ELECTRON PARAMAGNETIC RESONANCE STUDIES OF VO²⁺ IN SINGLE CRYSTALS OF NaCl, KCl AND RbCl*

BY A. V. JAGANNADHAM

(*Department of Physics, Indian Institute of Technology, Kanpur, India*)

AND

PUTCHA VENKATESWARLU,** F.A.SC.

(*Department of Physics, University of California, Santa Barbara, California*)

ABSTRACT

Electron paramagnetic resonance (EPR) of VO^{2-} radicals incorporated in face-centred single crystals of NaCl, KCl and RbCl has been studied in the temperature range of 77° K to 330° K. At liquid nitrogen temperature, anisotropic spectra have been recorded in each case while spectra recorded at room and higher temperatures are isotropic suggesting the existence of a fast readjustment of VO^{2+} molecular ions in the crystals at higher temperature while this motion gets hindered at liquid nitrogen temperatures. Spin-Hamiltonian constants are calculated from the recorded isotropic and anisotropic spectra. The line widths in each case are found to obey a parabolic law originally proposed by Kivelson. The constants which give a close fit have been evaluated. The random orientation and readjustment of V-0 bond in these alkali chloride crystals is explained on the assumption that the medium exhibits a "liquid-like" nature for VO^{2+} molecular ion as far as the electron paramagnetic resonance absorption is concerned.

INTRODUCTION

ELECTRON paramagnetic resonance (EPR) of VO^{2+} doped in NH_4Cl single crystal has been recently studied by Sastry and Venkateswarlu[1] and that in KNO_3 and $CSNO_3$ by Rao, Sastry and Venkateswarlu.[2] It has been found

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307

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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 orientation in Tutton salts[3] and in rubidium and cesium alums.[4] Very recently Rao, Sastry and Venkateswarlu[5] have also found from their EPR studies that the VO²⁺ ion has a preferred orientation in the potassium and ammonium alums. The present work has been undertaken to get information about the VO²⁺ complex in the alkali halide crystals, NaCl, KCl and RbCl. Further it was felt that if these systems exhibit a " liquid-like " behaviour they might represent better examples than $NH_4Cl : VO^{2+}$, $KNO_3 : VO^{2+}$ and $CSNO_3 : VO^{2+}$ to examine the applicability of Kivelson's theory[6] of paramagnetic relaxation in liquids as these crystals (alkali halides) do not have any phase transformation.

Experimental Procedure

0·5 mol percent of vanadyl chloride is added to E. Merck, A. R. quality chlorides of sodium, potassium and rubidium. Slow evaporation of aqueous solution yielded well-developed cubes. EPR measurements are carried at X band 9·5 kMc/sec nominal frequency with a Varian V-4502 EPR spectrometer and a V-3400 nine-inch rotating electromagnet using a 100 kc/sec field modulation. The magnetic field is calibrated using DPPH* as a field marker. The proton resonance is monitored with a Varian Fluxmeter model F-8 A connected to a Beckmann 10–110 Mc/sec convertor 7571. Spectra are recorded at various temperatures ranging from + 60° C to − 180° C with the help of a Varian V-4540 variable temperature accessory. General microwave 459 A thermoelectric power meter has been used for measuring the power output. IBM electronic computers 1620 and 7044 have been used for calculations and least square fit.

Theory

The electronic state of the VO²⁺ ion is mainly dependent on the $3d'$ electron of vanadium. In a crystalline field of symmetry less than cubic the lowest level will be an orbital singlet. In such a case only one fine structure transition can be expected in EPR, and the hyperfine structure would show eight lines because of the V⁵¹ nucleus whose spin is 7/2. As the EPR is due to the molecular ion which has itself an axial field, the spectrum cannot be expected to reveal cubic site symmetry even if VO²⁺ goes

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* Diphenylpicrylhydrazyl whose g-value is taken as 2·0036.

in substitutionally and the expected positive vacancy is too far off from it. If the VO^{2+} ion goes in substitutionally in the present alkali halides as Mn^{2+} in NaCl, it might get associated with a first neighbour positive vacancy in which case the site symmetry will be orthorhombic or it might get associated with a second neighbor positive vacancy in which case the site symmetry will be tetragonal. However the EPR spectra of VO^{2+} obtained in the present experiments are found to be independent of the crystal orientation with respect to the magnetic field indicating clearly that the VO^{2+} ion has no preferred orientation in the present crystals.

