

EFFECT ON EPR AND X-RAY DIFFRACTION DUE TO THE DOPANT CONCENTRATION OF Mn(II) ION IN TUTTON'S SALT

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ABSTRACT

Single crystal electron paramagnetic resonance (EPR) studies of Mn(II) doped zinc potassium sulphate hexahydrate have been carried out at room temperature. The effect of varying dopant concentration of Mn(II) is recorded by EPR and X-ray spectroscopic techniques. The EPR spectra of Mn(II) ions in salts show a remarkable concentration dependence. At lower concentrations of Mn(II) ions (less than 5 mol % of Mn(II) ions), the spectrum shows a sextet. The X-ray studies indicate a marginal increase in lattice parameters, when the dopant concentration is increased

Keywords: Tutton's salt, Lattice, Distorsion, sextet

1.INTRODUCTION

Electron Paramagnetic Resonance (EPR) studies are usually done by doping paramagnetic impurities into diamagnetic lattice, to minimize the dipolar broadening. However, in order to obtain an idea about the interaction between two paramagnetic ions, doping of a paramagnetic ion into a paramagnetic host lattice is necessary. These studies provide extra information, if the host paramagnetic lattice gives its EPR spectrum at lower temperatures. EPR studies provide a detail description about the nature of electric field symmetry produced by ligands around the paramagnetic ions. Paramagnetic compounds with divalent metal ion, such as Mn(II), are of more interest because the 3d electron shell responsible for paramagnetism is just half filled with five electrons and the resultant angular momentum is zero. Moreover the ground state of Mn(II) is ${}^6S_{5/2}$ and the S-state ions are characterized by long spin lattice relaxation times. This long spin-lattice relaxation time for Mn(II) ion makes the EPR spectra to be observed at room temperature itself. Its zero field tensor is highly sensitive to the strength and symmetry of the crystal field environments (1-2).

Electron paramagnetic resonance studies of Mn(II) have been reported earlier in several crystals [3-10]. Information was obtained about the position of the paramagnetic ion, spin-

Hamiltonian parameters and lattice defects. Single crystal R study of Mn(II) in Tutton's salt is carried out at room temperature. The single Tutton's salts are thoroughly investigated by mineralists, chemists and physicians in different points of view and described many physical and chemical properties. In the present work, Zinc Potassium Sulphate Hexahydrate $[ZnK_2(SO_4)_2 \cdot 6H_2O]$ abbreviated as ZPSH falls under the category of Tutton's salt, has been selected for detailed single crystal EPR analysis by doping a paramagnetic ion crystal rotations in three orthogonal planes indicate that the paramagnetic impurity, i.e., Mn(II), has entered the host lattice interstitially not a common observation. In the present work, effect of dopant concentration of the nature of EPR spectrum has been undertaken.

2.METHODS

Single crystals of the manganese ion doped Tutton salt $ZnK_2(SO_4)_2 \cdot 6H_2O$ (ZPSH) are grown by slow evaporation of a saturated solution of zinc sulphate respectively with potassium sulphate in equimolar amounts. To this solution 0.3, 0.5, 1.0 and 5% solution of $MnSO_4$ is added as a dopant. Crystals of Mn(II) doped ZPSH are colorless with well developed faces. EPR spectra are recorded on a JEOL JES-TE 100 ESR spectrometer operating at X-band frequencies, having a 100 KHZ field modulation to obtain a first derivative EPR spectrum. DPPH with a g value of 2.0036 is used for g-factor calculations.

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Crystal Structure

Tutton's salts have the general formula $M''M_2'(XO_4)_2/6H_2O$, where M'' is a divalent cation like Mg, Ca, Co, Ni, Zn; M' is a monovalent cation like K, Cs, Rb, NH_4 and X is S or Se. Tutton's Salts have monoclinic crystal structure with space group P21/n. The lattice parameters of MPSH (M'' is Mg, M' is K and X is S) are : $a = 0.613, b = 1.223, c = 0.909$ nm, $B = 104.78^\circ$ and $Z = 2$ [11]. Six water molecules in the form of distorted octahedral ion, as shown in Fig.1. The metal-oxygen bond distances (nm) are $M-O_6 = 0.206$, $M-O_7 = 0.2103$ and $M-O_8 = 0.2118$. Crystal structure data of $M(II)(H_2O)_6$ complex shows that the shortest bond corresponds to the $M-O_6$ direction in all the Tutton's salts. However, the longest bond is not unique, but may be in either $M-O_8$ or $M-O_7$ direction depending on M'' and M_1 .

