

ELECTRON PARAMAGNETIC RESONANCE OF Mn^{2+} AND Cu^{2+} IN $Cs_2C_2O_4 \cdot H_2O$ SINGLE CRYSTALS

V.K. JAIN AND V. KAPOOR

Department of Physics, M.D. University, Rohtak-124001, India

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The electron paramagnetic resonance spectra of Mn^{2+} and Cu^{2+} in $Cs_2C_2O_4 \cdot H_2O$ single crystals are studied at ~ 9.45 GHz and 290 K. The spectra at 77 K show no appreciable change. The ions appear to enter the lattice at interstitial sites. The spin-Hamiltonian parameters are evaluated at 290 K.

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1. Introduction

Cesium oxalate monohydrate $Cs_2C_2O_4 \cdot H_2O$, (COMH), belongs to a group of not very numerous crystal hydrates with a minimum number of water molecules. COMH crystallizes in monoclinic symmetry with space group $P2_1$ [1]. The unit cell contains two formula units. The lattice constants are [1] $a = 0.617$ nm, $b = 1.104$ nm, $c = 0.619$ nm, $\beta = 114.0^\circ$. The detailed atomic positions are not available. The electron paramagnetic resonance (EPR) of VO^{2+} ion in COMH has been reported earlier [2]. This paper reports the results of EPR of Mn^{2+} and Cu^{2+} in COMH single crystals at room temperature (~ 290 K).

2. Experimental

Single crystals of COMH doped with Mn^{2+} and Cu^{2+} were grown at room temperature by slow evaporation of an aqueous solution. The Mn^{2+} and Cu^{2+} were introduced into the host lattice by adding (0.5% by weight) the corresponding sulfates. The crystals are hygroscopic and grew in the form of thin needles with a axis parallel to the needle axis [1]. EPR measurements were carried out using a JEOL JES-FE 3X homodyne X-band spectrometer equipped with a TE₀₁₁ cylindrical cavity and 100 kHz field modulation. As a reference for the magnetic field strength the resonance line of DPPH with $g = 2.0036$ is used. The crystals were mounted on quartz rods. The angular variation studies were done using a JES-UCR-2X sample angular rotating device.

3. Results and discussion

3.1. Mn^{2+}

For an arbitrary orientation of the crystal, a spectrum corresponding to two identical but differently oriented magnetic complexes of Mn^{2+} is observed. The z axes of two complexes make an angle of $70 \pm 2^\circ$ with each other. When the magnetic field is in the ac plane or along the b axis, the two magnetic complexes become equivalent. The angular variation studies (Fig. 1) indicate that the observed spectrum has an orthorhombic symmetry. The spectrum shows no appreciable change at liquid nitrogen temperature.

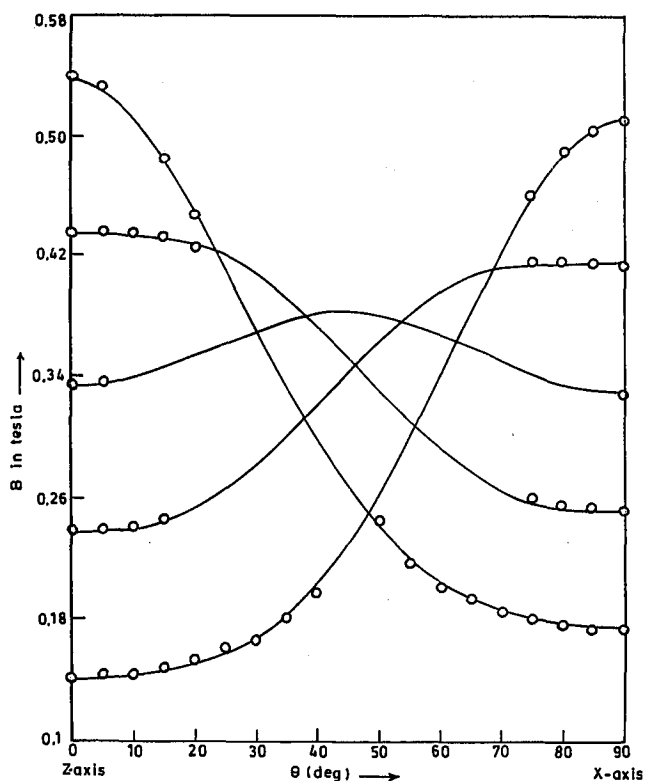


Fig. 1. Angular dependence of allowed fine structure transitions ($\Delta M = \pm 1$) of one of the two magnetically inequivalent Mn^{2+} centers in the zx plane at 290 K. Theoretical (—) and experimental (o) results.

