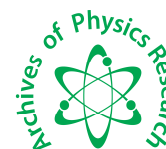




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Phase transition in rubidium carnallite doped with VO^{2+} by EPR method

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ABSTRACT

This work deals with EPR investigations of VO^{2+} doped rubidium carnallite. Vanadyl ion in some hosts e.g. NH_4Cl and $Mg(ClO_4).6H_2O$ etc. shows a rotatory behaviour, while in hosts like alums, sulphates, Tutton salts etc., it shows preferential orientation giving angle-dependent spectra. In the present host $RbMgCl_3.6H_2O$, the VO^{2+} shows an isotropic angle independent eight line hyperfine spectrum. It has already been reported that Mn^{2+} substitutes Mg^{2+} in $NH_4MgCl.6H_2O$ giving two distinct EPR spectra having angular variation. But in the present work the spectra of VO^{2+} in $RbMgCl_3.6H_2O$ does not show preferred orientation. This behaviour occurs due to VO^{2+} undergoing a rapid tumbling motion in the crystalline lattice. It has been also found that when the temperature is lowered to LNT, fast reorientations of V-O bond act progressively hindered and the anisotropies in \tilde{g} and \tilde{A} tensors are not averaged out and get reflected but it is angular independent. After analysing and comparing the spectrum it is found that VO^{2+} shows 'liquid like' behaviour in $RbMgCl_3.6H_2O$.

Keywords: EPR, VO^{2+} , Rb carnallite, Rapid tumbling motion, VEPI.

INTRODUCTION

Paramagnetic ion has a magnetic moment and therefore its ground state is degenerate. If this ion is placed in a strong static magnetic field, the degeneracy is lifted and the energy undergo a Zeeman splitting. Application of an external oscillating electromagnetic field (with magnetic component perpendicular to the field causing the Zeeman splitting) transitions between the Zeeman levels takes place and energy is absorbed from electromagnetic field. If the static magnetic field is slowly varied the absorption shows a series of maxima. The plot between the absorbed energy and the magnetic field is called the electron paramagnetic resonance spectrum. The phenomenon itself is called electron paramagnetic resonance (EPR). The VO^{2+} ion can be bound to a large variety of ligands. EPR and Optical investigations carried out on Mn^{2+} doped ammonium carnallite have already been reported. Using electron paramagnetic resonance spectroscopy, one can therefore study the delocalization of the single electron onto the ligand network, thereby estimating the π -bonding capabilities of the ligand [1].

Hydrated double chlorides $RbMgCl_3.6H_2O$ and $NH_4MgCl_3.6H_2O$ are isomorphic and are known as rubidium and ammonium carnallites respectively after the mineral carnallite ($KMgCl_3.6H_2O$) which is found in marine deposits formed by evaporation of sea water and has been an important source of potassium and magnesium. The crystals of rubidium and ammonium carnallite have been grown successfully in the laboratory and EPR and Optical investigations carried out on Mn^{2+} doped ammonium carnallite have already been reported [2]. This work deals with EPR investigations of VO^{2+} doped rubidium carnallite.

MATERIALS AND METHODS

Andrews and Saffe [3] have determined the crystal structure of ammonium carnallite $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$ and rubidium carnallite $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ and have reported that both are isomorphous with monoclinic unit cell parameters $a=1.330$ nm, $b=0.666$ nm $c=0.668$ nm, $\beta=90^\circ$ and $z=2$ for $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$ and $a=1.330$ nm, $b=0.665$ nm, $c=0.662$ nm, $\beta=90^\circ$ and $z=2$ for $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$.

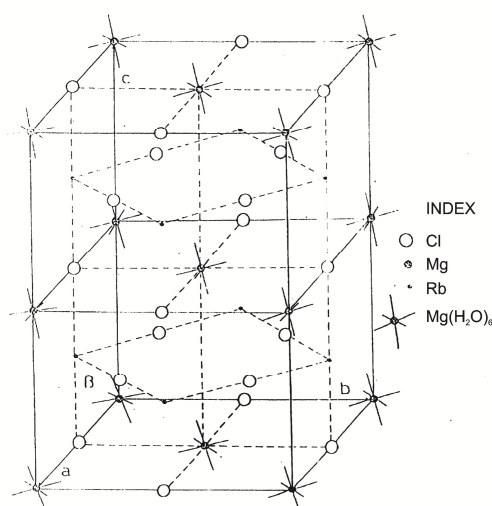


Fig. 1. Monoclinic Unit Cell of $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ (After X. Solans et al., Acta Cryst. C39, 1488 (1983).

* Hydrogens of NH_4 have not been shown.