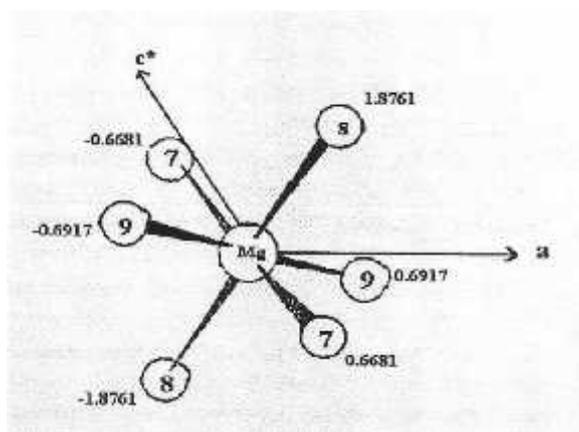


Fig.1: Divalent metal ion is surrounded by six water molecules in the form of an octahedron in MPSH crystal lattice projected in ac^* lane.

3.RESULTS AND DISCUSSION

EPR studies:

The paramagnetic ion, Mn(II), has five electrons in the 3d shell and the ground state is ${}^6S_{5/2}$. If the ground state is pure ${}^6S_{5/2}$, the five $\Delta M_s = \pm 1$ transitions will have same energy and the EPR spectrum would be a single line at the free spin value of 2.0023. However, the spectrum is complicated due to the fine and hyperfine structures. Fine structure arises because of the interaction of the electrons within themselves, whereas hyperfine structure is due to the interaction of the nuclear spin of the manganese nucleus with electron spin.

Since the $S = 5/2$ for Mn(II) ions, one expects five fine structure lines in an EPR spectrum. The $S = 5/2$ state splits into three Kramers' doublets $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$, separated by $2D$ and $4D$ respectively. Here, D is the zero-field splitting parameter. Once a magnetic field is applied, these three doublets split into six levels and transitions between them give rise to five fine structure lines. Each of these lines split into a sextet due to nuclear spin of ${}^{55}Mn(I = 5/2)$. Hence, a 30 line pattern is expected for a Mn(II) ion in a distorted octahedral environment. If the symmetry around the ion is perfect octahedral, only six lines are expected.

The observed EPR spectrum can be described by the spin-Hamiltonian [12]

$$H = \beta B g S + [A_{zz} S_z I_z + A_{xx} S_x I_x + A_{yy} S_y I_y] + D [S_z^2 - 1/3 S(S+1)] + E(S_x^2 - S_y^2) + (a/6) [S_x^4 + S_y^4 + S_z^4 - (1/5) S(S+1)(3S^2 + 3S - 1)] + (F/180) [35S_z^4 - 30S(S+1) S_z^2 + 25S_x^2 + 25S_y^2 - 6S(S+1) + 3S^2(S+1)^2]$$

Here the first term represents electron Zeeman, the second and third terms represent the hyperfine interaction and axial components of the zero-field splitting respectively. The fourth and the fifth term represent deviation from axial symmetry and the interaction with cubic crystal field, respectively. The sixth term represents the deviation from cubic symmetry.

Mn(II) doped ZPSH

EPR spectra are recorded on a JEOL JES - TE100 ESR spectrometer operating at X-band frequencies, having a 100 KHz field modulation to obtain a first derivative EPR spectrum. The powder spectrum of Mn(II)/ZPSH is recorded at room temperature. The room temperature EPR spectra for various concentrations are given in Figs.2.1-2.5. No EPR signals are detected in the spectra of undoped systems (Fig 2.1). The spectrum (Figs. 2.1 -2.5) consists of more than thirty lines with unsystematic distribution of intensities in the first few hyperfine resonances. The expected intensity ratio of Mn(II) fine structure lines is 5:8:9:8:5. A look at the figure indicates a different situation (assuming a quintet with sextet in each). In addition, the EPR spectrum is not symmetrical. Hence it may be suggested that the E term (which is half the difference between x and y components of D) is non zero. In addition, the unit cell contains two molecules and the central sextet shows abnormal intensity behavior.

