewlett-Packard frequency counter. The optical spectra were recorded at room temperature on a Unicam 5625 UV/Visible spectrophotometer in the wavelength range 325–925 nm.

### 4. Results

A typical EPR spectrum of ZPPH: $\text{VO}^{2+}$  single crystal in *ab* plane when magnetic field is parallel to **c** axis is shown in Fig. 1(a). The spectra consist of two prominent and distinguishable sets of octets ( $S = 1/2$ ,  $I = 7/2$ ) with different intensities indicated as site I and site II. The spectrum corresponding to site I is of higher intensity than that corresponding to site II. This indicates the presence of two magnetically inequivalent  $\text{VO}^{2+}$  sites with different spin populations. The EPR spectrum is simulated using EasySpin [19] with the values of parameters  $g_{\parallel} = 1.9664 \pm 0.0002$ ,  $g_{\perp} = 1.9973 \pm 0.0002$ ,  $A_{\parallel} = 150 \pm 2 \times 10^{-4}$  and  $A_{\perp} = 60 \pm 2 \times 10^{-4} \text{ cm}^{-1}$  for site I and  $g_{\parallel} = 1.9276 \pm 0.0002$ ,  $g_{\perp} = 1.9921 \pm 0.0002$ ,  $A_{\parallel} = 155 \pm 2 \times 10^{-4}$  and  $A_{\perp} = 62 \pm 2 \times 10^{-4} \text{ cm}^{-1}$  for site II (obtained as discussed later) and is given in Fig. 1(b). The simulated spectrum shows that the quality of the fit with the



**Fig. 1.** (a) EPR spectrum of  $\text{VO}^{2+}$  doped ZPPH single crystal when magnetic field is parallel to **c** axis (line position (mT): 281.2, 287.7, 297.2, 303.7, 310.7, 315.1, 318.7, 327.6, 335.1, 342.1, 346.0, 350.6, 359.6, 366.0, 378.5, 393.0). (b) The simulated EPR spectrum of  $\text{VO}^{2+}$  doped ZPPH single crystal when magnetic field is parallel to **c** axis (frequency 9.5 GHz, orientation [0, 0, 0]) (line position (mT): 282.2, 286.2, 296.7, 301.2, 310.1, 315.1, 325.6, 331.1, 340.6, 346.6, 355.0, 362.6, 369.6, 377.5, 384.0, 393.5).

recorded spectrum is not good (experimental and simulated line positions are given in Fig. 1). Figs. 2(a–c) show the angular variation plot in three mutually perpendicular planes.

The EPR spectrum of vanadyl complexes can be described in terms of an unpaired electron ( $S = 1/2$ ) interacting with the nuclear spin of a vanadium nucleus ( $I = 7/2$ ) with the spin Hamiltonian [20]

$$\mathcal{H} = \mu_B \mathbf{S} \cdot \tilde{g} \cdot \mathbf{B} + \mathbf{S} \cdot \tilde{A} \cdot \mathbf{I} + \mathcal{H}_Q + \mathcal{H}_N \quad (1)$$

in which the first and second terms represent electronic Zeeman and hyperfine interactions, respectively.  $\mathcal{H}_Q$  and  $\mathcal{H}_N$  are quadrupole and nuclear Zeeman interaction terms, respectively, given by

$$\mathcal{H}_Q = -\{e^2 Q / I(2I - 1)\} \langle r_q^{-3} \rangle \langle L_{\parallel} | \alpha | L_{\parallel} \rangle \times (1/2) \{3(\mathbf{L} \cdot \mathbf{I})^2 + 3/2(\mathbf{L} \cdot \mathbf{I}) - L(L + 1)I(I + 1)\} \quad (2)$$

$$\mathcal{H}_N = \gamma \mu_N \mathbf{B} \cdot \mathbf{I} \quad (3)$$

where the symbols have their usual meaning [20]. The magnitudes of quadrupole and nuclear Zeeman interactions for the present system are determined to be  $4.48 \times 10^{-20}$  and  $1.62 \times 10^{-15} \text{ cm}^{-1}$ , respectively, and thus are neglected due to being sufficiently small [21]. The principal values of spin Hamiltonian parameters are obtained by the diagonalization procedure of Schonland [22]. In this method  $g^2$  and  $g^2 A^2$  are measured for rotations of the magnetic vector in three crystal planes. From this  $g$  and  $gA$  tensors are calculated in terms of crystal coordinate system. Then the principal  $g$  and  $A$  values and their axes are obtained by diagonalizing the respective tensors. The evaluated spin Hamiltonian parameters are given in Table 1 together with the parameters obtained by earlier workers in similar systems for comparison purpose.

The optical absorption spectrum of  $\text{VO}^{2+}$  in ZPPH single crystal at room temperature is depicted in Fig. 3. Four characteristic bands are observed at 820(2), 655(3), 490(4) and 375(5) nm, respectively.

### 5. Discussion

According to crystal structure [16,18], there are two distinguishable  $\text{Zn}^{2+}$  atoms in the lattice of ZPPH. If the vanadyl ion enters the lattice substitutionally in place of  $\text{Zn}^{2+}$ , then the  $\text{V}=\text{O}$  can orient itself along any one of the four metal oxygen ligand directions. In this case, the EPR spectra will show two sites in general orientations and single site along three crystallographic axes. The  $\text{V}=\text{O}$  can also orient in any two of these directions  $\text{Zn}-\text{O}_w$  in which case one can observe two sets of eight hyperfine lines along the three crystallographic axes. Hence the observed two groups of eight hyperfine lines are due to two magnetically distinct vanadium complexes orienting in two different directions as shown in Fig. 4. Using the principal parameters in the spin Hamiltonian equation, the magnetic field positions were calculated for all orientations in the three planes. Angular variation of the field positions of hyperfine lines corresponding to two sets was plotted for different orientations of the magnetic field about the three crystallographic **a**, **b** and **c** axes. Reasonably good agreement is found between the calculated and observed magnetic field positions.

The exact  $\text{V}=\text{O}$  orientations can be found by correlating the experimentally obtained direction cosines with the calculated ones from the crystal structure data [16,18]. The calculated and experimental direction cosines are given in Table 2. From this table it is seen that the direction cosines of  $g_z$  for site I are in reasonable agreement with the direction cosines of the  $\text{Zn}-\text{O}_w(3)$  bond and the direction cosines of  $g_z$  for site II with the  $\text{Zn}-\text{O}_w(4)$  bond. This shows that the  $\text{V}=\text{O}$  orientation is along the  $\text{Zn}-\text{O}_w(3)$

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