EPR Study of Some Vanadyl Doped Single Crystals

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Abstract : Electron Paramagnetic resonance (EPR) study of some VO^{2+} doped single crystals of $M_6Sb_4(SO_4)_3 F_{12}$ (M = Cs, Rb, NH$_4$) have been carried out. An introduction and theoretical background related to the above investigations have also been discussed. The result, discussion and conclusions drawn are presented in this paper.

1. Introduction

Compounds having composition $3MSO_4 4SbF_3$ (M = Cs, Rb, NH$_4$) form hexagonal systems with closely similar cell constants and each unit cell containing three formula units[1]. The infrared spectra (IR) of $M_6Sb_4(SO_4)_3 F_{12}$ exhibit splitting of deformation and valence vibrations of the SO_4 groups into compounds[2], indicating that sulfate groups are coordinated with the antimony atoms hence the $M_6Sb_4(SO_4)_3 F_{12}$ compounds are not double salts of the $3MSO_4. 4SbF_3$ type. It is believed that SO_4 groups act as bridges which bind the antimony atoms. NQR Study[3] suggested that there are four types of antimony atoms differing in respect of their environment. These antimony sites have different coordination polyhedron having different strengths of binding and are similar to those in antimony sulfides[4-5]. Electron paramagnetic resonance has well established merits in the study of phase transitions[6] and the vanadyl ion (VO^{2+}) has been fruitful particularly in the study of ferroelectric phase transitions[7-8]. EPR study of VO^{2+} ions doped in $(NH_4)Sb_4 (SO_4)_3 F_{12}$ between room temperature (RT) and liquid nitrogen temperature (LNT) has been also reported by Agarwal and Chand[9].

2. Theory of EPR of Vanadyl Ion (VO^{2+})

Jorgenson[10] and Furlani[11] using simple crystal field model have given the energy level scheme for vanadyl ion. Model could not account for the observed magnetic properties of $VOSO_4 5H_2O$ and concluded that π bonding between vanadium and oxygen must be important. The energy level scheme in crystalline fields of octahedral and tetragonal symmetry is shown in Fig. 1. The parameters D_s and D_t show specifically the

degree of tetragonality present in the field[12]. For the ground state configuration one d electron in VO^{2+} is placed in the B_2 orbital and the predicted electronic transitions are

$$^2B_{2g} \rightarrow {}^2E_g \left(-3 D_s + 5 D_t \right)$$

$$^2B_{2g} \rightarrow {}^2B_1 \left(10 D_q \right)$$

and

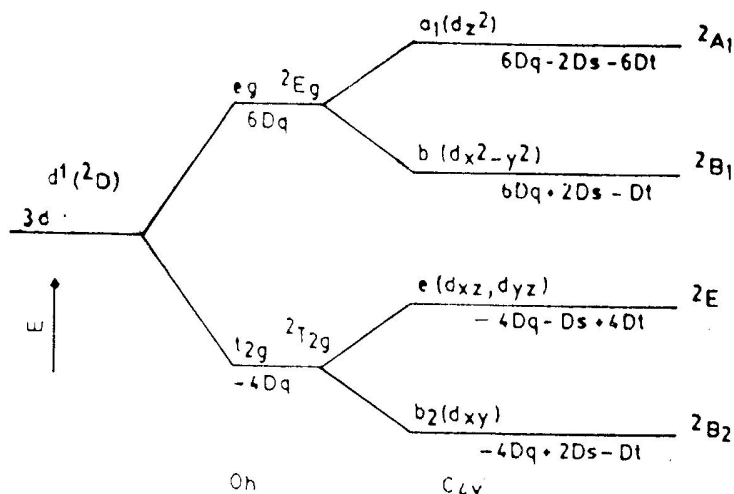$$^2B_{2g} \rightarrow {}^2A_{1g}, \left(10 D_q - 4 D_s - 5 D_t \right).$$

Fig 1. Energy level scheme of VO^{2+} in crystalline fields of octahedral and tetragonal symmetry (after Ballhausen and Gray [19])

The value of D_q is obtained directly from the transition $^2B_{2g} \rightarrow {}^2B_{1g}$ and the values of D_s and D_t can be calculated from the other two observed transitions. Ballhausen and Gray[13] have shown that a pure crystalline field model which only consider σ-bonding to be present is not adequate and for an accurate description of the electronic structure of the VO^{2+} ions and its complexes π-bonding must also be included. In vanadyl ion complexes the unpaired electron is in the orbital singlet state $^2B_{2g}$. On the application of magnetic field this spin doublet splits into two and paramagnetic resonance absorption can be observed between these two levels. As $S = 1/2$, the crystal field terms do not enter into the Spin Hamiltonian[14] and thus the resonance spectra are described by a Spin Hamiltonian of the form[15]

