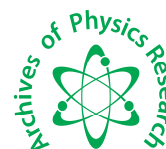




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Electron paramagnetic resonance and optical absorption study of VO²⁺ doped in cadmium ammonium sulphate hexahydrate

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ABSTRACT

Results of Electron Paramagnetic Resonance (EPR) and Optical Absorption (OA) studies of VO²⁺ ion doped in Cadmium Ammonium sulphate Hexahydrate (CdASH), which is the only Tutton salt in which the metal ion belongs to the second long period in the periodic system, in the powder form have shown that in all these hosts a pentahydrate vanadyl complex VO(H₂O)₅²⁺ doping the OA studies shows that these complexes reflect almost C_{4v} symmetry. Correlating the optical and EPR data, the molecular orbital coefficients have been obtained and discussed. It has been concluded that both EPR and optical results are in conformity with each other.

Keywords: EPR, Optical absorption, M. O. coefficients, VO²⁺, Cd(NH₄)₂(SO₄)₂.6H₂O

INTRODUCTION

The hexahydrated double sulphates (Tutton salts) [1-3] with the general formula M'M''(SO₄)₂.6H₂O where M' is K, Rb, Cs and NH₄ etc. and M'' is Mg, Zn and Cd etc. form an interesting isomorphous series of salts for EPR and OA studies. Few authors have made both EPR and OA investigations on the same host [4-6]. We have carried out EPR and OA studies of VO²⁺ doped in Cd(NH₄)₂(SO₄)₂.6H₂O written as CdASH. CdASH is the only Tutton salt in which the metal ion belongs to the second long period in the periodic system and the results are presented in this paper.

MATERIALS AND METHODS

CdASH belongs to the well known family of isomorphous Tutton salts. The unit cell of the Tutton salts is monoclinic and contains two formula units related by the space group symmetry p2₁a. The divalent cations are at positions (0 0 0) and (½ ½ 0) in the unit cell and are surrounded by distorted water octahedra with Cd-W distances between 0.2051-0.0033 nm. The unit cell parameters are a = 0.9324 nm, b = 1.2597 nm, c = 0.6244 nm, and β = 107° 8'. CdASH powder was prepared by slow evaporation of aqueous solution of equimolar CdSO₄ and (NH₄)₂SO₄, with doping of vanadyl sulphate (0.50%). The solution was filtered and allowed to crystallize. These crystals were then crushed into fine powder. The EPR spectra of this powder was recorded at X band (9.4 GHz) on JEOL-JESRE2XEPR set at RT (Fig.1). The optical absorption spectra of CdASH doped with VO²⁺ was recorded on CIBA corning spectrophotometer 2800 (England) at RT (Fig. 2)

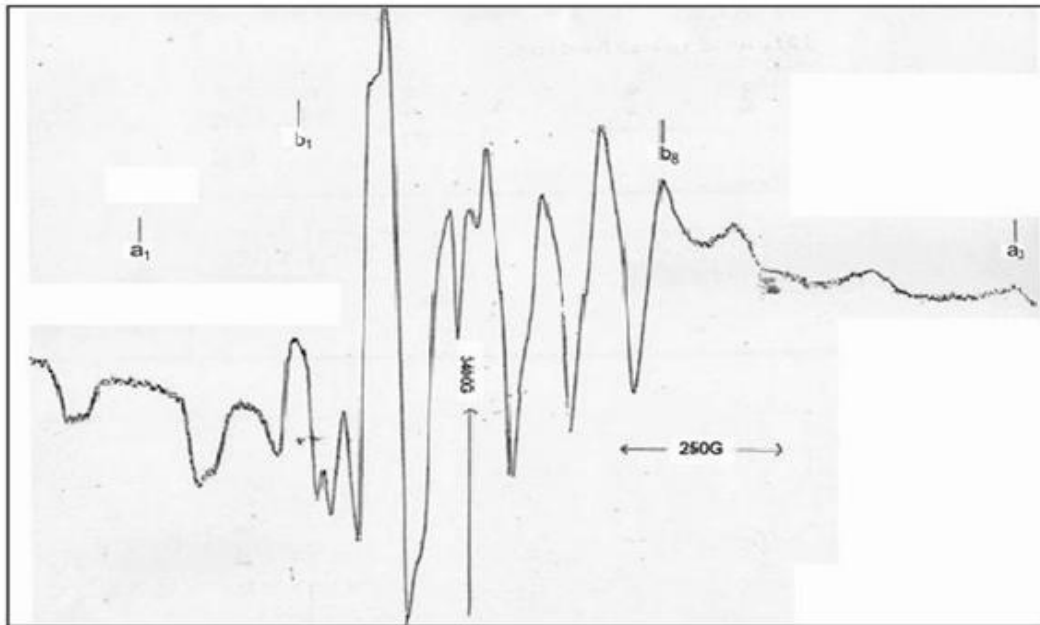


Fig 1. X-band EPR spectrum of Vanadyl doped CdASH powder at RT.

