

EPR AND OPTICAL ABSORPTION OF VANADYL DOPED MIXED TUTTON SALT

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Optical absorption and EPR studies in a mixed, Tutton salt doped with vanadyl ions were done. The results of both the studies have been further correlated to estimate the various molecular orbital and other parameters involving the doped vanadyl ion and the surrounding host lattice.

KEYWORDS : Vanadyl ion, electron paramagnetic resonance, line width.

INTRODUCTION

Vanadium found in many natural system [1] and the V^{51} nucleus, approximately 100% abundant, has a large nuclear magnetic moment and a nuclear spin of $7/2$. The electron paramagnetic resonance is ideally suited to identify vanadium through its characteristic eight line spectrum. The $4+$ oxidation state of vanadium almost exclusively exists in the VO^{2+} (Vanadyl) ion. The magnetic susceptibility data on various vanadyl complexes [2, 3] shows exhibits that the magnetic moment is close to the spin only value for a single unpaired electron. The vanadyl ion has consequently been used as an EPR probe in a variety of system to study phenomena ranging from phase transition to dynamics and structure of complex biological systems [1, 4].

The $4+$ state of vanadium has a single d - electron. It requires a non-cubic crystalline field for EPR to be observed and this requirement is fulfilled by vanadyl complexes. The chemistry and bonding of vanadyl complexes has been studied quite in detail by Selbin [3] and spectral properties of many vanadyl complexes have been discussed by him and Boucher *et al.* [3, 5].

The EPR results of vanadyl ions in alkali halides have been reported. For these systems too, the net crystalline electric field on the VO^{2+} site was non-cubic.

The Tutton salts are, further, a group of isomorphous compounds with monoclinic symmetry. In these salt doped vanadyl ions, are likely to occupy the divalent cation sites, which have a surrounding of distorted octahedron of water groups. The field at the divalent cation site of Tutton salt is thus inherently non-cubic and is likely to be further distorted due to the effect of $V=O$ bond itself, thus fulfilling the requirement for observing the EPR of doped vanadyl ions.

THEORY

In the work of Borcherts and Kikuchi [6] the formation of vanadylsulphatepenta hydrate complex has been reported. While considering the occupancy of B^{2+} ion sites in $Zn(NH_4)_2(SO_4)_2.6H_2O$ (ZASH) by vanadyl ion, this appears quite untenable. The B^{2+} ion sites

are surrounded by six water groups, thus there is no scope of SO_4 entering the octahedral cage of H_2O groups. The only tenable situation, however, is that one of the six water groups is made to leave its normal site for an interstitial position in the lattice. The $\text{V}=\text{O}$ would then point along such a vacant H_2O group site and in this process, a $\text{VO}(\text{H}_2\text{O})_5$ complex would be formed.

The types of water groups with oxygens as O(7), O(8) and O(9) may have to leave their normal sites on addition of vanadyl ions. It is known that the $\text{B}^{2+}-\text{O}(7, 8, 9)$ distances are not all equal in a Tutton salt. As per the crystal data reported $\text{B}-\text{O}(7)$ and $\text{B}-\text{O}(8)$ bonds are nearly equal and larger than the $\text{B}-\text{O}(9)$ bonds, which are the shortest in a Tutton salt. Further, all the three oxygens O(7), O(8), O(9) and also their water groups are bonded in the lattice differently through respective hydrogen bonding. Which of the three possible $\text{V}=\text{O}$ orientations will be more plausible in a Tutton salt and will obviously depend upon the bonding in the lattice of the oxygen O(7), O(8) or O(9) to be replaced. Now, as reported $\text{B}-\text{O}(9)$ is the shortest bond and the strongest. Accordingly, replacing the O(9) water groups by $\text{V}=\text{O}$ bond would be the most different process and $\text{V}=\text{O}$ alignment along this direction would be the rarest.

The observed 20 : 5 : 1 intensity for the EPR spectra of vanadyl ions in zinc ammonium sulphate hexahydrate Tutton salt accordingly suggests that the weakest spectrum should belong to the $\text{V}=\text{O}$ bond along the B-O (9) orientation. The B-O (7) and B-O (8) bonds would subsequently correspond to other orientations of $\text{V}=\text{O}$. Out of two remaining orientations, the stronger would depend upon, which of O(7) or O(8) can be made to leave the normal site with better ease.

