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ELECTRON PARAMAGNETIC RESONANCE STUDIES ON SOME TUTTON SALT SYSTEMS

Navin Pant[1a], A. L. Verma[2a*] and S. D.Pandey[3b]

[a]Department of Applied Physics, Amity Institute Of Applied Sciences, Noida-201313, INDIA. Email: navinpantksp@gmail.com[1]; alverma@amity.edu[2]
[b]PPN college P.G. Center, Kanpur University, Kanpur-208001, INDIA. Email: sdpandey41@gmail.com[3]
Corresponding Author: alverma@amity.edu

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ABSTRACT Electron paramagnetic resonance (EPR) studies were carried out on a vanadyl doped mixed Tutton salt ($Zn_{0.25}Mg_{0.75}(NH_4)_2(SO_4)_2.6H_2O$) system. The “g” and “A” parameters obtained from our studies were compared with other vanadyl doped Tutton salts and a critical analysis is presented. As *the EPR results depend upon the vicinity of V^{4+} of doped V=O ion in the host, the ‘g’ and ‘A’ parameters obtained from our studies reflect distorted octahedral surroundings of V^{4+} in the Tutton salt host and two major types of metal –water linkages are established.* Our findings are supported by the X-ray studies and electric field assisted de-aquation studies on Tutton salts by the earlier works. Critical analysis and correlation of the results indicate that the equatorial bonds and axial bonds between the oxygen of water molecules and the divalent cation in Tutton salts are of different nature, confirming that the octahedron formed by water molecules around the divalent ion in Tutton salts is distorted.

Keywords: Tutton salt, EPR, X-ray studies, de-aquation studies of Tutton Salts.

1. INTRODUCTION

The salts with the chemical formula $M^{//} M_2^{/} (XO_4)_2.6H_2O$ are a group of isomorphous compounds with monoclinic crystal structure (Tutton, 1928) and bear the name of Tutton. Here the $M^{//}$ is a divalent cation such as Mg, Zn, Cd or an ion of 3d group, $M^{/}$ is a monovalent cation such as K, Rb, Cs or NH_4 and X is S or Se.

The crystals of Tutton salt are prepared by slow evaporation of a saturated solution of mixed sulphates. The crystals growth with well-developed faces and are reported to be isomorphous (Margulis and Tmpleton, 1962). The detailed crystal structure of magnesium ammonium sulphate hexahydrate [MASH] is as shown in Figure 1 (Margulis & Templeton, 1962). Here each $M^{//}$ divalent cation is surrounded by an octahedron of water molecules. It is found that the octahedron is irregular; the equatorial $M^{//}$-H_2O bonds are longer as compared to the axial $M^{//}$-H_2O bonds. The details are given in Table 1. The isomorphism of Tutton salts suggests a similar crystal structure for all the Tutton salts. Furthermore, the de-aquation studies in some Tutton salts are reported which suggests non-equivalence of water molecules in the octahedra in some Tutton salts (Srivatsa & Pandey, 1984; Srivatsa & Pandey, 1985a; Srivatsa & Pandey 1985b).

The water molecules in Tutton salts form hydrogen bondings. In potassium Tutton salts, for example, the hydrogens of the water group are bonded on one side with its own oxygen and on the other side with the oxygen of SO_4^{2-} group. In Tutton salts containing ammonium ions, additional H bonding also exists; here H of NH_4^+ is linked on one side with the N and on the other side with the sulphate oxygen (Margulis & Templeton, 1962). Thus these Tutton salts have gathered the attention of various researchers. Recently, copper based Tutton salts (Chen et al., 2006) were used for the study of Jahn Teller distortion. The EPR studies on Cr^{3+}- doped Tutton salts are also reported (Ravi et al., 2006).

In the present work we have critically analyzed and correlated the results of our EPR work in VO-doped mixed Tutton salt $Zn_{0.25}Mg_{0.75}(NH_4)_2(SO_4)_2.6H_2O$ with the X-ray and electric field assisted de-aquation studies in Tutton salts reported earlier (Srivatsa & Pandey, 1984; Srivatsa & Pandey, 1985a; Srivatsa & Pandey 1985b). All these studies point towards a distorted octahedral structure of water molecules surrounding the divalent metal ion.

