

Theory and Simulation of EPR Axial Jahn-Teller Spectra of Cu^{2+} in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ Single Crystals in the temperature range 300-15 K

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Abstract

This paper presents the theory and simulation of the derivative line shape function of the EPR axial Jahn-Teller spectra of Cu^{2+} in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ single crystals. Computer simulation of the Cu^{2+} EPR spectra using the spectrum fitting technique has been carried out in the (111) direction and (100) direction at various temperatures. The results show excellent fit between the observed and simulated spectra. The insufficient resolution of the spectra limited simulation in the temperature intervals $15 \leq T \leq 60$ K in the (100) direction and $15 \leq T \leq 180$ K in the (111) direction.

Keywords: EPR, simulation, axial JT spectra, temperature

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 a crystalline lattice (Abragam and Bleaney, 1970; Al'tshuler and Kozyrev, 1972; Artherton, 1973). The size, mass and effective valency of the substitutional paramagnetic ion should match that of the nonmagnetic host lattice. EPR phenomenon 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 for EPR to occur is given by $g\beta H = h\nu$ 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 (Atherton, 1973;

Muller and Waldkirch, 1973; Owens, 1979; Oguama et al., 1997) and the most effective tool for studying JT effect (Oguama, 1997). The order parameter can be determined from EPR measurements for displacive and order-disorder systems (Muller and Waldkirch, 1973).

The complex cadmium ammonium sulphate hexahydrate with chemical formula $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ abbreviated as CASH belongs to a group of inorganic complexes commonly known as Tutton's salts (Oguama, 1997). 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 $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ complex (Dang *et al.*, 1974; De *et al.*, 1984). According to Oguama (1997), earlier investigations on zinc Tutton's ($\text{Zn}(\text{NH}_4)_2(\text{SO}_4)_6 \cdot 6\text{H}_2\text{O}$) 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 $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ 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 (Oguama, 1997). 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 $\text{Cu}^{2+}(\text{H}_2\text{O})_6$ complex associated with crystals such as Lanthanum magnesium nitrate, $\text{Mg}_3\text{La}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ and $\text{MgBi}_2(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 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 (Yerima *et al.*, 2014). 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. Breen et al (1969a/b) used the spin-echo technique to measure the rate of jumping between the three JT wells in Cu^{2+} doped $\text{Mg}_3\text{La}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ 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 our earlier work (Yerima et al. 2014) on the computer simulation of Cu^{2+} :CAS orthorhombic Jahn-Teller spectra we pointed out that the complex or insufficient resolved splitting patterns of the spectra constitute a major problem in the extraction of the relevant spectroscopic parameters (resonance frequency, coupling constants, linewidths) from the observed spectra as starting points in the computer simulation of the spectra. Therefore, a straightforward analysis is not possible in general (neither for the human expert nor for a conceivable computer expert system (Kirste, 1992)). It is against this background, several methods (spectrum contraction or elimination hyperfine splitting constants, extraction of hyperfine splitting constants, correlation method, maximum method, significance plots and "roll-up" transformation) have

been employed in the analysis of high resolution EPR spectra (Kirste, 1992; Wu, 2006). These methods may be more or less useful in providing estimates for the hyperfine coupling constants. On the other hand, the set of relevant spectroscopic parameters extracted from the spectra can be verified by spectrum simulation and comparison with the experimental spectrum which is the method adapted in this paper. We have adapted the spectrum fitting because it is considered an indispensable component in any scheme automated spectrum analysis.

Experiment

The EPR experimental spectra on Cu^{2+} ions doped in CASH that have been analyzed in this work was carried out by Oguama (1997) 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 $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$ 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 spectra 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.

Theory and Method of Computer Simulation of the Line Shape Function of Cu^{2+} in CASH

The detailed procedure of the experiment for determining Cu^{2+} spectra in CASH is available in Oguama (1997). The Oguama (1997) spectra of Cu^{2+} in this system at various temperatures were acquired for the computer simulation. The expression for the line shape function required for the computer simulation of the EPR spectra of Cu^{2+} in $\text{Cd}_2(\text{NH}_4)_2(\text{SO}_4)_3$ abbreviated as CAS with orthorhombic Jahn-Tellerspectra was derived earlier by (Yerima *et al.*, 2014)

