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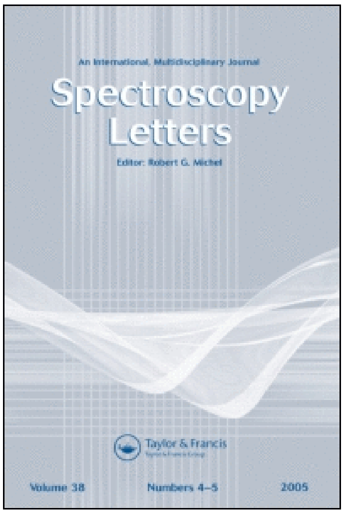

Spectroscopy Letters

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

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To cite this Article Kalkan, H. , Bulut, A. and Yavuz, M.(1998) 'EPR Study of the Dynamic Jahn-Teller Effect of Cu^2 in $Cd(HCOO)_2 2H_2O$ Single Crystals', Spectroscopy Letters, 31: 3, 547 — 557
To link to this Article: DOI: 10.1080/00387019808002748
URL: http://dx.doi.org/10.1080/00387019808002748

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SPECTROSCOPY LETTERS, 31(3), 547-557 (1998)

EPR STUDY OF THE DYNAMIC JAHN-TELLER EFFECT OF Cu^{2+} IN $Cd(HCOO)_2 2H_2O$ SINGLE CRYSTALS

KEY WORDS : Copper doped cadmium formate dihydrate, Jahn-Teller effect, EPR.

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ABSTRACT

The X-band EPR spectra of Cu^{2+} doped into cadmium formate dihydrate single crystal was studied at 113 °K. The powder spectrum of the same material was studied over the temperature range from 113 to 300 °K The observed values of the g and A hyperfine coupling constants and linewidths were found to be temperature dependent.

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The temperature dependence of Cu^{2+} EPR spectrum values were discussed in terms of dynamic Jahn-Teller effect. The tensor elements of g and A were calculated from the polycrystalline samples at various temperature and it is found that the spectrum at 113 °K has given followings, g_{xx}=2.108±0.002, g_{yy}=2.085±0.002, g_{zz} =2.431±0.002 and A_{xx}=48±1, A_{yy}=17±1, A_{zz}=11±1 Gauss.

INTRODUCTION

A number of studies [1-5] were carried out to understand Jahn-Teller effect and its ground state in low symmetry environments of Cu^{2+} doped single crystals by the EPR spectra. Especially, Silver and Getz (SG)[11] showed that in spite of low symmetry in Tutton salts, the complex exhibits temperature dependent EPR spectra which can be attributed to pseudo Jahn-Teller effect. It is stated in ref.[6] that when the crystal symmetry is octahedral, the Cu^{2+} ion, with d^9 electronic configuration, has the ground state arrangement of six electrons in the low lying t_{2g} orbital and the other three electrons in the doubly degenerate e_g orbital. The orbital degeneracy can be lifted either by the effects such as a lowering in symmetry arising due to charge compensating vacancies, crystalline fields or by Jahn-Teller (JT) distortion[7]. When the site symmetry is tetragonal, the ground state transforms either as d_{z^2} or $d_{x^2-y^2}$ 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 an admixture of both[8,9]. This admixture may also be occurred due to vibration of these states.

In this study, the single crystal and powder EPR studies of Cu^{2+} doped $Cd(HCOO)_2 2H_2O$, in the temperature range of 113 to 300 °K, are carried out. A $d_{x^2-y^2}$ ground state for copper was considered to interpret the results. The dependence of g and A values on the temperature have been explained in terms of dynamic JT distortion [10-12]. In this paper, the SG model is used to understand the dynamic aspects of distortion by assuming a $d_{x^2-y^2}$ ground state for the Cu^{2+} ion in $Cd(HCOO)_2 2H_2O$ (CFDH).

EXPERIMENTAL DETAILS

A weighed amount of cadmium carbonate was neutralised with formic acid and the single crystals were grown from aqueous solutions by isothermal evaporation at 300 °K. A little amount (≤ 0.2 wt %) of copper formate tetrahydrate having natural abundance of copper isotopes (^{63}Cu, 69 wt% and ^{65}Cu, 31 wt%) was added to the stock solutions for the purpose of doping. Colourless transparent crystals were obtained in about three weeks and those of sizes 4x3x2 mm^3 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° orientations of the external magnetic field in the three mutually perpendicular planes (*ab*, *ac** and *bc**) at 133 °K. The g values were found by comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

The CFDH single crystal has a monoclinic structure and belongs to the $P2_{1/c}$ space group[13]. The unit cell dimensions of the crystal are a=89.8, b=73.9, c=97.6 nm and β=97.3°. Post and Trotter[14] solved the crystal structure with two independent cadmium in the asymmetric unit, Z = 2 and there are four Cd per unit cell. The unit cell contains two pairs of symmetry related Cd^{2+} ion sites, both are slightly distorted octahedral. The two independent cadmium are six-coordinated: one type of cation indicated with Cd_{II} is surrounded by four water molecules and two formate oxygen atoms, and the other indicated with Cd_{I} by six formate oxygen atoms.

