

EPR Studies of Phase Transition and Jahn-Teller (JT) Effect of Copper II ion in Cadmium Ammonium Sulphate Hexahydrate [Cu²⁺:Cd₂(NH₄)₂(SO₄)₃.6H₂O] Spectra in the Temperature Range 300-15 K

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Abstract: In this paper, EPR study of the spectra of Cu²⁺ in Cadmium Ammonium Sulphate Hexahydrate (Cd₂(NH₄)₂(SO₄)₃.6H₂O) single crystals has been carried out in the temperature range 300-15 K. The spin Hamiltonian parameters of Cu²⁺ in this system were determined at different temperatures. The results show that this system exhibits JT effect and that the anisotropy in the g-factor and hyperfine tensor components decrease with increasing temperature similar to several known JT systems except g₁ and g<111> are different. This difference may be attributed to differences in the structural configurations of neighbouring ligands surrounding the paramagnetic Cu²⁺ in CASH and other related systems. It has been shown that the Cu-H₂O bond lengths in the three directions in many Tutton's salts are not equal while in known static JT systems they are equal. Consequently, we conclude that it is possible the Cu-H₂O bond lengths in CASH are different in the three directions which may be responsible for the observed differences in the g-values. We recommend that further x-ray and EPR or other related techniques be carried out to confirm the authenticity of the difference in Cu-H₂O bond lengths in this system.

Keywords: EPR, phase transition, temperature, Jahn-Teller effect, Cu-H₂O bond length

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 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 compound cadmium ammonium sulphate hexahydrate with chemical formula Cd₂(NH₄)₂(SO₄)₃.6H₂O 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 Cu²⁺ ions and in other systems containing the Cu²⁺(H₂O)₆ complex (Dang *et al.*, 1874; De *et al.*, 1984). According to Oguama (1997), earlier investigations on zinc Tutton's (Zn(NH₄)₂(SO₄)₃.6H₂O) 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, Cu²⁺ hyperfine tensor and ¹⁷O superfine tensor of Cu²⁺(H₂O)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 Cu²⁺(H₂O)₆ complex associated with crystals such as Lanthanum magnesium nitrate, Mg₃La(NO₃)₂.24H₂O and MgBi₂(NO₃)₆.6H₂O 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 Cu²⁺ doped Mg₃La(NO₃)₂·24H₂O 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 intervalley jumping contributes to the spin-lattice relaxation time T₁.

In this paper, a systematic description and interpretation of the EPR spectra of Cu²⁺ ions in CASH at different temperatures is presented. Also, the effect of substitution of Cd²⁺ for Zn²⁺ in the Tutton's salts on the modification of the phonon frequency and change in the phase transition characteristics using Cu²⁺ ion as a probe are discussed. In addition, the effect on the substitution of Cd²⁺ ion on the local site symmetry and the exploration of the possibility of JT effect coexisting with a soft mode phenomenon in this system have been reported.

2. Experiment

The EPR experimental spectra on Cu²⁺ 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 Cu²⁺:CASH were grown by slow evaporation at room temperature from aqueous solutions containing CdSO₄·8H₂O and (NH₄)₂SO₄ in equal molar ratio to which small quantity of CuSO₄ was added

such that the ratio of Cu²⁺ to Cd²⁺ 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.

3. Results and Discussion

The Cu²⁺(H₂O)₆ complex in isolation has the structure of a tetragonally distorted octahedron with a static JT distortion. The EPR spectra of Cu²⁺ doped in zinc Tutton's salt indicates that the structure of Cu²⁺(H₂O)₆ complex deviates considerably from D_{2h} symmetry due to lattice forces. For this reason, it is worthy to discuss the crystallographic data of Tutton's salts. The exact structure of the Cu²⁺(H₂O)₆ complex in cadmium Tutton's host lattice is not known but many researchers have worked on undiluted Tutton's salts and selected relevant results are given Table 1.

