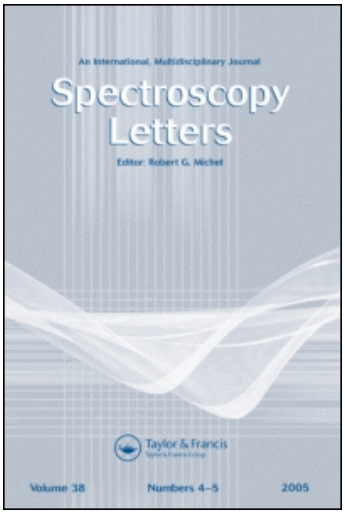


**Spectroscopy Letters**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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Online publication date: 05 April 2010

**To cite this Article** Kripal, Ram and Shukla, Ashutosh Kumar(2010) 'EPR and Optical Absorption Studies of $VO^{2+}$-Doped Diammonium Hexaaqua Magnesium(II) Sulfate', Spectroscopy Letters, 43: 3, 196 — 201
**To link to this Article: DOI:** 10.1080/00387010903284356
**URL:** http://dx.doi.org/10.1080/00387010903284356

*Spectroscopy Letters*, 43:196–201, 2010

ISSN: 0038-7010 print/1532-2289 online
DOI: 10.1080/00387010903284356

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# EPR and Optical Absorption Studies of $VO^{2+}$-Doped Diammonium Hexaaqua Magnesium(II) Sulfate

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**ABSTRACT** Electron paramagnetic resonance (EPR) studies of $VO^{2+}$ impurity ion in single crystals of diammonium hexaaqua magnesium(II) sulfate are carried out at 9.5 GHz (X-band) at room temperature. Different spin-Hamiltonian parameters are determined. $VO^{2+}$ is expected to enter the lattice substitutionally. Superhyperfine splitting is also observed. An EPR study of a powder sample is done that supports the data obtained from single crystal studies. Optical absorption studies are also performed at room temperature. The crystal field parameter ($D_q$), tetragonal parameters ($D_s$ and $D_t$), and various bonding parameters are evaluated to estimate the covalency and nature of bonding of $VO^{2+}$ with its different ligands.

**KEYWORDS** crystal field, distortion, optical absorption, spin Hamiltonian

## INTRODUCTION

Vanadyl ion is the most stable biatomic ion.[1] Due to short V=O bond, the unpaired electron is in a nondegenerate state. This leads to resolved electron paramagnetic resonance (EPR) spectra. The hyperfine interaction is anisotropic and therefore sensitive to orientation, conformation, and rotational relaxation.[2] As a result, interesting changes are found in the EPR and optical spectrum in different crystalline field environments.[3–7] An EPR study of vanadyl ion doped in diammonium hexaaqua magnesium (II) sulfate has been carried out by several workers[8–10] showing different results. Narayana et al.[8] have reported the presence of only one site, and Jayrama and Sobhanadri[9] and Misra and Sun[10] have reported the presence of two sites in this lattice. In order to confirm one of these results an X-band EPR and optical absorption study of vanadyl ion doped in diammonium hexaaqua magnesium(II) sulfate has been performed at room temperature. The present study shows the presence of two sites and the spin Hamiltonian parameters are found to be in agreement with Misra and Sun.[10] The study is further used to find the energy level ordering of different orbital levels and to discuss the nature of bonding of metal ion with its ligands.

Received 19 July 2009; accepted 24 August 2009.

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## CRYSTAL STRUCTURE

Diammonium hexaaqua magnesium(II) sulfate is a member of the isomorphous series $(NH_4)_2M''(SO_4)_2(H_2O)_6$, known as Tutton salt and the crystal structure is known to be monoclinic[11] with space group $P2_1/a$. The crystallographic axes are $a = 9.316$, $b = 12.596$, and $c = 6.198$A°, $Z = 2$, and the angle $\beta = 107.79°$.

