

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

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Abstract. Electron spin resonance studies were carried out on VO^{2+} in cadmium maleate dihydrate single crystals at 303 K. The spin hamiltonian parameters were evaluated. The results lead us to conclude that like Cu^{2+} , VO^{2+} enters the lattice interstitially.

Keywords. Electron spin resonance; cadmium maleate dihydrate; site location.

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1. Introduction

The electron spin resonance (ESR) studies on paramagnetic ions in carboxylic acids always yield interesting results (Bleaney and Bowers 1952; Sakaguchi *et al* 1973; Lau and Lin 1973). ESR studies on Cu^{2+} ion doped in cadmium maleate dihydrate single crystals at 303 K and 77 K (Chandra Mouli and Sivarama Sastry 1979) revealed that Cu^{2+} takes up a single site. It was concluded that Cu^{2+} enters the lattice interstitially. This paper describes the ESR of VO^{2+} in cadmium maleate dihydrate single crystals.

2. Experimental and structural data

Single crystals of the compound cadmium maleate dihydrate doped with vanadyl impurity (hereafter referred to as VO^{2+} in CMDH) were obtained by the procedure described by Post and Trotter (1974). The dopant was introduced in the form of aqueous solution of vanadyl sulphate during the growth. The crystallographic data is: Crystal system: monoclinic; Space group: $P_{21/c}$; $a = 8.729 \text{ \AA}$; $b = 14.285 \text{ \AA}$; $c = 11.622 \text{ \AA}$; $\beta = 102.66^\circ$; number of molecules in the unit cell = 8.

The structure of CMDH (figure 1) consists of two types of cadmium atoms and two types of maleate ligands, both pairs of which are crystallographically and chemically distinct. One cadmium atom is in distorted octahedral environment and the other in a distorted dodecahedral environment.

The ESR spectra of VO^{2+} in CMDH were recorded at 303 K with a conventional X-band ESR spectrometer assembled in this laboratory operating at 9.28 GHz and employing 100 kHz magnetic field modulation. The spectra were recorded at 10° intervals and DPPH was used as the g -marker.

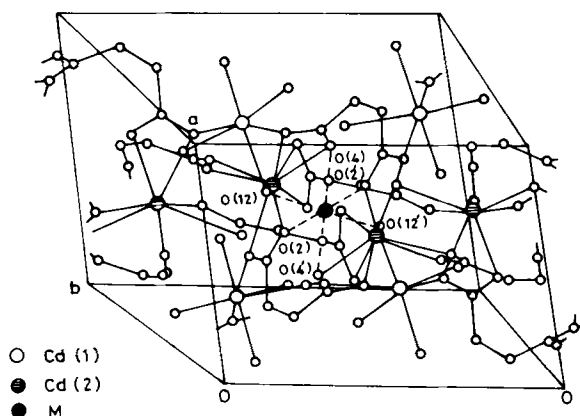


Figure 1. Schematic representation of crystal structure of CMDH and paramagnetic centre.

3. Results and discussion

The ESR spectra of VO^{2+} in CMDH consisted of a single set of eight hyperfine lines due to the ^{51}V ($I = 7/2$) nucleus, for all orientations of the magnetic field, with a peak-to-peak linewidth of approximately 4 G, indicating that VO^{2+} ion occupies a single site in the lattice. Figure 2 shows the ESR spectrum of VO^{2+} in CMDH recorded along the direction of maximum hyperfine splitting (minimum g -value) in ac plane at room temperature. The g and A tensors were coincident within experimental errors.

The angular variation of the ESR spectrum as the crystal is rotated in ac and bc^* (c^* being normal to a -axis in ac plane) is identical and follows the expressions

$$g^2(\theta) = g_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 \sin^2 \theta, \quad (1)$$

and
$$A^2 g^2 = g_{\parallel}^2 A_{\parallel}^2 \cos^2 \theta + g_{\perp}^2 A_{\perp}^2 \sin^2 \theta, \quad (2)$$

where θ is the angle between c^* axis and the magnetic field. The spectra recorded in ab plane show no anisotropy in g and A values indicating axial field symmetry around the VO^{2+} ion. Such a variation of g and A tensors can be represented by a spin hamiltonian having tetragonal symmetry with $s = 1/2$ and $I = 7/2$ as

$$\begin{aligned} \mathcal{H} = & g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} I_z S_z \\ & + A_{\perp} (I_x S_x + I_y S_y), \end{aligned} \quad (3)$$

where the terms have their usual meaning. This gives the field positions of resonance along the z -axis as

$$H_z(m) = H_0 - Am - [I(I+1) - m^2(A^2 + A'^2)]/4H_0, \quad (4)$$

where H_0 is the Gunn-diode frequency in gauss, A_{\parallel} and A_{\perp} are hyperfine field constants expressed in gauss. The other terms have their usual meaning.