Nakayasu, Suzukawa and Kobayashi [4] reinvestigated the crystal structure of $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$ and reported the structure to be triclinic P_1 with $a=0.665$ nm, $b=1.330$ nm, $c=0.6665$ nm, $\alpha=89.92^\circ$, $\beta=91.52^\circ$ and $\gamma=89.99^\circ$ and $z=2$. They found Mg-O bond lengths in the crystal are different. Two Mg-O bonds are shorter in length than the other four. Recent report of Marsh [5] investigates that the monoclinic unit cells for NH_4 and Rb carnallites reported by Andrews and Saffe correspond to primitive cell rather than to a C-centred cell. A monoclinic C-centered cell with space group $C 2/c$ is a proper unit cell. According to Solan's et al [6] $\text{NH}_4\text{MgCl}_3 \cdot 6\text{H}_2\text{O}$ is monoclinic $C2/c$ with parameters $a=0.9320$ nm, $b=0.9582$ nm, $c=1.3327$ nm, $\beta=90^\circ 12'$ and $z=4$. The structure consists of discrete $\text{Mg}(\text{H}_2\text{O})_6^{2+}$, Cl^- , and NH_4^+ or Rb ions linked by ionic forces and hydrogen-bond interaction. Each Mg^{2+} ion is surrounded by six water molecules in octahedral arrangement. The average Mg-O bond length and O-Mg-O bond angles are 0.253 nm and $89^\circ 7'$ respectively forming almost an equal orientation with the c-axis. Each NH_4^+ ion is surrounded by six Cl^- ions and has nearly regular octahedral arrangement with average Cl-N distance 0.334 nm and each Cl^- ion is hydrogen-bonded to six water molecules and two NH_4^+ ions. Table (I) shows atomic coordinates and Table (II) shows interatomic distances and angles. Fig.1 shows the crystal structure of $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$.

Colourless hygroscopic crystals were obtained by fractional crystallization and slow evaporation from a solution of NH_3 , H_3BO_3 and $\text{RbCl}_2 \cdot 6\text{H}_2\text{O}$ in water. In the first crystallization crystals of β - phase of rubidium pentaborate tetrahydrate were separated. In the second phase, crystals of $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ were obtained. The crystals were checked chemically and by X-ray diffraction. Electron paramagnetic resonance spectra (EPR) were recorded on X-band (~ 9.3 GHz) EPR spectrometer varian model E-109 with 100 KHz field modulation. The samples were capable

of being rotated about a vertical axes with the help of a goniometer inside a rectangular cavity, operating in TE_{102} mode ($Q \sim 7000$). Magnetic field was measured by a digital gaussmeter varian model E-500 and the microwave frequency was measured by using a DPPH standard marker ($g=2.0036 \pm 0.002$). EPR spectra was recorded at room temperature (RT) Fig. 2 and liquid nitrogen temperature (LNT) Fig. 3.

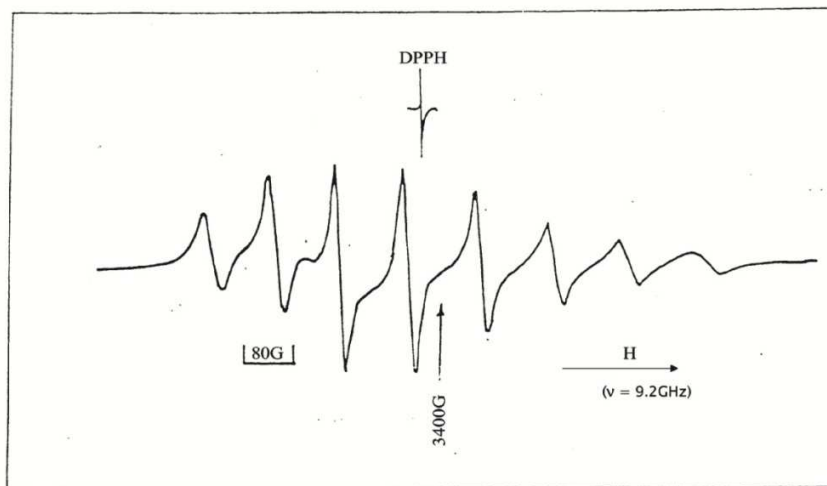


Fig. 2 Spectrum I, EPR Spectrum of VO^{2+} doped $RbMgCl_3 \cdot 6H_2O$ Single Crystals at RT.