RESULTS AND DISCUSSION

a) EPR spectra and angular variation at room temperature and 113 °K

For the Cu^{2+} doped single crystal of CFDH at all orientations of the crystal in the magnetic field at room temperature, only a broad EPR line was observed due to the short spin-lattice relaxation times involved. However, at low temperature we observed a spectrum, in general orientation, that consists of two sets of four equally spaced lines characteristic of copper hyperfine lines (I=3/2) of two sites. Along the three principal crystallographic axes, they are completely magnetically equivalent. Thus along the principal crystal directions, the EPR spectra will show a single set of four characteristic lines (a quartet). The spectra due to all the sites will overlap exactly along these directions and this fact was very useful in aligning the crystals. These results indicate that the Cu^{2+} ion has entered substitutional at Cd^{2+} ion. In addition, we have also observed some weak lines attributed to forbidden transitions, as observed by Bonomo *et al.*[15], which are more intense in the high field region. Especially, when the magnetic field lies in *ab* plane at 60° away from the *a* axis, where the forbidden transitions reach an intensity comparable with that of main transition as shown in Fig. 1, which are very similar to that observed in the Cu^{2+} doped cadmium acetate dihydrate[15].

Figure 2 shows EPR lines originated from $\mathrm{Cd}_{II'}$ and $\mathrm{Cd}_{I'}$ sites. These eight lines appears to be four equal lines along the axes. These lines are also seen as two lines at 20° making angle with *c** axis in *ac** plane. This is not an usual case. This may be explained as that for substitutional Cu^{2+} the contact term in the hyperfine interaction is zero. As explained in ref.[16], that is probably due to direction-dependent electron dipole-nuclear dipole magnetic interactions which may reduce to zero for this orientations of the crystal and hence $\mathrm{Cd}_{II'}$ and $\mathrm{Cd}_{I'}$ sites that have four lines each transform to the set "*" and the set "□" respectively as shown in Fig. 2.

The spin Hamiltonian of rhombic symmetry can be given by consideration the EPR parameters by

$$H = \beta(g_{xx}H_xS_x+g_{yy}H_yS_y+g_{zz}H_zS_z)+A_{zz}I_zS_z+A_{xx}I_xS_x+A_{yy}I_yS_y \qquad (1)$$

where all symbols have their usual meanings[12]. The principal values of *g* and *A* tensors and their direction cosines were found by diagonalization procedure[17] and the results are given in ref.[18].

