

Electron Paramagnetic Resonance Study of Cu²⁺ in CdCa(CH₃COO)₄ · 6H₂O Single Crystal

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Z. Naturforsch. 55a, 729–732 (2000); received April 4, 2000

The Electron Paramagnetic Resonance spectra of Cu²⁺ in CdCa(CH₃COO)₄ · 6H₂O (cadmium calcium tetraacetate hexahydrate) powder and single crystal have been recorded at 300 and 133 K. The angular variation of the spectra indicated the substitution of the host Cd²⁺ with Cu²⁺. The observed values of the **g** and **A** hyperfine tensors were found to be temperature dependent, and this dependence is discussed and explained on the basis of dynamic Jahn-Teller effects. The spin-Hamiltonian parameters were found to be axial symmetric at room temperature, whereas they showed deviations from axial symmetry at low temperature. The **g** and **A** tensors were found to be coaxial within the limits of experimental errors, and the ground state wave functions of the complex at 300 and 133 K have been constructed.

Key words: EPR; Crystal and Ligand Field; Jahn-Teller Effects.

1. Introductions

Electron paramagnetic resonance (EPR) techniques can be used to study paramagnetic ions in host crystals as probes [1–5]. This kind of studies gives valuable information about the site symmetries of the transition ions. Especially, the 3d⁹ configuration is of interest in transition-metal complexes because they represent a relatively simple one magnetic-hole system by means of which it is hoped to obtain information about the electron wave functions even in a ligand field of low symmetry. The Cu²⁺ ion has been used as an impurity probe to perform such studies in different symmetry environments by estimating the principal values of **g** and **A** of the ion. Several studies exist on CdCa(CH₃COO)₄ · 6H₂O with EPR and NMR (Nuclear Magnetic Resonance) techniques [6–12]. These studies were focused on the phase transition, and the EPR parameters were determined at different temperatures. Some researchers have not reported any phase change [9], others have reported the existence of only two inequivalent sites [8] just below 140 K; this was supported by EPR on γ -irradiated samples [13]. In addition, Gaura et al. studied the weak exchange in this complex by EPR technique [12].

Despite the previous studies [8–13] on the EPR spectra of Cu²⁺ in CdCa(CH₃COO)₄ · 6H₂O, several questions are still unanswered. Therefore we present an EPR study about the Jahn-Teller effect and ground state

wavefunctions in Cu²⁺-doped CdCa(CH₃COO)₄ · 6H₂O powder and single crystals at 113 to 300 K. The dependence of **g** and **A** on the temperature has been explained in terms of dynamic Jahn-Teller distortion [17, 18].

2. Experimental Details

Cadmium calcium tetraacetate hexahydrate crystals were obtained from a saturated solution containing Cd(II), Ca(II), and Cu(II) acetates in the mole ratios 1 : 1 : 0.001. Colorless transparent crystals were obtained in about a week, and those of sizes 5 × 3 × 1 mm³ were chosen for the present study.

The spectra were recorded using a Varian E-109C model X-band EPR spectrometer, equipped with a Varian temperature control unit. The magnetic field modulation frequency was 100 kHz. The single crystals were mounted on a goniometer and the spectra were recorded for every 10° orientation of the external magnetic field in the three mutually perpendicular planes (*ab*, *ac*, and *bc*) at room temperature. The **g** values were found by comparison with a diphenylpicrylhydrazyl sample of 2.0036 g. Powder spectra were recorded at room temperature as well as at 113 K.

Cadmium calcium tetraacetate hexahydrate single crystal is tetragonal with space group I4/m, containing four molecules per unit cell, the dimensions of which are:

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$a = b = 11.37$, $c = 16.08 \text{ \AA}$ [10]. In this lattice the cadmium ion displays eight-coordination with the acetate groups. The cadmium coordination geometry in this double salt has been described by Honkonen et al. [10] as a distorted dodecahedron. The Cd-O bond lengths are equally divided between 2.289 and 2.276 \AA [10]. Additionally, it is obtained from the NMR technique that the symmetry fixes the orientation of the shielding tensor in the tetragonal reference frame. The principal elements are required to be coincidental with the unit cell axes, with the unique elements, σ_{33} as can be seen in [10]. In this configuration the tensor orientations generated by the point group symmetry operators $C4$, m_c are magnetically equivalent.