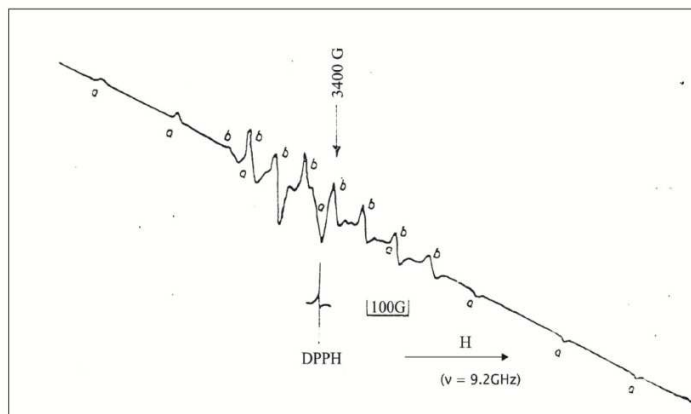


Fig. 3 Spectrum II, EPR Spectrum of VO^{2+} doped $RbMgCl_3 \cdot 6H_2O$ Single Crystals at LNT. Lines marked a are parallel transitions and lines marked b are perpendicular transitions.

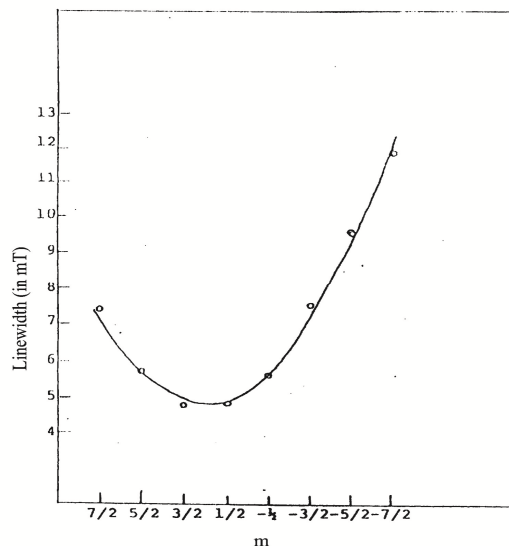


Fig. 4. Plot of Linewidth vs. m in the EPR of VO²⁺ doped in RbMgCl₃.6H₂O single crystal. The solid curve represents predicted parabolic variation of the Linewidth while circles denote the experimental values at RT.

THEORY

The spin-Hamilton for vanadyl ion with a single unpaired electron (S=1/2) interacting with nuclear spin I=7/2 can be written including the electron Zeeman and nuclear hyperfine terms, respectively terms, respectively.

$$H = \beta \vec{S} \cdot \vec{g} \cdot \vec{B} + \vec{S} \cdot \vec{A} \cdot \vec{I} \dots \dots \dots (1)$$

Where the symbols have their usual meaning. The \vec{g} and \vec{A} tensors are assumed to possess coincidental axes. The complete Hamiltonian requires additional nuclear and Zeeman and quadrupolar terms in equation (1), which are found to be sufficiently small for VO²⁺ ion, and are neglected [7]. Since the \vec{g} and \vec{A} tensors are nearly axial, spin-Hamiltons used by Bleaney [8] for the solution of the spin-Hamiltonian are used and the values determined at RT and LNT are given Table (III). The line widths are calculated with the help of

$$\Delta H = (1/T2) = \pi\sqrt{3} (a_1 + a_2m + a_3m^2) \dots \dots \dots (2)$$

$$\text{And derivative height} \times (\text{line width})^2 = \text{constant} \dots \dots \dots (3)$$

RESULTS AND DISCUSSION

R.P. Kohin has studied vanadyl ion in a variety of lattices [9]. In some hosts e.g. NH₄Cl [10] and Mg(ClO₄).6H₂O etc. It shows a rotatory behaviour, while in hosts like alums, sulphates, Tutton salts etc. It shows preferential orientation giving angle-dependent spectra. In the present host RbMgCl₃.6H₂O the VO²⁺ shows an isotropic angle independent eight line hyperfine spectrum designated as spectrum I at RT. Fig. 2 and is nearly similar as that studied by Nimai Chan Biswas [11]. NH₄⁺ and Mg are equivalent and Mg²⁺ occupies two distinct sites. In double salts with NH₄⁺ sites and divalent cation metal ions, VO²⁺ has chosen to occupy divalent cation site [12]. Therefore it may be expected to enter the lattice at Mg²⁺ sites in RbMgCl₃.6H₂O. It has already been shown that Mn²⁺ substitutes Mg²⁺ in NH₄MgCl₃.6H₂O giving two distinct EPR spectra having angular variation. But the present spectra of VO²⁺

in $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ does not show preferred orientation and is similar to that in NH_4Cl etc. This behaviour occur due to VO^{2+} undergoing a rapid tumbling motion in the crystalline lattice. When the temperature is lowered to LNT fast reorientations of V-O bond act progressively hindered and the anisotropies in \tilde{g} and \tilde{A} tensors are not averaged out and get reflected in spectrum II Fig.3 but it is angular independent. The spectrum reveals the characteristic parallel and perpendicular components levelled as ‘a’ and ‘b’ in Fig. 3. Spectrum II is analysed using eq. (1) and the parameters are given in Table (III). Comparing this spectrum with those of Reilly for vanadyl etioporphirin (VEPI) in benzene solution (low viscous medium), it is of the same nature while the features of spectrum (Fig 2) are similar to those of VEPI dissolved in high viscous oil. For this reason, VO^{2+} may be said to show ‘liquid like’ behaviour in $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ also. No effect of crystal field and association with ligands is shown in any manner, except in hindering the motion of VO^{2+} ion at low temperatures.