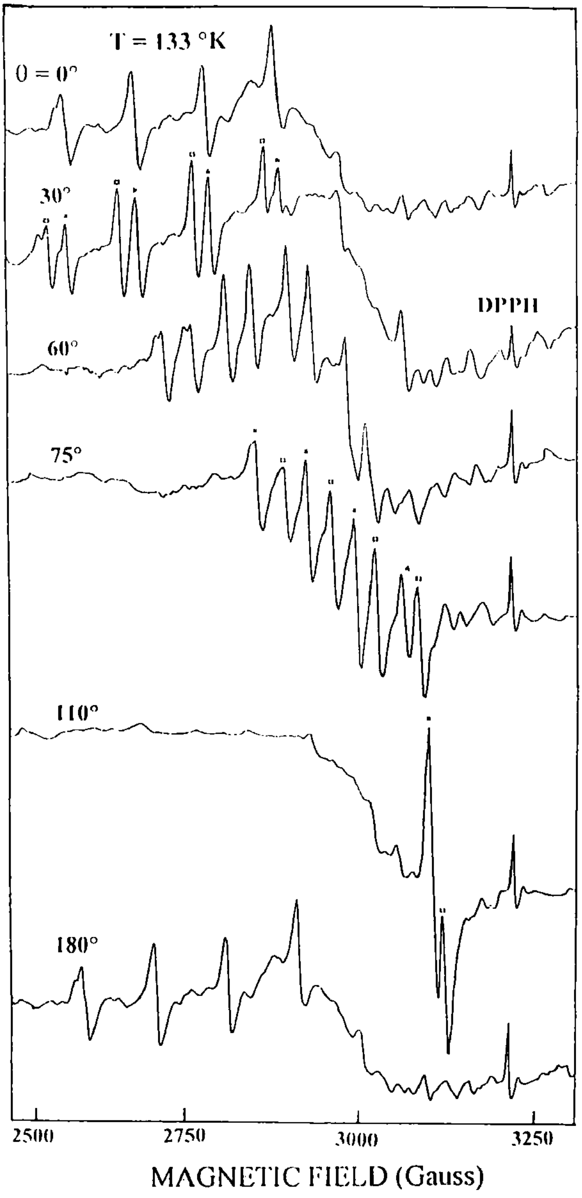

FIG. 1. EPR spectra of Cu^{2+} doped CFDH single crystal in the *ab* plane, 60°with *a* axis at 133 °K, where "*" and "I I" indicated Cd$_{II}$ and Cd$_{I}$ sites respectively. The other lines belong to forbidden transitions.

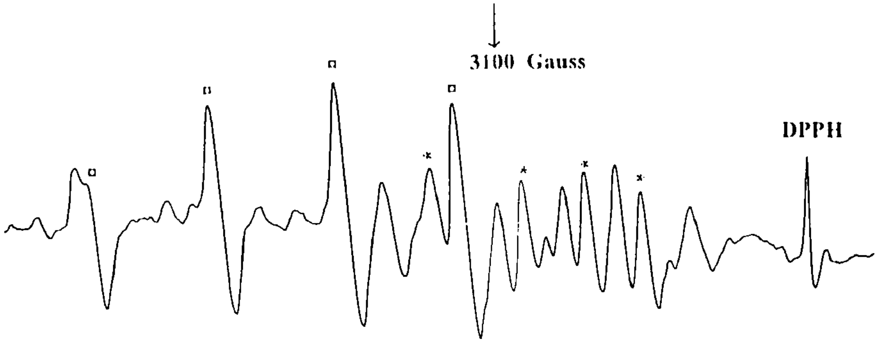

FIG. 2. EPR spectra for Cu^{2+} doped CFDH single crystal in the *ac** plane along the *c** axis in various angles.

b) Temperature dependence of *g* and *A* values and dynamic Jahn-Teller distortion

Temperature dependence of *g* and *A* values were carefully monitored by studying polycrystalline samples. The spectra at low temperatures are well defined while the spectra at higher temperatures are somewhat broadened. A selection of the X-band powder spectra at various temperatures are shown in Fig. 3. At low temperature, for a powder sample, three sets of four lines can be seen very clearly. This indicates that the copper complex has a tetragonal symmetry with rhombic distortion and ground state was found to be $d_{x^2-y^2}$[18]. In the single crystal, m_l dependent linewidth variations in the copper hyperfine components were observed in the temperature range of 113 to 293 °K. As can be seen from Table 1, there are strong temperature dependence of m_l variations in the copper hyperfine lines when the external field is along the *b* axis.