The EPR spectrum is very similar to others reported for Mn(II) ions in various systems [13-16]. The characteristic hyperfine structure (hfs) is due to the interaction of electron spin with the nuclear spin $I=5/2$ and was resolved for the $g \approx 2.0$ resonance line. The EPR spectra of Mn(II) ions in salts show a remarkable concentration dependence. At lower concentrations of Mn(II) ions (less than 5 mol % of Mn(II) ions), the spectrum shows a sextet. The ability to observe the ${}^{55}Mn$ hyperfine structure has two tangible benefits:

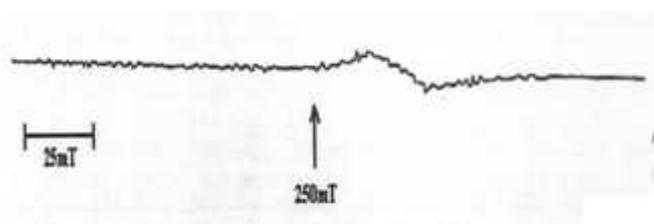
(i) It generally allows unambiguous assignments of positions of complex resonance lines to manganese and (ii) The magnitude of the hyperfine constant provides a measure of covalent bonding between Mn(II) ions and its surrounding ligands. An approximate relationship for the covalency c of a bond between the atoms p and q and their electronegativities χ_p and χ_q is given by

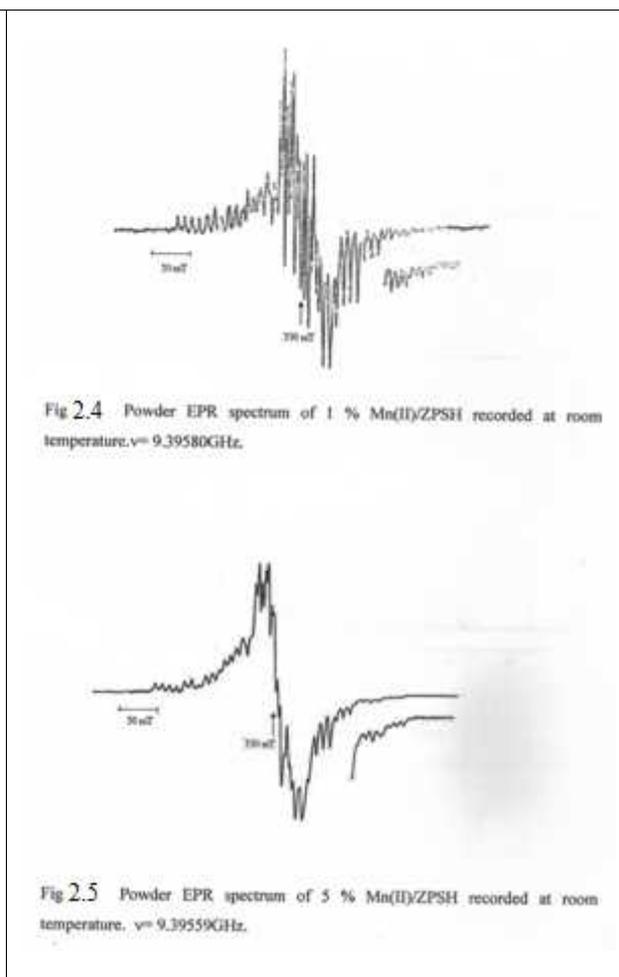
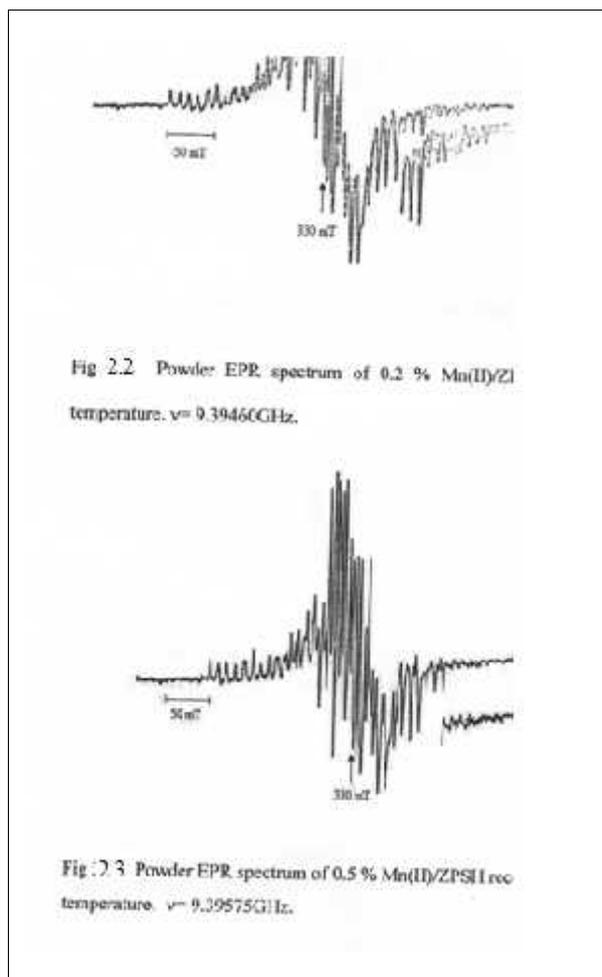
$$c = 1/n [1 - 0.16 (\chi_p - \chi_q) - 0.035 (\chi_p - \chi_q)^2]$$