(2.1) $$\mathcal{H} = \beta . B . \tilde{g} . S + S . \tilde{A} . I$$

the energy eigen-value for this Spin-Hamiltonian have been given by Pryce[16] and

Bleaney[17] explicitly to second order in the special case in which $\tilde{g}$ and $\tilde{A}$ are axially symmetric and have the same principal axes. In the case of VO^{2+} electronic spin $S = 1/2$ and Nuclear Spin is 7/2. There are eight transitions corresponding to $\Delta m = \pm 1$ (spin quantum) $\Delta m = 0$ (nuclear Spin quantum) selection rules are given by

$$(2.2) \quad B(m) = B_0 - \frac{k\,m}{g\,\beta} - \frac{\left(A_\perp^2\right)\left(A_{11}^2 + K^2\right)}{4\,B_0\,g^2\,\beta^2\,k^2}\left[I(I+1) - m^2\right]$$

$$- \frac{\left[\left(A_{11}^2 - A_\perp^2\right)\right]}{8\,B_0\,g^2\,\beta^2\,k^2}\left(g_{11}\,g_\perp\;/\;g^2\right)^2\left(\sin^2 2\,\theta\right)m^2$$

where

$$B_0 = h\,v/g\,\beta\,;\; k^2\,g^2 = g_{11}^2\,A_{11}^2\,\cos^2\theta + g_\perp^2\,A_\perp^2\,\sin^2\theta\,,$$

θ being the angle between the symmetry axis of $\tilde{A}$ and the direction of magnetic field B, $g^2 = g_{11}^2\,\cos^2\theta + g_\perp^2\,\sin^2\theta$ and B(m) is the resonance field corresponding to m values.

3. Experimental

Crystals of $M_6\,Sb_4\,(SO_4)_3\,F_{12}$ (to be called MSSF) were grown by slow evaporation of aqueous solution at RT. Appropriate amounts of M_2SO_4 and SbF_3 were dissolved in water and mixed together. Small amount (~ 0.1%) of $VOSO_4$ was dissolved and kept for evaporation in a constant temperature bath at $36 \pm 1°C$. To grow mixed crystals of NH_4 with Rb, appropriate amounts of respective sulfate were mixed together. The ammonium and rubidium crystals grow in the form of prisms and the cesium compounds formed cubic crystals. The crystals were slightly bluish in colour and were stable under the ambient atmosphere. The compounds crystallize in the hexagonal crystal system with the cell parameters[1].

$$a = 18.09 \text{ Å and } C = 7.56 \text{ Å for } NH_4 \text{ compound}$$

$$a = 17.02 \text{ Å and } C = 7.50 \text{ Å for Rb compound}$$

$$a = 17.49 \text{ Å and } C = 7.88 \text{ Å for Cs compound}$$

4. Results and Discussions

The crystals were checked by powder X-Ray diffraction technique. The X-Ray diffractograms are shown in Fig. 2. The observed X-Ray diffraction patterns are in good agreement with the earlier report[1]. EPR signals at X-band frequencies (~ 9GHz) reveal that at RT all crystals show orientation indpendent eight line spectra. The peak to peak line width were found to be quite different for the different lines of the spectrum (Fig 3). The EPR spectra were also recorded at LNT. It was observed that at LNT the EPR spectra are different as compared to RT (Fig. 4 and 5). However the observed EPR spectra were orientation independent spectra (OIS) even at LNT.
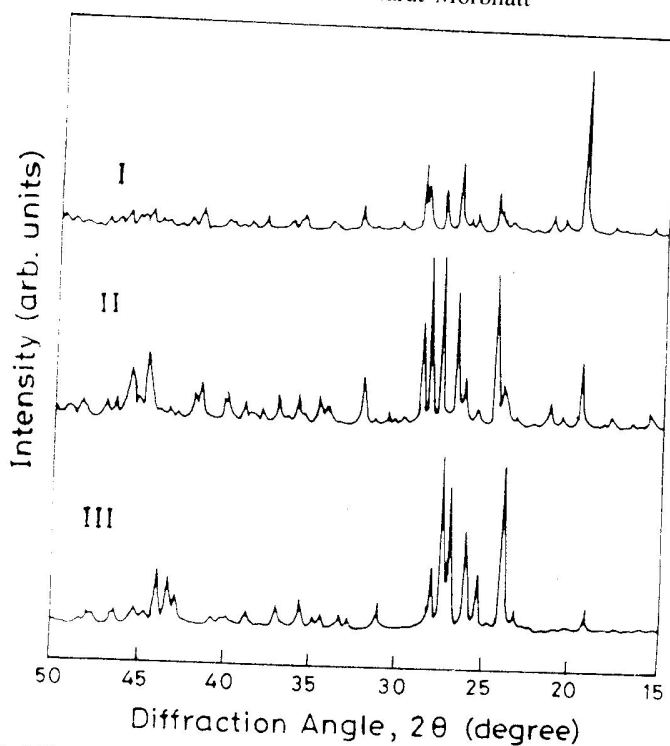
Fig.2 X-ray diffraction patterns of powder samples of (I)-NH₄SSF (II)-RbSSF (III)-GSSSF taken at RT with Cu-Kα radiation