Table 1: Bond lengths of some Tutton's salts M²⁺(M⁺)(SO₄)₂·6H₂O

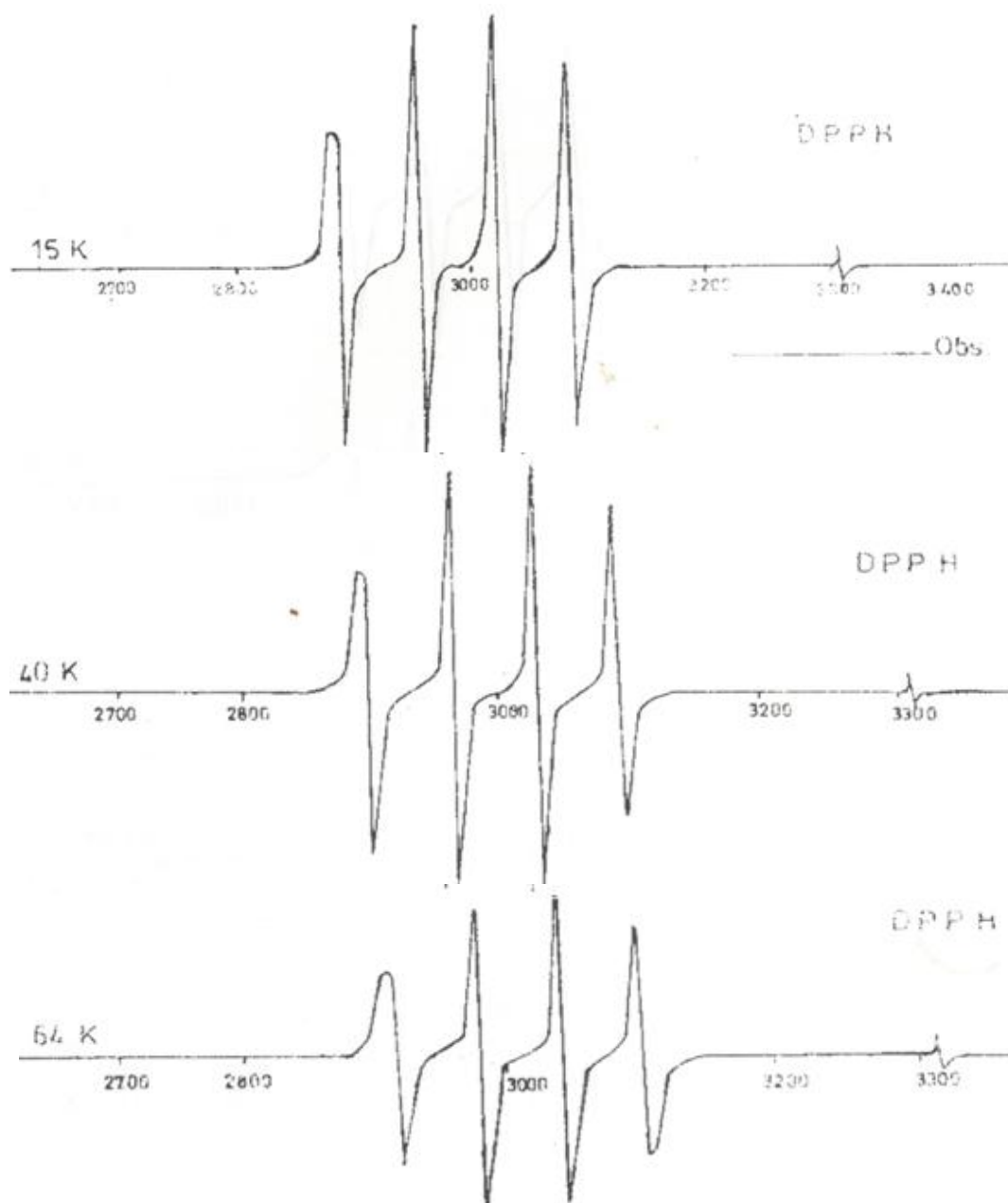
M ²⁺	M ⁺	Cu-O ₇	Cu-O ₈	Cu-O ₉	References
Cu	K	2.069	2.278	1.940	Robinson and Kennard (1972)
Cu	NH ₄	2.230	2.072	1.968	Brown and Chidambaram (1969)
Cu	NH ₄	2.219	2.095	1.961	Montgomery and Lingafelter (1966)
Mg	K	2.103	2.118	2.056	Kannan and Viswamitra (1965)
Mg	NH ₄	2.093	2.073	2.051	Magulis and Templeton (1962)
Zn	NH ₄	2.219	2.117	2.075	Montgomery and Lingafelter (1965)