$$F(H) = -\{2\alpha f_1\} \left[\frac{H - \frac{h\nu}{\beta g_z} + A_z M_I}{\left(\left(H - \frac{h\nu}{\beta g_z} + A_z M_I \right)^2 + R_1 \right)^2} \right] - \{2\alpha f_2\} \left[\frac{H - \frac{h\nu}{\beta g_x} + A_x M_I}{\left(\left(H - \frac{h\nu}{\beta g_x} + A_x M_I \right)^2 + R_2 \right)^2} \right] -$$

$$\{2\alpha f_3\} \left[\frac{H - \frac{h\nu}{\beta g_y} + A_y M_I}{\left(\left(H - \frac{h\nu}{\beta g_y} + A_y M_I \right)^2 + R_3 \right)^2} \right] \quad 1$$

where $f_1 = g_z^2(g_x^4 - g_y^2)\frac{\pi}{2} + \pi g_y^4$, $f_2 = g_x^2(g_z^4 - g_y^2)\frac{\pi}{2} + \pi g_y^4$, $f_3 = g_y^2(g_x^4 - g_z^2)\frac{\pi}{2} + \pi g_y^4$, α is the fractional relative abundance of copper isotopes $\alpha(\text{Cu}^{63}) = 0.69$ and $\alpha(\text{Cu}^{65}) = 0.31$; g_x , g_y , g_z are g-factors along the x-, y-, and z-axes respectively; H is the applied magnetic field; A_x , A_y , A_z are the hyperfine constants in the x-, y-, and z-axes respectively; R_1 , R_2 , R_3 are the linewidth parameters in the x-, y-, and z-axes respectively; $M_I = -3/2, -1/2, 1/2, 3/2$ and β is the Bohr magneton. The terms in the curly brackets represent the magnification factor of the line shape while the terms in square brackets determine the shape of the EPR line.

Now in the case of spectra with axial symmetry such as Cu^{2+} :CASH spectra, neglecting the isotopic and anisotropic effects, the second and third terms in equation (1) vanish and equation (1) reduces to

$$F(H) = -\{2\alpha f_1\} \left[\frac{H - \frac{h\nu}{\beta g_z} + A_z M_I}{\left(\left(H - \frac{h\nu}{\beta g_z} + A_z M_I \right)^2 + R_1 \right)^2} \right] \quad 2$$

Equation (2) represents the line shape function of spectra with axial symmetry consisting of only four resolved hyperfine lines. This implies that at the point of inflection the derivative line shape function is zero or cuts the H-axis four times. Thus, the values of H corresponding to the points of inflection or zero $F(H)$ can be determined. This means that the term in square bracket must be zero i.e. $H - \frac{h\nu}{\beta g} + AM = 0$. Using two values of H (H_1 and H_2) and M_I (M_{I_1} and M_{I_2}) corresponding to inflection points where $F(H)=0$, the corresponding expression for hyperfine constants is given by $A = \frac{H_2 - H_1}{M_{I_2} - M_{I_1}} = \frac{H_2 - H_1}{n - 1}$ where n is the number of complete resolved