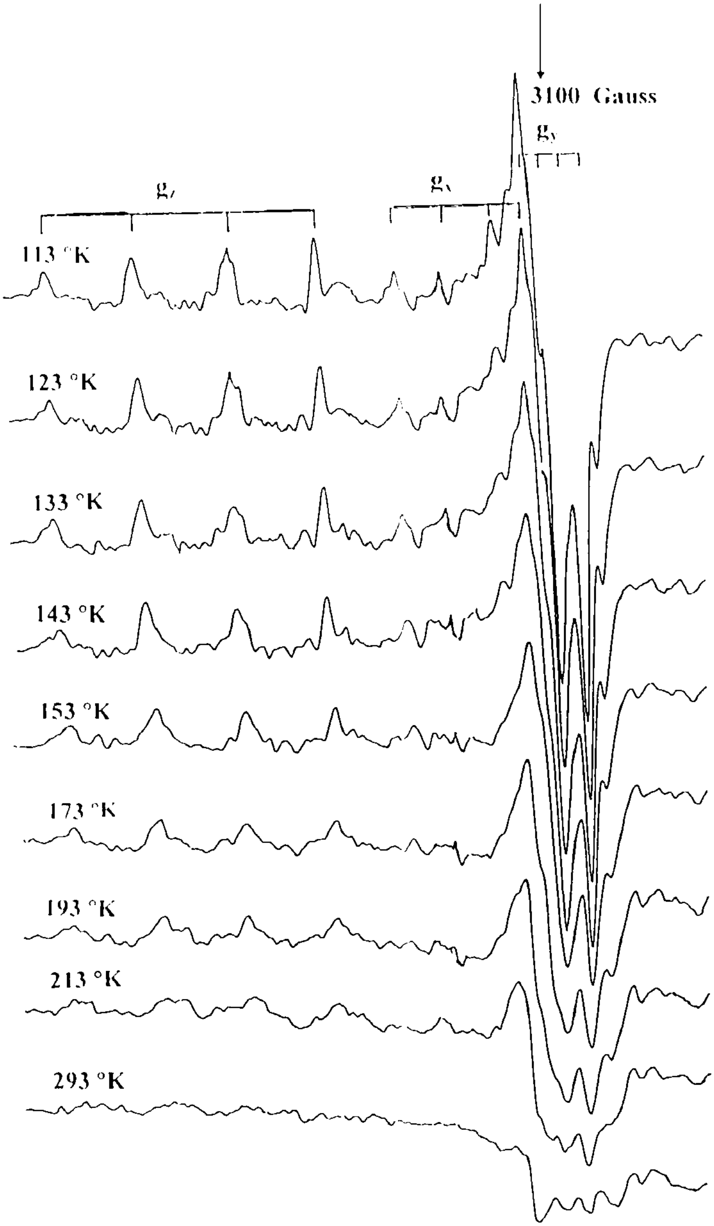

FIG. 3. EPR spectra of polycrystalline samples of Cu^{2+} in CFDH at various temperatures.

TABLE 1

Linewidths of Cu^{2+} hyperfine component in Cu^{2+}/ $Cd(HCOO)_2 2H_2O$ single crystal, as a function of temperature. The external magnetic field is along the *b* axis in *bc** plane.

T (°K)	m_I=3/2	m_I=1/2	m_I=-1/2	m_I=-3/2
113	5.00	3.25	3.25	4.75
123	5.50	3.50	3.25	5.00
143	7.00	5.25	5.00	6.50
153	8.75	7.50	7.00	7.75
173	11.25	8.75	8.00	9.75
193	12.50	9.00	8.00	10.00
213	13.75	9.50	8.50	11.50

The temperature dependence of the *g* factor in this compound are typical for complexes with vibronic coupling[19]. This coupling admixtures the excited d_{z^2} orbital state to the $d_{x^2-y^2}$ ground state. The mixing coefficients are determined by the thermal population of vibronic levels. The population of higher vibronic levels is expected to increase by mixing of d_{z^2} into $d_{x^2-y^2}$, causing the *g* values to vary with temperature. EPR spectra which temperature dependence of the tensor parameters were observed in copper doped zinc Tutton salt by Silver and Getz[11] who considered the experimental details of whole complex in term of the dynamic Jahn-Teller effect and showed that in spite of the low symmetry in this salt, the complex exhibits temperature dependent EPR spectra which can be attributed to dynamic Jahn-Teller effect. The important features of the temperature variation are brought out clearly by the powder spectra, which show that g_{xx}, A_{xx} and g_{zz}, A_{zz} values slowly

TABLE 2

Temperature dependence of principal values of g and A tensors for Cu^{2+} in $Cd(CHOO)_2 2H_2O$ polycrystalline samples.

T (°K)	g_{xx}	g_{yy}	g_{zz}	A_{xx}	A_{yy}	A_{zz}
113	2.085	2.145	2.384	15.5	56.1	105.8
123	2.086	2.145	2.383	16.6	56.1	105.0
133	2.087	2.145	2.382	17.1	56.1	103.6
153	2.089	2.145	2.377	17.9	56.1	103.3
173	2.011	2.145	2.376	20.0	56.1	101.9
193	2.013	2.145	2.375	21.6	56.1	101.1
213	2.015	2.145	2.374	23.2	56.1	100.0
293	2.101	2.145	2.366	28.9	56.1	96.1

increase linearly on heating, whereas g_{yy} and A_{yy} values were shown to be temperature independent as seen in Table 2. The temperature dependence of g, A and m_I values for the Cu^{2+} doped cadmium formate are very similar to those observed by Silver and Getz[11] for Cu^{2+} in isomorphous zinc Tutton's salt. We have also found that the SG model satisfactorily explains all the experimental results in terms of dynamic JT distortion, since the dynamic Jahn-Teller effect was originally invoked to account for the temperature dependence of the EPR spectrum of the crystals containing the $Cu^{2+}(H_2O)_6$ complex[11].

CONCLUSION

The results of the present study of the Cu^{2+} ions in CFDH indicate that Cu^{2+} enters instead of the Cd^{2+} ions as substitionally in host lattice. Temperature dependence in the spin-Hamiltonian parameters may be due to vibronic mixing of the first excited d_{z^2} wavefunction, through pseudo Jahn-Teller effects. Our results also support Silver and Getz model that satisfactorily explains all the experimental results in term of dynamic Jahn-Teller effect.

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Date Received: September 17, 1997
Date Accepted: November 10, 1997