Here, n is the number of ligands around Mn(II) ion. The percentage of covalency obtained from the above equation, assuming $\chi_{Mn} = 1.4$ and $\chi_o = 3.0$ is around 11. It has been reported during band energy calculations in the alkali sulphate crystals of $KLiSO_4$ [17] that the substantially flat energy bands will affect the covalency of Mn-O bond.

Here, one can notice more than six lines, at the centre portion, indicating two magnetically non-equivalent and chemically non-equivalent Mn(II) ions. The spin Hamiltonian parameters calculated for the different concentrations of 0.2, 0.5, 1 and 5 % on Mn(II) doped ZPSH are:

$$\begin{aligned} g &= 2.006; A = 10.08 \text{ mT}; D = 3.21 \text{ mT} \\ g &= 2.013; A = 9.68 \text{ mT}; D = 35.62 \text{ mT} \\ g &= 2.012; A = 9.97 \text{ mT}; D = 35.98 \text{ mT} \\ g &= 2.001; A = 10.11 \text{ mT}; D = 36.33 \text{ mT} \end{aligned}$$





X-Ray Diffraction:

The X-ray pattern of the pure and doped complexes indicates a slight change in the 2 θ values, suggesting a minor change in the lattice parameters. Initial calculations indicate a slight increase in the lattice parameters, as the dopant concentration increases. The X-ray studies indicate a marginal increase in lattice parameters, when the dopant concentration is increased. The X-ray patterns are given in Fig.3.1 & 3.2.

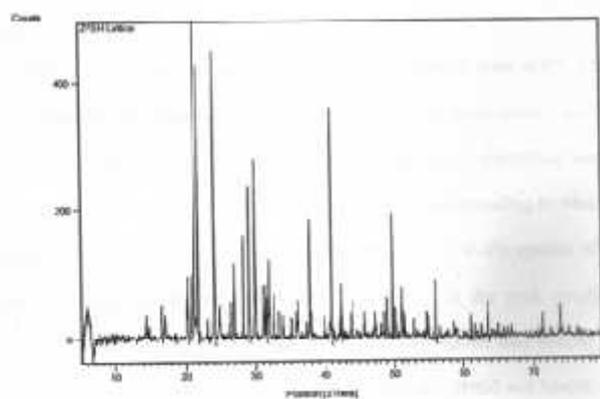


Fig 3.1 : X-ray diffraction of ZPSH lattice.

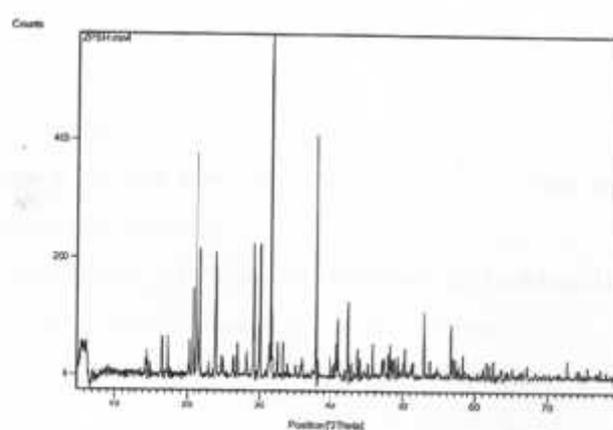


Fig 3.3 : X-ray diffraction of 5 % Mn(II)/ZPSH.

4.CONCLUSIONS :

The EPR study of Mn(II) doped ZPSH has been done at RT. The spin Hamiltonian parameters (g, A and D) have been determined. From the results, a distorted octahedral interstitial site is predicated for Mn(II) ions. The optical absorption study has been done at room temperature and the bands observed are corresponding to Mn(II) ion in ZPSH is octahedral symmetry.

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