EPR STUDIES OF THE HAMILTONIAN PARAMETERS OF THE SIMULTANEOUS AXIAL AND ORTHORHOMBIC JAHN-TELLER SPECTRA OF Cu^{2+} IN $Cd_2(NH_4)_2(SO_4)_3$ SINGLE CRYSTALS AT DIFFERENT TEMPERATURES

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ABSTRACT: *This paper presents the study of the effective Hamiltonian parameters (g_1, g_2, A_1, A_2) and the observed g and A tensors of the derivative axial and orthorhombic Jahn-Teller EPR spectra of Cu^{2+} in $Cd_2(NH_4)_2(SO_4)_3$ single crystals at different temperatures. The variations of these parameters with temperature in the three mutually perpendicular planes of the crystal confirm axial symmetry for $T>T_c$ and orthorhombic symmetry for $T<T_c$ in this system. The simultaneous axial and anisotropic symmetries of the spectra owe their origin to the behaviour of Cu^{2+} ions in the three JT potential wells because they can undergo reorientation from one well to another or quantum tunnelling among them which depends on temperature, burial height or thickness and energy of the ions. The results show that the components of the activation energy and Fermi-contact parameter increase with temperature while the decrease of the anisotropy parameter (u) is more than it compensates for the slight increase in the effective Hamiltonian parameters g_1 and g_2 with temperature.*

INTRODUCTION

The Langbeinite family of compounds with general formula $(X^+)_2(Y^{2+})_2(SO_4)_3$ where X^+ is ammonia or monovalent metal and Y^{2+} is a divalent metal were discovered by Jona and Pepinsky (1956). A host of authors have carried out a number of investigations on the microscopic properties of the langbeinite family of crystals (Babu *et al*, 1984). The complex cadmium ammonium sulphate, $Cd_2(NH_4)_2(SO_4)_3$ abbreviated as CAS is isomorphous to potassium magnesium sulphate, $K_2Mg_2(SO_4)_3$ abbreviated as PMS and both are members of the langbeinite family of crystals. The detailed x-ray data regarding the atomic positions in CAS does not seem to be available in the literature but that of PMS have been reported by Zemann and Zemann (Babu *et al*, 1984). Also they stated that some authors have reported that

the langbeinite family of compounds in cubic space group $P_{2/3}$ with a = 10.35 $Å$ have four molecules per unit cell. The structure consists of a group of $(SO_4)^{2-}$ tetrahedral and Cd^{2+} metal ions. There are two each crystallographically non-equivalent Cd^{2+} and $(NH_4)^+$ sites. Each Cd^{2+} is surrounded by six oxygen atoms which form a slightly distorted octahedron. Yerima (2005, 2007) stated that EPR studies of Misra and Korezak in 1986 using Mn^{2+} as a probe revealed a phase transition at 94.5 K whose mechanism was attributed to the freezing out of the rotation of the $(SO_4)^{2-}$ ion. Also he stated that EPR studies of Mouli and Sastry in 1962 using Cu^{2+} probe at room temperature and 77 K yielded eight poorly resolved hyperfine lines in a general direction and a set of four unresolved hyperfine lines in any crystallographic plane. Their computed values of the g-factor showed that $g_{//}>g_{\perp}$

