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Electron paramagnetic resonance study of VO^{2+} doped single crystal of ferroelectric guanidinium uranyl sulphate trihydrate

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Abstract

We report result obtained from an EPR study of vanadyl ion (VO^{2+}) in a single crystal of ferroelectric guanidinium uranyl sulphate trihydrate. The Spin-Hamiltonian parameters were also determined via EPR data. VO^{2+} enters the lattice interstitially at two distinguishable sites and resulting vanadyl complexes have nearly axial symmetry.

Key Words: EPR, crystal structure, spin hamiltonian, bonding coefficient

1. Introduction

Electron Paramagnetic Resonance (EPR) technique has been widely used in recent past for the investigation of ferroelectrics. The method is much easier and sensitive, in spite of the necessity to introduce paramagnetic defects or impurity as probe. In many cases these studies appeared somewhat inconclusive, as these were mainly restricted to spectroscopic determinations, as for as ferroelectricity is concerned [1]. However, in the class of hydrogen bonded ferroelectrics, new and important results were obtained by this method for the KH_2AsO_4 (KDA) crystal and the KH_2PO_4 (KDP) family, using (AsO_4) radical created by X-irradiation as a probe [2, 3]. Since VO^{2+} ions possess electric dipole moments, which interact with microscopic internal field at the trapping sites, VO^{2+} ions have been used as sensitive probe in the EPR study in ferroelectric [4]. Alkaline earth formats have already been extensively investigated by us [5–10]. A detailed description of the ground state and nature of the crystalline electric field produced by the ligands surrounding the metal ion are supposed

to be made quite accurately by EPR. As guanidinium uranyl sulphate trihydrate (GUSTH) is ferroelectric, it was thought worth while to carry out an EPR investigation on this crystal.

2. Crystal structure

The structure GUSTH $[\text{C}(\text{NH}_2)_3]_2 \text{UO}_2(\text{SO}_4)_2 \cdot 3\text{H}_2\text{O}$ is monoclinic with space group C_2/C with four formula units. The unit cell dimensions are $a = 11.220 \text{ \AA}$, $b = 8.027 \text{ \AA}$ and $c = 18.681 \text{ \AA}$, and $\beta = 101^\circ$ [11]. The uranium (U) atom is surrounded by a pentagonal bipyramid of oxygen (O) atoms. The upper half of the coordination polyhedron is related to the lower half by the two fold axis which bisects the pentagonal base through the U atom and a water molecule coordinated to it, thus forcing the uranyl group to be strictly linear. The sulphate group acts a bridging legend, joining bipyramids together with only two kinds of O atoms, involved in the bridging process. The gap between the layers is filled with guanidinium cations and remaining water of crystallization. The U—O distances lie between 1.75 \AA to 2.50 \AA .

3. Experimental

Single crystals of GUSTH were grown by slow evaporation method from a saturated aqueous solution at room temperature. Well developed crystals on (001) were obtained, showing a perfect cleavage. The dopant was introduced in the form of aqueous solution of vanadyl sulphate during growth.

EPR spectra were recorded on a Varian E-109 Century series EPR spectrometer operating in the X band ($\sim 9.4 \text{ GHz}$) with 100 kHz field modulation. Angular variation study of EPR spectra about three orthogonal axes \mathbf{a} , \mathbf{b} and \mathbf{c}' , where $\mathbf{c}' = \mathbf{a} \times \mathbf{b}$, was done by using a Varian model E-229 goniometer fitted to a Varian model E-231 multipurpose rectangular cavity operating in TE_{102} mode with unloaded $Q > 7,000$. The 100 kHz field modulation amplitude was kept below 0.05 mT . The magnetic field was calibrated using a Varian model E-500 digital gauss meter. The microwave resonant frequency was determined by using a standard field marker (DPPH, $g = 2.0036 \pm 0.0002$). EPR spectra at liquid nitrogen temperature were recorded by immersing the sample into liquid nitrogen in a quartz dewar fitted with rectangular cavity.

