EPR Study of the Dynamic Jahn-Teller Effect of Cu^{2+} in $CdBa(HCOO)_4{\cdot}2H_2O$ Single Crystals

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Electron Paramagnetic Resonance spectra of Cu^{2+} doped into cadmium barium formate dihydrate single crystal were studied at 300 K. The powder spectrum of this material was studied at 300 to 133 K. The values of the **g** and **A** hyperfine tensors were found to be temperature dependent. The temperature dependence of the Cu^{2+} EPR spectrum is discussed in terms of the dynamic Jahn-Teller effect. The angular variation of the spectra indicates the substitution of the host Cd^{2+} with Cu^{2+}. The spectra were fitted with a tetragonal spin-Hamiltonian, the parameters of which were determined at 300 K. The ground-state wave function of the copper complex has been constructed at 113 K and 300 K.

1. Introduction

Electron paramagnetic resonance (EPR) studies on transition metal ions doped into single crystals give valuable information about the environmental symmetry of transition ions and the bonding nature of their ligands. Especially, the $3d^9$ configuration is of interest in transition metal complexes because it represents 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 [1 - 4]. The Cu^{2+} ion also has been studied in alkaline formates [5 - 10]. The EPR parameters **g** and **A** indicate the symmetry and its variation as temperature or pressure is varied. The EPR spectra of Cu^{2+} in $Ba_2Zn(HCOO)_6{\cdot}4H_2O$ and zinc Tutton's salt were studied by Silver *et al.* [8, 11]. They postulated dynamic Jahn-Teller (JT) distortion and assigned the $d_{x^2-y^2}$ ground state. They also explained the temperature dependent **g** and **A** values in term of dynamic JT distortion.

In this study, the Silver-Getz(SG) model is used to understand the dynamic aspects of the distortion by assuming a $d_{x^2-y^2}$ ground state for Cu^{2+} in $CdBa(HCOO)_4.2H_2O$. To our knowledge, such an EPR study on Cu^{2+}-doped $CdBa(HCOO)_4{\cdot}2H_2O$ powder and single crystals does not exist. Since EPR can provide a detailed description of the crystal field around the metal ion and the state of the paramagnetic ion, a detailed EPR study of Cu^{2+} doped single crystals and powder samples of $CdBa(HCOO)_4{\cdot}2H_2O$ was carried out at 300 - 113 K, and the results are interpreted considering a $d_{x^2-y^2}$ ground state for copper.

2. Experimental Details

In the first step, cadmium formate (CF) and barium formate (BF) were obtained at room temperature [5, 9]. The aqueous solutions of these were obtained by equimolar mixing. A very small amount of $CuCl_2{\cdot}2H_2O$ was added to the stock solution. The crystals of cadmium barium formate dihydrate (CBFDH) doped with Cu^{2+} were grown by evaporation at room temperatures. Colourless transparent crystals of about $1 \times 3 \times 5$ mm^3 were obtained in about two weeks.

The CBFDH crystallizes in monoclinic symmetry with the unit cell dimensions $a = 0.89$, $b = 1$, $c = 0.54$-Å and $\beta = 90.28°$ [12].

The spectra were recorded with 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 in three mutually perpendicular planes (ac^*, ab, bc^*) at 10° intervals at 300 K. The **g** values were found by comparison with a dipenylpicrylhydrazyl sample of $g = 2.0036$.

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Table 1. Principal values of the **g** and **A** tensors and Hamiltonian parameters of Cu^{2+} doped $CdBa(HCOO)_4 \cdot 2H_2O$. The indicated errors are estimated by the use of a statistical method [22].

		Principal **g** value	Principal **A** value (mT)	α'^2	α	β	k
Single Crystal	Site I	$g_z = 2.356 \pm 0.002$	$A_z = 9.04 \pm 0.2$	0.729	0.987	0.155	0.392
		$g_x = 2.112 \pm 0.002$	$A_x = 4.29 \pm 0.2$				
		$g_y = 2.114 \pm 0.002$	$A_y = 4.03 \pm 0.2$				
	Site II	$g_z = 2.360 \pm 0.002$	$A_z = 9.05 \pm 0.2$	0.735	0.988	0.154	0.387
		$g_x = 2.210 \pm 0.002$	$A_x = 4.28 \pm 0.2$				
		$g_y = 2.111 \pm 0.002$	$A_y = 4.05 \pm 0.2$				
Powder	300 K	$g_z = 2.348 \pm 0.002$	$A_z = 9.06 \pm 0.2$	0.722	0.988	0.153	0.391
		$g_x = 2.106 \pm 0.002$	$A_x = 4.40 \pm 0.2$				
		$g_y = 2.118 \pm 0.002$	$A_y = 4.20 \pm 0.2$				
	113 K	$g_z = 2.461 \pm 0.002$	$A_z = 10.5 \pm 0.2$	0.887	0.993	0.119	0.387
		$g_x = 2.106 \pm 0.002$	$A_x = 4.20 \pm 0.2$				
		$g_y = 2.087 \pm 0.002$	$A_z = 2.50 \pm 0.2$				