## EXPERIMENTAL

$VO^{2+}$-doped diammonium hexaaqua magnesium(II) sulfate crystals were grown by slow evaporation of ammonium sulfate and magnesium sulfate solution together with .01 mole percent of vanadyl sulfate. The EPR measurements were carried out using an X-band EPR spectrometer (9.5 GHz) with 100-kHz field modulation at room temperature. Crystals were mounted at the end of a goniometer device along three mutually orthogonal *a, b*, and $c^*$ axes and spectra were recorded at every 10° rotation about these axes. The magnetic field was measured using a Varian flux meter and a proton probe with the help of Hewlett-Packard frequency counter. The optical absorption spectra were recorded on Unicam 5625 UV-Visible spectrophotometer (Cambridge, UK) in the wavelength range 325–925 nm.

## RESULTS AND DISCUSSION

The EPR spectrum of vanadyl ion doped in diammonium hexa aqua magnesium(II) sulfate recorded with B at 10° from b axis is shown in Fig. 1. Powder EPR spectrum were also recorded and are shown in Fig. 2. There is clear indication of the presence of two nonequivalent vanadium centers consisting of a pair of equivalent ions in the single crystal spectra (Fig. 1). The angular variation of EPR spectra for B in the $c^*a$ plane is shown in Fig. 3. In this plane, there are only two sets of eight hyperfine lines consistent with the crystal structure.[11] In order to obtain spin Hamiltonian parameters, the crystal was rotated for every 10° rotation in the three orthogonal planes. The spin Hamiltonian parameters are fitted with the following Hamiltonian

$$H = \mu_B(g_x B_x S_x + g_y B_y S_y + g_z B_z S_z) + A_x S_x I_x + A_y S_y I_y + A_z S_z I_z \quad (1)$$

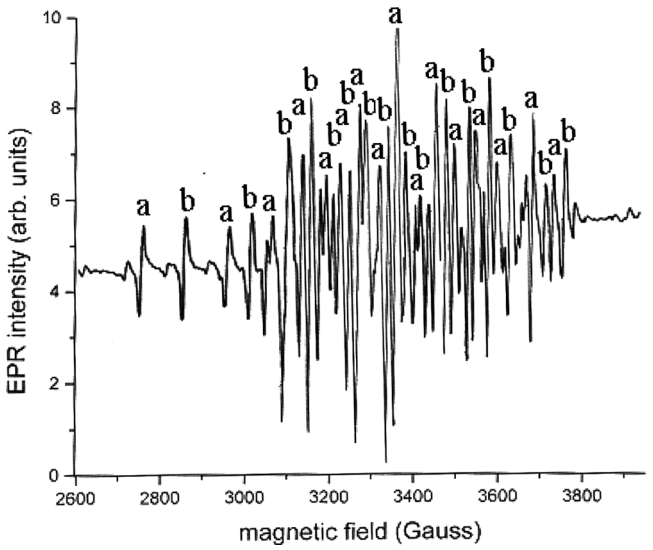


**FIGURE 1** **Single-crystal EPR spectrum of vanadyl ion in diammonium hexaaqua magnesium(II) sulfate (B at 10° from *b* axis). (a and b represent lines due to pair of equivalent ions of $VO^{2+}$ sites I and II, respectively).**

which includes only electronic Zeeman and hyperfine interaction terms. Additional terms of quadrupole and nuclear Zeeman interactions are neglected because these are sufficiently small.

