

Electron spin resonance studies of Cu^{2+} doped in cadmium maleate dihydrate single crystals

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MS received 15 September 1978; revised 18 December 1978

Abstract. Electron spin resonance studies have been carried out on Cu^{2+} ion doped in single crystals of cadmium maleate dihydrate at 303 and 77K. It has been found that Cu^{2+} enters this lattice interstitially. The spin Hamiltonian parameters have been evaluated and the ground state wave function is found to be predominantly $|X^2 - Y^2\rangle$ with a slight admixture of $|3Z^2 - r^2\rangle$.

Keywords. Electron spin resonance; Cu^{2+} : Cd maleate dihydrate; site location.

1. Introduction

The electron spin resonance (ESR) studies on Cu^{2+} ion in carboxylic acids always yield unusual results (Bleaney and Bowers 1952; Sakaguchi *et al* 1973). Eachus *et al* (1971) and Mabbs and Smail (1970) separately studied Cu^{2+} doped calcium cadmium acetate hexahydrate and found that Cu^{2+} enters the lattice in an unusual dodecahedral co-ordination. Narayana *et al* (1976) studied the ESR and optical absorption of Cu^{2+} in single crystals of strontium acetate tetra hydrate and suggested dodecahedral co-ordination.

In carboxylic acid cadmium salts, cadmium rarely exists in two different co-ordinations simultaneously. One such salt is cadmium maleate dihydrate (Post and Trotter 1974), in which cadmium atom exists at two sites having octahedral and dodecahedral co-ordination respectively. Cu^{2+} ion in cadmium maleate dihydrate would be also interesting because there are as many as four octahedral and four dodecahedral substitutional positions available for Cu^{2+} ion in a unit cell. In addition, interstitial sites with oxygen environments would also be available for Cu^{2+} ion.

In order to ascertain the preferential entry of Cu^{2+} ion, into the different possible sites mentioned above, the ESR study of Cu^{2+} ion in cadmium maleate dihydrate has been made and is reported here.

2. Experimental and structural data

Single crystals of the compound cadmium maleate dihydrate doped with Cu^{2+} (hereafter referred to as CMDH:Cu) are obtained by the procedure of Post and Trotter (1974). The compound was prepared by the addition of an aqueous solution of

maleic acid to an excess of finely divided cadmium carbonate, in suspension in water followed by heating to near boiling point, to which a few drops of copper acetate or copper sulphate aqueous solution are added as dopant (crystals with both dopants yielded the same results). Slow evaporation of the above solution at room temperature yielded transparent, approximately rectangular prisms elongated slightly along a -axis with (011) faces well developed; and the crystal structure data (Post and Trotter 1974) is given below.

Crystal system	Monoclinic
Space group:	$P2_1/c$
$a = 8.729 \text{ \AA}$	$b = 14.285 \text{ \AA}$
$c = 11.622 \text{ \AA}$	$\beta = 102.66^\circ$
Number of moles in the unit cell = $Z = 8$	

The structure (figure 1) consists of two cadmium atoms and two maleate ligands, both pairs of which are crystallographically and chemically distinct. One cadmium atom is six-coordinated through four water molecules and two bridging maleate oxygen atoms, while the other is eight-coordinated in distorted dodecahedral geometry, through four chelated carboxyl groups from two maleate ligands.

The ESR spectra of CMDH:Cu are recorded at 303 K and 77 K with a conventional X-band ESR spectrometer assembled in this laboratory operating at 9.28 GHz employing 100 kHz magnetic field modulation. The spectra are recorded at 10° intervals and DPPH is used as the g -marker.