and that the A_{max} is falling along g_{min}. They concluded that Cu^{2+} ions in this system may be in a compressed octahedral position or entered into the system interstitially rather than substitutionally. The shortcomings of the study of Mouli and Sastry include its limitation to 77 K and its failure to focus on JT effect that could be associated with Cu^{2+} in this crystal as earlier hinted by Babu *et al* (1984). Raman spectroscopy performed by Rabkin *et al* (1981) provided substantial information on the structural phase transition in this crystal. They observed that CAS exhibits a structural phase transition on lowering the temperature from space group $p_{2/3}$ to p_{21} at about 95 K, the lower the temperature phase being ferroelectric. Babu *et al* (1984) in their summary stated that Bhat *et al* (1973) EPR spectra of Mn^{2+} in the two phase groups of CAS observed at room temperature and at liquid nitrogen were slightly different, particularly in the magnitudes of their zero-field splitting, as a result of small orthorhombic component in the low temperature phase. The differences in the spectra indicated a phase transition from high temperature phase $p_{2/3}$ to a low temperature phase p_{21}. In another outlook, Yerima (2005) stated that Ng and Calvo in 1975 observed in their EPR studies using Mn^{2+} in the temperature range 300-77 K observed definite change in the spectral pattern from that of room temperature to that of liquid nitrogen temperature due to a phase transition from $p_{2/3}$ to a space group of lower symmetry at low temperature. They did not analyze the spectra nor determine the phase transition temperature due to the complexity of the spectra at liquid nitrogen temperature.

Babu *et al* (1984) study of phase transition in CAS using VO^{2-} as a probe in the temperature range of 573-77 K obtained a complex spectrum, in which they were unable to identify the phase transition temperature and suggested that

the lower temperature phase stabilizes at temperatures higher than 95 K. This was due to a local stabilization of the low symmetry phase by vandyl ions. They also found that the data of their experiment contained Cu^{2+} ion as contaminant and thus concluded that the complication in their results could have been due to a possible JT effect associated with Cu^{2+} ion in this crystal. Unfortunately, they did not carry out further investigation to establish or rule out the possibility of JT effect due to Cu^{2+} ion in this system.

In order to resolve the question of JT effect of Cu^{2+} in CAS De (2010) studied EPR spectra of Cu^{2+} doped in CAS at various temperatures in the range of 300-15 K with angular variations usually at steps of 5° and 0.5^o near JT extreme points in three mutually perpendicular planes of CAS single crystals. He reported that Cu^{2+} in CAS shows static JT effect and for the first time orthorhombic EPR JT spectra from a ^2D ion (with ^2E ground state) was reported in this system at 15 K. De also proposed that the Fermi-contact parameter k in this system exists in the form of s-wave which may not be easy to handle. So far, no attempt has been made to determine the components of the effective Hamiltonian parameters. In this paper, a theory that links the effective Hamiltonian parameters and the measured g and A tensors was developed from which the components of the Hamiltonian parameters were computed. The results show that the calculated components of the activation energy and the Fermi contact parameter increase with temperature. This confirms that the symmetry of the spectra of Cu^{2+} ions in CAS originates from their reorientation or quantum tunnelling in the three JT potential valleys which depends on the depths or thickness of the valleys, energy of the ions and the temperature.

METHOD

The experiment was carried out in the EPR laboratory of Prof H.W. Shields in Wake Forest University, North Carolina, USA (De, 2010). The experimental details is as follows: At the temperature of 358 K single crystals of CAS were grown by slow evaporation from the aqueous solution made up of stoichiometric amounts of $CdSO_4.8H_2O$ and $(NH_4)_2SO_4$ were added to specific amounts of $CuSO_4$ such that the ratio of Cu^{2+} ion to Cd^{2+} ion in the solution is 1:100. In about four weeks' time optically clear crystals were grown. A Ventury E-Century line spectrometer operating at 9.28 GHz was used to record the EPR spectra at various temperatures. The temperature of the cavity containing the sample was varied in the temperature range 300-15 K using an ADP cryogenic HC-4 closed cycle refrigerator. The minimum accuracy in temperature measurement was ±1 K. The spectra were observed in three mutually perpendicular planes ab, ac and bc of the crystals.

