

STUDY OF EPR OF VO²⁺ IN RBCL CRYSTALS

A.K. MISHRA & ANJOO

Department of Physics, N.A.S. College, Meerut (U.P), India

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EPR of VO²⁺ ions incorporated in single crystals of RbCl from RT to the LNT has been presented in the paper. At LNT, the spectrum recorded is anisotropic, exhibiting both parallel and perpendicular components. However, at RT the observed spectrum is isotropic, suggesting fast reorientation of VO molecular ions. The spin Hamiltonian parameters have been obtained for both the spectra in RbCl : VO²⁺ system and correlated with each other. Further, the line-widths of the RT spectra are found to obey a parabolic variation as proposed originally by Kivelson.

KEYWORDS: Rubidium chloride crystal, electron paramagnetic resonance, spectrum line width.

INTRODUCTION

It is known that when alkali halide crystals are doped with divalent impurities like Mn²⁺, alkali ion vacancies are created to account for charge neutrality. The divalent ions could go in substitutionally or interstitially in the crystal or could also go in clusters or precipitates. The vacancy could be a nearby neighbor to the divalent ion or it could be far away from it. The EPR spectra reported elsewhere [1-3] clearly indicate the different ways in which the impurity ions go into the crystal.

EPR of VO²⁺ doped in NH₄Cl single crystal was studied by Sastry and Venkateswarlu [4] and EPR of vanadyl doped in KNO₃ and CsNO₃ was studied by Rao, Sastry and Venkateswarlu [5]. It has been found from these studies that the molecular ion VO²⁺ does not have a fixed orientation in these crystals and undergoes a fast readjustment at room temperature, while it shows the effects of hindered rotation at low temperatures. On the other hand, VO²⁺ is known to have preferred orientations in Tutton salts [6] and in rubidium and cesium alums [7]. Again, Rao, Sastry and Venkateswarlu [8] have further found from their EPR studies that the VO²⁺ ion has preferred orientation in the potassium and ammonium aluminium alums & MAG alum. Pandey and Venkateswarlu [9] have reported distinct orientation of VO²⁺ in ammonium sulphate single crystals.

EPR of vanadium glasses elaborated by Bandyopadhyay [10] and interpreted that V⁴⁺ ion being complexed as a VO²⁺ ion within a tetragonally distorted octahedral sites. The interest of workers towards EPR studies in vanadyl doped samples continues even now. The EPR of VO²⁺ ions in KZnClSO₄.3H₂O single crystals have been reported by Deva Prasad Raju *et al* [11] and also have reported presence of more than three magnetic complexes which

correspond to distinct sites of VO^{2+} ion. However, recent EPR studies of VO^{2+} in potassium thiourea bromide single crystals [12] report a single eight line spectrum attributed to VO^{2+} complexed with sulphur atoms.

The work in this paper gives information about the VO^{2+} complex inside a simpler alkali halide crystal of RbCl [13], and the applicability of Kivelson's theory [14] of paramagnetic relaxation has also been examined for the system.

Table 1. g- and A-parameters of VO^{2+} in RbCl single crystal

Spectrum Type	g-parameters	A-parameter ($\times 10^{-4} \text{ cm}^{-1}$)
I	$g_o = 1.967 \pm 0.001$	$A_o = 107.2 \pm 1.0$
II	$g_{ } = 1.938 \pm 0.002$	$A_{ } = 189.2 \pm 2.0$
	$g_{\perp} = 1.969 \pm 0.002$	$A_{\perp} = 64.2 \pm 2.0$

Table 2. Experimental ΔB values for different hyperfine transitions in spectrum I of VO^{2+} : RbCl system.

S.No.	m_l for transition	ΔB (Gauss)
1	+7/2	24.8
2	+5/2	20.8
3	+3/2	18.5
4	+1/2	18.3
5	-1/2	21.1
6	-3/2	24.6
7	-5/2	29.6
8	-7/2	35.7

Table 3. Values of the coefficients a_1 , a_2 and a_3

Host	a_1 (mT)	a_2 (mT)	a_3 (mT)
RbCl	0.363	-0.033	+0.0163
RbBr	0.286	-0.035	+0.0139
RbI	0.217	-0.018	+0.0088

EXPERIMENTAL

VO^{2+} -doped rubidium chloride crystals were grown by slow evaporation of a saturated solution of rubidium chloride containing a known quantity (0.5 mole conc.) of vanadyl chloride. The rubidium chloride host was of E. Merck, A.R. quality. Nice cubic crystals with shining faces appeared after about 15 days of evaporation. The lower temperature of the surroundings improved the growth rate and the size of the crystals.