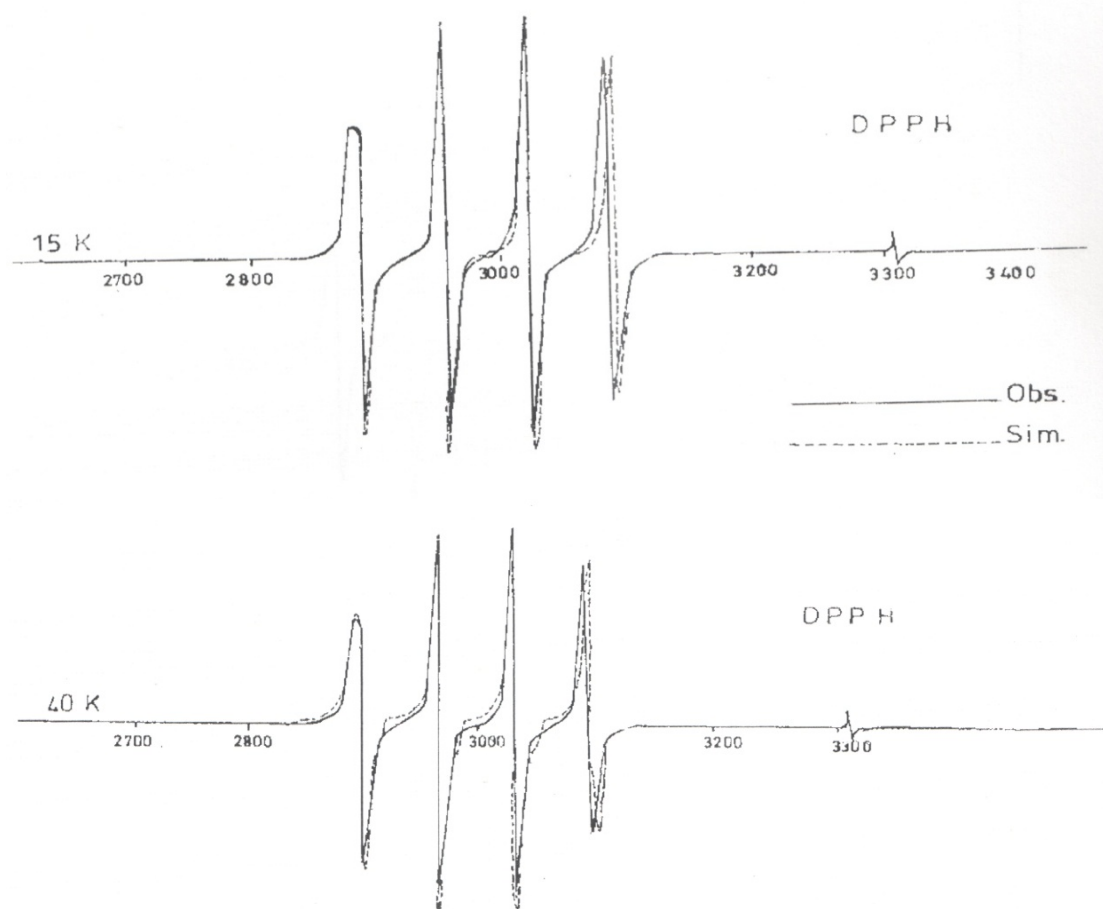
hyperfine lines and $n-1$ gives the number of hyperfine constants. Since we have only four hyperfine lines belonging to $\text{Cu}^{2+}(63)$ then $M_{I_1} = -3/2$, $M_{I_2} = -1/2$, $M_{I_3} = 1/2$ and $M_{I_4} = 3/2$ so that $n - 1 = M_{I_4} - M_{I_1} = 3$ or $n = 4$.

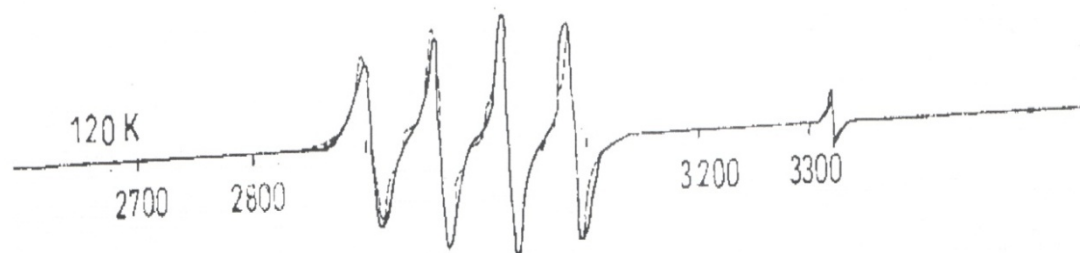
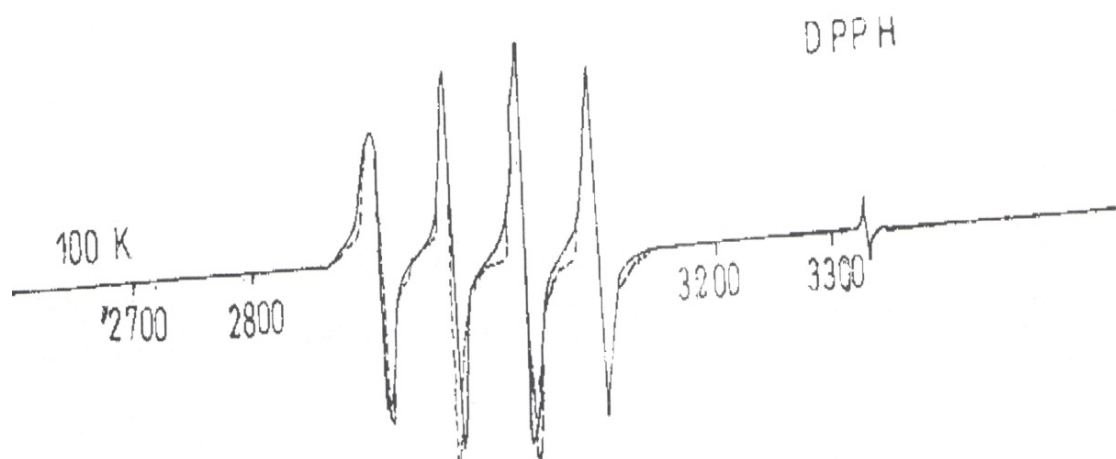
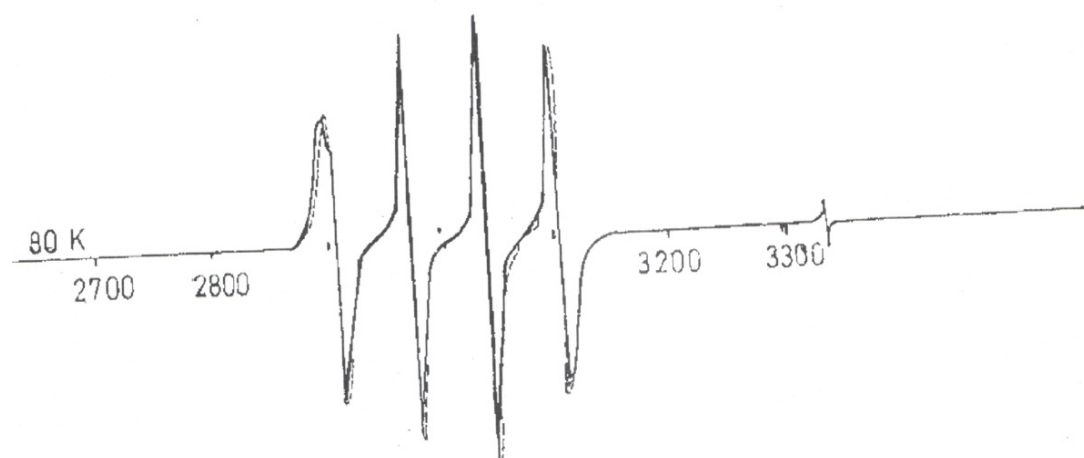
On the other hand, generally the g values are obtained by noting the middle field point H_{mf} of the hyperfine lines corresponding to $M_{I_1} = -1/2$ and $M_{I_2} = 1/2$ and using the relation $g = \frac{h\nu}{\beta H_{mf}}$. The calculated A and g values and estimated value of peak-to-peak