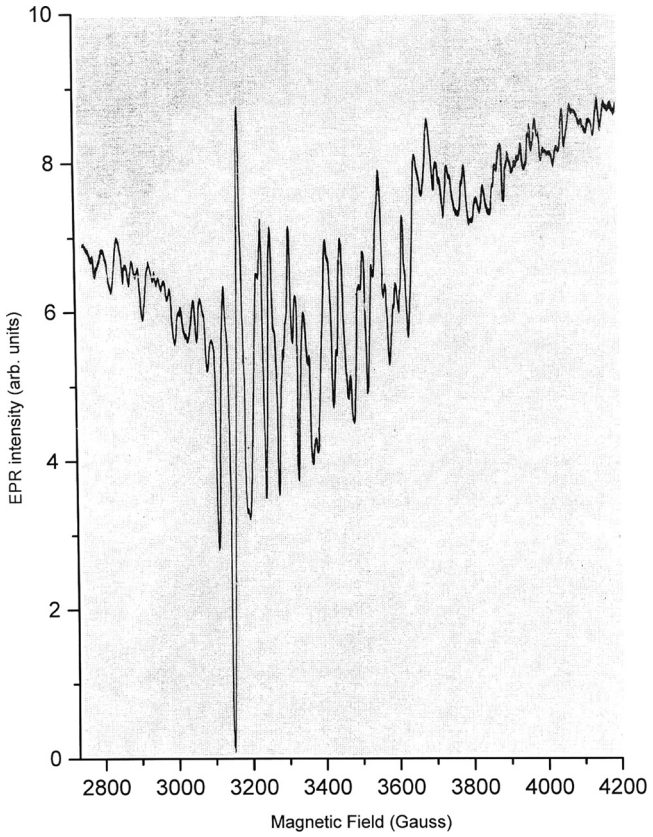


**FIGURE 2** **Powder EPR spectrum of vanadyl ion in diammonium hexaaqua magnesium(II) sulfate.**

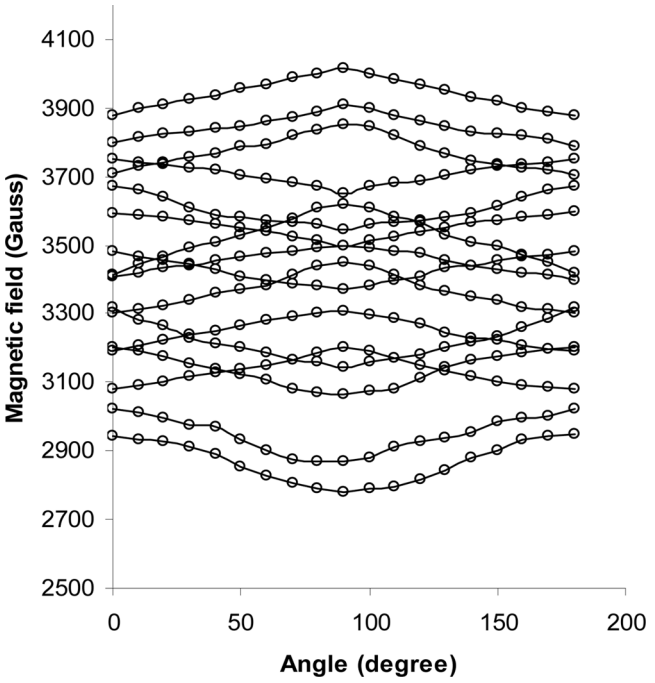


**FIGURE 3** **Angular variation of EPR line positions for vanadyl ion in diammonium hexaaqua magnesium(II) sulfate (B in the *c** *a* plane).**

Schonland's[12] procedure is adopted to obtain spin Hamiltonian parameters and the parameters obtained for both sites are shown in Table 1 along with the data obtained from powder spectrum. The results obtained by Misra and Sun,[10] Jayram and Sobhanadri,[9] and Narayana et al.[8] are also given in this table for comparison purposes. The involvement of ligands in hydrogen bonding results in a decrease of oxygen to vanadium donation along the *z*-axis, with an increase in the in-plane donation.[8] This results in a decrease of hyperfine splitting. Reduction in the hyperfine splitting is justified because the water molecules are involved in very strong hydrogen bonding.[11] In general, the stronger the in-plane donor atom, the less covalent the axial vanadium–oxygen bond is. This may be rationalized by considering charge buildup on the metal. As the charge on the metal increases, the charge donation from the axial oxygen decreases. Then as the in-plane ligand field increases, the axial ligand field should decrease.[13] The $g_y$ should therefore be larger for weak-field ligands binding to the in-plane positions of $VO^{2+}$. The in-plane ligand field strength is small for water.[13] This is consistent with the above discussion.

To further ascertain whether the vanadyl ion takes up a substitutional position in diammonium hexaaqua magnesium sulfate the direction cosines of different bonds are computed with the X-ray data[11] and compared with the value of direction cosine of V=O axis obtained from EPR study. These data are given in Table 2. Because the Mg-O(9) bond length is shorter than the Mg-O(8) and Mg-O(7) bond lengths, the former is stronger and therefore it is easy to replace the farthest water molecule from the metal atom to form the vanadyl sulfate pentahydrate along the direction of water molecules. Thus, the observed two sites can be correlated with the different metal water distances and the V=O orientations are confirmed by comparing the direction cosines. From Table 2 it is concluded that the V=O orientation is along the Mg-O(7) bond direction for site I and along the Mg-O(8) bond direction for site II.