The EPR measurements were carried out at X-band, 9.5 GHz frequency with a Varian E-line century series EPR spectrometer E-109 and a 9 inch rotating electromagnet using 100 KHz field modulation. The magnetic field was calibrated using DPPH as the field maker. The proton resonance monitoring with a fluxmeter helped to measure the magnetic field corresponding to the proton resonance and thus of all the EPR peaks in the observed spectrum.

The spectra were recorded at room temperature and at LNT (-180°C) with the help of a Varian variable temperature accessory.

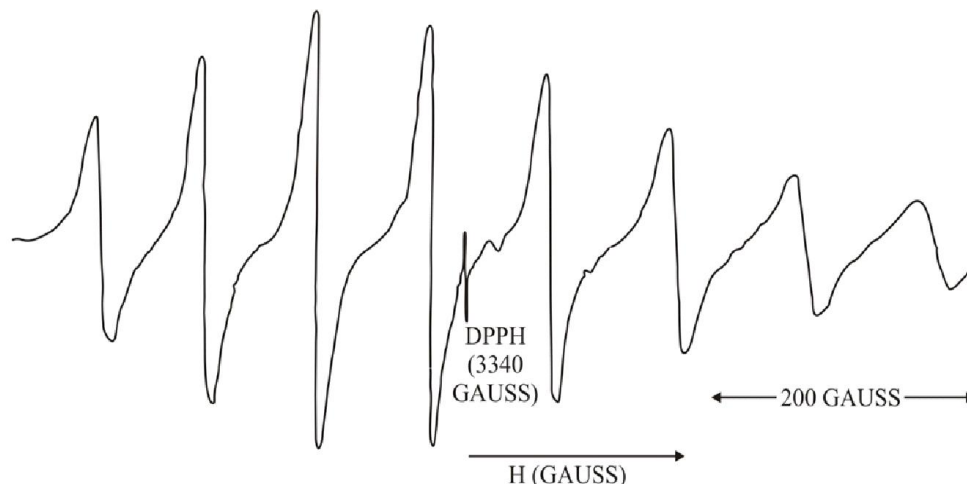


Fig. 1. Spectrum I : EPR Spectrum of VO^{2+} in RbCl at room temperature.

RESULTS AND DISCUSSION

The room temperature EPR spectra for RbCl : VO^{2+} furnish an isotropic angular independent octet. The corresponding spectrum termed as I, is shown in Fig. 1. As the temperature is lowered, the linewidths of hyperfine lines are found to increase leading to overall broadening of the spectrum I and its complete disappearance around -150°C . A new spectrum II, however, appears at the LNT. This new spectrum contains both parallel and perpendicular components. Fig. 2 shows such a spectrum II for RbCl : VO^{2+} with H perpendicular to a cubic face of the crystal. In this spectrum, the parallel component with greater spread is labeled as 'a' while the perpendicular component as 'b'.

At LNT, it was not practical to study the angular variation of EPR spectrum precisely. The LNT spectrum nevertheless appeared to exhibit a general identical appearance for different orientations of H. Finally, the change of EPR spectrum on cooling from type I to type II is found to be reversible; the type II spectrum changing to type I on heating.

The nature of isotropic spectrum I is similar to that reported by Rao *et al* [5] in the case of $\text{KNO}_3 : \text{VO}^{2+}$ and $\text{CsNO}_3 : \text{VO}^{2+}$ at RT and that reported by O' Reilly [15] for vanadyltiorphyrin I (VEPI) in benzene solution. This is also similar to eight line EPR spectrum reported for VO^{2+} in $\text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ [21] and in calcium oxalate monohydrate [16].

On the other hand, the spectrum II is similar to that obtained for VO^{2+} in KNO_3 , CsNO_3 and NH_4Cl hosts [4, 5] at LNT. Further, this spectrum resembles to that obtained by Hochstrasser [16] at room temperature itself for VO^{2+} in amorphous glass and that obtained by O' Reilly [15] for VEPI dissolved in highly viscous petroleum oil.

The spectrum I for VO^{2+} in RbCl is isotropic and independent of crystal orientation with respect to the applied d.c. magnetic field. This indicates that vanadyl molecules have no preferred orientation at room temperature in RbCl host. The origin of spectrum I is most likely due to fastly tumbling V-O bonds and RbCl appears to behave like a liquid for vanadyl ion.

