EPR Studies of the Effective Hamiltonian Parameters of the Orthorhombic Jahn-Teller Spectra of Cu2+:Cd2 (NH4)2(SO4)3.6H2O Single Crystals in the (100) Direction at Various Temperatures

Yerima J. B. [a]*, Solomon Simon[b], De D. K.[c]

[a,b]*Department of Physics, Modibbo Adama University of Technolohy,*
P M B 2076 Yola Admawa State, Yola +234, Nigeria.
[c]*Department of Physics, Kaduna State University, Kaduna State, Kaduna +234, Nigeria.*
[a]*Email: bjyerima@gmail.com*
[b]*Email: ssmutums@gmail.com*

Abstract

In this paper, EPR study of the effective Hamiltonian parameters of the spectra of Cu^{2+}: $Cd_2(NH_4)_2(SO_4)_3.6H_2O$ single crystals has been carried out at different temperatures. The results show that this system exhibits JT effect, isotropy (T≥122 K) and anisotropy (T<122 K) in the g-factor and hyperfine tensor (A) components in the (100) direction. The decrease in the g and A values with increasing temperature is similar to several known JT systems except the effective Hamiltonian parameter g_1 in the high field side and the cubic field splitting of the ^2E and $^2T_2$ orbital states Δ are different. This difference may be attributed to differences in the structural configurations of neighboring ligands surrounding the paramagnetic Cu^{2+} or the rapid quantum tunneling of Cu^{2+} ions and phonon induced reorientation in the three inequivalent JT potential wells or valleys in this system.

Keywords: EPR; Effective Hamiltonian parameter; Temperature; Jahn-Teller spectra; Quantum tunneling.

----

* Corresponding author.

1. Introduction

Electron paramagnetic resonance (EPR) finds increasingly wide applications as an analytical tool in studies of organic and inorganic materials containing radicals and paramagnetic ions. EPR is also an extremely useful technique in elucidating the magnetic properties of a substitutional paramagnetic ion and the local crystal field symmetry surrounding the ion when the ion is embedded in crystalline lattice [1,2,3]. The size and effective valency of the substitutional paramagnetic ion should match that of the nonmagnetic host lattice. EPR is observed when a frequency magnetic field induces transitions between the Zeeman splitting of magnetic ions or defects placed in an external magnetic field, H. In general, the resonance condition $g\beta H = h\nu$ holds good for EPR, where g is the spectroscopic splitting factor of the ion, which may depend on the orientation of H with respect to the symmetry axes of the crystal or ligand field of the ion, β is the Bohr magneton and h is the Planck's constant. EPR is a very sensitive tool in studying phase transition [3,11,14,13] and the most effective tool for studying JT effect [12]. The order parameter can be determined from EPR measurements for displacive and order-disorder systems [11].

The complex cadmium ammonium sulphate hexahydrate with chemical formula $Cd_2(NH_4)_2(SO4)_3.6H_2O$ abbreviated as CASH belongs to a group of inorganic complexes commonly known as Tutton's salts [12]. A host of researchers have reported Jahn-Teller (JT) effect in some salts of this group doped with Cu^{2+} ions and in other systems containing the $Cu^{2+}(H_2O)_6$ complex [9]. According to [12], earlier investigations on zinc Tutton's salts $Zn(NH_4)_2(SO_4).6H_2O$ have yielded some meaningful data on the values of g-tensors, copper hyperfine tensors and the quadrupole coupling.

Also studies on the spin relaxation time have shown that the crystal is a static JT system. Further, studies on the g-tensors, Cu^{2+} hyperfine tensor and ^{17}O superfine tensor of $Cu^{2+}(H_2O)_6$ in copper doped zinc Tutton's salts single crystals showed that this crystal is a dynamic JT type in contrast to the findings of Bagguley and Griffith in 1952 and Gill in 1965 in the temperature range 300-10 K [12]. They interpreted their results in terms of a rhombically distorted octahedron, in which the three JT configurations are energetically inequivalent and transitions are occurring within these configurations over the entire experimental temperature range. The $Cu^{2+}(H_2O)_6$ complex associated with crystals such as Lanthanum magnesium nitrate, $Mg_3La(NO_3).24H_2O$ and $MgBi_2(NO_3).6H_2O$ has a small trigonal distortion and it exhibits JT effect.