The spin-Hamiltonian suitable for the interpretation of EPR spectra of Mn^{2+} in COMH is [3]:

$$\mathcal{H} = \beta_e \mathbf{S} \cdot \hat{g} \cdot \mathbf{B} + D[S_z^2 - (1/3)S(S+1)] + E(S_x^2 - S_y^2) + (a/6)[S_x^4 + S_y^4 + S_z^4 - (1/5)S(S+1)(3S^2 + 3S - 1)] + \mathbf{S} \cdot \hat{A} \cdot \mathbf{I}, \quad (1)$$

where the symbols have their usual meaning and $S = I = 5/2$ for Mn^{2+} .

Magnetic field measurements were made for the allowed lines with B parallel to the z and x axes, respectively. No measurement could be made for B parallel to the y axis since the lines mixed up and consequently the various fine structure transitions could not be distinguished. Therefore, it was necessary to assume that $A_x = A_y$ and $g_x = g_y$ in the calculations (the hyperfine and \hat{g} tensors are normally isotropic for the Mn^{2+} ion). Using the expression for resonance field positions given by Pandey and Upreti [4] up to third-order perturbation for the above spin-Hamiltonian, the parameters obtained are (in units of 10^{-4} cm^{-1}):

$$D = -468(3), \quad E = 109(5), \quad a = 1.8(5),$$

$$g_z = 2.001(1), \quad g_x = 1.998(3),$$

$$A_z = -81(1), \quad A_x = -80(1).$$

The signs of the parameters are only relative. The relative signs of the parameters D and A_z were obtained by comparing the second-order shifts in the separation between hyperfine components for the various electronic transitions [3]. The sign of D is then obtained by assuming A_z to be negative as, in all the materials where the sign has been determined A_z has been found to be negative [3]. The sign of rhombic parameter E results from the sign of D and the choice of x and y axes.

3.2. Cu^{2+}

For an arbitrary orientation of the crystal, a spectrum corresponding to two identical but differently oriented magnetic complexes is observed. The intensity of two sets of hyperfine lines was found to be about the same indicating that the two sites, which the Cu^{2+} ions can occupy, are almost equally populated. These orientations become equivalent when the magnetic field is in the ac plane or along the b axis. Measurement of spectra at liquid nitrogen temperature did not indicate any appreciable change.

The parameters of the Cu^{2+} complex were determined by using the spin-Hamiltonian (1) neglecting the crystal field terms. For Cu^{2+} , $S = 1/2$, $I = 3/2$. The parameters of the spin-Hamiltonian at 290 K (hyperfine parameters in units of 10^{-4} cm^{-1}) are: $A_z = 139(1)$, $A_x = 9(2)$, $A_y = 7(2)$, $g_z = 2.344(1)$, $g_x = 2.063(3)$, $g_y = 2.079(3)$, $A^{65}/A^{63} = 1.0655$. The spin-Hamiltonian parameters were also determined from the spectrum of finely crushed COMH: Cu^{2+} single crystals. The parameters (hyperfine parameters are in units of 10^{-4} cm^{-1}) are: $A_z = 139.7$, $A_x = 9.0$, $A_y = 6.5$, $g_z = 2.347$, $g_x = 2.065$, $g_y = 2.079$. The accuracy of the parameters is limited by the linewidths. The powder spectra results are in good agreement with those of single crystals. Since Cu^{2+} has a d^9 configuration and $g_z > g_y > g_x$, the single hole must be in a $d_{x^2-y^2}$ type orbital. The values of the components of the g -factor indicate that Cu^{2+} in the lattice is surrounded by six oxygen atoms [5].

For COMH, no precise structure data are available to provide the exact positions of the various ions in the unit cell. In the host lattice, the interstitial site could be between oxygen ions belonging to either oxalate or water molecules similar to that of lattice of $K_2C_2O_4 \cdot H_2O$ [6]. The introduction of Mn^{2+} or Cu^{2+} in place of Cs^+ or in the interstitial site in the lattice causes a charge imbalance. The neutrality of the crystal can, however, be maintained by the formation of positive ion vacancies. In the lattice a positional substitution of the form $Cs^+ - Mn^{2+}$ (Cu^{2+}) or isomorphous substitution in the form $2Cs^+ - Mn^{2+}$ (Cu^{2+}) can take place.

It is reasonable to assume that Mn^{2+} (Cu^{2+}) enters the COMH lattice interstitially displacing two Cs^+ ions, similar to that in the lattice of $K_2C_2O_4 \cdot H_2O$ [6]. This is supported by the fact that for B in a general orientation only two magnetically inequivalent sets were observed. Had the Mn^{2+} (Cu^{2+}) ion substituted for a monovalent Cs^+ ion, four identical but magnetically inequivalent centers, rather than two, would have resulted, because of the presence of four inequivalent Cs^+ sites in the unit cell of COMH.

Acknowledgements

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