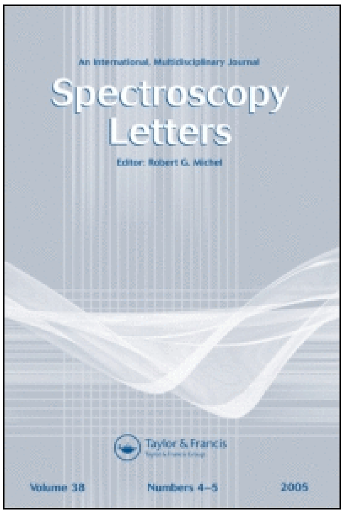

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AN EPR STUDY OF Cu^{2+} DOPED SODIUM HYDROGEN OXALATE MONOHYDRATE SINGLE CRYSTAL

KEY WORDS: EPR, Sodium Hydrogen Oxalate, Cu(II), ground state wave function

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ABSTRACT

The EPR spectra of Cu^{2+} in Sodium hydrogen oxalate monohydrate, $NaHC_2O_4.H_2O$ (SHOMH hereafter) single crystal was studied at room temperature. The angular variation of EPR spectra showed that the Cu^{2+} ion in SHOMH single crystal substitutes with Na^+ monovalent cation together with a monovalent vacancy to compensate oxygen in the crystal. Since the crystal symmetry is triclinic, only one site is observed in the EPR spectra in three perpendicular axis. The spin Hamiltonian parameters were obtained, and the ground state wave function of Cu^{2+} ion in the lattice was constructed.

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INTRODUCTION

It has been less than a few decades that the transition metal ions as a probe have been used to determine the different symmetry environments and structural phase transitions in the host lattices by electron paramagnetic resonance technique [1-9]. Cu^{2+} ion especially has been one of the most extensively used paramagnetic ions. In the majority of studies reported so far, Cu^{2+} impurity replaces with a divalent cation present in the lattice, whereas there are a few studies that report substitutional replacement of Cu^{2+} with monovalent cation. In this case a question about the charge imbalance arises, which can be explained by assuming that it is compensated by another monovalent cation vacancy. Moreover, in some cases, it has been found that the magnetic coupling tensors have their principal axis pointing along the impurity and monovalent cation vacancy directions [1-2].

In order to determine the site symmetry around the metal ion, one has to form the ground state wave function of the unpaired electron. Depending on the symmetry, the ground state wave function of Cu^{2+} ion in the host lattice can be formulated [8-9]. To our knowledge, such a study has not been carried out and reported. In this study, we undertake the construction of ground state wave function of the Cu^{2+} ion in SHOMH lattice.

EXPERIMENTAL DETAILS

The aqueous saturated solution of sodium oxalate and oxalic acid with equal molarity were prepared. A very small amount of $CuSO_4.5H_2O$ was added to the solution as impurity. The impurified saturated solution was then left for evaporation at room temperature. Well developed good crystals were obtained within 6-7 days. Figure 1 shows morphological structure and the selected axis set of Cu^{2+} doped SHOMH single crystal.

SHOMH belongs to the triclinic system (space group $P_{\bar{1}}$ [1]) and contains two molecules in a unit cell. The unit cell dimensions are $a = 6.5032\,\text{Å}$,

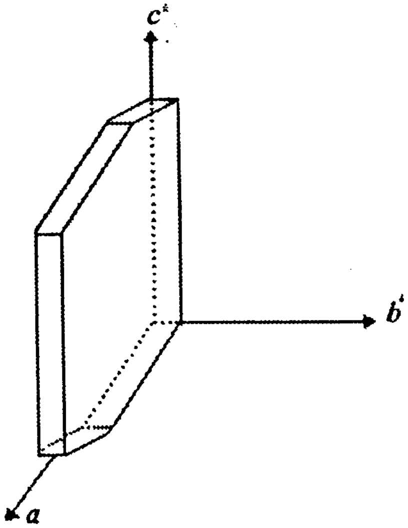

Figure 1. The morphological structure and the selected axes set of Cu^{2+} doped SHOMH single crystal.

$b = 6.6728\,\mathring{A}$, $c = 5.6982\,\mathring{A}$ and the angles are $\alpha = 85.036^\circ$, $\beta = 105.977^\circ$ and $\gamma = 105.016^\circ$ [10-11].

Varian E-109 C Model X-band EPR spectrometer was used to record the spectra. The magnetic field modulation frequency was 100 kHz. The single crystal was mounted on a goniometer and the spectra were recorded in the three perpendicular planes (*a*c*, b*c*, *a*b*) with 10° intervals at room temperature. A diphenylpicrylhydrazile sample (g=2.0036) was used as a reference to correct to the g values.