linewidths ΔH_{pp} were used as starting points in the computer simulation process. These values of g, A and ΔH_{pp} were substituted in the expression of $F(H)$ and the resulting line shape was compared or matched with observed EPR line. The values of g, A and ΔH_{pp} were varied by small amounts in the ranges ± 0.005 - 0.01 G, ± 0.5 - 1 G, and ± 5 - 10 G respectively around the initial values until the line that best fits the observed EPR line was obtained. The effective values of g, A and ΔH_{pp} corresponding to the simulated EPR lines of Cu^{2+} in CASH at different temperatures were recorded.

Results and discussions

Fig. 1 represents the observed (solid lines) and simulated (dashed lines) EPR spectra of $\text{Cu}^{2+}:\text{CASH}$ in the (111) direction or [111] axis of the $\text{Cu}^{2+}:\text{6H}_2\text{O}$ octahedral at different temperatures. The observed and simulated are in good agreement. The EPR spectra was observed when the crystal was rotated 60° off the parallel axis in plane 1 has a set of four resolved hyperfine lines at low temperatures and four unresolved hyperfine lines at high temperatures which almost appear as a single broad line at 300 K. With lowering temperature, the spectra show improved resolution of the hyperfine lines due to decrease in spin-lattice relaxation time as a function of temperature. The complete resolution of the axial spectra of the hyperfine lines in the temperature range ($15 \leq T \leq 180$ K) has made the computer simulation of the spectra possible. The main difficulty in computer assisted structure elucidation consists in the precise extraction of the relevant spectroscopic parameters such as resonance frequency, coupling constants and linewidths from the spectra. In this study, this problem has not been solved in totality because of highly complex or insufficiently resolved splitting of the g lines of $\text{Cu}^{2+}:\text{CASH}$ EPR spectra at high temperatures. However, the complete resolution of the hyperfine lines has provided reliable information that the number of equivalent nuclei in this system is three resulting to the four hyperfine lines of intensity ratios 1:3:3:1 in each of the three groups of four hyperfine lines.