Theory of Symmetry of EPR Spectra

We present the theory relating the Hamiltonian parameters (g_1, g_2, A_1, A_2) and the observed $g(g_{//}, g_\perp)$ and $A(A_{//}, A_\perp)$ values for both axial and orthorhombic symmetries, where $g_{//}(g_z)$ and $g_\perp(g_x, g_y)$. The first-order expressions for g_1, g_2, A_1, and A_2 assuming the cubic crystal-field interaction is large with respect to the spin-orbit coupling are given by (De *et al*, 1984; Yerima, 2007)

$$g_1 = 2.0023 - \frac{4\lambda}{\Delta} \tag{1}$$

$$g_2 = -\frac{4\lambda}{\Delta} = g_1 - 2.0023 \tag{2}$$

$$A_1 = \left(-\frac{2\beta\mu\langle r^{-3}\rangle}{I}\right)\left(k + \frac{4\lambda}{\Delta}\right) \tag{3}$$

$$A_2 = \left(-\frac{2\beta\mu\langle r^{-3}\rangle}{I}\right)\left(\frac{4}{7} + \frac{4\lambda}{\Delta}\right) \tag{4}$$

Where Δ, λ, μ, r and k respectively are cubic crystal field 10Dq, the spin-orbit coupling parameter, the nuclear magnetic dipole moment, the one-electron expectation value and the Femi contact parameter. The experimentally determined values of $g_{//}$, $g_\perp$, $A_{//}$, and $A_\perp$, at any temperature can be expressed in terms of other parameters of the systems. For example, the relationships between the observed $g_{//}$, $g_\perp$, $A_{//}$, and $A_\perp$ and the spin Hamiltonian parameters g_1, qg_2, A_1, qA_2 are given by (Ham, 1972; Reynolds and Boatner, 1975; Boatner *et al*, 1977).

$$g_{\parallel} = g_1 + 2qg_2 \tag{5}$$
$$g_\perp = g_1 - qg_2 \tag{6}$$
$$A_{\parallel} = A_1 + 2qA_2 \tag{7}$$
$$A_\perp = A_1 - qA_2 \tag{8}$$

Where q is the Ham reduction factor

(a) **Axial Symmetry of EPR Spectra:** In the case of axial symmetry, the temperature variation of $g_{//}$ and $g_\square$ is given by (De *et al*, 1984; Rubins *et al*, 1984).

$$g_{\parallel}(T) = g_1 + u(T)g_2, \qquad g_\perp(T) = g_1 - \frac{u(T)g_2}{2} \tag{9}$$

And to first order perturbation theory

$$g_1 - g_e = g_2 = -\frac{4\lambda'}{\Delta_{cub}} \tag{10}$$

Where $u = 2q$, $g_e = 2.0023$, $\lambda^{'}$ is the effective spin-orbit coupling constant and Δ_{cub} is the cubic field splitting of the ^2E and $^2T_2$ orbital states. We can easily deduce from equation (9) that

$$g_1 = \frac{g_\parallel(T)+2g_\perp(T)}{3}, \quad u(T)g_2 = \frac{2}{3}\left(g_\parallel(T) - g_\perp(T)\right) \tag{11}$$

So that

$$u = \frac{2g_1}{g_2}\left(\frac{g_\parallel(T)-g_\perp(T)}{g_\parallel(T)+2g_\perp(T)}\right) \tag{12}$$

Combining equations (10) and (11) yields

$$g_2 = \frac{g_\parallel(T)+2g_\perp(T)-3g_e}{3} \tag{13}$$

Substituting g_1 and g_2 from equations (11) and (13) respectively into equation (12) gives

$$u(T) = \frac{g_\parallel(T)-g_\perp(T)}{g_\parallel(T)+2g_\perp(T)-3g_e} \tag{14}$$

from which u(T) can be determined.