RESULTS AND DISCUSSION

The Cu^{2+} ion in SHOMH single crystal is in d^9 state. The recorded EPR spectra of Cu^{2+} doped SHOMH single crystal shows 4 lines in all orientations. Since the symmetry is triclinic, only one site is observable as in Fig. 2. The $\bar{\bar{g}}^2$ and $\bar{\bar{A}}^2$

Figure 2. The EPR spectra of Cu^{2+} doped SHOMH single crystal when the magnetic field making *ac** plane 110°, 120° and 130° with *a* axis in *ac** plane.

tensors were calculated from angular variation of the lines in three perpendicular planes. Figure 3 shows the variation of lines in three perpendicular planes.

Figure 2 shows the recorded EPR spectra of Cu^{2+} doped SHOMH single crystal when the magnetic field makes 110°, 120° and 130° with *a* axis in *ac** plane. There are two isotopes of copper ^{63}Cu and ^{65}Cu with the abundancies of 69.2 % and 30.8 % respectively. Although ^{65}Cu lines are distinguishable in some orientations., it is not clearly observable in all orientations due to overlapping. Cu^{2+} ion in SHOMH single crystal substitutes with Na^{+} monovalent cation together with a monovalent vacancy to compensate oxygens in the crystal structure. The complex structure is shown in Fig. 4. [11]. The principal values of g and hyperfine splitting, and directions cosines were calculated by diagonialization procedure [13-14] and results are given in Table 1. The parameters were fitted to

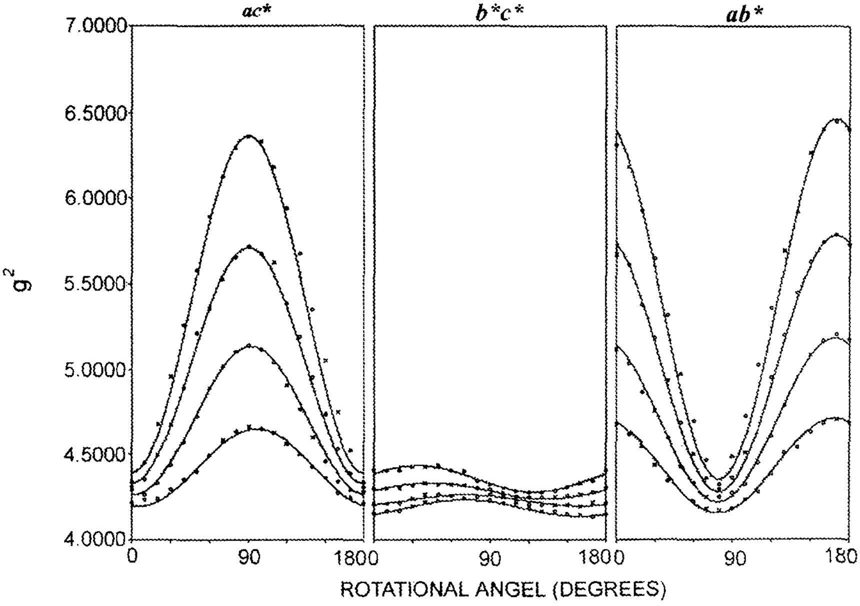

Figure 3. Angular variation of the g^2 values of four lines of in SHOMH single crystal at room temperature.

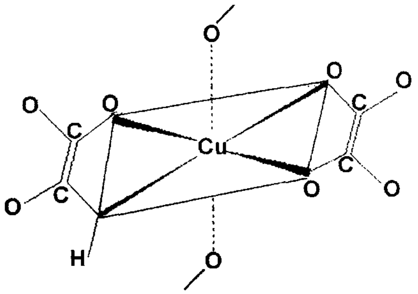

Figure 4. View of Cu^{2+} complex in SHOMH.

Table 1. Principal g and hyperfine (A) values, and direction cosines of Cu^{2+} in $NaHC_2O_4.H_2O$ at room temperature

Tensor	Principal values	Direction cosines in *a*, *b**,*c** axis system *a*	*b**	*c**
g_{xx}	2.0562	0.891	0.101	0.441
g_{yy}	2.0729	-0.452	0.153	0.878
g_{zz}	2.3378	0.021	-0.982	0.182
A_{xx}	36.4 G	0.996	0.054	0.066
A_{yy}	42.5 G	-0.075	0.168	0.982
A_{zz}	153.8 G	0.042	-0.984	0.172

the spin Hamiltonian corresponding to rhombic symmetry of the form [12]

$$\mathcal{H} = \beta(g_{zz}H_zS_z + g_{xx}H_xS_x + g_{yy}H_yS_y) + A_{zz}I_zS_z + A_{xx}I_xS_x + A_{yy}I_yS_y . \qquad (1)$$

Figure 5 shows the powder EPR spectrum of Cu^{2+} doped SHOMH crystal. It can be seen from the spectrum and from the principal g and hyperfine values, Table 2, that the complex symmetry in the crystal is obviously rhombic.