Spectrum II (Fig.3) is very much similar to those of solid asphaltenes containing vanadium porphins [13] and VO^{2+} in polycrystalline Tutton salts [14] therefore it may be said to correspond to powder spectrum. EPR line widths in spectrum I (Fig. 2) has been found to show a variation with nuclear magnetic quantum number m and follow the Kivelson’s theory [15, 16]. The constants a_1 , a_2 and a_3 and ΔH values are determined by equations (2) & (3). The values of line widths in units of mT are-

$$a_1 = 0.967, \quad a_2 = -0.128 \quad \text{and} \quad a_3 = 0.066$$

Fig. shows the experimental and predicted variation of line widths and according to Kivelson’s theory these values suggest a liquid like behaviour of VO^{2+} in $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$.

Table (I) Final Atomic Coordinates ($\times 10^4$) of $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$

	x	y	z
Cl(1)	5000	0	5000
Cl (2)	2544 (1)	7384 (2)	7467 (1)
Mg	5000	5000	5000
N	5000	13 (6)	7500
O (1)	4103 (3)	6876 (2)	5381 (2)
O (2)	3194 (3)	3990 (2)	5511 (2)
O (3)	4084 (3)	5134 (3)	5381 (2)

Table (II) Interatomic Distances (a) and Angles ($^\circ$) in the unit cell of $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$

Mg-O (1)	2.047 (2)	Cl (2 ⁱ)...O (1)	3.177 (3)
Mg-O (2)	2.059 (2)	Cl (2 ⁱⁱ)...O (2)	3.180 (3)
Mg-O (3)	2.053 (2)	Cl (2 ⁱⁱⁱ)...O (3)	3.186 (3)
Cl (1 ⁱ) ... N	3.332 (2)	Cl (2 ^{iv})...O (3)	3.159 (3)
Cl (2 ^v)...N	3.404 (3)	O (1) – Mg-O (2)	89.8 (1)
Cl (1 ⁱⁱⁱ)...N	3.284 (3)	O (1) – Mg-O (3)	90.1 (1)
Cl (1 ^{iv}) ...O (1)	3.149 (2)	O (2) – Mg-O (3)	89.5 (1)
Cl (1 ^v) ...O (2)	3.202 (2)		

Symmetry Code :

- (i) x, y, z (ii) x, y-1, z (iii) x+1/2, y-1/2, z (iv) x, y+1, z
 (v) x-1/2, y+1/2, z (vi) 1/2 -x, y-1/2, 3/2-z (vii) x, 1-y, z-1/2 (viii) 1/2-x, 1/2-y, 1-z

Table (III) Spin Hamiltonian Parameters for VO^{2+} in $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ single crystal
 (Values of A_0 , A and A are in units of gauss)

Spectrum I RT	$g_0 = 1.926 \pm 0.005$	$A_0 = 118.18 \pm 0.60$
Spectrum II LNT	$g = 1.891 \pm 0.005$	$A = 200.87 \pm 1.80$
	$g = 1.949 \pm 0.005$	$A = 76.78 \pm 0.20$

where

$$g_o = (g_{||} + 2g_{\perp})/3$$

$$\text{And } A_o = (A_{||} + 2 A_{\perp})/3$$

CONCLUSION

Present study shows that the spectra of VO^{2+} in $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ does not show preferred orientation and is similar to that in NH_4Cl etc. This behaviour occurs due to VO^{2+} undergoing a rapid tumbling motion in the crystalline lattice. When the temperature is lowered to LNT it is found that spectrum II is angular independent. Comparing this spectrum with those of Reilly for vanadyl etioporphirin (VEPI) in benzene solution (low viscous medium), it is of the same nature while the features of spectrum I are similar to those of VEPI dissolved in high viscous oil. For this reason, VO^{2+} may be said to show 'liquid like' behaviour in $\text{RbMgCl}_3 \cdot 6\text{H}_2\text{O}$ also. No effect of crystal field and association with ligands is shown in any manner, except in hindering the motion of VO^{2+} ion at low temperatures.

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