Similarly the following equations have been established (Yerima, 2007)

$$A_\parallel(T) = A_1 + u(T)A_2, \quad A_\perp = A_1 - \frac{u(T)}{2}A_2 \tag{15}$$

and $\quad A_1 = c(k - g_2), \quad A_2 = c\left(\frac{4}{7} - \frac{34}{28}g_2\right) \tag{16}$

Where c is equal to the constant term $(-2\mu_B\mu\langle r^{-3}\rangle/I)$ in equations (3) and (4)
Similarly from equation (15) we can easily show that

$$A_1 = \frac{A_\parallel(T)-2A_\perp(T)}{3}, \quad u(T)A_2 = \frac{2}{3}\left(A_\parallel(T) - A_\perp(T)\right) \tag{17}$$

so that

$$u(T) = \frac{2A_1}{A_2}\left(\frac{A_\parallel(T)-A_\perp(T)}{A_\parallel(T)+2A_\perp(T)}\right) \tag{18}$$

Also from equations (16) we have

$$\frac{A_1}{A_2} = (k - g_2)/\left(\frac{4}{7} - \frac{34}{28}g_2\right) \tag{19}$$

Substituting the ratio A_1/A_2 in equation (19) into equation (18) yields

$$u(T) = 2\left(\frac{k-g_2}{\frac{4}{7}-\frac{34}{28}g_2}\right)\left(\frac{A_\parallel(T)-A_\perp(T)}{A_\parallel(T)+2A_\perp(T)}\right) \tag{20}$$

from which k can be determined using u(T) value obtained from equation (18). Hence the parameter c in equation (16) can be evaluated using k value determined from equation (20).

The anisotropy parameter $u(T)$ can be fitted to an exponential function of the form (De *et al,* 1984)

$$u(T) = \frac{1-e^{\frac{-E}{kT}}}{1+2e^{\frac{-E}{kT}}} \qquad (21)$$

Where E is the energy splitting of the JT potential well sometimes called the activation energy. Equation (21) can be written as

$$E = kT ln\left(\frac{1+2u(T)}{1-u(T)}\right) \qquad (22)$$

(b) Orthorhombic Symmetry of EPR Spectra: In the case of orthorhombic symmetry, the axial symmetry theory we have developed cannot be sufficient enough to explain the anisotropic

symmetry in EPR spectra of Cu^{2+} in CAS system. The present system is unique owing to its orthorhombic symmetry where by the Cu^{2+} spectra exhibits two set of four hyperfine $g_\perp$ lines instead of one set in axial symmetry. Thus it is expected that in the orthorhombic symmetry the three JT potential wells are completely inequivalent. In Fig.1(a), at $T>T_c$ all the three JT potential wells are equivalent and (b) at $T<T_c$ two of the three wells are lowered to different energy levels instead of only one becoming lower than the other two as earlier observed by De (1987) in axial symmetry in Zinc fluotitanate hexahydrate (ZFTH) crystals.
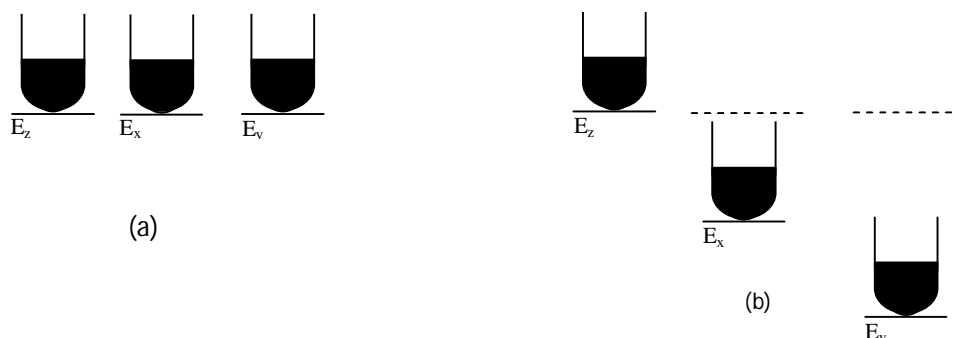

Fig. 1: Axial Symmetry (a) and Orthorhombic Symmetry (b) of JT Potential Wells of Cu^{2+} in CAS

