

## Electron spin resonance and optical absorption studies on copper-doped lithium hydrazinium sulphate single crystals

V CHANDRA MOULI\* and G SIVARAMA SASTRY

Department of Physics, University College of Science, Osmania University, Hyderabad 500 007, India

\* Post Graduate Centre, Godavari Khani 505 209, Karim Nagar (Dist), India

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**Abstract.** ESR and optical absorption studies have been carried out on  $\text{Cu}^{2+}$ -doped lithium hydrazinium sulphate single crystals at 303 K. The spin-Hamiltonian parameters evaluated indicate a  $\text{N}_2\text{O}_2$  square planar environment for  $\text{Cu}^{2+}$  ion in this lattice. The correlation of ESR and crystal structure data leads us to conclude that  $\text{Cu}^{2+}$  ion enters the lattice interstitially. Charge compensation is achieved by the release of protons. Using the optical absorption and ESR data, bonding parameters and orbital reduction factors are also evaluated.

**Keywords.** Electron spin resonance; lithium hydrazinium sulphate; site location.

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### 1. Introduction

Doping is in general a fairly specific process, whether the impurity ion enters substitutionally or interstitially. The dopant and its host must be compatible as regards size and charge. It was, therefore, somewhat surprising when a number of transition metal ions and some rare earth ions were found to dope readily in monovalent lattices (Volkel and Windsch 1971; Faracas *et al* 1972; Chandra Mouli and Sastry 1982; Suryanarayana and Sobhanadri 1974; Kuwabara 1971). The symmetry of the environment and the charge compensation mechanism can be very well understood by doping a cation impurity in a monovalent lattice, using ESR absorption spectroscopy. The ESR and optical absorption studies on  $\text{Cu}^{2+}$  doped in potassium hydrogen maleate (Chandra Mouli and Sastry 1982) and  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$  (Chandra Mouli and Sastry 1978) showed that the charge compensation for  $\text{Cu}^{2+}$  ion can be achieved by the release of protons. This paper reports the ESR and optical absorption study of copper-doped lithium hydrazinium sulphate single crystals.

### 2. Experimental and structural data

Lithium hydrazinium sulphate (LHS) was prepared by the method of Sommer and Weise (1916) and single crystals were grown by evaporation of the aqueous solution. The paramagnetic impurity was introduced during the crystal growth by the addition of a few drops of copper sulphate solution. As shown by Brown (1964) and Vanden

Hende and Boutin (1964), LHS crystallizes in the orthorhombic space group  $Pbn2_1$  with  $a = 8.99 \text{ \AA}$ ;  $b = 9.94 \text{ \AA}$ ;  $c = 5.18 \text{ \AA}$  and the number of molecules per unit cell is 4. The crystals are found to be elongated along the  $C$ -axis with the prominent (100), (110) and (101) faces. The crystallographic axes are identified by x-ray analysis.

The crystal structure (figure 1) consists of lithium and sulphur atoms both surrounded by tetrahedra of oxygens. The tetrahedra share apices to form a three-dimensional framework containing channels running parallel to  $C$ -axis. The hydrazinium ions lie in these channels with their N–N bond perpendicular to  $C$ -axis.

ESR spectra of  $\text{Cu}^{2+}$  in LHS were recorded on an X-band ESR spectrometer which was assembled in this laboratory employing 100 kHz magnetic modulation. DPPH is used as the  $g$ -marker. The spectra are recorded in the three crystallographic planes i.e.,  $ab$ ,  $ac$  and  $bc$  at  $10^\circ$  intervals. The optical absorption spectra are obtained using a Cary-17 spectrophotometer.

### 3. Results and discussion

Figure 2 shows the ESR spectra of single crystals of  $\text{Cu}^{2+}$  in LHS at 303 K along  $C$ -axis in  $bc$  plane. The ESR spectra recorded in a general direction consists of sixteen lines while in all the crystallographic planes (viz  $ab$ ,  $ac$  and  $bc$ ) they consist of resolved eight lines (excluding the lines due to the ligand hyperfine structure), which can be divided into two quartets, one being more prominent. The ESR spectra recorded along all the crystallographic axes consists of a well-resolved single set of four lines due to  $^{63}\text{Cu}$  ( $S = 1/2$ ;  $I = 3/2$ ). With this information, all the four groups are assigned to  $\text{Cu}^{2+}$  centres trapped at four physically distinct but crystallographically related pairs. Each line of the above quartet (figure 2) has a quintet structure with an intensity distribution in the ratio 1 : 2 : 3 : 2 : 1; clearly showing that the quintet is due to the interaction of the unpaired  $\text{Cu}^{2+}$  ion and the two equivalent  $^{14}\text{N}$  ( $I = 1$ ) nuclei. The experimental angular variation of  $g^2$  and  $g^2 A^2$  values has been fitted by the equations

$$g_x^2(\theta) = (g^2)_{yy} \cos^2 \theta + 2(g^2)_{yz} \sin \theta \cos \theta + (g^2)_{zz} \sin^2 \theta, \quad (1a)$$

