

# ESR STUDY OF DIBARIUM COPPER FORMATE TETRAHYDRATE

## Part II. Optical Absorption and Temperature Dependence of Spin-Hamiltonian parameters

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### ABSTRACT

The variations in certain spin-Hamiltonian parameters of the  $\text{Cu}^{++}$  ion in dibarium copper formate tetrahydrate with temperature have been studied. Optical absorption investigations on single crystals of the salt at room temperature and  $90^\circ\text{K}$ . are reported. The results are discussed in terms of a model in which vibronic mixing of certain electron levels of the  $\text{Cu}^{++}$  ion play an important role.

### INTRODUCTION

ESR investigations of single crystals of dibarium copper formate tetrahydrate diluted with the isomorphous zinc compound, reported in Part I (Reddy and Srinivasan, 1967), showed that the spin-Hamiltonian parameters at  $90^\circ\text{K}$ . are significantly different from those at room temperatures. This temperature dependence of the spin-Hamiltonian parameters has been studied more closely and an explanation has been given for this in terms of vibronic effects whereby vibrations of the ligand octahedron of certain symmetries mix the upper  $3d_{z^2}$  level into the ground  $3d_{x^2-y^2}$  level. (Reddy and Srinivasan, 1966). The observed  $g$ -value is a resultant of the  $g$ -values of the states weighted according to the amount of mixing, which depends on the temperature.

These effects have so far not been reported in literature and even in the few cases (Bowers and Owen, 1955; Gerritson and Sabisky, 1962; Sroubek and Zdansky, 1966) where different  $g$ -values have been reported at different temperatures of investigation, a systematic investigation has not been attempted. DBCF has been very favourable for such investigations, as it has only one molecule per unit cell with near tetragonal symmetry around the  $\text{Cu}^{++}$  ion. Further the crystal does not show any change in gross crystal

structure or in molecular arrangement with changes in temperature, in contrast to the situation in copper Tutton salts (Bowers and Owen, 1955) where there appears to be a change in the orientation of the principal axes of the  $\text{Cu}^{++}$  ion at low temperatures.

Polarised optical absorption investigations have also been carried out on single crystals of DBCF to supplement the ESR results.

### ESR STUDY

*Experimental arrangements.*—ESR measurements have been carried out at four different temperatures, *viz.*, 340° K., 301° K., 203° K. and 90° K. The ESR spectrometer used has been described in Part I. The  $H_{011}$  rectangular brass cavity was used for the work at elevated temperatures and the  $H_{111}$  cylindrical perspex cavity, silvered inside, has been used for measurement at low temperatures. For investigations at 340° the cavity was enclosed in a double-walled glass jacket. Alcohol was kept boiling in the interspace between the walls, by means of a heater wound on the outside of the outer jacket. Arrangements were made to condense the alcohol vapours back into the jacket. The temperature was measured by means of a copper-constantan couple, placed at the bottom of the cavity outside it and very near the sample. For work at 203° K. a bath of mixture of solid  $\text{CO}_2$  and alcohol was employed and the cavity was directly dipped into the mixture contained in a double-walled dewar.

*Measurements and Results.*—The temperature variation of only the parameters  $g_{\parallel}$  and  $A$  has been studied as these parameters could be obtained accurately. The crystal was therefore mounted in the  $g_{\parallel}$  direction and the measurements were made at various temperatures. A careful check was also made of any possible change in the orientation of the crystal or in the principal axis direction as the temperature was varied. Further the changes in ESR spectra due to the variation in temperature were completely reversible. The values of the parameters  $g_{\parallel}$  and  $A$  are given in Table I.

### OPTICAL ABSORPTION STUDIES

*Experimental arrangement.*—Investigations of polarised optical absorption in single crystals of DBCF have been carried out both at room temperature and 90° K. At room temperature the spectra have been recorded using a Beckmann spectrophotometer. A slit of the same size as the crystal was kept in the blank. A polaroid sheet was employed for the polarization studies and it covered the blank slit as well as the crystal simultaneously. Investigations at 90° K. have been made by conduction cooling the crystal

placed in vacuum. The spectra in this case were recorded by means of a Feuss spectrograph using a tungsten filament lamp as the source and recording the spectrum photographically.

TABLE I  
*g<sub>||</sub> and A values at different temperatures*

Sl. No.	Temperature	$G_{  }$	$A \times 10^4 \text{ cm.}^{-1}$	$x^2$	Calculated $A \times 10^4 \text{ cm.}^{-1}$
1	340° K.	2.328	89	0.165	91
2	301° K.	2.340	98	0.14	98
3	203° K.	2.370	117	0.06	119
4	90° K.	2.390	131	0.012	131

*Measurements and Results.*—The crystals employed in the optical absorption studies were in the form of thin plates of less than 1 mm. thickness and  $5 \times 5 \text{ mm.}^2$  cross-section. Such crystals were obtained by picking them out during the early stages of crystallization. They were ideal for the optical absorption studies as no grinding or polishing was necessary. The crystals were very transparent indicating the absence of any strong absorption in the visible region.