For a paramagnetic ion placed in a matrix which does not exhibit directional properties the spectra can be interpreted using a simple model of random array[7] of magnetic ions. The EPR spectrum of VO^{2+} in tetragonal symmetry or of randomly oriented VO^{2+} molecular ions in solutions can be described by the spin-Hamiltonian, [8–10] of the type

$$\mathcal{H} = g_{\parallel}\beta H_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A I_z S_z + B (I_x S_x + I_y S_y).$$

$$(1)$$

The Hamiltonian (1) leads to the following magnetic field resonance[10] values for the hyperfine structure components in the EPR spectrum of VO^{2+} :

$$H = H_0 - \frac{K m_I}{g\beta} - \frac{B^2 (A^2 + K^2)}{4 H_0 g^2 \beta^2 K^2} [I(I+1) - m_I^2]$$

$$- \frac{(A^2 - B^2) g_{\parallel}^2 g_{\perp}^2}{2 H_0 g^2 \beta^2 K^2 g^4} \sin^2 \theta \cos^2 \theta m_I^2 \qquad (2)$$

where

$$H_0 = \frac{h\nu}{g\beta},$$

$$g^2 = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta$$

and

$$K^2 g^2 = A^2 g_{\parallel}^2 \cos^2 \theta + B^2 g_{\perp}^2 \sin^2 \theta,$$

θ being the angle between crystalline or molecular field z-axis and the direction of the magnetic field.

When the system examined has statistically oriented ions, the resonance lines are in general distributed for each m_I value between two extreme positions[8, 11, 12] which are characteristic of the parallel and perpendi-

cular orientations. Thus when I = 7/2 the derivative of the spectrum consists of eight lines of the absorption type which are characteristic of the $\perp$ positions and eight other lines of the dispersion type which are characteristic of the parallel positions. By an analysis of these lines it is possible to evaluate the components of g ($g_\perp$ and $g_{||}$) and of A ($A_{||}$ = A and $A_\perp$ = B).

RESULTS AND DISCUSSION

All the systems studied have given similar spectra at room temperature, an isotropic angular independent octet, designated I. As the temperature is lowered, the line widths increase and finally the spectrum nearly disappears at $-160°$ C. A new spectrum appears in each case at liquid nitrogen temperature and contains both parallel and perpendicular components. This anisotropic spectrum, designated II, is also angular independent. Figures 1 (a) and 1 (b) show the typical spectra obtained in the case of NaCl : VO^{2+} system. The parallel and perpendicular components are
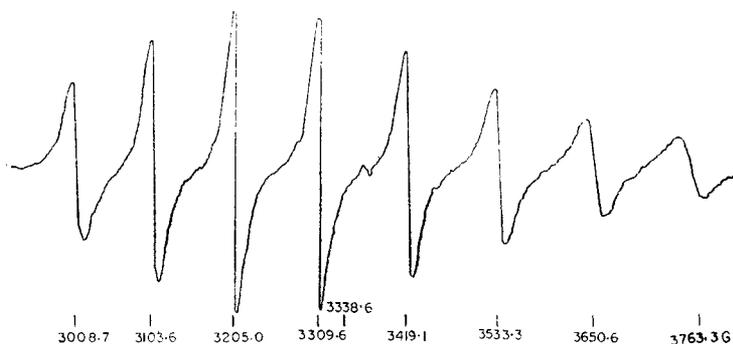

FIG. 1. Spectrum I, electron paramagnetic resonance spectrum of VO^{2+} in NaCl at room temperature. The x-coordinate represents magnetic field values in gauss.

labelled "a" and "b" respectively. The gradual change of spectrum I to spectrum II with lowering of temperature is reversible. The isotropic spectrum I is similar to those reported by Rao et al.[2] in the case of CSNO$_3$: VO^{2+} and KNO$_3$: VO^{2+} at room temperature, and O'Reilly[8] for Vanadyl etioporphirin I (VEPI) in benzene solution. On the other hand the anisotropic spectrum II obtained at liquid nitrogen temperature as in the case[1, 2] of KNO$_3$, CSNO$_3$ and NH$_4$Cl is similar to the spectrum obtained by Hochstrasier[11] for VO^{2+} in amorphous glass and to those obtained by O'Reilly[8] for VEPI dissolved in high viscous petroleum oil and for solid asphaltenes containing vanadium. This similarity suggests that the VO^{2+} in alkali chlorides behaves as if it were in a liquid medium as far as the results of