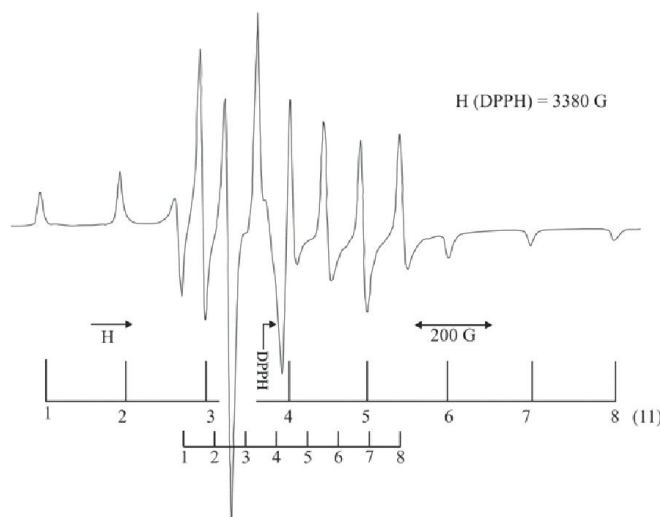


Fig. 1. EPR spectam of VO^{2+} doped in mixed system of $(\text{NH}_4)_2\text{Mg}_{0.5}\text{Zn}_{0.5}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

The observation of only sites in VO^{2+} : cobalt ammonium sulphate hexahydrate (CASH) with intensity ratio 1 : 1 further suggests that B-O(9) bond is strongest in this host and cannot be broken. However, the other two bonds B-O(7) and B-O(8) being equally strongly breakable, attribute equal probability for the two orientations of $\text{V}=\text{O}$ occupancy.

The results of EPR studies by Saraswat & Upreti [7] in the system VO^{2+} - CKSH further suggest a quite strong B-O(9) bond and the remaining two B-O(7) and B-O(8) bonds to have bond-strengths in the reverse ratio of 5:3 and thus to be actually 3 : 5. The unique case of nikil ammonium sulphate hexahydrate (NASH) and nikilpotassium sulphate hexahydrate (NKSH)

hosts suggests that all B-O bonds are quite strong in such salts and are not broken at all, with energy exchanges involved during substitution of V=O in Tutton salts.

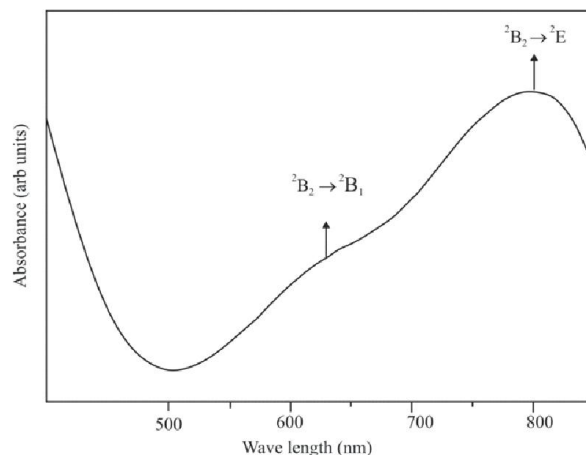


Fig. 2. Optical absorption spectrum of VO^{2+} doped in mixed Mg, Zn Ammoniumtutton salt single crystals at room temperature, showing clearly two bands corresponding to the tetragonal symmetry as $12,530 \text{ cm}^{-1}$ and $15,870 \text{ cm}^{-1}$.

The transition of energy levels is drawn in Fig. 1 with 2B_2 as the lowest level and 2E , 2B_1 and 2A_1 as the higher vacant levels. The expected transitions with energy changes E_1 , E_2 and E_3 are depicted here for the transitions ${}^2B_2 \rightarrow {}^2E$, and ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2A_1$ respectively.

The reported optical absorption spectra for vanadyl ions are due to Ballhausen & Gray [9]. These workers have reported spectra for the complex $\text{VO}(\text{H}_2\text{O})_5^{2+}$ as two broad maxima at approximately $13,000 \text{ cm}^{-1}$ and $16,000 \text{ cm}^{-1}$ which correspond respectively to $b_2 \rightarrow e_\pi^*$ and $b_2 \rightarrow b_1^*$ electron transitions. It is compared well with the results of other workers [10-15] about optical absorption of VO^{2+} in a variety of hosts, including solvents, glasses and single crystals.

EXPERIMENTAL

VO^{2+} - doped $(\text{NH}_4)_2\text{Mg}_{0.5}\text{Zn}_{0.5}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ crystals were grown by slow evaporation of a saturated solution in distilled water, containing $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 and ZnSO_4 in the molar ratio 2 : 1 : 1 About 1% by weight of vanadylsulphate was also added to the solution before the growth of crystals. In a typical growth process about 50 ml of saturated solution as above were kept for evaporation in a beaker at 10°C . Good crystals with shining faces appeared after about 15 days and majority of these had prismatic appearance.

As the EPR spectrum of a powdered sample itself furnishes sufficient information about the parameter g_{\parallel} , g_{\perp} , A and A_{\perp} , the present studies were devoted to the powdered samples. This avoided critical alignment conditions. The spectra were recorded at RT using Varian E-line century series spectrometer E-109. The DPPH was used as the field marker and its magnetic field was calibrated with the help of Varian E - 500 digital NMR gaussmeter. The optical absorption spectra were recorded with the help of a Hitachi UV-Visible spectrometer in very thin slices of crystal samples.