In the EPR spectrum, superhyperfine splitting is also seen. This splitting may result from the delocalization of vanadium electron over the ligands. This superhyperfine splitting has been evaluated and found to be about 5 gauss, which is in agreement with the previous results of Misra and Sun.[10]

To estimate the covalency, the Fermi contact term *k* is calculated, which relates the amount of unpaired

**TABLE 1** **Spin Hailtonian Parameters for Vanadyl Ions in Diammonium Hexaaqua Magnesium(II) Sulfate**

| | $g_z$ | $g_x$ | $g_y$ | $A_z$ (G) | $A_x$ (G) | $A_y$ (G) |
|---|---|---|---|---|---|---|
| Site I | 1.9673 ± .0002 | 1.9940 ± .0002 | 2.0105 ± .0002 | 153 ± 2 | 106 ± 2 | 106 ± 2 |
| Site II | 1.9723 ± .0002 | 1.9887 ± .0002 | 2.0174 ± .0002 | 101 ± 2 | 83 ± 2 | 83[a] ± 2 |
| Powder | 1.9542 ± .0002 | 1.9827 ± .0002 | 1.9827 ± .0002 | 90 ± 2 | 58 ± 2 | 58 ± 2 |
| Site I | 1.9424 ± .0020 | 1.9826 ± .0020 | 1.9859 ± .0020 | 186 | 79 | 74[9] |
| Site II | 1.9384 ± .0020 | 1.9827 ± .0020 | 1.9862 ± .0020 | 189 | 79 | 69 |
| Site I | 1.9420 | 2.0062 | 1.9875 | 200 | 78 | 80[8] |
| Site II | 1.9372 | 2.0025 | 1.9972 | 197 | 78 | 88 |
| Site I | 1.936 ± .002 | 1.981 ± .002 | 1.979 ± .002 | 196 ± 2 | 81 ± 2 | 79[7] ± 2 |

[a]Present study.

**TABLE 2** Direction Cosines of Different Bonds in Diammonium Hexaaqua Magnesium(II) Sulfate

| | *a* | *b* | *c** |
|---|---|---|---|
| Mg-O(7) | .7580 | .6322 | .4969 |
| Site I | .7829 | .5088 | .3581 |
| Mg-O(8) | .7179 | .6620 | .0900 |
| Site II | .7525 | .5626 | .3420 |

electron density at the nucleus and bonding coefficients.[14] Neglecting the spin–orbit effects of ligands, Maki and McGarvey[15] have given the following expressions

$$A_{\|} = -Pk - \frac{4}{7}\beta_2^2 P - (g_e - g_{\|})P - \frac{3}{7}(g_e - g_{\perp})P$$
$$A_{\perp} = -Pk + \frac{2}{7}\beta_2^2 P - \frac{11}{14}(g_e - g_{\perp})P \quad (2)$$

where $P = 2g_n\beta_n\beta\langle r^{-3}\rangle$ $P$ is the dipolar term that accounts for the direct dipole–dipole interaction of electron and nuclear moments. The hyperfine coupling constants are related to the direct dipolar term and an indirect dipolar interaction due to anisotropy in g value. Using the relations

$$g_0 = \frac{1}{3}(g_{\|} + 2g_{\perp}) \quad (3)$$

and

$$A_0 = \frac{1}{3}(A_{\|} + 2A_{\perp}) \quad (4)$$

and combining with the equation mentioned above one gets the following expression:[16]

$$A_0 = -Pk - (g_e - g_0)P \quad (5)$$

In order to compute the value of Fermi contact term, $A_{\|}$ and $A_{\perp}$ are taken to be negative and the value of spin–orbit coupling constant is taken to be 136 G.[17] The value of Fermi contact term has been found to be 0.88 (site I) and 0.63 (site II). These values are smaller than the values obtained for VO $(H_2O)_5^{2+}$ complex, where no covalency effects are observed. This is in agreement with the values obtained in complexes with appreciable covalency effects.[13] The non-zero value of the Fermi contact term is assumed to arise from spin polarization. With increase in covalency the value of $k$ decreases. Therefore, in the present case the decrease in $k$ value may be expected due to involvement of water molecules in strong hydrogen bonding.