To validate these assumptions our new theory requires that the parameters u(T), A_1/A_2, E, k, c and so on each will have two components representing the lowering of two of the JT potential wells. Following the procedures similar to the axial symmetry, we can easily show that the components of these parameters in the orthorhombic symmetry are given as follows:

$$u_x(T) = \frac{2\left(g_\parallel(T)-g_x(T)\right)}{g_\parallel(T)+2g_x(T)-3g_e}, \qquad u_y(T) = \frac{2\left(g_\parallel(T)-g_y(T)\right)}{g_\parallel(T)+2g_y(T)-3g_e} \qquad (23)$$

$$\left(\frac{A_1}{A_2}\right)_x = \frac{u_x}{2}\left(\frac{A_\parallel(T)+2A_\perp(T)}{A_\parallel(T)-A_\perp(T)}\right), \qquad \left(\frac{A_1}{A_2}\right)_y = \frac{u_y}{2}\left(\frac{A_\parallel(T)+2A_\perp(T)}{A_\parallel(T)-A_\perp(T)}\right) \tag{24}$$

$$E_x = kTln\left(\frac{1+2u_x(T)}{1-u_x(T)}\right), \qquad E_y = kTln\left(\frac{1+2u_y(T)}{1-u_y(T)}\right) \tag{25}$$

$$\left(\frac{A_1}{A_2}\right)_x = \frac{3k_x-g_\parallel(T)-2g_x(T)+3g_e}{\frac{4}{7}-\frac{17}{42}(g_\parallel(T)+2g_x(T)-3g_e)}, \qquad \left(\frac{A_1}{A_2}\right)_y = \frac{3k_y-g_\parallel(T)-2g_y(T)+3g_e}{\frac{4}{7}-\frac{17}{42}(g_\parallel(T)+2g_y(T)-3g_e)} \tag{26}$$

$$c_x = \frac{A_\parallel+2A_x(T)}{3k_x-g_\parallel(T)-2g_x(T)+3g_e}, \qquad c_y = \frac{A_\parallel+2A_y(T)}{3k_y-g_\parallel(T)-2g_y(T)+3g_e} \tag{27}$$

$$\left(\frac{\lambda'}{\Delta}\right)_x = \frac{3g_e-g_\parallel-2g_x(T)}{12}, \qquad \left(\frac{\lambda'}{\Delta}\right)_y = \frac{3g_c-g_\parallel-2g_y(T)}{12}, \tag{28}$$

The components of the effective Hamiltonian parameters in equations (23) to (28) can be determined using the values of the measured $g_{//}$, $g_\perp$, $A_{//}$ and $A_\perp$ extracted from the EPR lines recorded at different temperatures.

RESULTS AND DISCUSSION

The EPR spectra of Cu^{2+} in CAS measured by Oguama in 1997 in an ac plane according to De (2010) show three groups of four well resolved hyperfine lines at low temperatures in such a way that one set appeared at the low magnetic field and the remaining two at high magnetic field. The high resolution of the spectra in the (100) direction at 15 K results to reduction in broadening due to spin lattice relaxation time. The complete anisotropic spectra at low temperatures as a result of the phonon-induced reorientation rate of the Cu^{2+} among the three JT potential wells and Cu^{2+} would then stabilize statistically among the three JT wells. It is expected Cu^{2+} being a JT ion, when the crystal is oriented from this direction (which is one of the [100] type of axes of [Cu^{2+}, H$_2$O] chromophore), the lowest field hyperfine lines move to higher fields and the highest field lines move to lower fields until all the three sets of spectra merge into one set of four hyperfine lines when the crystal is oriented to about 50$^{\text{o}}$ from the earlier direction in the ac plane to the (111) direction. The merging of the four set of spectra into one set demonstrates Cu^{2+} in CAS exhibits static JT effect. This is the first time finely resolved JT orthorhombic spectra are observed in this system (De, 2010). The presence of highly resolved EPR spectra is a mark of striking difference from that of ZnTiF$_6$.6H$_2$O and other systems exhibiting phase transition and JT effect mentioned earlier. More remarkable is the three groups of four hyperfine lines clearly observed at 15 K, which has not been observed in copper complexes containing a single ion per unit cell, even though multiple (up to five) groups of four hyperfine lines have been observed in Cu^{2+}:ZnTiF$_6$.6H$_2$O which contained two magnetically inequivalent Cu^{2+} per unit cell (De et al, 1984). The values of g(g$_x$, g$_y$, g$_z$) and A(A$_x$, A$_y$, A$_z$) observed in different directions were extracted from the EPR spectra of Oguama (1997) and De (2010) and the values of g<111> and A<111> were calculated from equations (37) and (38) respectively at various temperatures (Table 1).