It has been observed that such systems yield isotropic EPR signal at high temperatures which becomes anisotropic at sufficiently low temperatures and no change in crystal structures has been observed so far in these crystals even at the lowest temperature of investigation. The isotropic signal arises from rapid tunneling and phonon induced orientation among the three JT potential wells or troughs which are energetically equivalent in such systems [20]. In CASH, the JT potential valleys are expected to be energetically inequivalent and the transition from isotropic to anisotropic signal is expected to take place at much higher temperatures unlike the systems mentioned earlier. [5,6] used the spin-echo technique to measure the rate of jumping between the three JT wells in Cu^{2+} doped $Mg_3La(NO_3).24H_2O$ and found it to be linearly dependent on temperature up to 10 K and the direct phonon process is prevailing. In addition, these authors reported that inter-valley jumping contributes to the spin-lattice relaxation time T_1.

In this paper, the values of the effective Hamiltonian or magnetic solid state parameters of the simultaneous axial and orthorhombic EPR spectra of Cu^{2+}:CASH in the (100) direction at different temperatures were determined. The study reveals that these parameters are temperature dependent.

2.   Experiment

The EPR experimental spectra on Cu^{2+} ions doped in CASH that have been analyzed in this work was carried out by [12] at Olin Physical Laboratory, WFU, USA. However, for the sake of clarity the experimental details are given as follows: Single crystals of Cu^{2+}:CASH were grown by slow evaporation at room temperature from aqueous solutions containing $CdSO_4.8H_2O$ and $(NH_4)_2SO_4$ in equal molar ratio to which small quantity of $CuSO_4$ was added such that the ratio of Cu^{2+} to Cd^{2+} is 1:100 in the solution. The crystals were grown within a period of two weeks.

The EPR studies of CASH were carried out in the temperature range of 300-15 K using a Varian E-Century line spectrometer operating at 9.28 GHz. An APD cryogenic HC-X closed cycle refrigerator was used to vary the temperature. The EPR spectra measurements were performed in two mutually perpendicular planes viz: plane 1 and plane 2. Plane 1 is one perpendicular to the long axis as well as the natural plane of the crystal while plane 2 contains the long axis and perpendicular to plane 1.

In each plane, the angular variations of the spectra were recorded at different temperatures. In the case of phase transition studies, the EPR spectra were recorded in plane 1 at a fixed orientation (the orientation in which largest hyperfine splitting, a mark of phase transition) as a function of temperature. This orientation was achieved when the magnetic field was 40° off the parallel axis. In each of the orientations mentioned, a small amount of DPPH (Diphenyl Picryl Hydrazil) was placed beside the sample and the corresponding EPR signal was recorded.

3.   Theory of Symmetry of EPR Spect

We present the theory relating the effective Hamiltonian parameters (g_1, g_2, A_1, A_2) and the observed spin Hamiltonian parameters $g(g_\parallel, g_\perp)$ and $A(A_\parallel, A_\perp)$ values for both axial and orthorhombic symmetries, where $g_\parallel(g_z)$ and $g_\perp(g_x, g_y)$ are the g-values in the low and high magnetic fields respectively. 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 reference [9,19].

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

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

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

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

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 $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ at any temperature can be expressed in terms of other parameters of the system. For example, the relationships between the observed $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$ and the effective spin Hamiltonian parameters g_1, qg_2, A_1, qA_2 are given by [10,15,4]

$$g_\parallel = g_1 + 2qg_2 \qquad\qquad 5$$

$$g_\perp = g_1 - qg_2 \qquad\qquad 6$$

$$A_\parallel = A_1 + 2qA_2 \qquad\qquad 7$$

$$A_\perp = A_1 - qA_2 \qquad\qquad 8$$

where q is the Ham reduction factor.

In the case of axial symmetry EPR spectra, the temperature variation of $g_\parallel$ and $g_\perp$ is given by (De et al, 1984; Rubins et al, 1984)

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

and to first order perturbation theory

$$g_2 = g_1 - g_e = -\frac{4\lambda'}{\Delta} \qquad\qquad 10$$

where $u = 2q$, $g_e = 2.0023$, λ' is the effective spin-orbit coupling constant and Δ is the cubic field splitting of the ^2E and $^2T_2$ orbital states. We can easily deduce from equation (9) that

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

so that

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

Combining equations (10) and (11) yields

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

from which g_2 can be calculated.