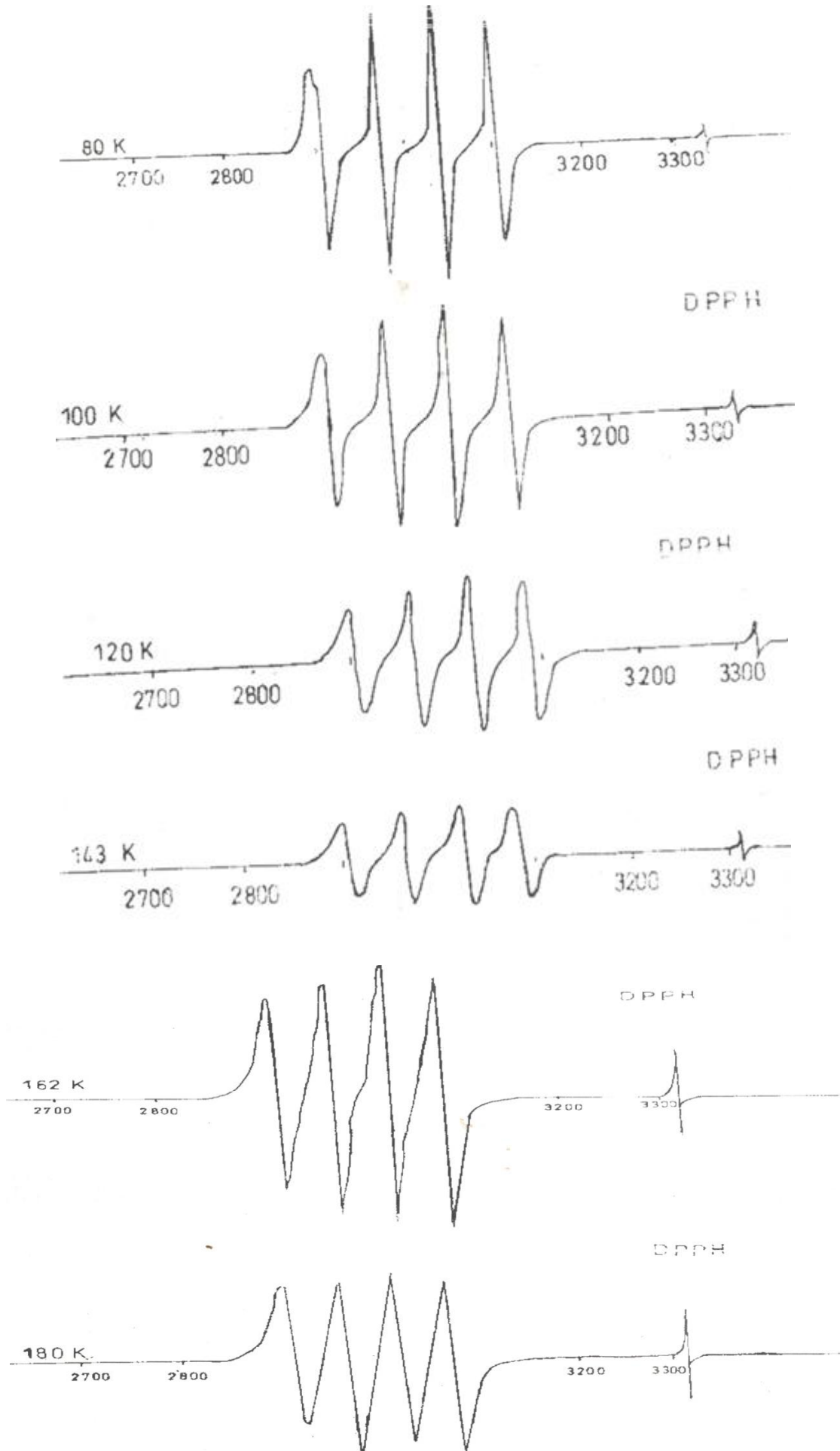
In this paper, the data for cadmium Tutton's salt is not available but were derived from existing data (Table 1) by analogy to the nature of Cd₂(NH₄)₂(SO₄)₃·6H₂O lattice. In Cu²⁺ salts the six oxygen atoms are arranged in the form of elongated octahedron with a rhombic distortion. In all the salts, the shortest bond is linked to O(9) but in Zn²⁺ and Mg²⁺ salts, the arrangement of the atoms is closer to that of a compressed octahedron. Also, it is observed that the relative bond lengths of O(7) and O(8) increase in going from NH₄⁺ to K⁺. Therefore, by analogy, one can assume that for cadmium ammonium Tutton's salt, the bond to O(8) is shorter than to O(7), which is similar to one found in Zinc ammonium salt. The shortest of the bond to O(9) is due to the proximity of another oxygen to O(9).