The ground state wave function of an ion with orthorhombic symmetry can be obtained by the equations given in ref 8. Rao *et al* [9] have modified the wave function and developed the most general expression for the ground state as

$$\Psi = (\alpha'^2)^{1/2}[\alpha|x^2 - y^2\rangle + \beta|3z^2 - r^2\rangle] \qquad (2)$$

where α'^2 is the covalency parameter which indicates the probability of finding an electron on Cu^{2+} d orbital. α and β are the mixing coefficients for $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ orbitals. Rao *et al* assumed $\alpha \approx 1$, $\beta \approx 0$ and analysed the spectra only for the compressed octahedral symmetry with rhombic distortion superimposed on it [4]. Using equation 2 together with the experimental parameters obtained from EPR spectra, α'^2, α, β and k parameters were calculated. The resultant

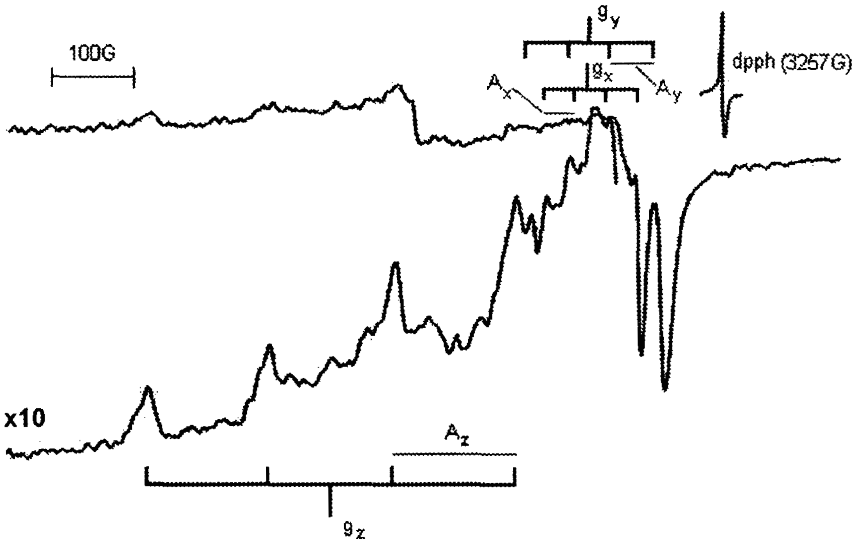

Figure 5. The powder EPR spectrum of Cu^{2+} doped SHOMH at room temperature.

Table 2. The principal g and hyperfine values of powder EPR spectrum of Cu^{2+} doped SHOMH crystal.

g_a	g_{b^*}	g_{c^*}	g_{iso}	A_a	A_{b^*}	A_{c^*}	A_{iso}
2.0072	2.0075	2.3359	2.1817	37 G	50 G	147 G	78 G

parameters and the parameters found in other studies for comparison are given in Table 3. The ground state wave function of Cu^{2+}, in SHOMH lattice can be constructed as

$$\Psi = (0.966)^{1/2}[0.990|x^2 - y^2\rangle + 0.100|3z^2 - r^2\rangle]. \quad (3)$$

The unpaired electron in the Cu^{2+} ion spends some of its time on $d_{3z^2-r^2}$ orbital and on $d_{x^2-y^2}$ orbital. This wave function shows that the electron spends 3.4

Table 3. The comparison of the ground state wave function parameters obtained in this study and in other studies.

Complex	k	α'^2	α	β	δg_{exp}	δg_{cal}	Ref.
$NaHC_2O_4.H_2O$	0.26	0.966	0.990	0.134	0. 016	0.024	this study
$CdK_2(SO_4)_2.6H_2O$	0.315	0.769	0.996	0.077	0.07	0.084	Ref. 3
$Rb_2Zn(SO_4)_2.6D_2O$	0.29	0.95	0.981	0.194	0.110	0.114	Ref. 9
$K_2Zn(ZrF_6)_2.6H_2O$	0.38	0.84	0.990	0.118	0.066	0.065	Ref.9

percent of its time on the ligands, whereas it spends 96.6 percent of its time on $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals of the copper ion. The time spent on d orbital is shared as 99.4 percent in $d_{x^2-y^2}$ and 1.34 percent in $d_{3z^2-r^2}$ orbitals. From these results, it can be concluded that the electron spends most of its time on $d_{x^2-y^2}$ orbital.

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