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

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

from which u(T) can be determined.

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

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

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

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

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

so that

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

Also from equations (16) we have

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

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

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

The anisotropy parameter u(T) can be fitted to an exponential function of the form [9]

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

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

$$\Delta = kTln\left(\frac{1 + 2u(T)}{1 - u(T)}\right) \qquad\qquad 22$$

Now from equation (21) it is clear that u(T)=1 as T→0 and u(T)=0 as T→∞, i.e. 0≤u(T)≤1 for T≥0. This confirms our earlier assertion that u=2q=1 for q=0.5 for strong JT system. Substituting u=1 in equation (22), Δ becomes infinite and for u=0, Δ=0. Equations (21) and (22) were used to calculate the values of u(T) and Δ at different temperatures and the values recorded in Table 2.
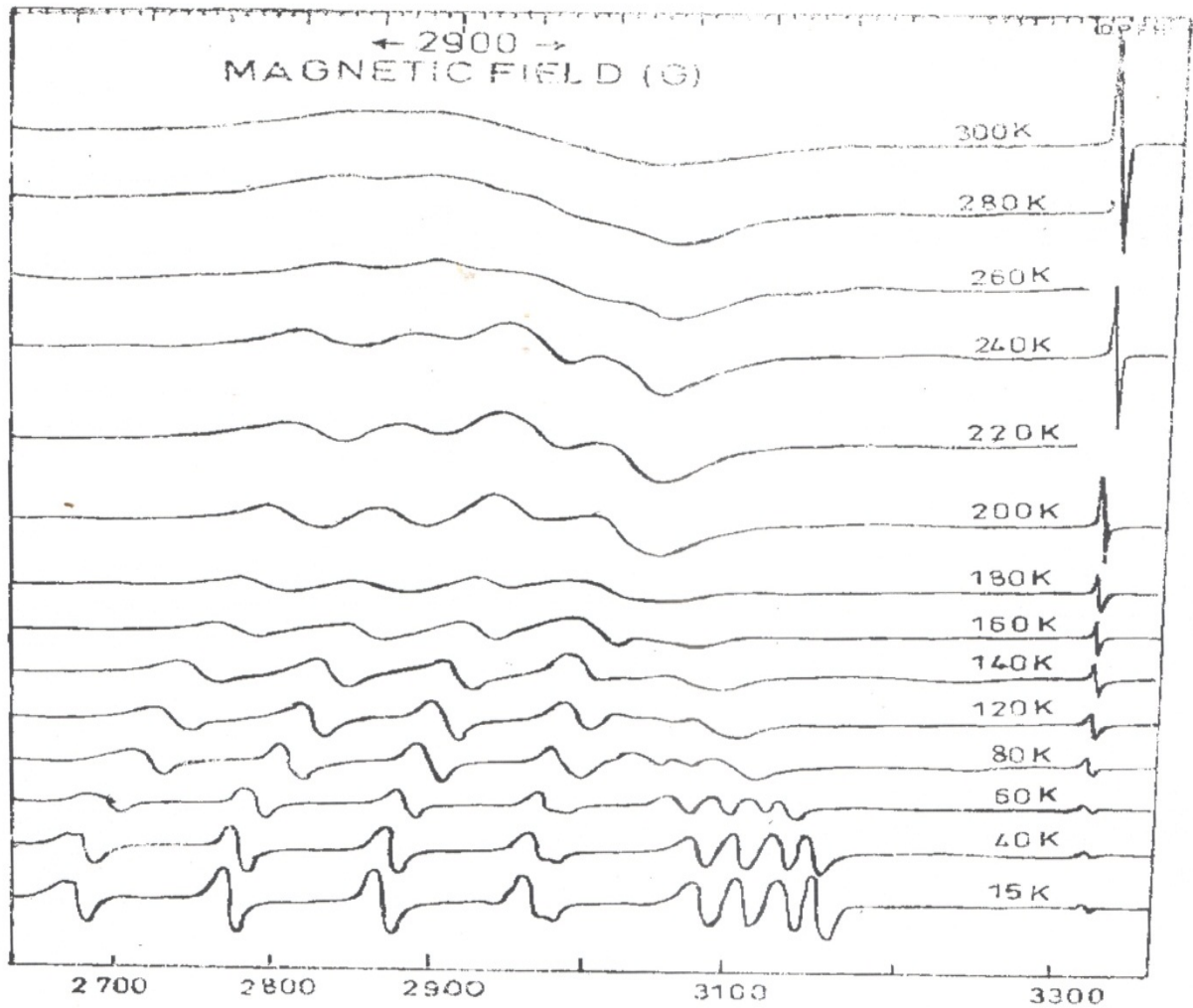
4.   Results and discussion