The flat face of the crystal was found to be the *bc*-plane and the ESR results, described in Part I, have shown the tetragonal axis lies in this plane. This made possible a direct study of the polarization characteristics of the absorption bands. In fact, the crystal when viewed under polarised light changed in colour from blue to almost colourless as the direction of polarisation was changed in the *bc*-plane of the crystal. This indicated that the absorption in the visible region was strongly polarised. The optical absorption studies have therefore been carried out in this plane using (1) unpolarised light, (2) polarised light with the electric vector along the tetragonal axis and (3) polarised light with the electric vector perpendicular to tetragonal axis. Fig. 1 shows the optical absorption spectra at room temperature of DBCF for the above three cases, obtained using the Beckmann spectrophotometer. The unpolarised spectrum clearly indicates a band at  $13,330 \text{ cm.}^{-1}$  ( $750 \text{ m}\mu$ ) with a shoulder at  $11,050 \text{ cm.}^{-1}$  ( $905 \text{ m}\mu$ ). The polarised spectrum shows that the band at  $13,330 \text{ cm.}^{-1}$  is strongly polarised. This

band is strongly present when the polarisation is perpendicular to the tetragonal axis and forbidden when it is parallel. The shoulder at  $11,050\text{ cm.}^{-1}$  seems to be almost unaffected by the polarization. In fact, this band shows up more clearly when the other band is forbidden.

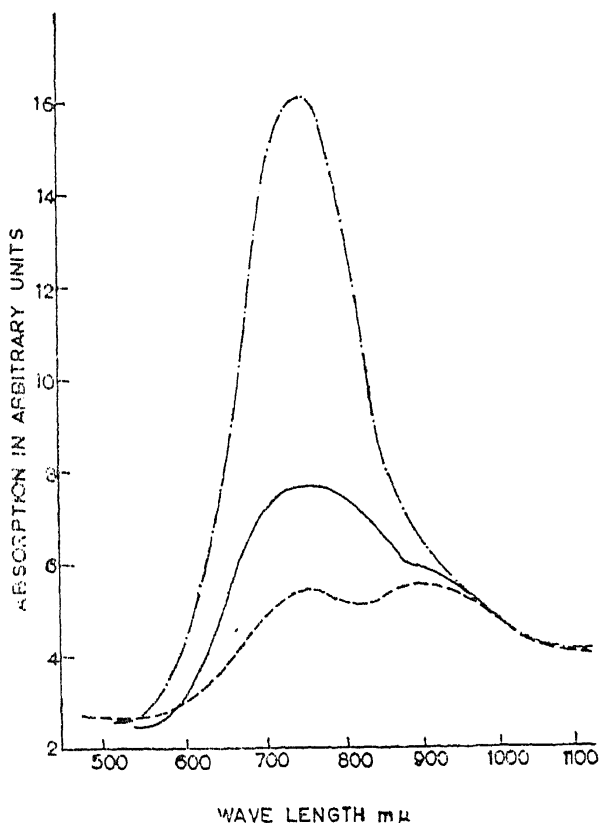


FIG. 1. Optical absorption in the  $bc$ -plane in single crystal of DBCF. — Unpolarised, ---- Electric vector parallel to the tetragonal axis, -·-·-·- Electric vector perpendicular to the tetragonal axis.

The results thus indicate that the band at  $13,330\text{ cm.}^{-1}$  is  $(x, y)$  polarised whereas the band at  $11,050\text{ cm.}^{-1}$  is unpolarised.

The crystal structure of DBCF shows that the  $\text{Cu}^{++}$  ion is at the centre of symmetry. Under such conditions the  $d-d$  transitions should be forbidden in the absence of odd vibrations of the octahedron of ligands surrounding the  $\text{Cu}^{++}$  ion. These odd vibrations violate the centre of symmetry around the  $\text{Cu}^{++}$  ion instantaneously and the transitions become allowed. The  $d-d$  transitions which are allowed due to the vibronic interaction are in general weak and the intensities are temperature dependent (Liehr and Ballhausen, 1957), the intensity of the absorption band falling off as the temperature is lowered.

The optical absorption investigations at liquid oxygen temperature confirmed that the transitions are allowed by vibronic couplings. No

change in the position of the absorption band was observed on cooling. The spectra were recorded using a Feuss spectrograph on the same photographic plate under identical conditions at (1) room temperature first, (2) then at liquid oxygen temperature and (3) again after warming the crystal to room temperature, keeping all the other parameters like optical arrangement, time of exposure, etc., same. The results indicated that the intensity of the optical absorption bands decreased considerably at 90° K. compared to room temperature, and that this change was completely reversible. This clearly indicated that the observed  $d-d$  transitions had become allowed through vibronic coupling.