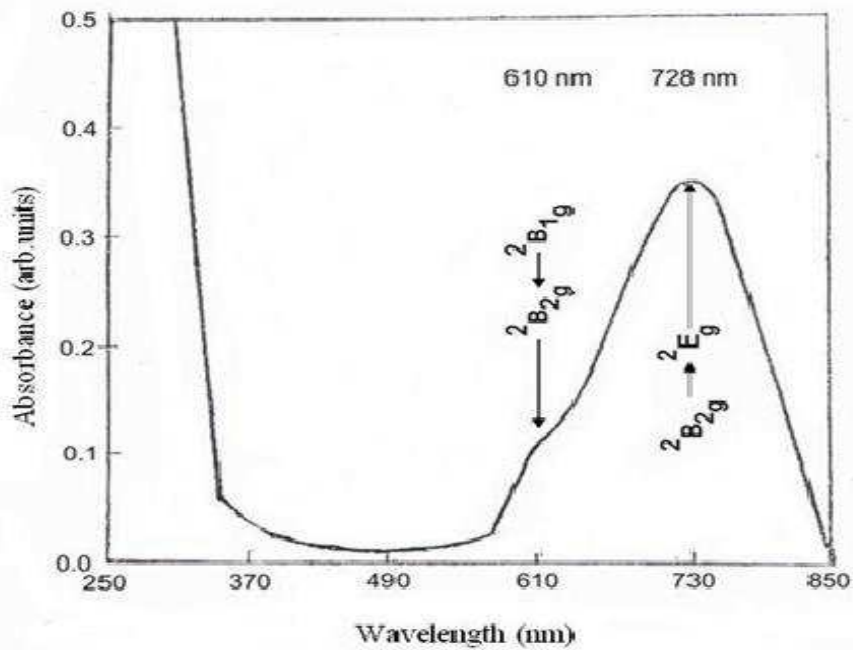


Fig 2. The optical absorption spectrum of Vanadyl doped CdASH

Theory

Vanadium ($Z=23$), a member of d block transition series, in its tetravalent (V^{4+}) state has a great affinity to oxygen and is invariably found to exist in a stable molecular ion form VO^{2+} , known as vanadyl ion, which is supposed to have a tetravalent vanadium ion $V^{4+}[(Ar)^{18}3d^1]$ and a closed shell O^{2-} ion $[(Ne)^{10}]$ and has been the subject of

extensive EPR and optical investigation in a variety of hosts [2-6]. The description of the molecular ion VO^{2+} is based on a LCAO-MO (Linear combination of atomic orbitals - molecular orbitals) theory of $\text{VO}(\text{H}_2\text{O})_5^{2+}$ by Ballhausen and Gray. They have shown that the d electron occupies a non-bonding orbital of b_2 symmetry and the resulting ground state is an orbital singlet. Under the molecular orbital scheme for $\text{VO}(\text{H}_2\text{O})_5^{2+}$, the 3d, 4s and 4p metal orbitals take part in bonding with $2s, 2p\sigma$ ($2p_z$) and $2p\pi$ - ($2p_x, 2p_y$) orbitals of (metal) oxide oxygen, and the sp hybrid orbitals for the water oxygen. The longer vanadium to oxygen bond length (0.23nm) and the orientation of combining orbitals (forming a π bond) has a little overlap and appears to be unlikely. The transformation scheme for the vanadium, while specifying the form of molecular orbitals, is shown in Table 1.

In $\text{VO}(\text{H}_2\text{O})_5^{2+}$, the V=O bond is strongest (bond length 0.167 nm), the four waters in the square plane are equivalent being attached more strongly (bond length 0.23nm) than the axial water molecule, which is the weakest bond (bond length 0.24 nm) of all. With these considerations, the bonding in $\text{VO}(\text{H}_2\text{O})_5^{2+}$ can be pictured as in table 1.

For vanadyl ion with a single unpaired electron ($S=1/2$) interacting with nuclear spin $I = 7/2$, the spin - Hamiltonian including the electron Zeeman and nuclear hyperfine terms respectively, can be written as

$$\mathbb{H} = \vec{S} \cdot \vec{g} \cdot \vec{H} + \vec{S} \cdot \vec{A} \cdot \vec{I} \quad (1)$$

Where symbols have their usual meanings. The g and A possess coincidental axes. The complete Hamiltonian requires additional nuclear Zeeman and Quadrupolar terms in equation (1), which are found to be sufficiently small for VO^{2+} ion, and are neglected [8]. Since the g and A tensors were found to be axial within experimental errors, the expressions given by Bleaney [9] for the solution of the spin Hamiltonian were used and the values were determined which are found to be

$$A_{\parallel} = 188.09 \pm 0.1\% (10^{-4} \text{ cm}^{-1}) ; \quad g_{\parallel} = 1.930 \pm 0.1\%$$

$$A_{\perp} = 79.11 \pm 0.1\% (10^{-4} \text{ cm}^{-1}) ; \quad g_{\perp} = 1.980 \pm 0.1\%$$

The single unpaired d electron of VO^{2+} ion occupies two energy levels viz. 2E_g and ${}^2T_{2g}$ the latter, being the ground state. In an octahedral symmetry, these levels split further in (${}^2B_{2g}, {}^2E_g$) and (${}^2B_{1g}, {}^2A_{1g}$) giving rise to two transitions Δ_{\parallel} and Δ_{\perp} , shown in Fig 2. These levels have been interpreted satisfactorily on the basis of crystal field theory (CFT).