Figure 1: Temperature variation of EPR spectra of Jahn-Teller effect of Cu^{2+} doped in CASH in the (100) direction (plane 2)

Figure 1 represents the EPR spectra of Cu^{2+} in CASH single crystals in the (100) direction which shows improved resolution of the hyperfine lines with lowering temperature due to decrease in spin-lattice relaxation time. The resolved hyperfine lines occurring at lower side of the field correspond to $g_{\parallel}$ and $A_{\parallel}$ in the (100) direction. [12] has reported earlier that this system is a JT system with a second order phase transition at about 71±1 K. The spectra is a broad single line spectrum at room temperature 300 K which is replaced by two sets of four hyperfine lines at the lowest and highest fields corresponding to $g_{\parallel}$ and $g_{\perp}$ lines respectively.

The appearance of the two sets of four hyperfine lines at the lowest and highest magnetic fields for the same orientation belongs to one of the (100) type axes of [Cu^{2+}:H_2O] coordination and that the complex is exhibiting JT effect similar to well-known JT systems such as $ZnTiF_6.6H_2O$ and $Zn(BrO)_2.6H_2O$ [7]. In plane 2, as the crystal was gradually rotated at 15 K all the two sets of four hyperfine lines merged into a group of four lines only when the magnetic field is just 5° off the long axis of the crystal. This is equivalent to (111) direction in a perfect cube which is ideally 54.7^o away from the (100) type axis. The merging of the two sets of four hyperfine lines into a group of only four hyperfine lines have been observed in the Cu^{2+}spectra of JT systems with axillary g and A values [18,9,17]. Also the g-mean is almost constant while $g_\parallel$ and $A_\parallel$ values both increase with decreasing temperature as expected of a JT system [9,17]. The observed characteristics of the EPR spectra reveal that this crystal is a static JT system with axial g and A tensors like $ZnTiF_6.6H_2O$ and $Zn(BrO)_2.6H_2O$ crystals. This is different from Cu^{2+}:CAS crystals where orthorhombic g and A tensors have been observed. For a true static JT system, at points of zero line shape the values of $g_\parallel$, $g_\perp$, $A_\parallel$ and $A_\perp$ (Table 1) in the (100) direction at different temperatures were deduced from the observed spectra using the following equations

$$g_\parallel = \frac{h\nu}{\beta H_\parallel}, \qquad g_\perp = \frac{h\nu}{\beta H_\perp} \qquad\qquad 23$$

$$A_\parallel = \frac{H_{3/2} - H_{-3/2}}{3}, \quad A_\perp = \frac{H_{3/2} - H_{-3/2}}{3} \qquad\qquad 24$$

where $H_\parallel$ and $H_\perp$ are sets of low field lines and high field lines respectively. For example, the value of the magnetic field half way between two fields $H_{-1/2}$ and $H_{1/2}$ corresponding to quantum number m=-1/2 and m=1/2 respectively, $H_{-3/2}$ and $H_{3/2}$ respectively correspond to m=-3/2 and m=3/2 at the lowest and highest magnetic fields. The appearance of two sets of four hyperfine lines at low magnetic field (T<122 K) and one set of hyperfine lines at high magnetic field (T≥122 K) suggests that this system manifests both axial and orthorhombic symmetries. The presence of two sets of four hyperfine lines in the low and high field sides at low temperatures (T<122 K) suggests that one of the three JT potential wells becomes lower than the remaining two on cooling. This implies that $g_x = g_y$ and $A_x = A_y$ i.e. the system manifests two-fold anisotropy unlike three-fold anisotropy observed in Cu^{2+}:$Cd_2(NH_4)_2(SO_4)_3$ [20].