2. EXPERIMENTAL METHODS

Vanadyl ion doped $Zn_{0.25}Mg_{0.75}(NH_4)_2(SO_4)_2.6H_2O$ crystals were grown by slow evaporation of a saturated solution in distilled water with 1:3:4 molar ratio of $ZnSO_4$, $MgSO_4$ & $(NH_4)_2SO_4$. Vanadyl sulphate 1% by weight, was also added into the saturated solution. The solution was then left at 10 ^{0}C leading to the formation of shinning facets of single crystals after 15 days. The crystals grown had prismatic appearance, in general.

As it is known, the EPR spectrum of a powdered sample furnishes important information about the spin Hamiltonian parameters $g_{||}$, $g_\perp$, $A_{||}$ and $A_\perp$ related to the crystal structure, the present studies have been undertaken on powdered samples (Jain et al., 1984). The spectra shown in Figure 2 were recorded at room temperature using Varian E-line century series spectrometer E-109 and DPPH was used as the field maker, whose resonance field was obtained by E-500 digital NMR Gauss meter.

3. RESULTS AND DISCUSSIONS

3.1 EPR of Vanadyl Doped Tutton Salt System

The orientation of doped vanadyl ion (V=O) depends on the formation of the V=O group in the complex VO $(H_2O)_5$ in the lattice. Four equatorial water groups from the total of six are linked to the V of the V=O group in one plane, while one water group is perpendicular to the plane and the remaining V=O group is at 180° opposite to fifth water group.

Figure 2 shows the EPR spectrum of VO-doped $Zn_{0.25}Mg_{0.75}(NH_4)_2(SO_4)_2.6H_2O$ system in the powdered polycrystalline phase. In such samples, both the upper and lower contours are not simultaneously seen in the first derivative curve of the EPR absorption of magnetic field (Jain et al., 1984). The turning points of both parallel and perpendicular spectra are, however well defined. Using the field positions and the expressions for resonance transitions ($m \rightarrow m$), (Pake, 1962), the $g_{||}$, $g_\perp$, $A_{||}$ and $A_\perp$ parameters are calculated as:

$g_{||}$ = 1.93 ± 0.01

$g_{\perp}$ = 1.98 ± 0.01

$A_{||}$ = 201.8 ± 3.0 G

$A_{\perp}$ = 78.5 ± 3.0 G

In energy units.

$A_{||} = (-181.4 \pm 2.8) \times 10^{-4}\ \mathrm{cm}^{-1}$

$A_{\perp} = (-70.6 \pm 2.8) \times 10^{-4}\ \mathrm{cm}^{-1}$

The signs of $A_{||}$ and $A_{\perp}$ are obtained by considering the nature of the hyperfine parameter as the sum of dipolar and Fermi-contact contributions. The 'g' and 'A' parameters of the vanadyl ion are for different Tutton salts are given in Table 2. These results are similar and confirms the replacement of $M^{//}$ in the Tutton salt lattice by vanadyl and forming bonds with neighboring water groups.

In the EPR literature, different authors present two to three types of V=O orientations with respect to the water octahedron (Borcherts & Kikuchi, 1964; Upreti & Saraswat, 1984). However, this is unlikely because during free crystal growth, the V=O group is always perpendicular to nearest square plane of water groups. The two types of V=O sites reported by the above mentioned workers are probably due to two symmetry related sites of $M^{//}$ cation in the lattice (Borcherts & Kikuchi 1964,; Upreti & Saraswat, 1984). In a general orientation of magnetic field, therefore, two distinct type of spectra will be observed which could probably merge into a single spectrum for a particular single orientation of the magnetic field.

It seems, earlier workers did not pay much attention to the possible distorted nature of water octahedra around the $M^{//}$ ions and thus wrongly interpreted their results by stipulating the different stable orientations of V=O groups with respect to the $M^{//}$-H_2O bonds in Tutton salts.

The third orientation of V=O was discussed, though only with weak intensity of EPR signal (Borcherts & Kikuchi, 1964) in VO doped ZASH. This can be understood if we note that, though the equatorial $M^{//}$-H_2O bonds are longer than the axial $M^{//}$-H_2O bonds in a general Tutton salt (Borcherts & Kikuchi, 1964), the difference between the equatorial and axial bonds is much smaller in the ZASH as per Table 1. Thus four H_2O groups forming a square plane around V could involve both equatorial and axial water groups, leading to an unusual orientation of the V=O in such a Tutton salt.