The optical absorption spectrum at RT has been analysed using the following relations.

$$\Delta g_{\parallel} = -8\lambda\beta^2 / (\Delta_{\parallel}) \quad (2)$$

$$A_{\parallel} = P \left[-\left(\frac{4}{7} + K\right) - \frac{8\lambda\beta^2}{\Delta_{\parallel}} - \frac{6A_{\perp}}{7\Delta_{\perp}} \right] \quad (3)$$

$$\Delta g_{\perp} = -\frac{2A_{\perp}}{\Delta_{\perp}} \quad (4)$$

$$A_{\perp} = P \left[\left(\frac{2}{7} - K\right) - \frac{11}{7} - \frac{A_{\perp}}{\Delta_{\perp}} \right] \quad (5)$$

β^2 and γ^2 are the bonding coefficients of the excited orbitals,

Δ_{\parallel} and Δ_{\perp} are the energy splitting in the host as discussed above,

λ is the spin orbit coupling parameter which is assumed to be equal to 170 cm^{-1} for vanadyl ion,

P is dipolar coupling constant, K is Fermi contact parameter. The values of $\Delta_{\parallel} = 16393 \text{ cm}^{-1}$ and $\Delta_{\perp} = 13740 \text{ cm}^{-1}$ are obtained from EPR spectra of VO^{2+} given in Fig.(1)

RESULTS AND DISCUSSION

The EPR and optical absorption data are used to solve equations (1-5) and we have obtained $K = 0.88$, $\beta^2 = 0.87$ and $\gamma^2 = 0.76$ and $P = -123 \times 10^{-4} \text{ cm}^{-1}$. The parameter β^2 and γ^2 represent the in-plane σ and out of plane π bonding respectively. K related to the unpaired electron density at the vanadium nucleus, has been found to be very sensitive to even small deformations of the electron orbitals of VO^{2+} which results in a change of spin polarization of inner s-shells caused by the unpaired electron. The typical values of K ranges from 0.60 to 0.88 for various vanadyl complexes, the values of β^2 and γ^2 indicate [12] that both in-plane σ – and out of plane π -bonding are of covalent nature. $(1-\beta^2)$ and $(1-\gamma^2)$ are the measures of covalent bonding, so that the unpaired electron is delocalised. The values MO parameters obtained by us do not differ much from those other such hosts in which the ion is surrounded by water molecules in an identical manner (Table 1). Hence, it may be concluded that vanadyl VO^{2+} complexes in this salt possesses a C_{4v} symmetry and the oxygen atom of VO^{2+} ion replaces a water molecule of water molecule of water octahedron to form $\text{VO}(\text{H}_2\text{O})_5^{2+}$ groups. Further a diluted $\text{NH}_4\text{SO}_4\text{VO}(\text{H}_2\text{O})_5$ complex in the host lattice is formed as a result of VO^{2+} ion doping. Hence we conclude that both EPR and optical results are in conformity with each other. Transformation scheme for metal and ligand orbitals in C_{4v} symmetry has been given in the following table-

Table 1: Metal and ligand orbitals in C_{4v} symmetry

Presentation	Vanadium orbitals	Ligand orbitals
a_1	$3d_z^2+4s$ $4s-3d_z^2$ $4p_x$	σ_5 $(\sigma_1+\sigma_2+\sigma_3+\sigma_4)/2$ σ_6
e	$3d_{xz}, 3d_{yz}$ $4p_x, 4p_y$	$\Pi_5(2p_x, 2p_y)$ $(\sigma_1-\sigma_2)/2^{1/2}, (\sigma_2-\sigma_4)/2^{1/2}$
b_1	$3d_x^2-y^2$	$(\sigma_1-\sigma_2+\sigma_2-\sigma_4)/2^{1/2}$
b_2	$3d_{xy}$

Table 2 A comparison of g and A values and MMO parameters of VO^{2+} doped in other hexahydrated compounds

S.N.	Compound	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}	β^2	γ^2	K	Reference
1.	$\text{Cs}_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.935	1.98	182	73	0.82	0.64	0.88	4
2.	$(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.933	1.981	183	72	0.81	0.88	0.87	4
3.	$\text{Cs}_2\text{Cd}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.921	1.987	177	70	0.91	0.60	0.88	4
4.	$\text{Cd}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$	1.937	1.850	188	79	0.87	0.76	0.88	Present work

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