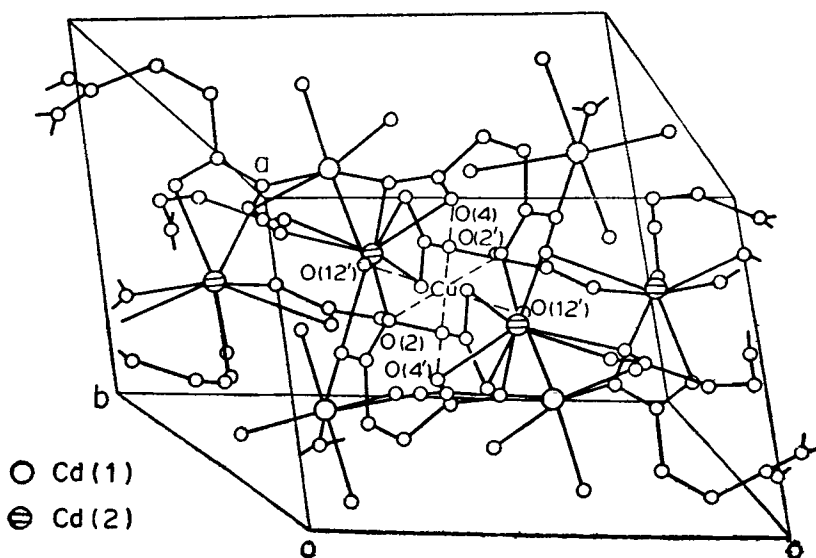


Figure 1. Stereoscopic view of the lattice CMDH

3. Results

ESR spectra recorded at room temperature gave a broad line in all orientations and a single set of poorly resolved hyperfine lines along g -maximum direction. The ESR spectra recorded at 77 K, for all orientations of magnetic field, showed a single set of four hyperfine lines ($S=\frac{1}{2}$, $I=\frac{3}{2}$) with a peak-to-peak line width of approximately 8 G. Figure 2 shows the ESR spectrum recorded along the direction of maximum g and A values at 77 K, the g and A tensors being coincident within the limits of experimental error. The hyperfine lines of ^{65}Cu ($S=\frac{1}{2}$, $I=\frac{3}{2}$ with 31% abundance) are resolved sufficiently clearly only for the $M_I=+\frac{3}{2}$ and $-\frac{3}{2}$ lines.

The angular variation of the spectra as the crystal is rotated in the ac and bc^* (c^* being normal to a -axis in ac plane) planes are identical and follow the expression

$$g^2(\theta) = g_{\max}^2 \cos^2 \theta + g_{\min}^2 \sin^2 \theta,$$

where θ is the angle made by the c^* -axis with the magnetic field. In ab plane there is no variation of g -value indicating an axial symmetry for the electric field around Cu^{2+} ion. The variation of the field positions of the hyperfine lines in ac plane is shown in figure 3 and can be represented by the equation

$$K^2 g^2(\theta) = A_{\max}^2 g_{\max}^2 \cos^2 \theta + A_{\min}^2 g_{\min}^2 \sin^2 \theta.$$

Such a variation of A and g tensors can be represented by the spin Hamiltonian having tetragonal symmetry with $S=\frac{1}{2}$ and $I=\frac{3}{2}$ and ignoring the quadrupole, interaction can be written as

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y)$$

where the terms have their usual meaning. The spin Hamiltonian constants are evaluated using Schonland's (1959) procedure and are given in table 1. The directional cosines of the ligand bonds are also given in this table.

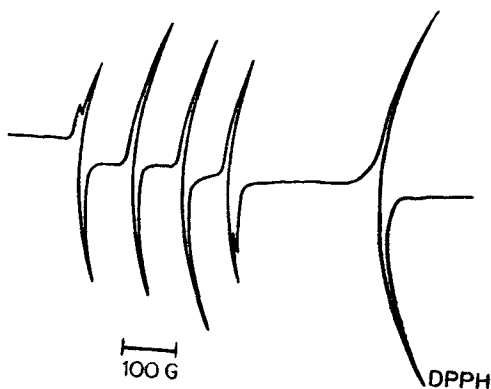


Figure 2. ESR Spectra of Cu^{2+} ion in CMDH along the direction of maximum g - and A -value at 77K

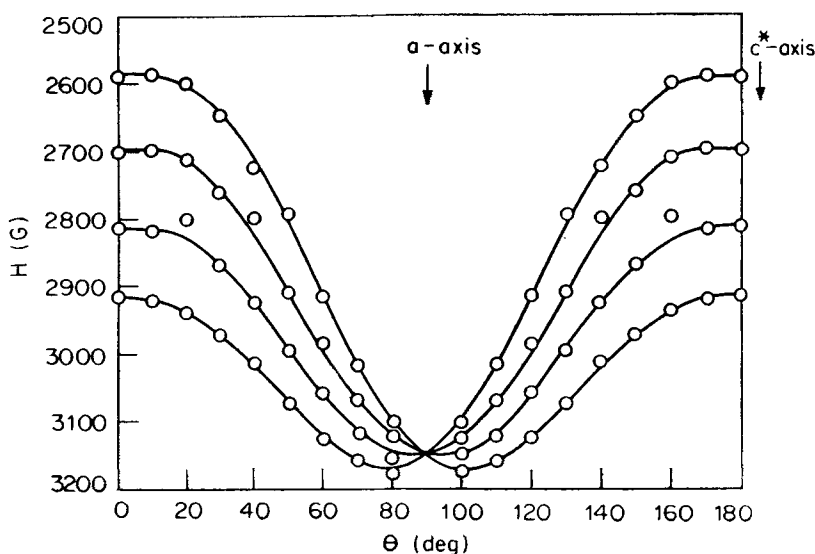


Figure 3. Variation of hyperfine field positions in ac -plane at 77K

Table 1. Spin-Hamiltonian parameters and the directional cosines of the ligand bonds

		Directional cosines		
		a	b	c
g_x	2.091 ± 0.002	0.9992	-0.0490	0.2896
g_y	2.091 ± 0.002	0.3740	0.3101	0.8734
g_z	2.409 ± 0.002	0.7177	0.0972	0.6369
A_x	$11 \pm 2 \times 10^{-4} \text{ cm}^{-1}$	—	—	—
A_y	$11 \pm 2 \times 10^{-4} \text{ cm}^{-1}$	—	—	—
A_z	$126 \pm 2 \times 10^{-4} \text{ cm}^{-1}$	—	—	—
<i>Substitutional (Cd 1) site</i>				
Cd(1) — 0(10)		0.8045	-0.2958	0.3870
Cd(1) — 0(9)		-0.9987	0.3720	0.9924
Cd(1) — 0(1)		0.9173	-0.1154	0.2588
<i>Interstitial site</i>				
0(4) — 0(4')		0.9939	-0.0510	0.1914
0(2) — 0(2')		0.4648	0.4115	0.8804
0(12) — 0(12')		-0.3616	0.9838	0.9602