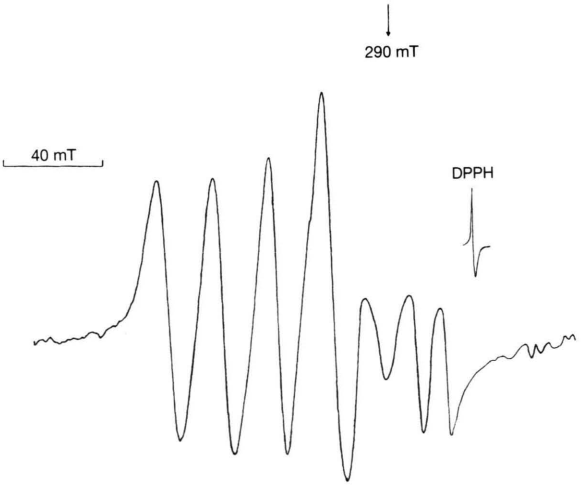

Fig. 1. EPR Spectrum of Cu^{2+} doped $CdBa(HCOO)_4 \cdot 2H_2O$ single crystal in the *ab* plane, 60° with the *a* axis at 300 K.

3. Results and Discussion

EPR Spectra of the Cu^{2+} doped CBFHD were recorded at room temperature. The spectra show two sets of four equally spaced lines characteristic of copper hyperfine lines(due to ^{65}Cu, $I = 3/2$) in any general direction from two sites. An example of the spectra at room temperature is shown in Fig. 1, where the magnetic field is in the *ab* plane, 60° with the *a* axis. In most of the orientations in the principal. *ac**, *ab*, and *bc** planes, the hyperfine lines could be resolved. The angular variations of the EPR spectra were studied at room temperature in the crystallographic *ac**, *ab*, and *bc** planes for every 10° intervals, and these are shown in Figure 2. It can be seen that two sets of four hf lines were observed for all orientations in the *ab* and *bc** planes, whereas only a single set of four hf lines was observed in the *ac** plane. When the magnetic field was parallel to any of the crystallographic axes, all of the sets became equivalent and only one set was observed. These results are in complete agreement with the above-explained monoclinic structure of the host crystals.

The spectrum could be fitted to a spin Hamiltonian of tetragonal symmetry [13]

$$\mathcal{H} = g_{\parallel}\beta \hat{H}_z \hat{S}_z + g_{\perp}\beta(\hat{H}_x \hat{S}_x + \hat{H}_y \hat{S}_y) + A_{\parallel}\hat{I}_z \hat{S}_z + A_{\perp}(\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y). \quad (1)$$

The principal values of the **g** and **A** tensors and their direction cosines were found by the diagonalization procedure [14]. The results, presented in Table 1, show that the principal values of **g** and **A** obtained from the present study are in good agreement with those previously reported for doped $Cd(HCOO)_2 \cdot 2H_2O$ single crystal by Kalkan *et al.* [5].Therefore we can state that the Cu^{2+} ions enter substititutionally into Cd^{2+} sites in the crystal.

4. Temperature Dependence of g and A and the Dynamic Jahn-Teller Effect

The temperature dependencies of **g** and **A** were investigated by studying the powder sample. The spectra at 300 and 113 K are shown in Figure 3. At room temperature, an axial symmetric spectrum was observed within the experimental errors limits, whereas at the low temperature three sets of four lines can be