3. Results and Discussion

The EPR spectrum of Cu^{2+} in single crystal of $\text{CdCa}(\text{CH}_3\text{COO})_4 \cdot 6\text{H}_2\text{O}$ was recorded at 300 and at 113 K. $I4/m$ space group of the host lattice contains four equivalent cadmium sites per unit cell, which are magnetically equivalent in the three crystallographic planes and along the three principal crystallographic axes [10]. Thus, along the principal crystal directions and in the three crystallographic planes the EPR spectrum will show a single set of four characteristic lines because the spectra due to all the four sites will overlap exactly in all positions [13]. An example of the spectra at room temperature is shown in Fig. 1 when the magnetic field is in the ac plane, 30° with the a axis. It is seen that the hyper-

fine lines due to the less abundant isotope ^{65}Cu are also resolved in the outer two lines of the quartet on the low field side. This could not be followed completely, as they are not resolved for other directions. The angular variations of the spectra were studied at every 10° orientation of the magnetic field in three mutually perpendicular planes (ab , ac , and bc), cf. Figure 2. These results are in complete agreement with the above explained tetragonal structure of the host crystal. The EPR spectrum in the crystallographic ac plane consisted of a set of incompletely resolved lines whose position is invariant to rotation in this plane.

The whole spectra can be fitted to the rhombic symmetry spin-Hamiltonian

$$\mathcal{H} = \beta B \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I}, \quad (1)$$

where all the symbols have their usual meaning [13], the principal values of the \mathbf{g} and \mathbf{A} tensors and their direction cosines were found by the diagonalization procedure [15, 16]. The results are given in Table 1.

The temperature dependencies of \mathbf{g} and \mathbf{A} were carefully monitored by studying the powder samples. The principal values of \mathbf{g} and \mathbf{A} obtained from single crystal spectra were compared with the powder values at 300 K. Excellent agreement within the experimental errors was found. This shows clearly that the single crystal analysis is correct. The values of \mathbf{g} and \mathbf{A} were found to be very temperature depended, are shown for the components g_z and A_z in Table 2. The temperature dependencies of \mathbf{g} and \mathbf{A} for Cu^{2+} doped cadmium calcium tetraacetate hexahydrate are very similar to those observed by Silver et al. [17] and Schlick et al. [18] for Cu^{2+} in isomorphous zinc tutons's salt. We have also found that this model [17, 18] satisfactorily explains at our experimental results in terms of dynamic Jahn-Teller distortion, since this effect was originally invoked to account for the temperature dependence of the EPR spectrum of the crystals containing the $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ complex [17].

At room and low temperature, for a powder sample three sets of four lines can clearly be seen. They are shown in Figure 3. This indicates that the copper complex has a tetragonal symmetry with rhombic distortion. The ground state was found to be $|x^2 - y^2\rangle$ [5]. As the obtained data indicate rhombic symmetry and the \mathbf{A} hyperfine tensor coincides with the \mathbf{g} tensor, the ground state wavefunction of Cu^{2+} should be a linear combination of the $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ orbitals. The ground state wavefunction given by Rao et al. [19] is

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

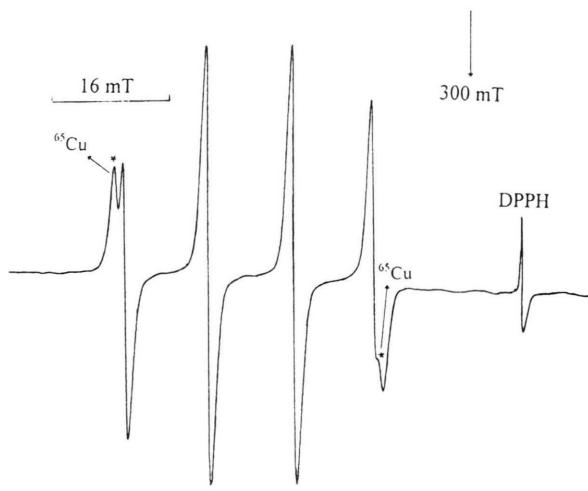


Fig. 1. EPR spectra of Cu^{2+} doped $\text{CdCa}(\text{CH}_3\text{COO})_4 \cdot 6\text{H}_2\text{O}$ single crystal in the ac plane, 30° with the a axis, at 300 K. The shoulders (*) on the extreme lines correspond to ^{65}Cu isotope.