The spin-hamiltonian parameters of VO^{2+} in CMDH are given in table 1 and compared with the corresponding parameters of VO^{2+} doped in tris sarcosin calcium chloride (TSCC), (Sathyanarayana *et al* 1978), hexauria aluminium per chlorate (HUAP) (Sathyanarayana *et al* 1976), ammonium zinc sulphate hexahydrate (AZSH) (Borchert

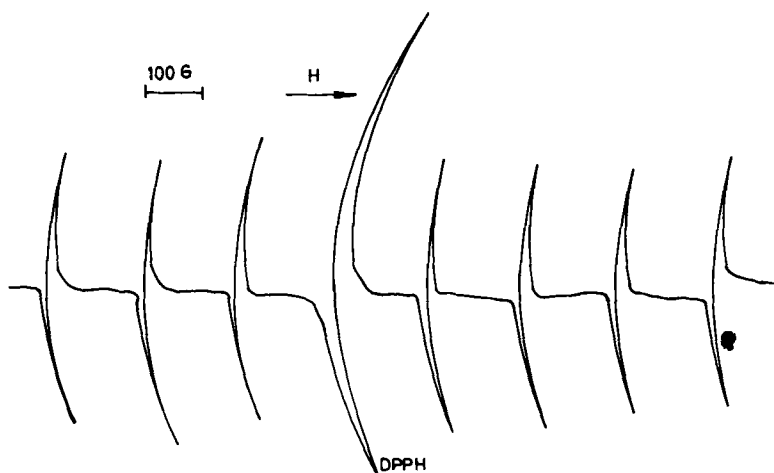


Figure 2. ESR spectra of VO^{2+} in CMDH along the direction of maximum hyperfine splitting (A) in *ac* plane at 303 K.

Table 1. Spin-hamiltonian parameters of VO^{2+} in different VO-O_n complexes.

Lattice	g_{\parallel}	g_{\perp}	A_{\parallel} ($\times 10^4 \text{ cm}^{-1}$)	A_{\perp} (B) ($\times 10^4 \text{ cm}^{-1}$)
CMDH VO-O_5	1.931	1.992	183	78
	± 0.002	± 0.002	± 2	± 2
TSCC VO-O_5	1.930	1.991	178	72
HUAP VO-O_5	1.932	1.987	175	65
AZSH VO-O_5	1.933	1.981	188	72
KTO VO-O_4	1.940	1.972	168	61

and Kikuchi 1964) and potassium titanyl oxalate (κTO) (Golding 1962). The κTO represents a VO-O_4 complex formation while all the others represent formation of a VO-O_5 complex.

It is evident from the ESR spectra of VO^{2+} in CMDH that vanadium entered the lattice as VO^{2+} . Table 1 shows that the complex formed is clearly VO-O_5 rather than the VO-O_4 (κTO).

As can be seen from crystal structure of CMDH, Cd(1) is in distorted octahedron, while Cd(2) is in dodecahedron of oxygens. Assuming that VO^{2+} ion enters the lattice substitutionally in Cd(1) position according to the symmetry requirement of the crystal system, at least two sets of VO^{2+} hyperfine lines should be recorded in any plane except in *ac*-plane (*ac*-plane being a mirror plane). Since only a single set of eight hyperfine lines was obtained in all planes the octahedral substitutional position seems unlikely. The same argument holds against VO^{2+} ion entering CMDH substitutionally in the Cd(2) dodecahedral position. Further axial g and A values would be inconsistent with Cd(1) and Cd(2) substitution.

An attempt was made to locate the most probable interstitial site. It is suggested that VO^{2+} ion may coordinate with the ligands O(4), O(4'); O(2), O(2') belonging to two Cd (2) atoms and O(12) and O(12') belonging to two Cd(1) atoms. We have arrived at a similar conclusion in the study of Cu^{2+} ion in CMDH. As discussed in a previous paper (Chandra Mouli and Sivarama Sastry 1979), the charge neutrality will be achieved by the release of two protons belonging to hydroxyl groups.

References

- Bleaney B and Bowers K D 1952 *Proc. R. Soc. (London)* **A214** 451
Borchert R H and Kikuchi C 1964 *J. Chem. Phys.* **40** 2270
Chandra Mouli V and Sivarama Sastry G 1979 *Pramana (J. Phys.)* **12** 165
Golding M R 1962 *Mol. Phys.* **5** 369
Lau P W and Lin W C 1973a *J. Chem. Phys.* **59** 3981, 3988
Post M L and Trotter J 1974 *J. Chem. Soc. (Dalton)* p. 674
Sakaguchi U, Arato Y and Fujiwara S 1973 *J. Mag. Reson.* **10** 139
Sathyanarayana S G, Krishnan V G and Sivarama Sastry G 1976 *J. Chem. Phys.* **65** 4181
Sathyanarayana S G, Narayana M and Sivarama Sastry G 1978 *J. Chem. Phys.* **68** 3122