4. Result and discussion

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

$$\mathbf{H} = \beta \mathbf{SgB} + hc\mathbf{SAI}. \quad (1)$$

In the given equation, the first and second terms are the electron Zeeman and nuclear hyperfine interactions, respectively. The hyperfine tensor \mathbf{A} has units of cm^{-1} and \mathbf{B} is in Teslas. The positions (in magnetic field units) B_m of the observed allowed hyperfine transitions ($\Delta m = 0$) are obtained by solving equation (1) under the assumption that tensors \mathbf{g} and \mathbf{A} are axially symmetric; and correct to the second order, are given

by [12]

$$B_m = B_0 - Km - \frac{A_{\perp}^2}{16B_0} \left[\frac{K^2 + A_{//}^2}{K^2 g^2} \right] (63 - 4m^2) - \frac{m^2}{8B_0} \left[\frac{(A_{//}^2 - A_{\perp}^2) g_{//} g_{\perp} \sin 2\theta}{K^2 g^2} \right]^2,$$

where $B_0 = h\nu/g\beta$, ν being the microwave resonant frequency. Magnitude of \mathbf{g} , and K , are given by the relations

$$\begin{aligned} g^2 &= g_{//}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta \\ K^2 g^2 &= A_{//}^2 g_{//}^2 \cos^2 \theta + A_{\perp}^2 g_{\perp}^2 \sin^2 \theta, \end{aligned} \quad (2)$$

where $m = -7/2, \dots, 7/2$ and θ is the angle between the symmetry axis of the vanadyl complexes and the magnetic field \mathbf{B} . Here, m is the magnetic quantum number of vanadium nucleus and $A_{//}, g_{//}$ positions were taken which correspond to maximum first derivative curves of the parallel component for a given m value whereas the A_{\perp}, g_{\perp} positions are between the first derivatives perpendicular peak and its zero [13].

The spectra associated with VO^{2+} ion doped in GUSTH showed two intense sets of eight lines when magnetic field \mathbf{B} was away from crystallographic axis in \mathbf{bc}' , \mathbf{ac}' and \mathbf{ab} planes. These two intense sets of eight lines show two magnetically inequivalent vanadyl complexes present in the host lattice. These sites become equivalent along the three orthogonal axes and show a single set of eight lines. Angular variation of hyperfine lines of spectra is shown in Figure 1 in all three planes. The spectra when \mathbf{B} is along \mathbf{c}' axis in \mathbf{bc}' plane and 2° away from \mathbf{c}' in \mathbf{ac}' plane are shown in Figure 2.

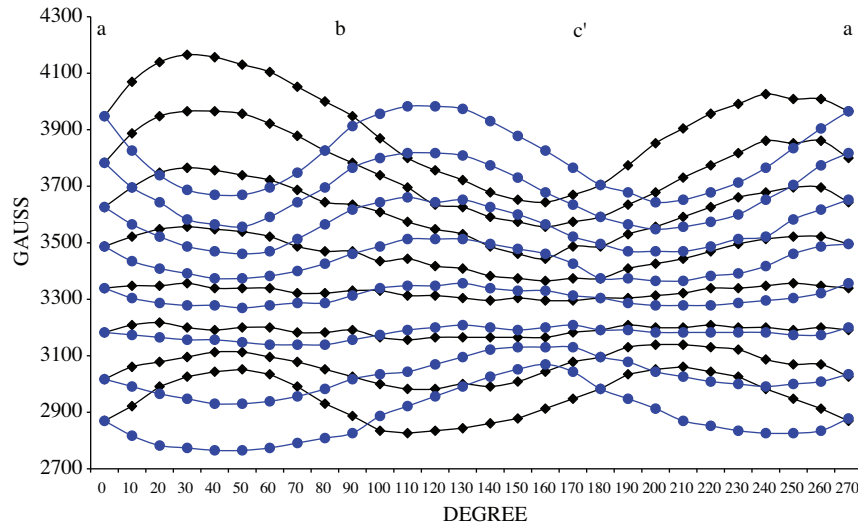


Figure 1. Angular variation of hyperfine lines of VO^{2+} doped in GUSTH in \mathbf{ba} , \mathbf{ac}' and $\mathbf{c}'\mathbf{b}$ planes.