The optical absorption spectrum of vanadyl ions in single crystals of diammonium hexaaqua magnesium(II) sulfate is shown in Fig. 4. It consists of four bands in contradiction to a previous study reported by Agarwal and Chand.[18] They have reported only three bands at 13,000, 16,100, and 30,000 $cm^{-1}$, whereas in our case four bands are observed at 12,270, 15,698, 20,790, and 26,455 $cm^{-1}$, respectively. Except for the higher energy band at 26,455 $cm^{-1}$, all other bands are attributed to the d-d transitions. Based on crystal field theory the first three bands at 12,270, 15,698, and 20,790 $cm^{-1}$ are assigned to transitions $^2B_2 \rightarrow {}^2E$ ($d_{xy} \rightarrow d_{xz,yz}$), $^2B_2 \rightarrow {}^2B_1$ ($d_{xy} \rightarrow d_x^2 - y^2$), and $^2B_2 \rightarrow {}^2A_1$ ($d_{xy} \rightarrow d_z^2$), respectively. The higher energy band at 26,455 $cm^{-1}$ is probably the charge transfer band[19] arising due to the promotion of electron from the filled bonding level $e_{\pi}^b$ to nonbonding level $b_2$. Thus, this band is assigned to $e_{\pi}^b \rightarrow {}^2B_2(b_2)$ (from filled level to $d_{xy}$ level). Using the following expressions[11] for the various transitions the octahedral field parameter

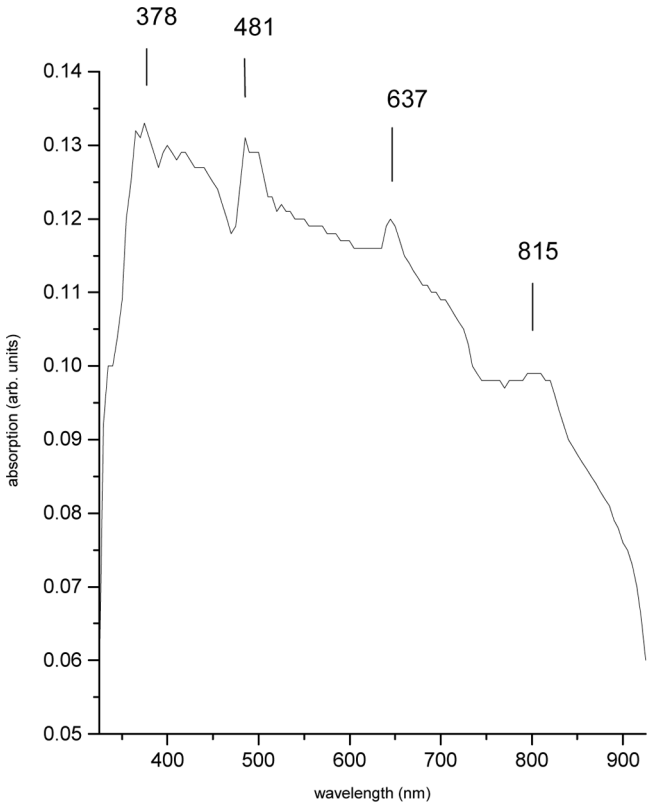


**FIGURE 4** Optical absorption spectrum of vanadyl ion in diammonium hexaaqua magnesium(II) sulfate.

($D_q$) and tetragonal field parameters ($D_s$ and $D_t$) are evaluated.

$$
\begin{aligned}
{}^2B_2 &\rightarrow {}^2E : -3D_s + 5D_t \\
{}^2B_2 &\rightarrow {}^2B_1 : 10D_q \\
{}^2B_2 &\rightarrow {}^2A_1 : 10D_q - 4D_s - 5D_t
\end{aligned} \tag{6}
$$

The parameters are $D_q = 1570$, $D_s = -2480$, and $D_t = 968\ cm^{-1}$.

The energy matrices have been solved using a computer to confirm these assignments.[19]

The calculated band positions shown in Table 3 are in good agreement with the observed ones.