3.2 Correlation Of EPR, X-ray And Electric Field Assisted De-aquation Studies In Tutton Salts

A critical view of de-aquation in $Zn(NH_4)_2(SO_4)_2.6H_2O$ [ZASH] is available (Srivatsa & Pandey, 1984). In this work the samples were grown by the crystallization of saturated solution of a mixture of $ZnSO_4$ and $(NH_4)_2SO_4$ in a stoichiometric ratio and a thin coating of silver paint was laid on a pellet surface before measuring the electric field assisted de-aquation process. In the experiment, the current through the pellet was measured while heating the sample at a linear rate of 1 ^{0}C/min. Figure 3 shows the curve of current versus time 't' for the ZASH sample (Srivatsa & Pandey, 1984). This figure shows a sharp peak at 98 °C while a composite peak around 131 °C. Curves 'B' and 'C' were obtained after the deconvolution of the curve in the temperature range between 125 °C to 140 °C and two clear peaks are identified at 127 °C and 136 °C. The curve denoted by 'A' represents the temperature for the dissociation of four equatorial water molecules while the curves 'B' and 'C' represent the temperatures for dissociation of two unequal axial water molecules in the distorted water octahedra.

The peaks in the current versus time graph arise due to current flow from the H^+ and OH^- ions, when water groups are dissociated at a characteristic temperature depending upon its bonding inside the crystal. Though, the dissociation energy of a free water group is as high as 1.2 eV, a water group in a Tutton salt crystal is under electrostatic attraction by the neighboring ions. This produces the easy dissociation of water groups into H^+ and OH^- ions which occurs at a much lower energy.

At the characteristic temperature of the current versus time/temperature graph, the particular water groups are loosened and simultaneously dissociated giving rise to a current flow through the sample (Srivatsa and Pandey, 1984). A revised model on the dissociation of water groups in a hydrated system is recently provided (Mishra et al., 2008). This theoretical model was used by us to analyze this electric field assisted current versus time graph (Srivasta & Pandey, 1984; Mishra et al., 2008).

We are of the view that the four equatorial water groups are slightly loosely bound in a Tutton salt lattice and are thus released at a lower temperature compared to the axial water groups. The peak at 98 °C in the current versus temperature graph is attributable to four equatorial water groups and the second peak at 131 °C to two axial water groups. We believe that the two axial water groups are not similar and the contour due to charge flow can be resolved into two peaks which is also evident in Figure 3. These results along with our EPR data clearly show that the six water molecules form a distorted octahedra around the divalent cation. The charge flowing through the two resolved peaks are calculated and the dissociation energies of the water groups are estimated using the present available formulae (Mishra et al., 2008).

4. CONCLUSIONS

Based on the EPR, X-ray, and electric field assisted de-aquation studies in vanadyl doped system, we have correlated the results from all these studies which strongly support the distorted nature of water octahedra around the divalent cation in the Tutton salts.

5. ACKNOWLEDGEMENTS

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Table 1. Interatomic distances (A^0) in MASH Tutton salt single crystal,

(a) SO_4^{--} Tetrahedron:-

Atoms forming the bond	Distances (Å)	Atoms forming the bond	Distances (Å)
S-O_3	1.459 ± 0.005	O_3-O_5	2.419 ± 0.006
S-O_4	1.474 ± 0.005	O_3-O_6	2.396 ± 0.007
S-O_5	1.481 ± 0.005	O_4-O_5	2.417 ± 0.006
S-O_6	1.476 ± 0.005	O_4-O_6	2.393 ± 0.006
O_3-O_4	2.387 ± 0.005	O_5-O_6	2.417 ± 0.006

(b) Mg $(H_2O)_6^{++}$ Octahedron:-

Atoms forming the bond	Distances (Å)	Atoms forming the bond	Distances (Å)
Mg-O_7	2.083± 0.005	O_7-O_9	2.924 ± 0.007
Mg-O_8	2.073± 0.005	O_7-O'_9	2.922 ± 0.007
Mg-O_9	2.051± 0.005	O_8-O_9	2.953 ± 0.007
O_7-O_8	2.945± 0.007	O_8-O'_9	2.879 ± 0.007
O_7-O'_8	2.932± 0.007		