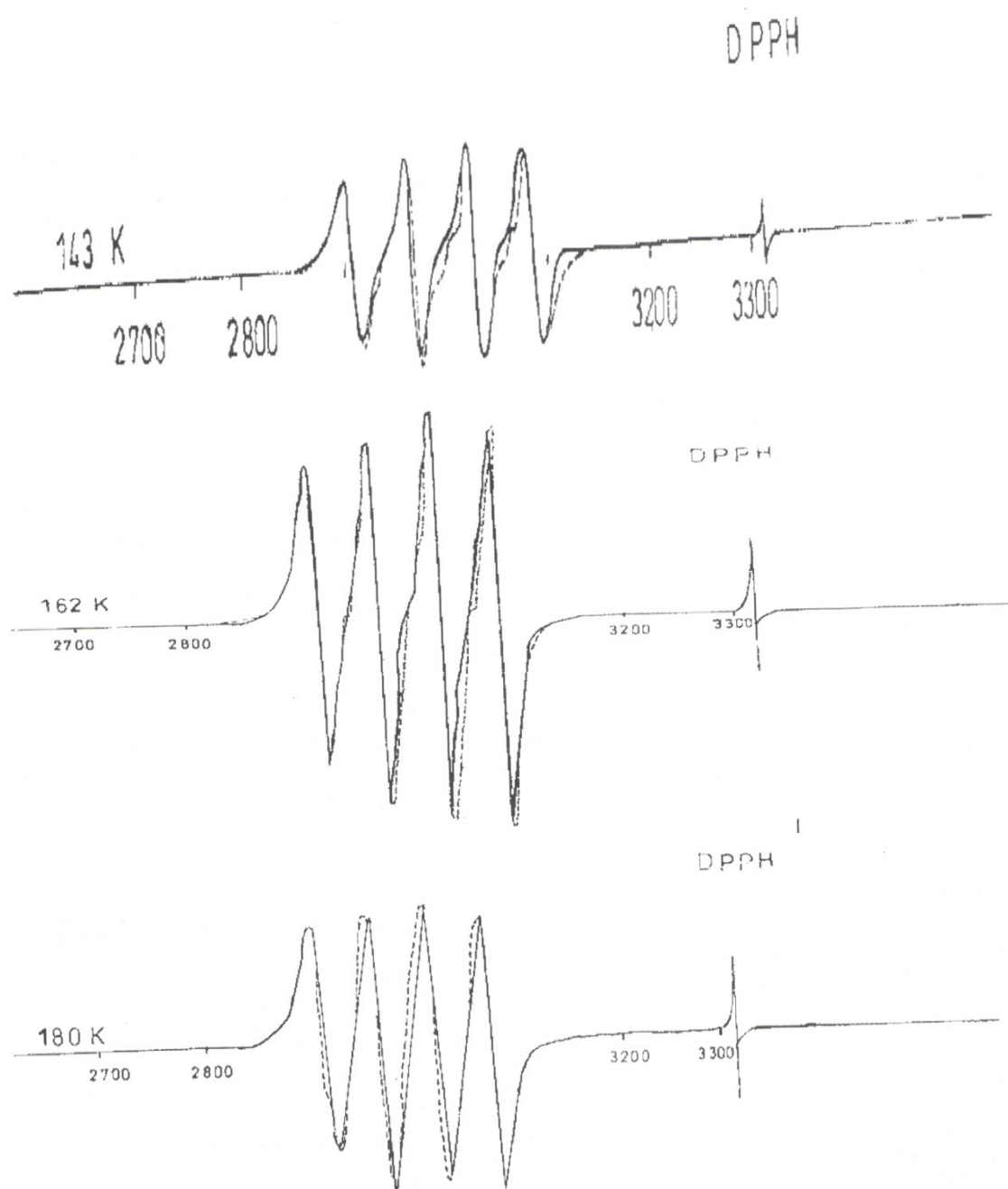


Fig. 1 Observed (solidlines) and simulated (dashed lines) spectra of $\text{Cu}^{2+}:\text{CASH}$ in the (111) direction at different temperatures