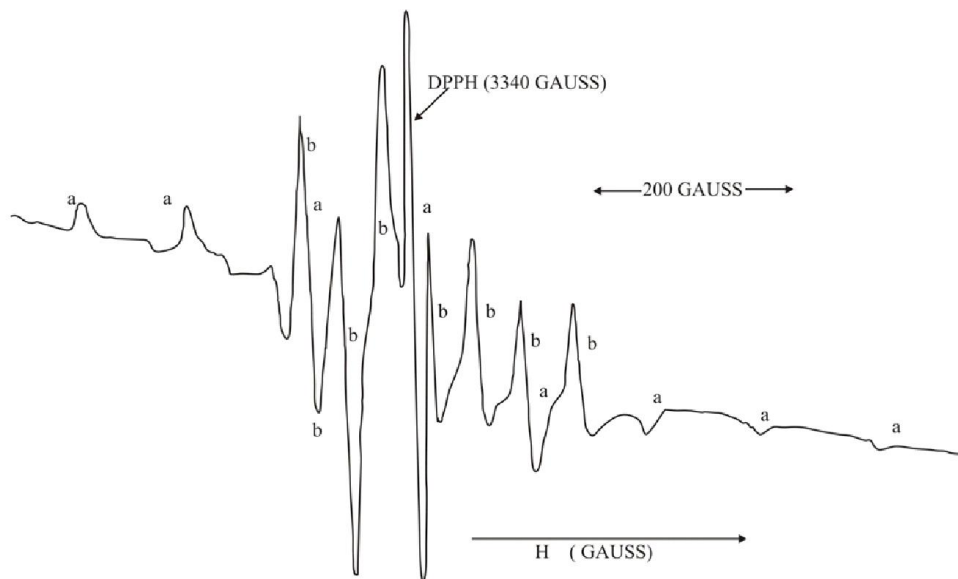


Fig. 2. Spectrum II : EPR of VO^{2+} in RbCl at liquid nitrogen temperature. Lines marked 'a' are parallel transitions and those Marked 'b' are perpendicular transitions.

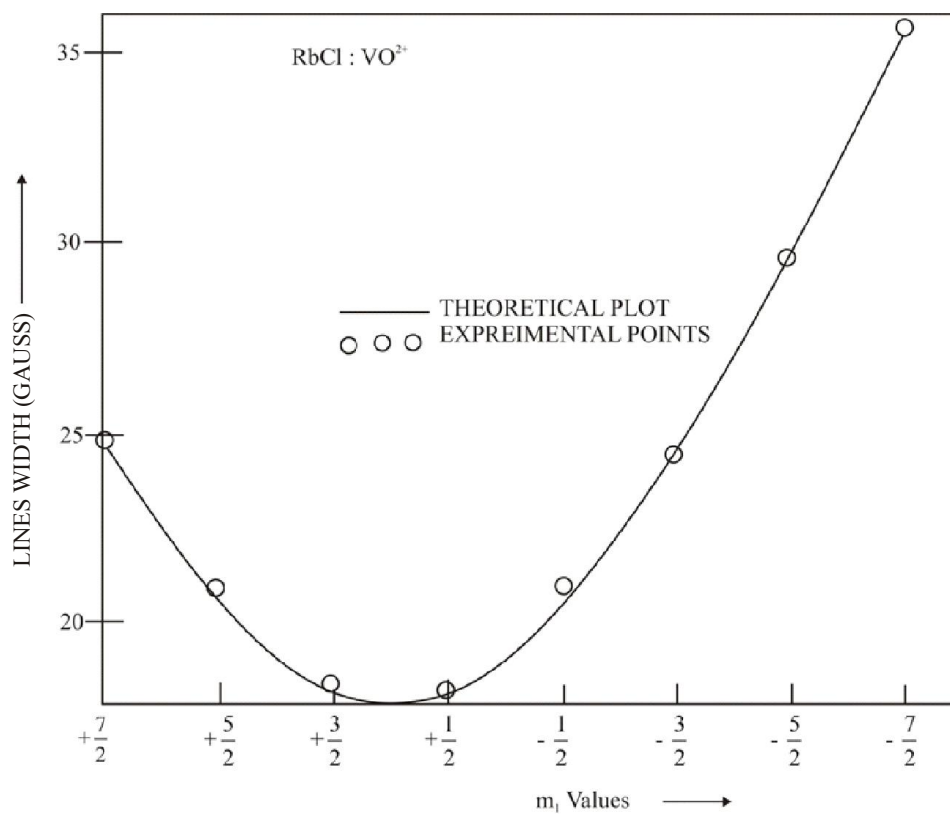


Fig. 3. Plot of Linewidth versus m_l in the EPR of RbCl : VO^{2+} at RT

With the lowering of temperature, the line widths of the hyperfine lines of spectrum I increased, resulting in total broadening of the spectrum at about -100°C . However, on further cooling the sample to LNT, a two octet spectrum II had appeared. This spectrum consisted of eight hyperfine lines, marked 'a', of parallel configuration with H parallel to V=O molecular axis and another eight hyperfine lines, marked 'b', of perpendicular configuration with H perpendicular to molecular axis.