(c) H_2O Hydrogen Bonding :-

Atoms forming the bond	Distances (Å)	Atoms forming the bond	Distances (Å)
O_7-O_3	2.722± 0.006	O_8-H_{19}	0.8 ± 0.1
O_7-O_5	2.756± 0.006	O_9-H_{12}	0.8 ± 0.1
O_8-O_4	2.792± 0.006	O_9-H_{18}	0.9 ± 0.1
O_8-O_5	2.844± 0.006	O_3-H_{13}	1.8 ± 0.1
O_9-O_4	2.777± 0.006	O_4-H_{11}	2.0 ± 0.1
O_9-O_6	2.713± 0.006	O_5-H_{15}	1.9 ± 0.1
O_7-H_{13}	1.0± 0.1	O_6-H_{12}	1.9 ± 0.1
O_7-H_{15}	0.9± 0.1	O_4-H_{18}	1.9 ± 0.1
O_8-H_{11}	0.8± 0.1	O_5-H_{19}	2.0 ± 0.1

(d) NH^{+}_{4} Hydrogen Bonding :-

Atoms forming the bond	Distances (Å)	Atoms forming the bond	Distances (Å)
N-O_3	3.102± 0.009	N-H_{17}	1.0 ± 0.1
N-O_4	2.837± 0.008	N-H_{20}	0.8 ± 0.1
N-O_5	2.916± 0.008	O_5-H_{14}	2.0 ± 0.1
N-O_6	2.949± 0.008	O_6-H_{16}	2.1 ± 0.1
N-O'_8	3.057± 0.009	O_4-H_{17}	1.9 ± 0.1
N-H_{14}	1.0± 0.01	O_3-H_{20}	2.4± 0.1
N-H_{16}	0.9± 0.01	O_6-H_{20}	2.3 ± 0.1

Table 2. The g and A parameters for $V0^{2+}$ in different Tutton salts.

Host	Site	$g_{\parallel}$ /g_z	$g_{\perp}$		$A_{\parallel}$/A_z	$A_{\perp}$	-	Ref.
ZASH	I	1.9331	1.9813(g_x)	1.9808(g_y)	182.81	71.37(A_x)	72.56 (A_y)	(Borcherts & Kikuchi, 1964)
	II	1.9313	1.9808	1.9797	182.75	71.04	72.55	
	III	1.9299	1.9810	–	184.40	72.55	–	
CASH	-	1.932	1.982	–	174	72		(Upreti & Saraswat, 1984)
FASH	-	1.941	1.990	–	180	73		(Upreti & Saraswat, 1984)
CdASH	I	1.935	1.986	1.988	180.0	71.3	69.0	(Vimal et.al., 1981)
	II	1.931	1.982	1.984	183.9	71.4	69.5	
ZASeH	I	1.935	1.983	1.985	182.0	73.0	72.0	(Jain et al., 1984)

	II	1.935	1.986	1.984	181.0	71.0	70.0	
ZRSH	I	1.931	1.978	1.982	180.0	70.3	-	(Jain et al., 1979)
	II	1.937	1.985	-	179.6	71.0	-	
ZCSeH	-	1.938	1.975	1.978	178.0	71.3	70.4	(Jain & Yadav, 1985)

Abbreviations

CASH :Cobalt Ammonium Sulphate Hexahydrate

FASH :Ferrous Ammonium Sulphate Hexahydrate

CdASH :Cadmium Ammonium Sulphate Hexahydrate

ZASeH :Zinc Ammonium Selenate Hexahydrate

ZRSH :Zinc Rubidium Sulphate Hexahydrate

ZCSeH :Zinc Caesium Selenate Hexahydrate

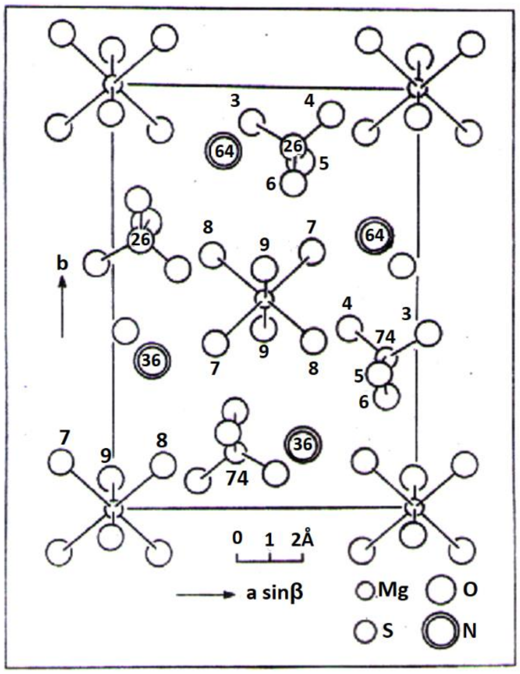

Fig.1 Crystal Structure of MASH. The number at the sulphur and nitrogen items indicate their Z-Coordinates