Table 1

Spin Hamiltonian parameters for VO^{2+} *in* M_6 Sb_4 $(SO_4)_3$ F_{12} *for OIS (I-type at RT)*

Host (M)	g_0	A_0	Remarks
NH₄	1.970 ± 0.001	110.80 ± 2(10^{-4} cm⁻¹)	Ref. 9
Rb	1.978	120 (G)	Present work
Cs	1.965	112 (G)	"
(NH₄)₀.₉₅ Rb₀.₀₅	1.965	112 (G)	"

The EPR spectra of single crystals of MSSF were found to be OIS and at RT comprised eight resonance lines (Octets) each. The line widths within an octet differed for different values of m. The observation of OIS for VO^{2+} in single crystals is not new and explained on the basis of tumbling of VO^{2+} ion in crystalline hosts similar to in solutions. The RT spectra are to be called I-type. On cooling the crystals the intensity of I-type spectra decreased progressively and the spectra disappeared in the temperature range 253-223°K. On further cooling a new kind of EPR spectrum (to be called II-type) originated and its intensity improved progressively upto LNT. Isotropic parameters g_0 and | A_0 | obtained from the analysis of RT spectra are given in Table 1.
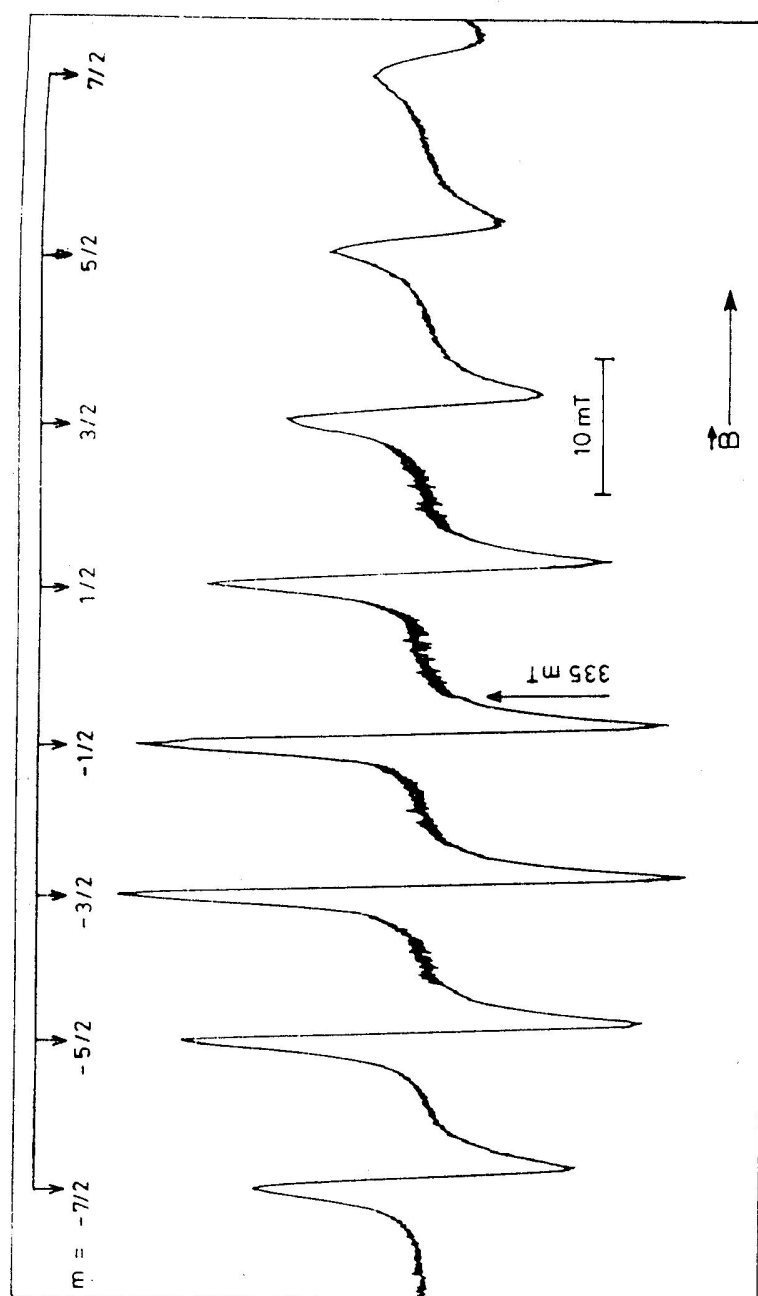
Fig. 3 X-band EPR spectrum of VO^{2+} doped by Rb SSF single crystal at RT.
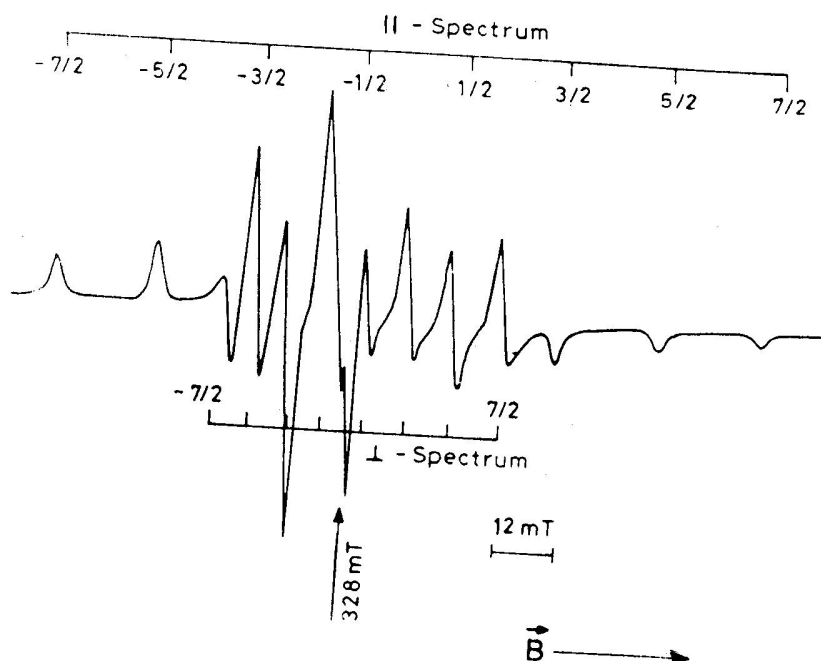*m* denotes the nuclear spin quantum number associated with the hyperfine peak.