The group 'a' of hyperfine lines of spectrum II (Fig. 2) does not possess the usual first derivative appearance of an absorption peak, to show up both positive and negative area. In such hyperfine lines only positive contours are visible. This shows that the absorption in the group 'a' of lines is not due only to single peaks, but represents continuous absorption build up, probably due to various angular parts alongwith different hyperfine lines. Such line shapes are representative of powder spectra and were extensively investigated by Poole, Jr. and Farach [17] and also by Taylor et al [18] through computer simulation. These workers have shown that the computer simulated spectra of powdered samples show peak positions corresponding to the so called turning points in the angular dependence of the single crystal resonance fields.

Thus, the transition 'a' of VO^{2+} in RbCl at LNT corresponds to the Z-axis ($\theta = 0$) spectrum, also called the // spectrum and the spectrum 'b' corresponds to the X/Y – axis ($\theta = 90^{\circ}$) spectrum, also called the \perp spectrum. This is shown in fig. 2 clearly. Both the sets of eight hyperfine lines 'a' and 'b' were suitably fitted to Hamiltonian equation. The Parameters $A_{//}$, A_{\perp} , $g_{//}$ and g_{\perp} were also found. Their values are given in Table 1 alongwith A_0 and g_0 calculated for **spectrum I**. Mc Connell [20] and O' Reilly [15] had obtained relations which relate g_0 and A_0 for a fastly reorienting vanadyl ion with its $g_{//}$, g and $\perp A_{//}$, A . These are given as –

$$g_0 = \frac{g + 2g_{\perp}}{3}$$

$$A_0 = \frac{A_{//} + 2A_{\perp}}{3}$$

It is observed that the values of different parameters obtained presently follow above Equation reasonably well.

The nature of various hyperfine lines with regard to line-width variation is similar to what has been reported earlier in the case of NH_4Cl [4], KNO_3 and CsNO_3 hosts [5]. Thus, it was interesting to see the applicability of Kivelson's theory [14] of paramagnetic relaxation in liquids to the present RbCl crystal system. According to this theory the line-width of a hyperfine component [21] is given by –

$$\Delta B = \pi \sqrt{3} (a_1 + a_2 m_l + a_3 m_l^2) \quad \dots (1)$$

where the factors a_1 , a_2 and a_3 depend on the anisotropic g factor, anisotropic hyperfine interaction, the correlation time τ_c and the resonance frequency. The experimental line widths of different hyperfine components at room temperature in the present spectrum I, are obtained by using the relation

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

given by Rogers and Pake [20]. Here, it is assumed that the population difference between different m_l levels of the system is negligible.

The line-width and derivative height of one hyperfine component $+1/2 \leftrightarrow -1/2$ in the observed **spectrum I** (Fig.1) was measured directly. Then, using the observed derivative heights, the line-widths of the other hyperfine transitions were calculated through Eq. (2)

above. Thus obtained values of ΔB for the line-widths of the various hyperfine components are given in Table 2. The constants a_1 , a_2 and a_3 were then calculated by fitting the experimental data to the required equation (1) and the values obtained are given in Table 3. Fig. 3 [19]. The parabolic plot for variation of ΔB with m_1 values and this lies close to the experimental data as shown in fig. 3.

It is seen that a_1 parameter is positive and increases monotonously in the series of hosts RbCl, RbBr and RbI. The a_2 parameter is however negative for all the hosts. It varies very slightly from RbCl to RbBr, but changes abruptly from RbBr to RbI. The parameter a_3 is positive for all the hosts and decreases in the series of hosts RbCl, RbBr and RbI. Using the expression of Rogers and Pake [22], the correlation time τ_c has been calculated and is found to be 0.70×10^{-11} sec. This value is close to the value of τ_c estimated by Kivelson [14] for a vanadyl complex in benzene solution to be 6×10^{-11} sec. The same order of τ_c in both RbCl and benzene hosts, supports the assumption that vanadyl ion exhibits liquid-like behavior in RbCl lattice at room temperature.

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