EPR are concerned. The isotropic spectrum at room temperature is probably due to a fast reorientation of the V-0 bond which results in the averaging out of anisotropies in g and A tensors. As the temperature is lowered, the fast reorientation gets hindered and at liquid nitrogen temperature the reorientation rate is slow enough that the anisotropies in g and A tensors are not averaged and can be seen in the spectrum. However even at liquid nitrogen temperature the orientation of the VO bond is random enough to make the EPR spectrum angular independent. It may be mentioned that the anisotropic spectrum obtained here is similar to that obtained by Borcherts and Kikuch[3] for VO^{2+} in polycrystalline Tutton salts; but the probability of the formation of polycrystals at low temperature in the present experiments is ruled out as the transformation of the spectrum I to II is found to be reversible. The appearance of spectrum II only at liquid, nitrogen temperature is probably due to the hindrance of the motion of VO^{2+} ion due to the lowering of temperature and as such appears to be a purely temperature effect as unlike in NH_4Cl there are no phase transformations in the crystals studied here.
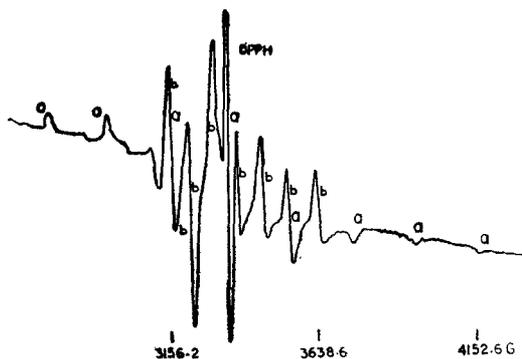

FIG. 2. Spectrum II, electron paramagnetic resonance of VO^{2+} in NaCl at liquid nitrogen temperature. Lines marked a are parallel transitions and those marked (b) are perpendicular transitions. The x-coordinate represents magnetic field values in gauss.

O'Reilly[8] and McConnel[13] obtained the following expressions for the isotropic values of g and A in terms of g_{π} and $g_{\perp}$ for the cases where the molecule is rotating with a correlation time much shorter than the reciprocal of the frequency spread of this spectrum:

$$g_0 = \frac{g_{\pi} + 2g_{\perp}}{3} \tag{3A}$$

$$A_0 = \frac{A + 2B}{3}. \tag{3B}$$

The values obtained for g_0 and A_0 from the analysis of the spectrum I are listed in Table I for the different alkali halides studied.

Table I

Spin-Hamiltonian Constants for VO^{2+} in NaCl, KCl and RbCl single crystals
(Values of A_0, $A_{||}$ and $A_{\perp}$ are in units of $10^{-4}\,cm.^{-1}$)

Crystal System	Spectrum I	Spectrum II
NaCl : VO^{2+}	$g_0 = 1\cdot971 \pm 0\cdot001$ $A_0 = 104\cdot0\pm1\cdot0$	$g_{||} = 1\cdot925 \pm0\cdot002$ $g_{\perp} = 1\cdot996 \pm0\cdot002$ $A_{||} = 176\cdot8\pm2\cdot0$ $A_{\perp} = 64\cdot2\pm2\cdot0$
KCl : VO^{2+}	$g_0 = 1\cdot969 \pm0\cdot002$ $A_0 = 106\cdot8\pm2\cdot0$	$g_{||} = 1\cdot932 \pm0\cdot002$ $g_{\perp} = 1\cdot988 \pm0\cdot002$ $A_{||} = 186\cdot8\pm3\cdot0$ $A_{\perp} = 70\cdot4\pm5\cdot0$
RbCl : VO^{2+}	$g_0 = 1\cdot967 \pm0\cdot002$ $A_0 = 106\cdot0\pm2\cdot0$	$g_{||} = 1\cdot939 \pm0\cdot002$ $g_{\perp} = 1\cdot968 \pm0\cdot002$ $A_{||} = 188\cdot7\pm3\cdot0$ $A_{\perp} = 63\cdot9\pm3\cdot0$

The Hamiltonian (1) remains anisotropic for cases where the correlation time is long. The existence of anisotropic spectra at liquid nitrogen temperature in all cases is confirmed by varying the microwave power level from $1\cdot0\,\mu$ to $110\,\mu$ mW. There were no saturation effects and the intensities followed the power levels, their relative values remaining the same.