Table 1: Observed g and A Values

T (K)	g_z	g_x	g_y	g<111>	A_z	A_x	A_y	A<111>
15	2.415	2.144	2.094	2.221	104	20	17	62
40	2.412	2.145	2.095	2.221	102	18	14	61
60	2.408	2.146	2.097	2.221	100	18	12	60
80	2.401	2.150	2.101	2.221	96	*	*	*
100	2.397	2.151	2.103	2.221	94	*	*	*

The results show that the g and A tensors are temperature dependent similar to that of other systems known to exhibit phase transition and JT effect (De *et al.* 1984; Rubins and De, 1985). However, there is a striking difference in that CAS manifests static JT effect with complete orthorhombic spectra at low temperatures unlike the axial spectra observed earlier in most of the JT systems (Breen, 1969a/b; Ham, 1972; Dang *et al,* 1974; De *et al,* 1984; Rubins *et al,* 1984; De, 1986; Misra and Wang, 1990). Along [111] direction, the two sets of four hyperfine lines merge into one set of hyperfine lines with g and A values satisfying equations (35) and (36).

$$g^2[111] = \left(g_z^2 + g_x^2 + g_y^2\right)/3 \qquad (35)$$

$$A^2[111] = \left(g_z^2 A_z^2 + g_x^2 A_x^2 + g_y^2 A_y^2\right)/3g^2[111] \quad (36)$$

This is the case of static JT effect with a ^{2}E ion with axial g and A tensors. A host of authors have observed such EPR static JT spectra from a ^{2}D ion with axially symmetric g and A tensors (De, 1987; Rubins et al, 1985; De, 2010). In the case of EPR spectra from ^{2}E ground state ion with orthorhombic JT distortions g ana A tensors are also orthorhombic and equations (35) and (36) are modified to

$$g^2[111] = \left(g_{//}^2 + 2g_\perp^2\right)/3 \qquad (37)$$

$$A^2[111] = \left(g_\parallel^2 A_\parallel^2 + 2g_\perp^2 A_\perp^2\right)/3g^2[111] \quad (38)$$

The orthorhombic JT EPR spectra reminds us of the multiple EPR lines observed in the case of static JT systems Cu^{2+}:$ZnTiF_6.6H_2O$ (De, 1987) and Cu^{2+}:$MgSiF_6.6H_2O$ (Rubins *et al,* 1985). In these systems, the EPR spectra were attributed to the axial JT distortions of two non-equivalent Cu^{2+} per unit cell such that the principal g and A values are the same for each ion. In the present case, we believe that the EPR spectra correspond to one JT Cu^{2+} per unit cell with orthorhombic JT distortions leading to the observed orthorhombic g and A tensors.

Recall we have earlier shown in our theory that the presence of JT effect of a ^{2}E ground state ion with orthorhombic g and A tensors as seen in CAS requires the three JT potentials to be energetically non-equivalent, meaning that their minima occur at different energies (Fig. 1b). De (2010) stated that many authors have reported orthorhombic JT distortions in GaAs system doped with different impurities (Cr^{3+}, $Ni^{2+}(^3T_1)$). However, none of the systems mentioned earlier showed complete resolved orthorhombic JT EPR spectra as their temperatures varied as observed in CAS system. De (2010) has stated that this is the first report of a clear and direct observation of static orthorhombic JT EPR spectra with a Cu^{2+} in ^{2}E ground state at lower temperatures whose effective Hamiltonian parameters have not been considered. This is done in this paper (Table 2).