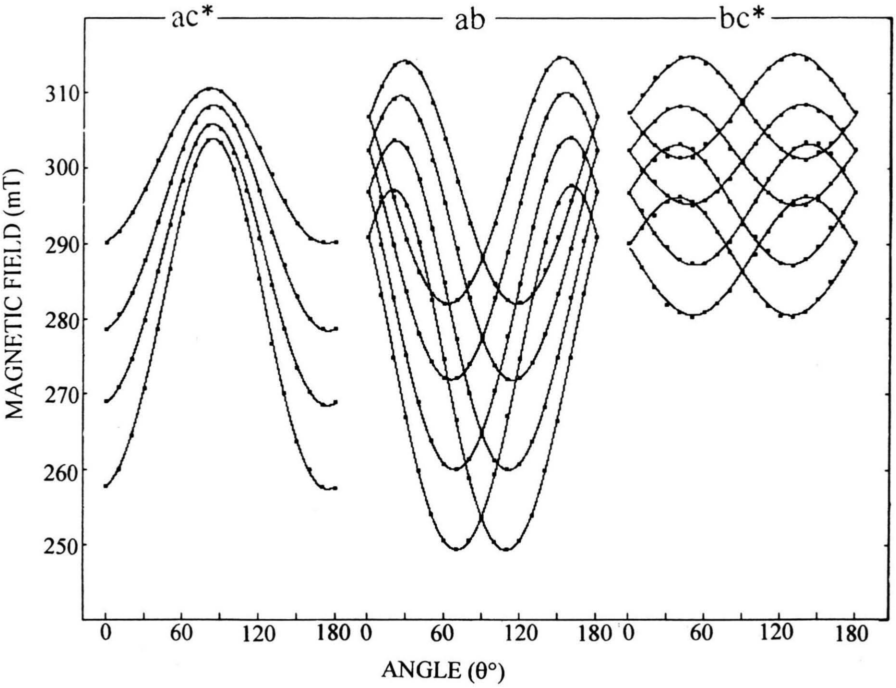

Fig. 2. Angular variations of the EPR spectra of Cu^{2+} doped $CdBa(HCOO)_4 \cdot 2H_2O$ single crystal in the *ac**, *ab* and *bc** planes at 300 K.

seen very clearly. This indicates that the copper complex has a tetragonal symmetry with rhombic distortion. The results are interpreted in terms of a rhombically distorted octahedron in which three Jhan-Teller configurations have different energies, and transitions are taking place between these configurations over the whole experimental temperature range. In the case of tetragonal distortions , the ground state is described by a warped potential with three identical minima, corresponding to elongation along each of the axes *x*, *y*, and *z* [15]. The principal values of **g** and of **A** obtained from the single crystal spectra were compared with those obtained from the powder at room temperatures and was found to be in excellent agreement. This shows clearly that the single crystal analysis is correct. The values of **g** and **A** were found to be highly temperature dependent. The temperature variation of **g** and **A** is shown graphically in Figs. 4 and 5, respectively. The temperature variations of the **g** and **A** tensors very such that g_z, A_z and g_y, A_y vary significantly with temperature, whilst g_x, A_x remain practically constant over the range 113 - 300 K. Variation of the **g** and **A** tensors with temperature in $3d^9$ ions is explained in term of the Jahn-Teller effect [16], and this temperature dependence in the spin-Hamiltonien parameters may be due to vibronic mixing of the first exited $|3z^2 - r^2\rangle$ wavefunction, through a pseudo Jahn-Teller effect. The temperature dependence of **g** and **A** for the Cu^{2+} doped CBFDH are very similar to those observed by Silver and Getz [11] for Cu^{2+} in isomorphous zinc Tutton's salt. Since the dynamic Jahn-Teller effect was originally invoked to account for the temperature dependence of the EPR spectrum of crystals containing the Cu^{2+} complex [17], we found that the SG model satisfactorily explain all of the experimental results in terms of dynamic JT distortion.

5. Ground State Wave Function

The spin-Hamiltonian parameters at 113 K indicate rhombic symmetry. It is known [18] that for $R = (g_x - g_y)/(g_z - g_x) > 1$ a predominantly d_{z^2} ground state, and for $R < 1$ a predominantly $d_{x^2-y^2}$ ground state is expected for rhombic g values (with $g_z > g_x > g_y$). The observed value of R_1=0.053 in the present case is smaller than unity for both complexes at 113 K, and therefore the suggestion for the ground state of Cu^{2+} ion is $d_{x^2-y^2}$. When the symmetry is tetragonal, the ground state transforms either to d_{z^2} or to $d_{x^2-y^2}$ depending on whether the distortion is compressional or elongational. If the symmetry is rhombic or lower, then the ground state will be neither d_{z^2} nor $d_{x^2-y^2}$ but good a mixture of both [16, 19].