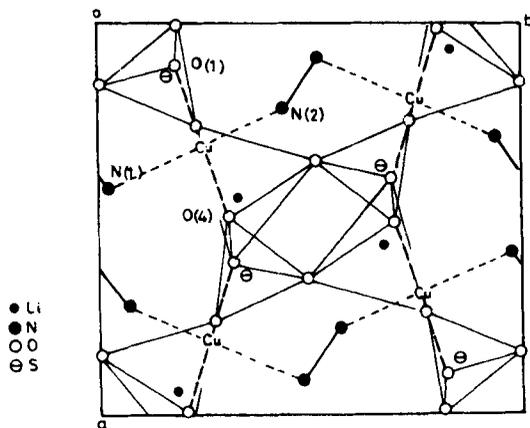


Figure 1. Projection of crystal structure of LHS in  $ab$  plane.

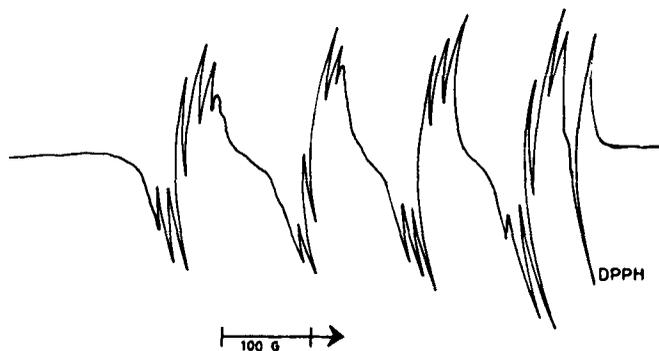


Figure 2. ESR spectra of  $\text{Cu}^{2+}$  in LHS along  $C$ -axis at 303 K.

and

$$g_x^2 A_x^2(\theta) = (gA^2g)_{yy} \cos^2 \theta + 2(gA^2g)_{yz} \sin \theta \cos \theta + (gA^2g)_{zz} \sin^2 \theta. \quad (1b)$$

The spin Hamiltonian parameters are evaluated using the Schonland (1959) procedure for only one site. Due to the presence of ligand hyperfine structure, the less prominent site could not be followed.

The angular dependence of the super-hyperfine constant  $A^N$  for rotation of the crystal in  $ab$  and  $bc$  planes was investigated. A fairly large anisotropy was observed in the  $bc$ -plane, and the maximum value of  $A^N$  found to be 11.9 G.

Table 1 shows the spin Hamiltonian parameters for the  $\text{Cu}^{2+}$  in LHS along with those of  $\text{Cu}^{2+}$  dimethyl alanine (Fujimoto and Janecka 1971) and triglycine sulphate (Stankowski and Wieckowski 1974). The latter two copper-doped complexes are in  $\text{N}_2\text{O}_2$  quadrangular site consisting of two nitrogens and two oxygens in transposition around the cupric ion. The good agreement found in the spin Hamiltonian parameters clearly indicates a similar  $\text{N}_2\text{O}_2$  environment for  $\text{Cu}^{2+}$  ion in  $\text{Cu}^{2+}$  in LHS. Further the quintet structure with intensity ratio 1:2:3:2:1 observed for most of the directions is a clear evidence of the presence of two equivalent nitrogens in trans-position.

The crystal structure of LHS (figure 1) indicates that the only possible substitutional position for  $\text{Cu}^{2+}$  is the monovalent lithium site surrounded by oxygen tetrahedron. But the spin Hamiltonian parameters (table 1) and the observed  $^{14}\text{N}$  ligand hyperfine structure completely rule out such a substitutional possibility for  $\text{Cu}^{2+}$  ion in this lattice.

Alternatively  $\text{Cu}^{2+}$  can enter the lattice interstitially. The crystal structure (figure 1) reveals that as many as sixteen oxygens and eight nitrogens per unit cell are available for coordination with the  $\text{Cu}^{2+}$  ion for interstitial occupation. The correlation of angular variation of ESR spectra of LHS: Cu and the crystal structure suggest that  $\text{Cu}^{2+}$  can enter the lattice interstitially as shown in figure 1. In the first interstitial site  $\text{Cu}^{2+}$  coordinates with the ligands N(1) and N(2) of two hydrazinium groups and O(1) and O(4) belonging to sulphur and lithium oxygen tetrahedra groups respectively. A close observation of the direction cosines of the components of the principal magnetic tensor (table 1) shows that the tetragonal  $g_z$  axis is almost parallel to the  $C$ -axis. Since the tetragonal axis normally lies along the  $\text{Cu}^{2+}$ -vacancy direction, the  $\text{N}_2\text{O}_2$  plane around

Table 1. Spin Hamiltonian parameters for  $\text{Cu}^{2+}$  at  $\text{N}_2\text{O}_2$  quadrangular site