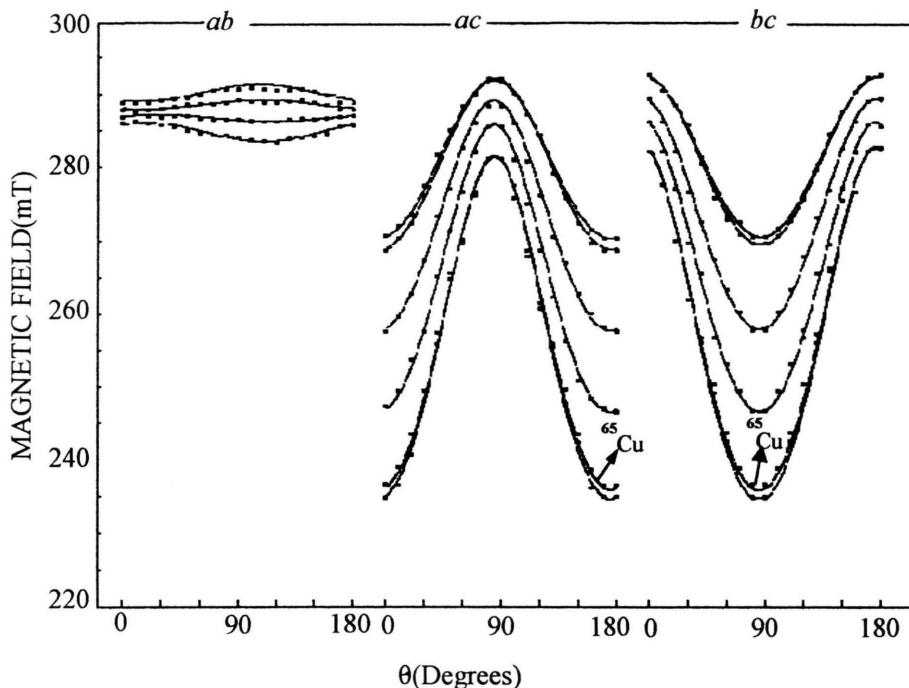


Fig. 2. Angular variations of the EPR spectra of Cu²⁺ doped CdCa (CH₃COO)₄ · 6H₂O single crystal in the ab, ac, and bc planes at 300 K.

Table 1. Spin-Hamiltonian Parameters of Cu²⁺ doped in CdCa (CH₃COO)₄ · 6H₂O.

	(K)	A _x (mT)	A _y (mT)	A _z (mT)	g _x (mT)	g _y (mT)	g _z (mT)
Mabbs F. Eç [6]	300	1.5		14.3	2.064		2.365
Eachus R. S. [7]	300	1.14	1.14	-14.3	2.065		2.366
	77	1.52	1.66	-15.1	2.057	2.054	2.256
Roy A. K. [8]	300	1.3	1.3	11.9	2.060		2.360
Sushil K. M. [9]	300	2.9	2.9	12.0	2.064		2.354
	77	5.3	5.3	16.0	2.066		2.363
	5.4	4.6	4.6	15.4	2.064		2.350
Present Work	300 (Cryst.)	1.40	2.2	12.8	2.083	2.075	2.400
	300 (Powder)	1.24	2.0	12.8	2.083	2.074	2.390
	113 (Powder)	1.7	2.0	13.9	2.085	2.077	2.388

where α'^2 is the covalency parameter which indicates the probability of finding the electron-spin density on the metal Cu²⁺ d orbital, α and β are the mixing coefficients for the $|x^2 - y^2\rangle$ and $|3z^2 - r^2\rangle$ orbitals, respectively, and $\alpha^2 + \beta^2 = 1$. In order to evaluate the above parameters in the present case, using the literature values and expressions to construct these wavefunctions [7, 19], we obtain