Table 2: Calculated Orthorhombic JT EPR Parameters at Different Temperatures

T(K)	g_1	g_2	u_x	u_y	E_x (cm^{-1})	E_y (cm^{-1})	$(A_1/A_2)_x$	$(A_1/A_2)_y$	k_x	k_y	c_x	c_y	$(\lambda/\Delta)_x$	$(\lambda/\Delta)_y$
15	2.2177	0.2155	0.78	1.08	25.3	*	0.67	0.85	-1.03	-1.37	-19.4	-18.1	-0.0580	-0.0497
40	2.2174	0.2151	0.77	1.07	66.0	*	0.63	0.79	-0..96	-1.25	-21.4	--18.7	-0.0579	-0.0496
60	2.2171	0.2148	0.76	1.05	96.5	*	0.64	0.74	-0.98	-1.15	-19.6	-20.7	-0.0578	-0.0496
80	2.2174	0.2151	0.72	1.07	120.3	*	0.52	0.50	-0.75	-0.72	-29.4	-40.4	-0.0578	-0.497
100	2.2158	0.2134	0.70	0.98	144.5	343.3	0.35	0.49	-0.44	-0.70	-61.2	-40.8	-0.0573	-0.0493

The quantities g_1, g_2 and u are in good agreement with that of De *et al* (1984) for Cu^{2+} in Zinc Fluotitanate hexahydrate (ZFTH) crystals. The decrease of u with increasing temperature is more than it compensates for the slight increase of g_1 and g_2. The component of E in the x-direction increases with temperature instead of decreasing as reported in $ZnGeF_6.6H_2O$ (Ziatdinov *et al*, 1983). However, its value at 100 K is 145 cm^{-1} which is very close to 143cm^{-1} in ZFTH (De, 1987). On the other hand, the y-component is undefined for T<80 K because the ratio (1+2u)/(1-u) in equation (25) becomes negative rendering the natural logarithm undefined. However, at higher temperatures E_y becomes finite and greater than E_x. This behaviour of E_y is attributed to $u_y>1$ which has not been observed in any system before. In other words, the lowering of the JT potential well of magnitude E_y is much faster than that of magnitude E_x. To understand this finding, investigation into the behaviour of the components of u in this system is recommended, since orthorhombic JT EPR spectra has its origin in the components of u, which in turn has its origin in the components of E. The quantities (A_1/A_2) and u appear to be the same in behaviour. The quantity c decreases with temperature while (λ'/Δ) appears to be independent of temperature. The quantity k called Fermi contact term is known to be in the form of s-wave and existence of its components based on our theory may not be that simple even though our theory gives reasonable values. One reason for this may be due to some p-wave admixture to the s-wave through s-wave spin-orbit interaction. We recommend further research work to exactly determine its components taking into consideration s-wave for comparison with our findings.

CONCLUSION

The theory linking observed g and A tensors with the Hamiltonian parameters (g_1, g_2, A_1, A_2, Δ, k, λ) was developed for both axial and anisotropic symmetries of Cu^{2+} spectra in CAS system. The Hamiltonian parameters including the Fermi contact parameter k were computed. The results show most of these parameters are temperature dependent and they owe their origin in the non-equivalent orthorhombic JT potential wells which may be attributed to coupling between orbital states and phonons arising out of strong spin-orbit interactions or certain random strains which can cause magnetic field transition in copper II orbital states from tetragonal to orthorhombic symmetry. It is worthy to note, in particular, that even though our theory did not take into consideration the s-wave nature of k, the computed values of its components are reasonable. For instance, the value of the calculated activation energy in this system at 100 K is 145 cm^{-1} compared to 143 cm^{-1} in ZTFH in which copper ion is known to be a static JT ion (De, 1987).

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