Table 1: Observed g and A values in Cu^{2+}: CASH in (100) direction, where * represents values

T±1K	$g_\parallel \pm 0.005\,G$	$A_\parallel \pm 2\,G$	$g_\perp \pm 0.005\,G$	$A_\perp \pm 2\,G$
15	2.358	98.0	2.136	26.0
40	2.355	98.0	2.137	25.0
71	2.347	93.0	2.148	25.0
103	2.334	90.0	2.158	25.0
122	*	85.0	*	*
140	*	83.0	*	*

Table 2: Effective Spin Hamiltonian parameters in Cu^{2+}:CASH in (100) direction, where * represents missing values.

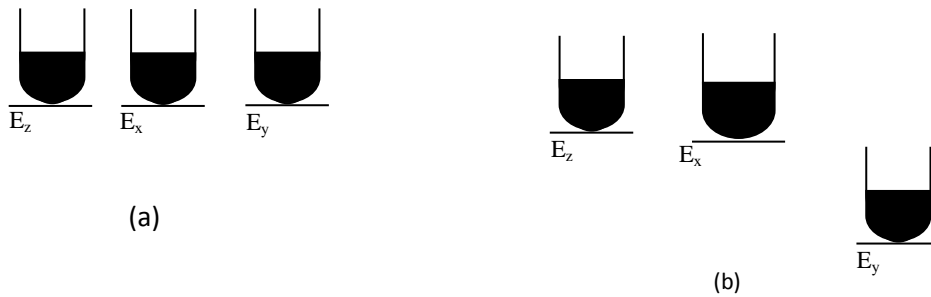| $T\pm 1K$	A_1(G)	A_2 (G)	g_1	g_2	c	k	U	λ'	Δ (cm^{-1})
15	50.0	48.0	2.210	0.148	122.5	0.556	0.713	-0.026	2221
40	49.3	48.9	2.210	0.145	123.2	0.547	0.701	-0.025	5784
71	47.7	45.3	2.214	0.133	110.5	0.564	0.626	-0.021	8844
103	46.7	43.3	2.217	0.117	101.0	0.579	0.547	-0.018	10955
122	*	*	*	*	*	*	*	*	*

Figure 2: (a) Axial symmetry and (b) anisotropy symmetry of JT potential wells

The effective spin Hamiltonian parameters (A_1, A_2, g_1, g_2, c, k, λ', u) except Δ in Table 2 and the observed spin Hamiltonian parameters ($g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$) in Table 1 decrease with increasing temperature in the same pattern. We have mentioned earlier that the resolution of the Cu^{2+}:CASH spectra at temperatures greater than 103 K is poor and for this reason we are able to measure only four spin Hamiltonian parameters corresponding to fairly resolved spectra at 15, 40, 60 and 80 K. The values of u in Table 2 lie in the range $0 \leq u \leq 1$ for $T \geq 0$ in agreement with the boundary conditions that T tends to zero and infinity in equation (21). The increase of Δ with increasing temperature indicates that the separation between the ^2E and $^2T_2$ states increases on warming the system.

5. Conclusion

The effective Hamiltonian parameters (g_1, g_2, A_1, A_2, q, u, k, λ', Δ, α) characterizing the magnetic and spectroscopic properties of Cu^{2+} ion in this crystal were determined in the (100) direction at different temperatures. The results show static JT effect [17] and anisotropy in the g and A values which increase with decreasing temperature similar to other JT systems [7,9,17,16]. The decrease in the parameters (u, A_1, A_2, g_2, c) or increase in (g_1, k, λ', Δ) with increasing temperature is attributed due to (i) differences in the structural configurations of the neighbouring ligands surrounding the paramagnetic Cu^{2+} ion in CASH i.e. the Cu-H_2O bond lengths in the three directions in many Tutton's salts are not always equal [18,9,17,8]. (ii) quantum tunneling or reorientation of Cu^{2+} ions among the two upper JT potential wells and one lower JT potential well. The values of u(T) have been used to determine the thermally energy difference between one of the JT potential minima and the two other JT potential minima.