Using the energy differences obtained from optical absorption spectrum and EPR data the bonding parameters $\beta_1^{*2}$ and $e_\pi^{*2}$ are estimated with the help of the following expressions:[15]

$$
\begin{aligned}
g_e - g_\parallel &= \frac{4g_e\lambda\beta_1^{*2}\beta_2^{*2}}{\Delta_\parallel} \\
g_e - g_\perp &= \frac{g_e\lambda e_\pi^{*2}\beta_2^{*2}}{\Delta_\perp}
\end{aligned} \tag{7}
$$

where $\Delta_\parallel$ and $\Delta_\perp$ correspond to the energy differences ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$, respectively. Taking the values of $g_\parallel$ and $g_\perp$ from powder study and the energies from Table 3, the bonding parameters are found to be $\beta_1^{*2} = 0.56$ and $e_\pi^{*2} = 0.70$ with $\beta_2^{*2} = 1 \cdot \beta_2^{*2}$ taken to be 1 when $b_2$ orbital is strictly non-(in-plane) bonding as predicted by Ballhausen and Gray[4] and accepted by others.[20,21] The expressions $(1 - \beta_1^{*2})$ and $(1 - e_\pi^{*2})$ are the covalency rates;[20] the former gives an indication of the influence of $\sigma$ bonding between the vanadium atom and the equatorial ligands, whereas the latter indicates the influence of $\pi$ bonding with the vanadyl oxygen. The values of these parameters suggest that both the in-plane $\sigma$ and out-of-plane $\pi$ bonding are partly covalent.

**TABLE 3** **Band Positions and Assignments of Transitions of Vanadyl Ions in the Diammonium Hexaaqua Magnesium(II) Sulfate**

| Band positions | | | | |
|---|---|---|---|---|
| Observed | | | | |
| (nm) | ($cm^{-1}$) | Calculated ($cm^{-1}$) | Assignment | |
| 815 | 12,270 | 12,356 | ${}^2B_2 \rightarrow {}^2E$ | ($d_{xy} \rightarrow d_{xz,yz}$) |
| 637 | 15,698 | 15,701 | ${}^2B_2 \rightarrow {}^2B_1$ | ($d_{xy} \rightarrow d_x^2 - y^2$) |
| 481 | 20,790 | 20,791 | ${}^2B_2 \rightarrow {}^2A_1$ | ($d_{xy} \rightarrow d_z^2$) |
| 378 | 26,455 | | CT band | Filled bonding levels $\rightarrow d_{xy}$ $\{e_\pi^b \rightarrow {}^2B_2(b_2)\}$ |

## CONCLUSION

EPR and optical absorption studies of $VO^{2+}$-doped diammonium hexaaqua magnesium(II) sulfate have been done. By comparing the direction cosines obtained from single-crystal EPR data with those calculated from crystal structure data, the $VO^{2+}$ ions are expected to take up substitutional $Mg^{2+}$ sites in the lattice. The crystal field parameter ($D_q$), tetragonal parameters ($D_s$ and $D_t$), and bonding parameters have been evaluated to estimate the covalency. The values of bonding parameters suggest that both the in-plane $\sigma$ and out-of-plane $\pi$ bonding are partly covalent.

## ACKNOWLEDGMENTS

The authors are thankful to Dr. T. K. Gundu Rao, R.S.I.C., I.I.T., Mumbai, for recording of EPR spectra. One of the authors (AKS) is thankful to the University Grants Commission for financial assistance in the form of a minor research project.