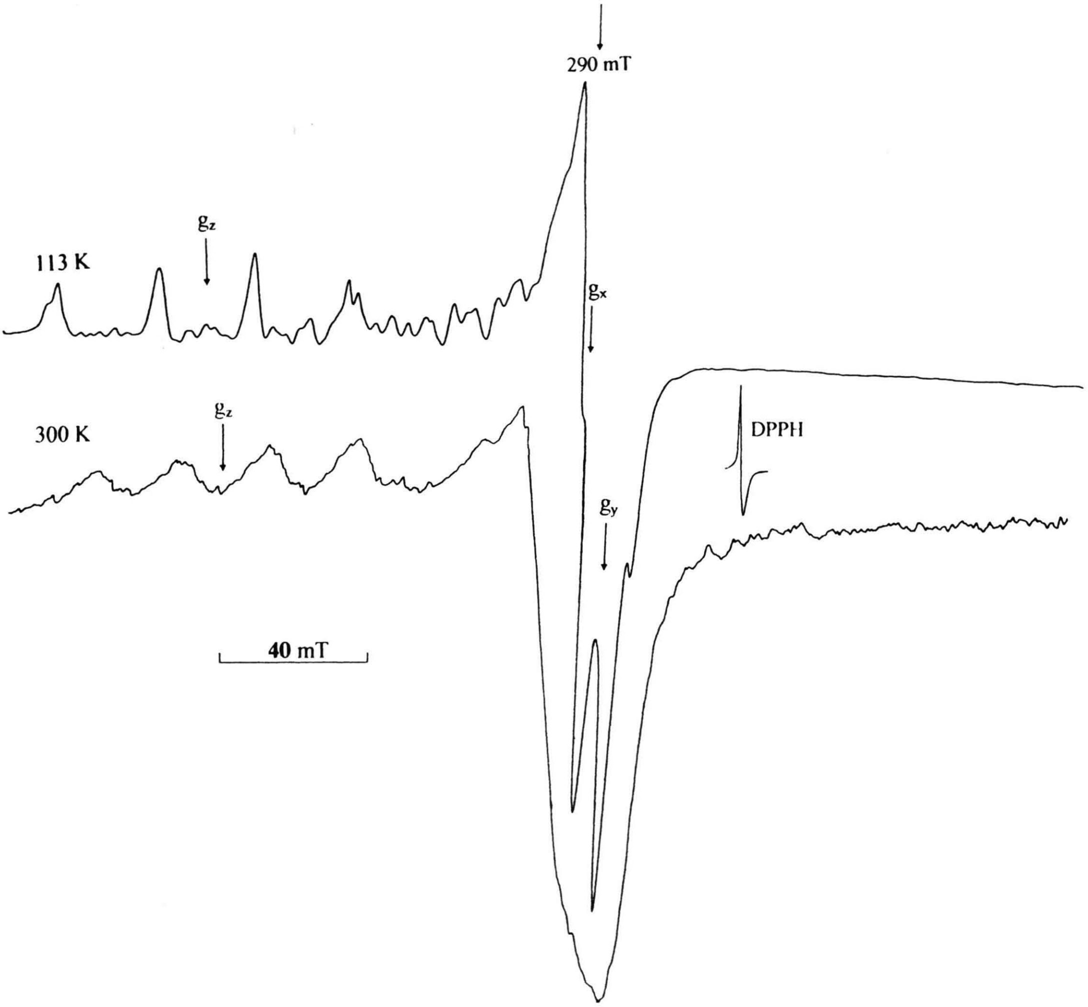

Fig. 3. EPR spectra of powdered samples of Cu^{2+}-doped $CdBa(HCOO)_4 \cdot 2H_2O$ at 300 and 113 K.

The large anisotropy of the **g** and **A** tensors permits a quantitative determination of the appropriate ground state wavefunction, which can be written in a modified form [20] as

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

where the parameter α'^2 is the covalency parameters, which indicates the probability of finding the electron-spin density of Cu^{2+} in the d-orbital and $(1-\alpha'^2)$ is the probablity of its being in the ligand orbitals. α and β are the mixing coefficients for the $|x^2-y^2\rangle$ and $|3z^2-r^2\rangle$ orbitals, respectively. In other words, the ground state in low symmetries is never a pure d-orbital [21] and must be described as a linear compination of all five d-orbitals. We use the literature values and expressions[21] to construct this wave function:

$$\Psi_{300\,K} = \sqrt{0.722}\left[0.988|x^2-y^2\rangle + 0.153|3z^2-r^2\rangle\right], \quad (3)$$

$$\Psi_{113\,K} = \sqrt{0.887}\left[0.993|x^2-y^2\rangle + 0.119|3z^2-r^2\rangle\right], \quad (4)$$

at 300 and 113 K respectively. This means that at 300 K the electron spends 72% of its time in the metal d orbital and the remaining 28% in the ligand orbital, whereas at 113 K the electron spends 89%