Fig.4 X-band EPR spectrum of VO^{2+} doped by Rb SSF single crystal at LNT.
The spectrum is powderlike and the $\parallel$ and $\perp$ parts of the spectrum are identified.
The value of m corresponding to each transition is also indicated

Table 2

Spin Hamiltonian parameters for VO^{2+} *in* $M_6\ Sb_4\ (SO_4)_3\ F_{12}$ *at LNT (OIS-II-type)*

Host (M)	g_{11}	$g_\perp$	A_{11}	$A_\perp$	$g_{av} = [(g_{11} + 2g_\perp)/3]$	$A_{av} = [(A_{11} + 2A_\perp)/3]$
NH_4	1.942 ± 0.001	1.981 ± 0.001	192.33 ± 2	$71\pm 2^*$	1.968	119.23^*
Rb	1.940 ± 0.001	1.980 ± 0.001	185 ± 2 (gauss)	67 ± 2 (gauss)	1.967	106
Cs	1.935 ± 0.001	1.970 ± 0.001	120 ± 2 (gauss)	53 ± 2 (gauss)	1.958	75
$\cdot(NH_4)_{0.95}$ $Rb_{0.05}$	1.938 ± 0.001	1.975 ± 0.001	200 ± 2 (gauss)	70 ± 2 (gauss)	1.963	113