4. Discussion

The spin Hamiltonian parameters suggest an elongated octahedral coordination for Cu^{2+} ion in this lattice. As can be seen from the crystal structure (figure 1), the Cd(1) atom is surrounded by six oxygens (octahedron) and the Cd(2) atom is eight coordinated. Suppose the Cu^{2+} ion enters the lattice substitutionally in Cd(1) position, then it will be in a distorted octahedral environment having for its ligands 0(9), 0(10), 0(11), 0(12), 0(1) and 0(3). According to the crystal system the four Cd(1)

atoms per unit cell are not equivalent in ab and bc planes while they are equivalent in ac -plane. This symmetry requires at least two sets of Cu^{2+} hyperfine lines (excluding the lines due to the ^{65}Cu isotope) in any plane except in ac -plane. Since only one set of four hyperfine lines could be recorded in all planes, this octahedral substitutional position for Cu^{2+} ion seems to be doubtful. The directional cosines of the coordinating bonds to this Cd(1) site are calculated and listed in table 1. It can be seen that there is a clear disagreement between the latter values and the principal g -values direction further supporting that Cu^{2+} ion is not entering the lattice substitutionally in Cd(1) site.

The other possibility for Cu^{2+} ion is to occupy CMDH substitutionally in the Cd(2) dodecahedral position: which has also to be ruled out on the same basis of inconsistency observed between the symmetry of the recorded ESR spectra and unit cell. It is very unusual for Cu^{2+} ion to enter such a dodecahedral Cd position. In fact only in the case of calcium cadmium acetate hexa hydrate it has been reported (Eachus *et al* 1971; Mabbs and Smail 1970) that Cu^{2+} ion enters a dodecahedral Cd position giving a hyperfine maximum of $151.8 \times 10^{-4} \text{ cm}^{-1}$ at 77 K, whereas in CMDH:Cu the hyperfine maximum is found to be only $126 \times 10^{-4} \text{ cm}^{-1}$ which indicates an octahedral environment. Further, a similar calculation of the coordinating ligand bond directions for this site also gives values that do not agree with any of the principal g -value directions.

In addition, the spin Hamiltonian parameters in CMDH:Cu suggests a purely axial symmetry around Cu^{2+} ion, and expectation of such an axial g - and A -values either from Cd(1) distorted octahedral or from Cd(2) dodecahedral site is highly improbable as can be seen from the crystal structure data. It is thus more probable for Cu^{2+} ion to enter the lattice interstitially rather than substitutionally. Therefore an attempt has been made to locate the most probable interstitial site. It was found that the Cu^{2+} ion may coordinate with the ligands 0(4) and 0(4'), 0(2) and 0(2') belonging to two Cd(2) atoms and 0(12) and 0(12') belonging to two Cd(1) atoms. The comparison of the directional cosines of the g -values with that of the coordinating ligands for this site indicate reasonable agreement (table 1). Moreover, for this particular interstitial site the metal ion is approximately located at the centre of the unit cell (having coordinates roughly $1/2, 1/2, 1/2$) giving an unique type of site per unit cell. Finally when a bivalent metal ion goes into an interstitial site, two positive charges must be set free in order to achieve the charge neutrality. It is possible that the hydroxyl groups in the CMDH:Cu be used for such a charge compensation. The protons of the 0(12) and 0(12') hydroxyl groups could be the ones which are set free in the process of doping. A similar result was reported (Lau and Lin 1973) in which ESR of Cu^{2+} , Mn^{2+} , and Ni^{2+} doped calcium tartrate was studied and it was postulated that the divalent metal ion enters the lattice interstitially and two protons of hydroxyl groups were set free to bring about the charge neutrality.

The spin Hamiltonian parameters of Cu^{2+} ion in this lattice indicate a $|X^2 - Y^2\rangle$ ground state with a slight admixture from $|3Z^2 - r^2\rangle$. The ground state wave function may be written as

$$\alpha |X^2 - Y^2\rangle + \beta |3Z^2 - r^2\rangle$$

where α and β are the mixing coefficients. The departure (Δg_i) of each of the three principal g values g_i , from the free spin value 2.0023, and the principal A values

are substituted in the simultaneous equations due to Bleaney *et al* (1955), with the necessary modification suggested by Sroubeck and Zdansky (1966) and solved. We get $\alpha=0.895$, $\beta=0.104$. As the signs of A_x , A_y and A_z are not known, various trial combinations were used in the above equations. Only when A_x and A_y were chosen positive and A_z negative, the condition $\alpha \approx 1$ and $B \ll 1$ could be met.

Acknowledgements

The authors thank Prof. K V Krishna Rao for his interest and encouragement and one of them (VCM) is grateful to the University Grants commission, New Delhi, for financial assistance.

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