Fig. 1 represents the experimental CASH spectra in the (111) direction when the crystal was rotated 60° off the parallel axis in plane 1. The spectra at 60° orientation show four unresolved hyperfine lines 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 rate as a function of temperature. With this orientation fixed, the crystal was cooled to 15 K and the four lines remained unchanged except for the gradual increase in the normalized intensity (Table 2). This direction may be identified as the [111] axis of the Cu²⁺:6H₂O octahedra. This feature is common with many systems exhibiting JT effect (De, 1986, 1987, 1988).

In practice, the appearance of parallel and perpendicular lines along (110) direction and convergence of these lines into one set of hyperfine lines along (111) direction at low temperatures and the isotropic nature of the lines at room temperature indicate that $\text{Cu}^{2+}:\text{CASH}$ is a JT system. The g and A values decrease with increasing temperature in (110) and (111) directions. The change in the EPR line shape (complete disappearance of the g_{\perp} lines while warming from the low temperature at about 71 ± 1 K in the (100) shows the possibility of a second order phase transition in the crystal. There is need for further investigation to ascertain whether the gradual splitting of the Cu^{2+} hyperfine lines with temperature starting from 180 K is a JT transition 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 $\text{Cu}^{2+}:\text{CASH}$ as a function of Cu^{2+} ion concentration is recommended for further investigations.

Fig. 2 represents the observed EPR in the (100) direction 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 (i.e., g_{\parallel} axis) 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). With the (100) axes, all the spectra from differently oriented Cu^{2+} ions would merge and one would observe only one set of four hyperfine lines with g and A values given by equations (1) and (2).