Lattice	$g$	$A(G)$	$A^N(G)$	Cu-ligand bond	$a$	$b$	$c$
LHS: Cu	2.042	$22 \pm 2$	7.5		0.9283	0.3925	0.0832
	$\pm 0.002$			Cu-O(4)	(0.9499)	(0.2978)	(0.1078)
	2.050	$28 \pm 2$	7.5		-0.3614	0.9194	0.0038
Dimethyl alanine	$\pm 0.002$			Cu-N(2)	(-0.3987)	(0.9218)	(0.0047)
	2.246	$157 \pm 2$	11.9		0.0872	0.0175	0.9965
	$\pm 0.002$						
Triglycine sulphate	2.044	20	7.5				
	2.051	18	7.5				
	2.204	152	10.3				
Triglycine sulphate	2.064	5.2	7.5				
	2.054	30.8	7.5				
	2.261	169.4	11.5				

\* The direction cosines of Cu-ligand bonds are given in parantheses.

the  $\text{Cu}^{2+}$  ion must be almost perpendicular to  $C$ -axis or nearly parallel to  $ab$  plane. The plane formed by N(1), O(1), N(2) and O(4) is almost parallel to  $ab$  plane and the two nitrogens are in transposition as required by the ESR data further support the proposed interstitial site for  $\text{Cu}^{2+}$  in LHS for site I.

In table 1 the directional cosines of the principal  $g$ -tensors (site I) are compared with the Cu–O(4) and Cu–N(2) bond directions and a reasonably good agreement is found clearly indicating that  $\text{Cu}^{2+}$  enters the lattice interstitially into the  $\text{N}_2\text{O}_2$  square planar site. An attempt has also been made to locate other  $\text{Cu}^{2+}$  sites, with the help of both ESR and crystal structure data and these are shown in figure 1.

The optical absorption spectrum of  $\text{Cu}^{2+}$  in LHS consists of two bands centred at  $15400\text{ cm}^{-1}$  and  $26000\text{ cm}^{-1}$  respectively. The spin Hamiltonian parameters indicate that the ground state in the present case is predominantly  $|X^2 - Y^2\rangle$ . The band at  $15400\text{ cm}^{-1}$  is assigned as  $|X^2 - Y^2\rangle \leftrightarrow |XY\rangle$  transition and  $26000\text{ cm}^{-1}$  band to  $|X^2 - Y^2\rangle \leftrightarrow |XY, XZ\rangle$  transition.

The molecular orbital parameters are evaluated using the equation due to Maki and McGarvey (1958) and Kivelson and Neiman (1961). The equations are solved taking  $P = 360 \times 10^{-4}\text{ cm}^{-1}$  and  $\lambda = -828\text{ cm}^{-1}$  with  $E(\parallel) = 15400\text{ cm}^{-1}$  and  $E(\perp) = 26000\text{ cm}^{-1}$ . The molecular orbital parameters thus obtained were found to be  $\alpha^2 = 0.74$ ;  $\beta_1^2 = 0.81$ ;  $\beta^2 = 0.81$ . The orbital reduction factors calculated were found to be  $K_{\parallel} = 0.75$  and  $K_{\perp} = 0.82$ .

The value of  $\alpha^2 = 0.74$  indicates large covalency in Cu–N bonds in the in-plane  $\sigma$  bonding supported by the observation of superhyperfine structure due to  $^{14}\text{N}$ . When a divalent ion enters the lattice in an interstitial position, two positive charges must be set free to preserve charge neutrality (Lau and Lin 1973). In this lattice two types of positive charges are available, namely protons of hydrazinium groups and lithium ion. As the tetragonal axis ( $g_z$ ) passing through the Cu-vacancy direction is along the  $C$ -axis, the positive charges along this line are expected to be released. According to the crystal structure of LHS, the hydrazinium ions lie in channels parallel to  $C$ -axis and the  $\text{NH}_2$  groups of hydrazinium ion are linked into infinite chains by hydrogen bonding, thus making a number of protons available for charge neutrality. Hence it can be concluded that the charge neutrality is achieved by the release of two protons lying along the  $g_z$  direction.

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### References

- Brown I D 1964 *Acta Crystallogr.* **17** 654
- Chandra Mouli V and Sastry G S 1978 *Phys. Status Solidi* **B80** K127
- Chandra Mouli V and Sastry G S 1982 *J. Mol. Struct.* **82** 251
- Farrucas S I, Darabant A and Nicolo A 1972 *Phys. Status Solidi* **B50** 755
- Fujimoto M and Janecka J 1971 *J. Chem. Phys.* **55** 1152
- Kivelson D and Neiman R 1961 *J. Chem. Phys.* **35** 149
- Kuwabara G 1971 *J. Phys. Soc. (Jpn)* **31** 1074

- Lau P W and Lin W C 1973 *J. Chem. Phys.* **59** 3981  
Maki A and McGarvey B R 1958 *J. Chem. Phys.* **24** 35  
Schonland D S 1959 *Proc. Phys. Soc.* **73** 788  
Sommer F and Weise K 1916 *Z. Anorg. Chem.* **94** 51  
Stankowski J and Wieckowski A 1974 *J. Mag. Reson.* **15** 498  
Suryanarayana D and Sobhanadri J 1974 *J. Mag. Reson.* **14** 1  
Vanden Hende J H and Boutin 1964 *Acta Crystallogr.* **17** 663  
Volkel G and Windsch W 1971 *Phys. Status Solidi* **B43** 263