## REFERENCES

1. Selbin, I. The chemistry of oxovanadium(IV). *Chem. Rev.* **1965**, *65*, 153–175.
2. Prasad, L. S.; Subramanian, S. EPR of $VO^{2+}$ in $Zn(antipyrine)_2(NO_3)_2$: On the orientation of vanadyl doped in a low symmetry crystal field. *J. Chem. Phys.* **1987**, *86*, 629–633.
3. Jorgenson, C. K. Comparative ligand field studies. IV. Vanadium(IV), titanium(IV), molybdenum(V) and other systems with one d-electron. *Acta Chem. Scand.* **1995**, *11*, 73–85.
4. Ballhausen, C. J.; Gray, H. B. The electronic structure of the vanadyl ion. *Inorg. Chem.* **1962**, *1*, 111–122.
5. Ortolano, T. R.; Selbin, J.; McGlynn, S. P. Electronic structure, spectra and magnetic properties of oxycations. V. The electronic spectra of some vanadyl complexes. *J. Chem. Phys.* **1964**, *41*, 262–268.
6. Vanquickenborne, L. G.; Mc.Glynn, S. P. Semi-empirical molecular orbital computations. *Theor. Chim. Acta* **1968**, *9*, 390–400.
7. Feng, W. L. Theoretical studies of the optical and EPR spectra for vanadyl ions in alkaline-earth aluminoborate glasses. *Phil. Mag.* **2009**, *89*, 1391–1394.
8. Narayana, M.; Sathyanarayan, S. G.; Sastry, G. S. Covalency effects on the ESR spectra of $VO^{2+}$ in hexaaquo magnesium dihydrogen ethylene diamine tetraacetic acid. *Mol. Phys.* **1976**, *31*, 203–207.
9. Jayaram, B.; Sobhanadri, J. Host lattice effects on the EPR of vanadyl in Tutton salts. *Crystal Lattice Defects and Amorphous Materials* **1983**, *10*, 47–57.
10. Misra, S. K.; Sun, J. EPR of $VO^{2+}$ in $Cd(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and $Mg(NH_4)_2(SO_4)_2 \cdot 6H_2O$ single crystals. Ligand superhyperfine interaction and bonding coefficients. *Physica B* **1990**, *162*, 331–343.

11. Maslen, E. N.; Ridout, S. C.; Watson, K. J.; Moore, F. H. The structure of Tutton's salts. I. Diammonium hexaaquamagnesium(II) sulfate. *Acta Crystallogr.* **1988**, *C44*, 409–412.
12. Schonland, D. S. On the determination of principal g-values in electron spin resonance. *Proc. Phys. Soc.* **1989**, *73*, 788–792.
13. Boucher, L. J.; Tynan, E. C.; Yen, T. F. Spectral properties of oxovanadium (IV) complexes. IV. Correlation of ESR spectra with ligand type. In *Electron Spin Resonance of Metal Complexes, Vol. 97*; Yen, T. F., Ed.; Plenum Press: 1969.
14. Vishwanath, A. K. EPR studies of $VO^{2+}$ in single crystals of $ZnSO_4 \cdot 7H_2O$ and certain polycrystalline sulfates. *J. Chem. Phys.* **1977**, *67*, 3744–3757.
15. Maki, A. H.; McGarvey, B. R. Electron spin resonance in transition metal chelates. I. copper(II) bis-acetylacetonate. *J. Chem. Phys.* **1958**, *29*, 31–34; Maki, A. H.; McGarvey, B. R. Electron spin resonance in transition metal chelates. II. copper(II) bis-salicylaldehyde-imine. *J. Chem. Phys.* **1958**, ***29***, 35–38.
16. Sathyanarayan, S. G.; Krishnan, V. G.; Sastry, G. S. Single crystal ESR of $VO^{2+}$ in hexa-urea aluminium perchlorate. *J. Chem. Phys.* **1976**, *65*, 4181–4183.
17. McGarvey, B. R. The isotropic hyperfine interaction. *J. Phys. Chem.* **1967**, *71*, 51–66.
18. Agarwal, O. P.; Chand, P. Optical spectra of vanadyl (impurities) in three host crystal compounds. *Z. Naturforsch.* **1985**, *40a*, 1164–1166.
19. Satyanarayana, N.; Radhakrishna, S. EPR and electronic absorption studies of vanadyl ions in the $Cd(NH_4)_2(SO_4)_2 \cdot 6H_2O$ single crystals *J. Chem. Phys.* **1985**, *83*, 529–534.
20. Seth, V. P.; Jain, V. K.; Yadav, A.; Bansal, R. S. ESR study of vanadyl ion in potassium succinate. *Phys. Status Solidi B* **1985**, *132*, K139–K142.
21. Jain, V. K. Electron spin resonance of $VO^{2+}$ in $(NH_4)_2SeO_4$. *J. Phys. Soc. Jpn.* **1979**, *46*, 1250–1253.