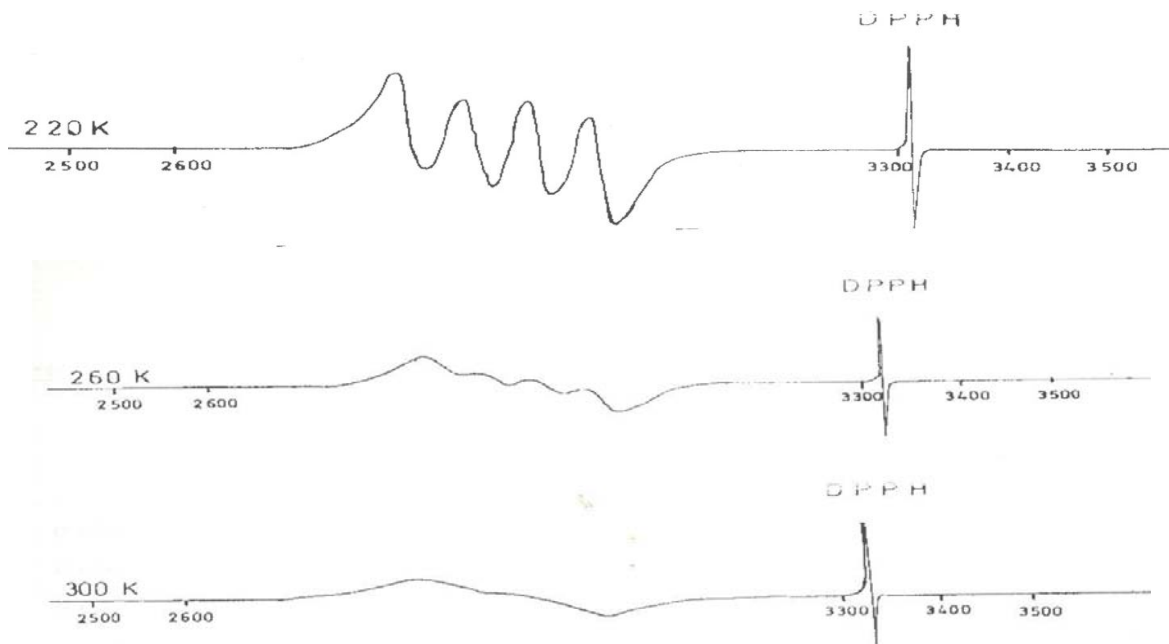


Figure 1: Temperature variation of the experimental EPR spectra of Cu(II) in CASH in (111) direction (plane 1) with magnetic field 60° off the parallel axis