References

[1] Abragam A and Bleaney B. 1970. *Electron Paramagnetic Resonance of transition metal ions*. Clearendon press, Oxford. 168.

[2] Al'tshuler S A and Kozyrev B M. 1972. "Electron paramagnetic resonance in the compounds" *of transition elements,* 2nd ed. Vol 2. John Willey & Sons, New York,

[3] Artherton E M. 1973. *Electron spin resonance*. Willey, New York.

[4] Boatner L A; Reynolds R W; Chen Y and Abraham M M. 1977. *Static quasi-static and quasi-dynamic jahn-Teller in the EPR spectra of Ag^{2+} SrO, CaO, and MgO. Phys. Rev. B16*, 1:86,

[5] Breen D P, Drupka D C and Williams F I B. 1969a. *Relaxation in Jahn-Teller system I, cfopper in octahedral water coordination*. Phys. Rev. 179(2): 241-251..

[6] Breen D P, Drupka D C and Williams F I B. 1969b. *Relaxation in Jahn-Teller system II*, Phys. Rev. 179(2): 255-271.

[7] De D K. 1986. *Powder EPR study of Jahn-Teller effect and phase transition in Cu^{2+}:ZnTiF6.6H$_2$O.* Phys. Rev. B 34:4655.

[8] De D K. 1987. *Jahn-Teller impurity dependence of the transition temperature T$_{cl}$, critical exponent and pseudo-Jahn-Teller potential well splitting in ZnTiF$_6$.6H$_2$O.* J. Phys. C Solid state physics 20:5911-5921.

[9] De D K, Rubins R S and Black T D. 1984. *EPR study of the Jahn-Teller effect of Cu(II) in ZnTiF$_6$.6H$_2$O.* Phys. Rev. 29B:71-78.

[10] Ham F S. 1972. "Electron paramagnetic resonance" *edited by S Greschwind.* Plenum press, New York,

[11] Muller K A and Waldkirch T. 1973. "Local properties at phase transitions". Proceedings of the Enrico Fermi International School of Physics Course LIX, Varenna edite by K A Muller and A Rigamonti, NH, Asterdam,

[12] Oguama F A. 1997. "EPR studies on the effect of magnetic Jahn-Teller and Jahn-Teller impurities on solid state phase transitions" Doc. Dissert. WFU, USA.

[13] Oguama F A; Shields W H and De D K. 1997. *EPR studies of phase transitions in cadmium calcium acetate hexahydrate as a function of different paramagnetic impurity ion concentrations*. Phys. Rev. B56: 2611.

[14] Owens F J. 1979. "Magnetic resonance of phase transitions". Academic press, New York, edited By C P Poole Jr and H A Farach.

[15] Reynolds R. W and Boatner L. A. 1975. *Dynamic, intermediate and static Jahn-Teller in the EPR spectra of ^2E orbital states*. Phys. Rev B12:4735,

[16] Rubins R S and Drumheller J E. 1987. *The temperature dependence of the EPR spectrum of Cu^{2+}in $ZnTiF_6.6H_2O$ between 4 and 160 K*. J. Chem. Phys. 86:6660.

[17] Rubins R S; Tello L N; De D K and Black T D. 1984. *EPR studies of Cu(II) $MgGeF_6.6H_2O$ crystals*. J. Chem. Phys. 81:4230.

[18] Ziatdinov A M; Zaripov M M; Davidovich R L and Yablokov Yu V. 1976. *The depression of the dynamic Jahn-Teller effect*. Phys. Stat. sol. (b) 78:K69-71.

[19] Yerima J B. 2007. "EPR studies of the effect of paramagnetic impurity concentrations in phase transition and Jahn-Teller effect in crystalline solids". Doc. Dis. FUTY.

[20] Yerima J B; Dikko A B and De D K. 2014. *EPR studies of the Hamiltonian parameters of the simultaneous axal and orthorhombic Jahn-Teller spectra of Cu^{2+} in $Cd_2(NH_4)_2(SO_4)_3$*. J. Engineering & Applied Scientific Research. 1:6.