The energy of transition from the level 2B_2 to 2E is denoted by E_1 , from the level 2B_2 to 2B_1 as E_2 and that from 2B_2 to 2A_1 as E_3 . Kivelson and Lee [12] have described how the overlapping of ligand orbitals leads to the modification of g and A - tensor components for VO^{2+} ion complex with tetragonal symmetry.

RESULTS AND DISCUSSION

The results obtained from the EPR and optical absorption studies in the mixed system of $(NH_4)_2Mg_{0.5}Zn_{0.5}(SO_4)_2 \cdot 6H_2O$ are discussed as under.

(i) EPR Studies :

The EPR spectrum of VO^{2+} - doped mixed Tutton salt system, in the powdered polycrystalline phase as shown in fig. 1 and also upper and lower contours are not simultaneously seen in the first derivative absorption spectrum. The turning points of both parallel and perpendicular spectra are well defined. Now, using the positions of these turning points for the eight hyperfine lines and field expressions for such transitions $g \parallel$, $g \perp$, & $A \parallel$ & $A \perp$ have been evaluated as for an EPR centre with g -value of $\cong 2$, the value of 1 gauss is equivalent to $0.9 \times 10^{-4} \text{ cm}^{-1}$ and then in energy units the signs of A and $A \perp$ have however been found to be negative.

(ii) Optical Studies :

The optical absorption spectrum in the UV-Visible range for the system $(NH_4)_2Mg_{0.5}Zn_{0.5}(SO_4)_2 \cdot 6H_2O : VO^{2+}$ is given in Fig. 2. Two prominent bands at $12,530 \text{ cm}^{-1}$ and $15,870 \text{ cm}^{-1}$ have been observed and correspond to the energy differences E_1 and E_2 respectively.

(iii) Correlation of EPR and Optical Studies :

The turning points with only one side (up/down) contours indicate the positions of parallel components of the most populated Mg/Zn sites in the mixed Tutton salt. The perpendicular components however present both up and down contours. The components of g and A tensors calculated from the turning point positions, thus represent the behaviour of such a type of site for VO^{2+} .

So far optical absorption spectrum is concerned only two broad bands have been observed. This indicates that the crystalline environment of VO^{2+} in both Mg^{2+} & Zn^{2+} types of octahedral of water groups are nearly identical and the observed bands are due to overlap of such pairs of bands of VO^{2+} spectra.

CONCLUSION

It is seen that both g and A terms possess three unique principal values for all these systems. Further, barring the case of $KMgClSO_4 \cdot 3H_2O$ host the g and A tensors in general possess near tetragonal symmetry.

The Fermi-contact parameter K for the above systems has been found to range between 0.72 and 0.86. It is related to unpaired electron density at the vanadium nucleus and is due to s-character of the magnetic spin of the vanadium. The s-character results basically from the partial unpairing or polarization of the inner electrons as a result of interaction with unpaired d-electrons. The quite large value of 0.86 for K in the mixed Tutton salt doped with VO^{2+} , indicates that there is a large contribution to hyperfine coupling constant due to unpaired s-electron, probably through spin polarization.

The value of P which represents dipole-dipole interaction of electronic and nuclear moments has been found to be $120.4 \times 10^{-4} \text{ cm}^{-1}$ for VO^{2+} in the mixed Tutton salt. The standard value of P for a free VO^{2+} ion is however $160 \times 10^{-4} \text{ cm}^{-1}$ [13]. The observed value of P for VO^{2+} in the mixed Tutton salt is thus considerably reduced up to 75% of the ideal value. This indicates a significant amount of covalent bonding in the VO complexes doped in the mixed Tutton salt.

The covalency parameters α and γ show large variation from one system to another [13, 17-19]. However, α and γ values in different systems cannot be compared due to their dependence on λ , the spin-orbit coupling parameter. We assumed λ to be 249 cm^{-1} in congruence with Khasa *et al* [14] and Mancaster & Parke [16]. However, Kivelson & Lee [12] and Dev Prasad Raju *et al* [13] assumed this to be 170 cm^{-1} only.

The dipolar terms A_{\parallel} and A_{\perp} are about the same for all the systems reported [14, 15, 20, 21], except the case of $\text{LiPbBTe} : 9 \text{ Mol } \% \text{ V}_2\text{O}_5$, wherein these are quite lower. The PK values range between $87.0 \times 10^{-4} \text{ cm}^{-1}$ to $105.83 \times 10^{-4} \text{ cm}^{-1}$ for these systems. The $\Delta g_{\parallel} / \Delta g_{\perp}$ values further show a large variation to be between 1.256 & 3.017 for different systems. The theoretical value of $\Delta g_{\parallel} / \Delta g_{\perp}$ is 1 of a regular octahedral system. The deviation of this ratio ($\Delta g_{\parallel} / \Delta g_{\perp}$) from 1 indicates departures from the regular octahedral coordination of VO^{2+} . The ratio is maximum for VO^{2+} in the present mixed Tutton salt host and indicates that among the systems mentioned, the present one has the extreme tetragonal distortion of electric field at the vanadium site.

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