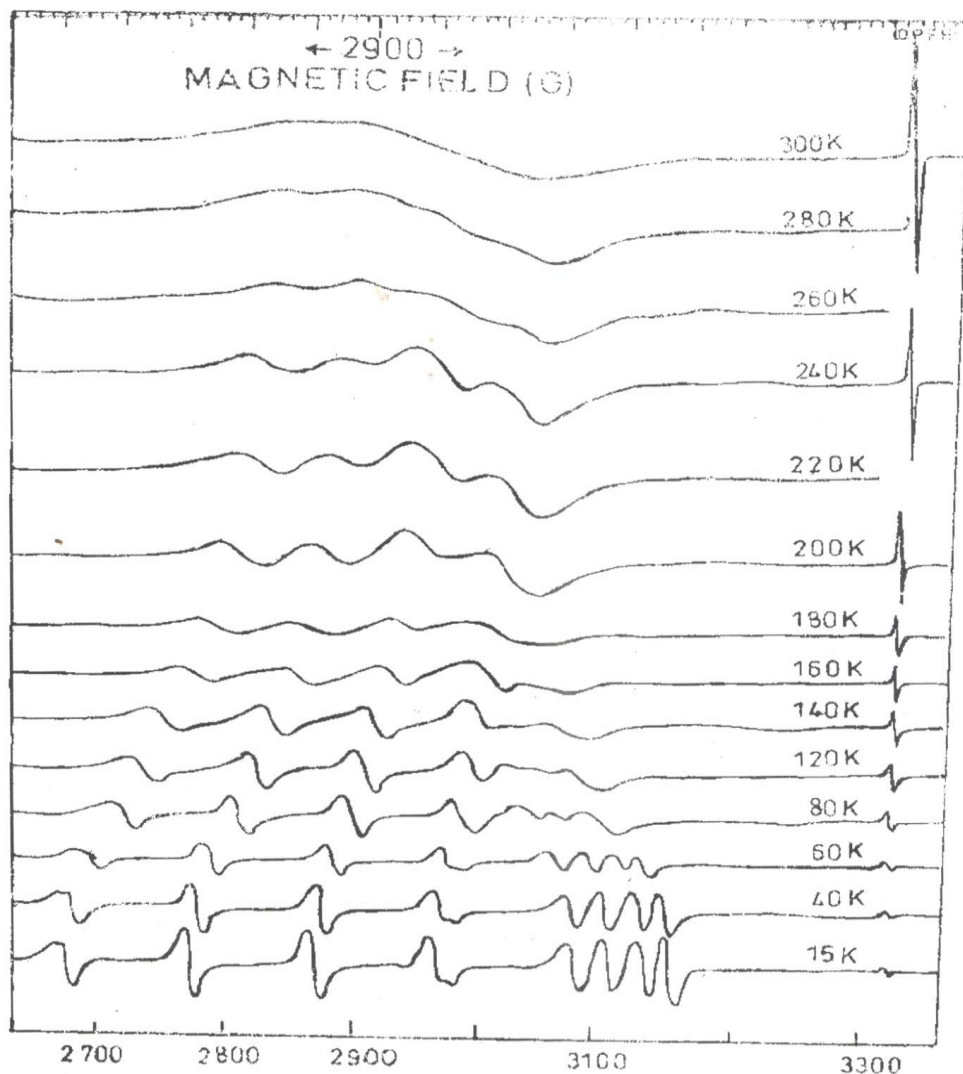


Figure 2: Temperature variation of EPR spectra of Jahn-Teller effect of Cu²⁺ doped in CASH in the (100) direction (plane 2)

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° 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 Cu²⁺ spectra in JT systems with axial g and A values (Ziatdnov *et al.*, 1976; De *et al.*, 1984; Rubins *et al.*, 1984). 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 (De *et al.*, 1984; Rubins *et al.*, 1984). The evolution of spin Hamiltonian parameters with temperature can yield a host of information on the solid state interactions in the system. The observed characteristics of the EPR spectra suggests that this crystal is a static JT system and the (111) axis of the [Cu, 6H₂O] coordination lies about 5° from the long axis of the crystal with axial g and A tensors like that of ZnTiF₆·6H₂O and Zn(BrO)₂·6H₂O crystals. This is different from Cu²⁺:CAS crystals where orthorhombic g and A tensors have been observed (Yerima *et al.*, 2014). The splitting of the hyperfine lines increased slightly with lowering of temperature. The resolved hyperfine lines occurring at lower side of the field correspond to g_{\parallel} and A_{\parallel} in the (100) direction. The CASH EPR spectra at different temperatures show axial symmetry i.e. $g_x = g_y$ and $A_x = A_y$. At points of inflection or zero line shape the values of g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} in the (111) direction at different temperatures were computed using the following equations

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

$$A_{\parallel} = \frac{H_{3/2} - H_{-3/2}}{3}$$

$$A_{\perp} = \frac{H_{3/2} - H_{-3/2}}{3} \cdot 2$$

where H_{\parallel} and H_{\perp} are sets of magnetic field values in the low and high magnetic field sides respectively each has value half way between two fields $H_{-1/2}$ and $H_{1/2}$ corresponding to zero line shape for quantum magnetic numbers $m = -1/2$ and $m = 1/2$ while H_m are two magnetic field values corresponding to the first ($m = -3/2$) and last ($m = 3/2$) zero line shape in each set of the spectrum in the low and high magnetic fields.