$^*10^{-4}$ cm^{-1} from ref.9

The SHP obtained from the analysis of II-type spectra at LNT are given in Table 2.
It is seen that the SHP of VO^{2+} in all the hosts under study are in good agreement with
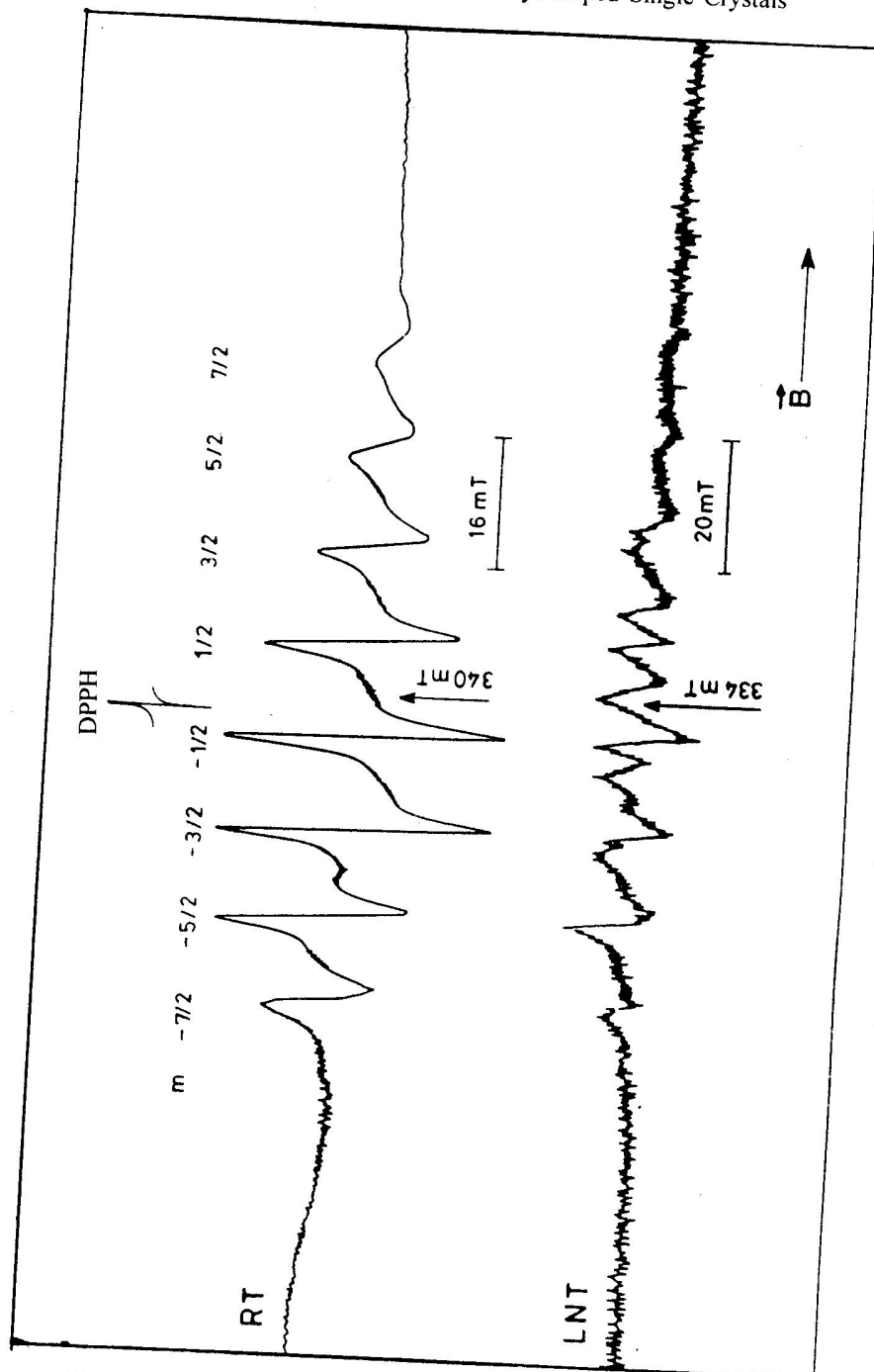
Fig. 5. X-band EPR spectrum of VO^{2+} doped by Cs SSF single crystal at RT and at LNT. m denotes the nuclear spin quantum number assigned to transition. In LNT spectrum the $\parallel$ and $\perp$ parts of the spectrum are also identified.

each other. The reason may be that the spectra of I-type are recorded at RT and those of II- type are recorded at LNT therefore the temperature dependence of SHP may cause the disagreement.

5. Conclusion

From the observed orientation independent EPR spectra it is concluded that VO^{2+} shows a liquid like behaviour in MSSF in higher temperature phases. EPR study of VO^{2+} ion doped $M_6Sb_4 (SO_4)_3 F_{12}$ (M = Rb, Cs, NH_4) single crystals has shown that vanadyl ion tumbles rapidly in the high temperature phase of the MSSF materials and the motion is quenched at lower temperature (230°K).

Acknowledgement

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