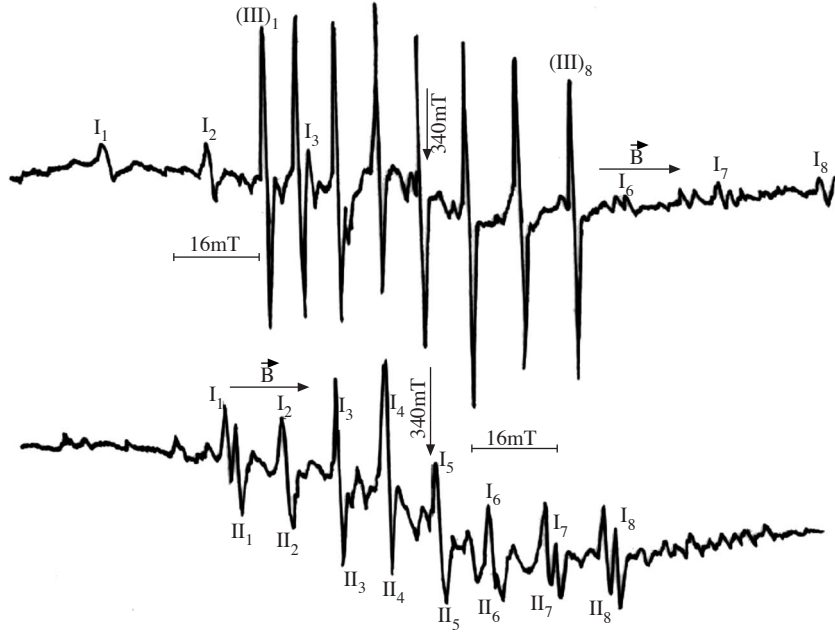


Figure 2. EPR Spectra of VO^{2+} doped in GUSTH, when B is along c' axis and 2° away from c' .

If VO^{2+} enters substitutionally, the crystal structure of GUSTH requires that four symmetry related equivalent orientations, given by the space group symmetry operation, should be obtained. In arbitrary orientation there should be four sets of eight hyperfine lines each. The observation of only two distinguishable vanadyl complexes, namely complex I and complex II, indicates that these vanadyl complexes result in interstitial incorporation of vanadyl ions in the host lattice. As only two sets of eight hyperfine lines were observed in all planes, the substitution incorporation of VO^{2+} seems unlikely. At liquid nitrogen temperature no appreciable change in the spectra were observed.

The spin Hamiltonian parameters obtained for both the complexes using the method of Waller and Rogers [14] were found to be the same for both the complexes within the experimental error and are $A_{//} = 193 \pm 1$, $A_{\perp} = 76 \pm 1$ in the unit of 10^{-4} cm^{-1} and $g_{//} = 1.938 \pm 0.001$, $g_{\perp} = 1.983 \pm 0.001$. Considering the eigenvector of the GK matrix, the $V = O$ bond direction is defined with respect to \mathbf{a} , \mathbf{b} and \mathbf{c}' axes, respectively, with the value $\theta = 46^\circ$ and $\phi = 80^\circ$ with the shortest $U-O$ (I) bond direction. Within experimental error the spin Hamiltonian parameters are found to be axial and same for both vanadyl complexes [15].

The Fermi contact parameter k and dipolar interaction parameter P are estimated from the following expression [16, 17]:

$$A_{//} = P[-\beta_2^2(4/7 + k) + (g_{//} - g_e) + (3/7)(g_{\perp} - g_e)] \quad (3)$$

$$A_{\perp} = P[\beta_2^2(2/7 - k) + (11/14)(g_{\perp} - g_e)], \quad (4)$$

where, $g_e = 2.0023$ and β_2^2 is taken as unity. Substituting the values of $g_{//}$, g_{\perp} , $A_{//}$ and A_{\perp} in the above equations, we get $P = -127 \times 10^{-4} \text{ cm}^{-1}$ and $k = 0.86$. Parameter P is the measure of the radial distribution of the unpaired electron wave function and is given by

$$P = 2.0023g_N\beta\beta_N \langle r^{-3} \rangle, \quad (5)$$

from which one obtains $\langle r^{-3} \rangle \approx 2.92 \text{ \AA}$. The calculated value of $\langle r^{-3} \rangle$ is rather low compared to the theoretical free ion value $\langle r^{-3} \rangle \approx 3.67 \text{ \AA}$ [18]. Such a reduction in $\langle r^{-3} \rangle$ is often attributed to the bonding effect in the solid state.

5. Conclusion

VO^{2+} enters the GUSTH interstitially at two distinguishable sites and the resulting vanadyl complexes have axial symmetry. The larger value of k indicates a large contribution to the hyperfine constants by the unpaired S electron and also due to the contribution from spin polarization.

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