For a true static JT system the parameters $g_{\langle 111 \rangle}$ and $A_{\langle 111 \rangle}$ in the (111) direction is related to the g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} as follows:

$$g_{\langle 111 \rangle}^2 = \frac{g_{\parallel}^2 + 2g_{\perp}^2}{3}$$

$$A_{\langle 111 \rangle}^2 = \frac{g_{\parallel}^2 + 2g_{\perp}^2 A_{\parallel}^2}{3g_{\langle 111 \rangle}^2} \cdot 4$$

Now, using the values of H_{\parallel} , H_{\perp} and H_m deduced from the observed spectra in equations (1) and (2) the g and A values (g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp}) were calculated and finally putting these values in equations (3) and (4) we obtained the $g_{\langle 111 \rangle}$ and $A_{\langle 111 \rangle}$ values in the (111) direction at different temperatures (Table 2). The observed mean values of $g_{\langle 111 \rangle}$ and $A_{\langle 111 \rangle}$

Table 2: Spin Hamiltonian parameters from observed CASH spectra in the (111) direction

T±1 K	$g_{\langle 111 \rangle}$	$A_{\langle 111 \rangle}$	ΔH_{pp}	I_N
15	2.2184	67	5	11.900
40	2.2129	65	10	3.600
80	2.2055	65	10	3.400
120	2.2000	62	10	1.050
140	2.1946	58	10	1.050
160	2.2092	55	15	0.180
180	2.2055	53	25	0.098

respectively are 2.23±0.01 and 75±2 G while the calculated values from equations (3) and (4) respectively are 2.22±0.01 and 74±2 G which are in good agreement within experimental error. The experimentally determined values of g_{\parallel} , g_{\perp} , A_{\parallel} and A_{\perp} at the lowest attainable temperature, say 15 K in this case, can be used to determine other important solid state parameters of the system (Ham, 1972; Boatner *et al.*, 1977) such as g_1 , g_2 , A_1 , A_2 , Δ , q , α and λ . The theory and the method of determination of these solid state parameters are in progress and will be reported separately.

4. Conclusion

The EPR of Cu²⁺:CASH single crystals at various temperatures in the range 300-15 K has been reported. The spin Hamiltonian parameters (g_{\parallel} , g_{\perp} , A_{\parallel} , A_{\perp} , $g_{\langle 111 \rangle}$, $A_{\langle 111 \rangle}$) were determined using the values of H_{\parallel} , H_{\perp} and H_m extracted from the observed EPR spectra. The analysis of the data shows convincing evidence for the presence of static JT effect in this system. Similar to other known JT systems (Rubins *et al.*, 1984), the anisotropy in the g and A hyperfine tensor components increase with decreasing temperature. Likewise the A_{\parallel} and A_{\perp} values are similar to those in other JT systems (De *et al.*, 1984; Rubins *et al.*, 1984; Rubins and Drumheller, 1987) while the g_{\parallel} and g_{\perp} are somewhat dissimilar. The spin-orbit reduction parameter is lower in the present system compared to that of Cu²⁺:ZnTiF₆·6H₂O signifying parameter higher covalent reduction of spin-orbit interaction parameter of the Cu²⁺. This may be due to differences in the structural configurations of the neighbouring ligands surrounding the paramagnetic Cu²⁺ ion in CASH and other related systems. It can be clearly seen in Table 1 that the Cu-H₂O bond lengths in three directions in many Tutton's salts are not equal while in familiar static JT systems they are equal (Ziatdnov *et al.*, 1976; De *et al.*, 1984; Rubins *et al.*, 1984; De, 1987). Thus, in CASH it is possible that Cu-H₂O bond lengths are different in the three directions which may be responsible for the observed differences in the g-values. However, for detailed account on the difference in site symmetry we recommend precise x-ray measurements. In this crystal, the EPR spectra manifests gradual splitting of the Cu²⁺ hyperfine lines at 181±1 K which could be a signature for a possible second order phase transition. However, further investigation is recommended to ascertain whether the gradual splitting of Cu²⁺ hyperfine lines at this temperature is a JT transition even though JT transition has never been reported at such high temperature at least in the systems so far studied (Gebhardt, 1969; Ham, 1972; Englman, 1972; Thomas, 1977; Reinen, 1991). This

particular observation could be related to significant reduction in spin-lattice relaxation rate at this temperature. In this vein, to throw more light on this, detailed EPR or any other allied techniques is required to study CASH spectra as a function of Cu^{2+} concentrations.

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