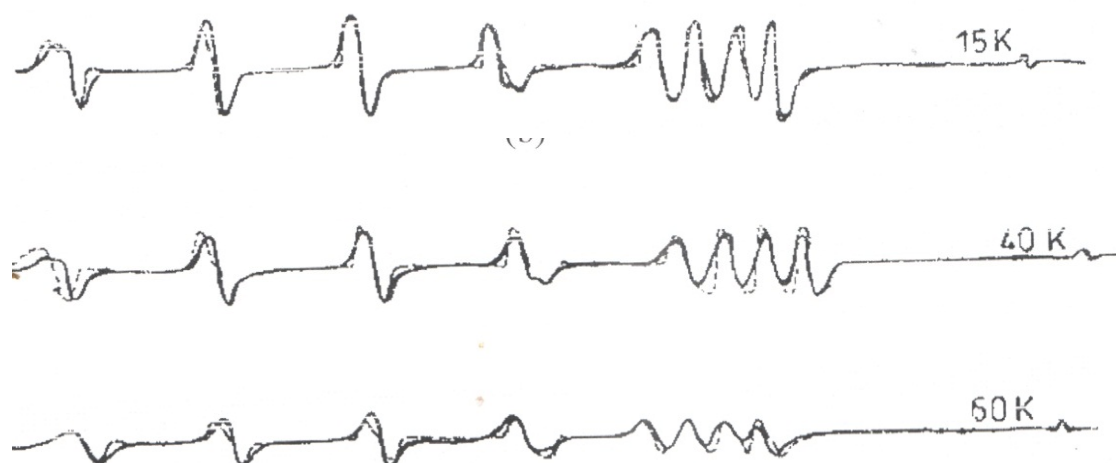


Fig. 2 Observed (solid lines) and simulated (dashed lines) Cu^{2+} :CASH spectra in the (100) direction at selected different temperatures

Table 1 Calculated spin Hamiltonian parameters from simulated CASH Spectra in the (111) direction

T±1 K	$g_{\langle 111 \rangle}$	$A_{\langle 111 \rangle}$
15	2.2184	67
40	2.2129	65
80	2.2055	65
120	2.2000	62
140	2.1946	58
160	2.2092	55
180	2.2055	53

The mean values of the hyperfine coupling constant (A) and g-factor (g) obtained from the simulated spectra at various temperatures are recorded in Table 1. The decrease in the g and A values measured in this direction at different temperatures points to the possibility of JT effect and a second order phase transition temperature (180 K) in this system (Oguama 1997) even though JT transition has never been reported at such high temperature (Ham, 1972; Englman, 1972; Thomas, 1977; Reinen, 1991). Therefore, to establish the reality of JT transition in this system at high temperature a detailed study of Cu^{2+} :CASH as a function of Cu^{2+} ion concentration was recommended for further investigations.

Fig. 2 represents the Cu^{2+} : H_2O EPR spectra observed (solid lines) and simulated (dashed lines) in the (100) direction at different temperatures when the magnetic field is 60° off the parallel axis in plane 2. 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 $[\text{Cu}^{2+}:\text{H}_2\text{O}]$ coordination and that the complex is exhibiting JT effect similar to well-known JT systems such as $\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ and $\text{Zn}(\text{BrO})_2 \cdot 6\text{H}_2\text{O}$ (De, 1986). The disappearing of the set of four g lines in the high magnetic field side in the (100) direction restricted the computer simulation of the spectra to only few temperatures. In this direction, the g values increase with temperature while the A values decrease with temperature (Table 2).

Table 2 observed and simulated g and A values in $\text{Cu}^{2+}:\text{CASH}$ in (100) direction

$T \pm 1 \text{ K}$	$g_{\parallel} \pm 0005$	$A_{\parallel} \pm 2G$	$g_{\perp} \pm 0005$	$A_{\perp} \pm 2G$	$g_{\langle 111 \rangle}$	$A_{\langle 111 \rangle}$
15	2.358 2.356	98.0 98.3	2.136 2.135	26.0 26.7	2.210 2.211	63.7 64.0
40	2.355 2.352	98.0 98.3	2.137 2.155	25.0 25.0	2.210 2.221	63.4 63.3
71	2.347 2.344	93.0 93.0	2.148 2.159	25.0 25.0	2.214 2.222	62.3 60.0
103	2.334 *	90.0 *	2.158 *	25.0 *	2.217 *	58.2 *
122	2.326	85.0	*	*	*	*
140	2.319	83.0	*	*	*	*

where bold face values belong to simulated EPR lines and * missing values

Conclusion

In this paper, the theoretical expression for the line shape function of the axial JT spectra of Cu^{2+} in CASH have been reported. The JT spectra of $\text{Cu}^{2+}:\text{CASH}$ were simulated by the aid of computer using spectrum fitting technique at different temperatures. The results show excellent fitting between the simulated spectra and the observed spectra especially at the lowtemperature regions $T \leq 180 \text{ K}$ in the (111) direction and $T \leq 60 \text{ K}$ in the (100) direction where the hyperfine lines are sufficiently resolved.

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