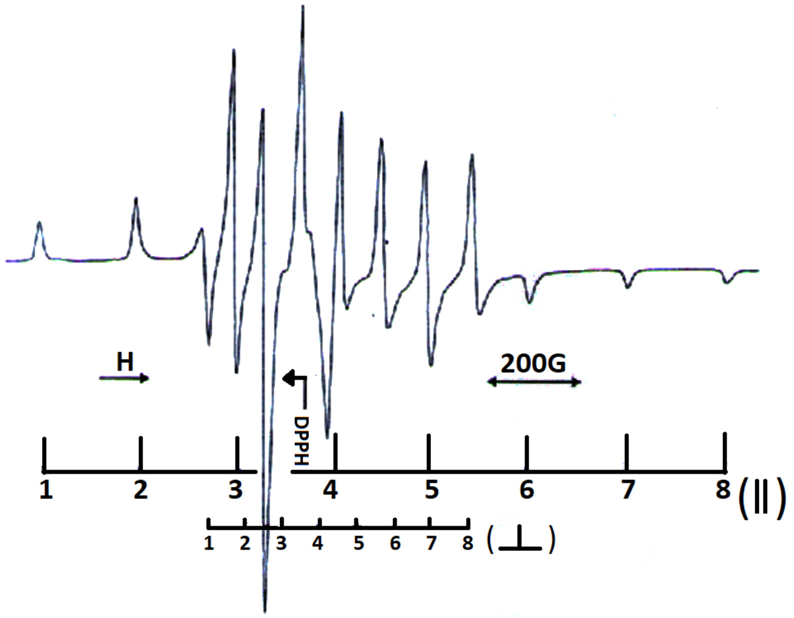

Fig.2 EPR of vanadyl doped $Zn_{0.25}Mg_{0.75}(NH_4)_2(SO_4)_2.6H_2O$ [H(DPPH)= 3385G]. Parallel and penpendicular hyperfine groups are marked by vertical lines below the spectrum.

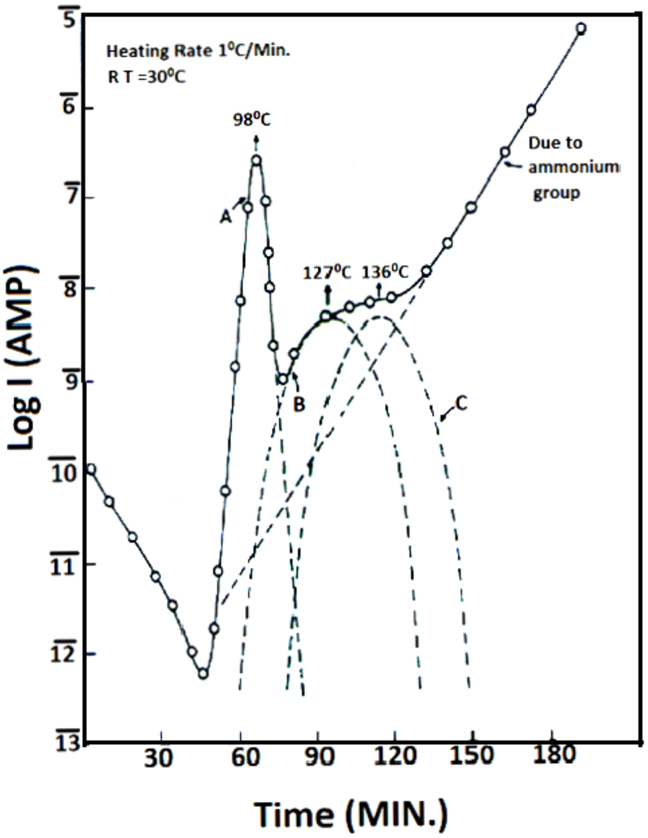

Fig.3 Temperature variation for current vs. time for zinc ammonium sulphate hexahydrate pellet. The composite peak at 131^{0}C is shown as deconvoluted into curves 'B' and 'C'