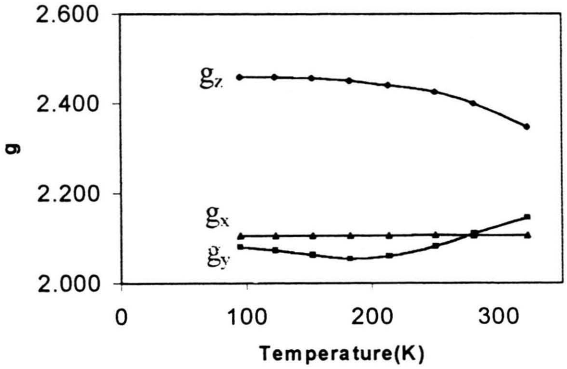

Fig. 4. Temperature variation of the **g** values in Cu^{2+}-doped $CdBa(HCOO)_4{\cdot}2H_2O$ powder spectra.

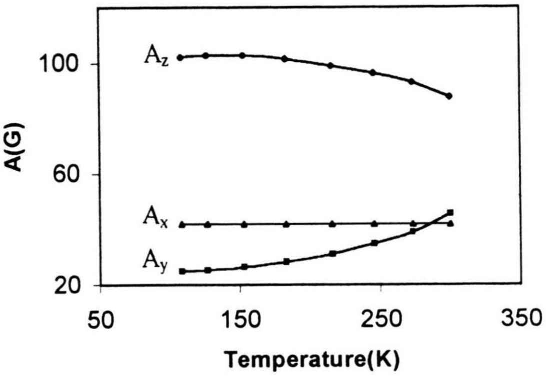

Fig. 5. Temperature variation of the **A** values in Cu^{2+}-doped $CdBa(HCOO)_4{\cdot}2H_2O$ powder spectra.

of its time in the metal d orbital and the remaining 11% in the ligand orbitals. The ground state wave function is not a pure $|x^2-y^2\rangle$ wave function; about 1% $|3z^2-r^2\rangle$ is admixed to it. Small variations in the **g** and **A** tensors have been explained [16] by assuming that higher vibrational state of the complex become populated at higher temperatures, coupling the ground state $|x^2-y^2\rangle$ to the $|3z^2-r^2\rangle$ state, with subsequent change in the EPR parameters. α'^2, α, β and k were calculated for several temperatures, and temperature dependence of α'^2 is shown in Figure 6. As can be seen Fig. 6, the covalency of Cu^{2+} slightly changes between 113 and 250 K, whereas it abruptly changes above 250 K.

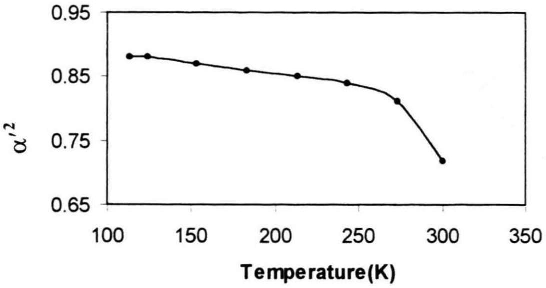

Fig. 6. Temperature variation of α'^2 of Cu^{2+}-doped in $CdBa(HCOO)_4{\cdot}2H_2O$ powder spectra.

6. Concluding Remarks

- The results of the present study indicate that Cu^{2+} ions replace Cd^{2+} ions substitutionally in CBFDH.
- The principal spin-Hamilton parameters are tetragonal at room temperature, whereas at low temperature they indicate rhombic symmetry.
- The temperature variation of the **g** tensor was such that the two larger **g** values vary significantly with temperature, whereas the small value is effectively constant at 113 - 300 K.
- The temperature dependence of the Cu^{2+} EPR spectrum was discussed in terms of the dynamic Jahn-Teller effect.
- As a conclusion we can state that the results of the present study indicate that the Cu^{2+}ions exhibit a more covalent nature at 113 K than at 300 K. In addition, the population of higher vibronic levels is expected to increase by mixing of $|3z^2-r^2\rangle$ to $|x^2-y^2\rangle$, causing the **g** value to vary with temperature.

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