$$|\Psi_{\text{room}}\rangle = (0.865)^{1/2} [0.999|x^2 - y^2\rangle + 0.040|3z^2 - r^2\rangle],$$

$$|\Psi_{\text{low}}\rangle = (0.886)^{1/2} [0.998|x^2 - y^2\rangle + 0.053|3z^2 - r^2\rangle]$$

at room and low temperature, respectively. This means that at room temperature the electron spends 87% of its time in the metal d orbital, whereas the remaining 14% is spread over the ligand orbital, while at 113 K the electron spends 89% of its time in the metal d orbital and the remaining 11% is spread over the ligand orbitals. However, α'^2 , α , β , and k were calculated for several temperatures. As can be seen in Table 2, the covalence of Cu²⁺ slightly changes between 113 and 213 K, whereas it abruptly changes above 213 K. The ground state

Table 2. Temperature dependence of the coefficients of the ground state wavefunction and spin-Hamiltonian Parameters of Cu²⁺ in CdCa(CH₃COO)₄ · 6H₂O powdered samples.

T (K)	α'^2	α	β	k	g_z	A_z (mT)
300	0.8657	0.99921	0.0395	0.34199	2.3702	128
270	0.8663	0.99918	0.0399	0.34204	2.33656	129
243	0.8672	0.99914	0.0413	0.34207	2.3633	131
213	0.8742	0.99902	0.0420	0.34166	2.3619	133
193	0.8769	0.99878	0.0493	0.34124	2.3601	134.5
173	0.8790	0.99873	0.0497	0.34128	2.3597	136
163	0.8809	0.99874	0.0500	0.34130	2.3585	136.4
153	0.8830	0.99872	0.0505	0.34139	2.3584	136.8
143	0.8834	0.99869	0.0511	0.34150	2.3583	137
133	0.8855	0.99866	0.0516	0.34142	2.3582	137.5
123	0.8859	0.99863	0.0522	0.34145	2.3581	138
113	0.8861	0.99861	0.0528	0.34150	2.3580	139

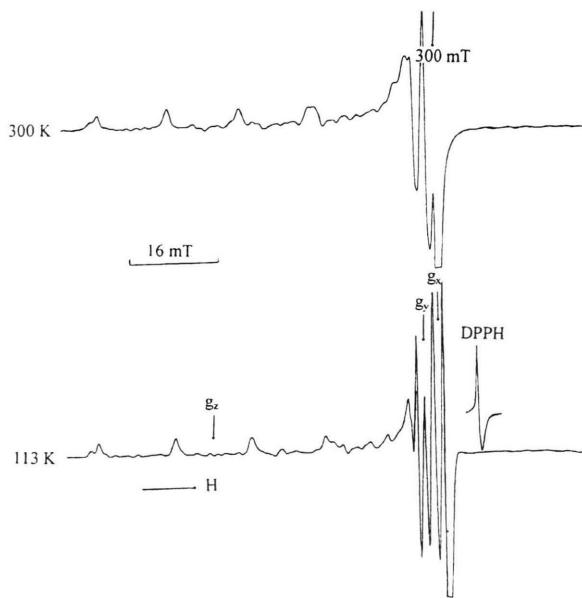


Fig. 3. EPR spectra of powdered samples of Cu²⁺ in CdCa(CH₃COO)₄ · 6H₂O at 300 and 113 K.

wavefunction is not a pure $|x^2 - y^2\rangle$ wavefunction but about 1% $|3z^2 - r^2\rangle$ is admixed to it. The admixture of $|3z^2 - r^2\rangle$ to $|x^2 - y^2\rangle$ through vibronic interaction increases with temperature, resulting in a corresponding increase in the g_z values and decrease in the g_x and g_y values as can be seen in Table 1. As conclusion we can

state that the results of the present study indicate the incorporation of the Cu²⁺ ions in the host lattice, and that the Cu²⁺ complex shows in CdCa(CH₃COO)₄ · 6H₂O a more covalent nature at room temperature than at 113 K.

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