All the spectra obtained, type I and type II, have been analyzed using equation (2) and the results are tabulated in Table I.

Line Width Studies

The spin resonance studies have clearly shown that VO^{2+} in alkali chlorides exhibit a "liquid-like" nature as far as the para-magnetic resonance and relaxation are concerned similar to what has been reported earlier in the case of NH_4Cl, KNO_3 and $CSNO_3$[2]. An attempt is therefore made to see the applicability of Kivelson's theory[6] of par magnetic relaxation in liquids, to the single crystal systems of the present study.

It has been shown[6,13] that the anisotropies in g and A tensors contribute to the line broadening in the EPR spectra. When there are considerable

anisotropies in g and A, the line widths can be given by the following expression[14]

$$\frac{1}{T_2} = (a_1 + a_2 m_I + a_3 m_I^2).$$ (4)

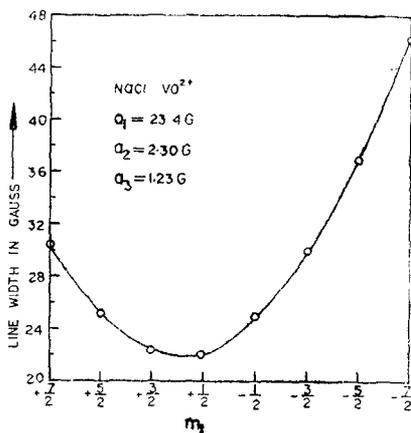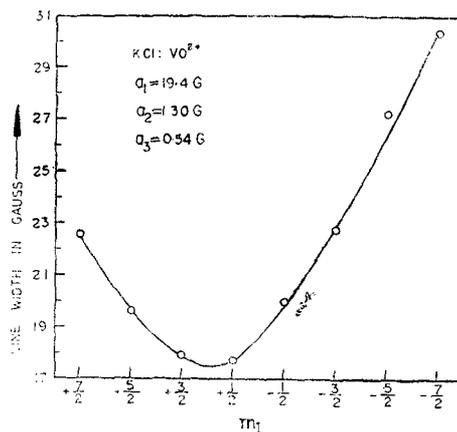where a's depend upon the factors $(g_{||} - g_{\perp})$ and $(A - B)$.

Fig. 3

Fig. 4

Fig. 3. Plot of line width *versus* m_I in the EPR of NaCl : VO^{2+} system. The sold curve represents predicted variation of the line width while circles indicate actual experimental values at room temperature.

Fig. 4. Plot of line width *versus* m_I in the EPR of KCl : VO^{2+} system. The solid curve represents predicted variation of the line width while circles indicate actual experimental values at room temperature.

Fig. 5

Fig. 5. Plot of line width *versus* m_I in the EPR of RbCl : VO^{2+} system. The solid curve represents predicted variation of the line width while circles indicate actual experimental values at room temperature.
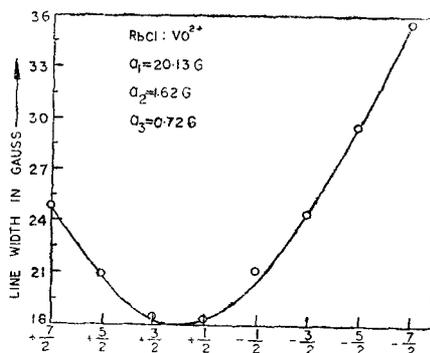
The experimental line widths are measured by the method used by Rogers and Pake[14] and Rao, et al.[2] where it is assumed that the population difference between the different m_I levels is small. The m dependence of the line widths is shown in Figs. 2 (a), (b) and (c). These curves fit in very well with eq. (4), and a least-square calculation yields the constants a_1, a_2 and a_3 given in Table II. Wilson and Kivelson[15] have added a cubic term to the polynomial in eq. (4), but such a term is not found to be necessary in the present case.

TABLE II

Line Width Parameters of the EPR of VO^{2+} in Alkali Halides

	a_1 in gauss	a_2 in gauss	a_3 gauss
NaCl	23·4	2·30	1·23
KCl	19·4	1·30	0·54
RbCl	20·13	1·62	0·72

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