*Discussion.*—Assuming tetragonal symmetry around the  $\text{Cu}^{++}$  ion, as indicated by ESR results, the point group symmetry of the  $\text{CuO}_6$  complex can be taken to be  $D_{4h}$  and the selection rules for the  $d-d$  transitions can be worked out (Cotton, 1963). In  $D_{4h}$  symmetry, the  ${}^2D$  ground term for the  $\text{Cu}^{++}$  ion splits up into the levels  $B_{1g}$ ,  $A_{1g}$ ,  $B_{2g}$ ,  $E_g$ . With the ground state as  $B_{1g}$ , the following transitions can be visualised:  $B_{1g} - A_{1g}$ ,  $B_{1g} - B_{2g}$ ,  $B_{1g} - E_g$ .

The representation for the pure electronic dipole integral for various transitions can then be evaluated; the absence of the  $A_{1g}$  representation in the product clearly indicates that the transitions as such are forbidden. The consideration of vibronic coupling however, brings about the transitions, if the representation for any normal mode of vibration of the octahedron, *i.e.*,  $A_{1g}$ ,  $A_{2u}$ ,  $B_{1g}$ ,  $B_{1u}$ ,  $B_{2g}$ ,  $E_g$ ,  $E_u$ , occurs in the product representation for the electronic dipole integral. The selection rules can now be readily written down for the various transitions and they are given in Table II.

TABLE II  
*Selection rules for the d-d transitions*

Transition	Polarization with vibronic coupling	
	$z$	$(x, y)$
$B_{1g} - A_{1g}$	Forbidden	Allowed
$B_{1g} - B_{2g}$	Forbidden	Allowed
$B_{1g} - E_g$	Allowed	Allowed

Using the selection rules given in Table II the bands at  $13,330\text{ cm.}^{-1}$  and  $11,050\text{ cm.}^{-1}$  have been assigned as the  $B_{1g} - B_{2g}$  and  $B_{1g} - E_g$  transitions respectively; the former being  $(x, y)$  polarised and the latter unpolarised. The band corresponding to  $B_{1g} - A_{1g}$  occurs at much longer wavelength and further it is not involved in the interpretation of the ESR results. These results are later used in the calculation of the  $g$ -values.

#### DISCUSSION OF THE RESULTS

As already mentioned the temperature dependence of the spin-Hamiltonian parameters has been explained as due to vibronic effects. The effects of the change in the mean position of the ligands with temperature due to anharmonic vibration is too small to explain our results (Englman, 1960). Optical absorption investigations did not indicate any shift in the peak of absorption band on cooling to liquid oxygen temperatures, appreciable enough to explain the change in the  $g$ -values. Another model where the change in the covalency with temperature is considered also cannot explain the observed results. This is because one expects the covalency in the  $[\text{CuO}_6]$  complex to increase as the temperature is lowered, due to decrease in the metal ligand distance. This in turn should cause the  $g$ -values to approach the free spin value whereas the observed variation is in the other direction.

Hence we conclude that the temperature dependence of the  $g$ -values is due to vibronic effects. In fact, the observation of the reduced intensity of the optical absorption bands on cooling indicates pronounced vibronic mixing of the electronic levels of the  $\text{Cu}^{++}$  ion.

The  $\text{Cu}^{++}$  ion in dibarium copper formate tetrahydrate is in a tetragonally distorted elongated octahedron. The resulting ground state under this static distortion is  $3d_{x^2-y^2}$ . If the tetragonal distortion is small, the next excited state  $3d_{z^2}$  is fairly close to the ground state, compared to the other excited  $d\epsilon$  states ( $d_{xy}$ ,  $d_{yz}$ ,  $d_{xz}$ ), which are separated from the ground  $d\gamma$  state by the octahedral splitting. Spin-orbit interaction couples the ground state to only the  $d\epsilon$  states, but not to the  $d_{z^2}$  state. However, the  $B_{1g}$  vibrational mode of the octahedron formed by the ligand oxygens, brings about the mixing of the  $3d_{z^2}$  ( $A_{1g}$ ) level into the  $3d_{x^2-y^2}$  ( $B_{1g}$ ) level; the resulting ground state can therefore be written as  $(1 - x^2)^{\frac{1}{2}} d_{x^2-y^2} + x d_{z^2}$ . The amount of mixing depends on the excitation of this mode, which in turn is temperature dependent. The observed  $g$ -value which is a resultant of the  $g$ -values of the two states weighted according to the amount of mixing, depends on temperature,

At the lowest temperatures the mixing of  $3d_{z^2}$  into  $3d_{x^2-y^2}$  is governed by the amplitude of the zero point vibration in the mode. Larger mixing at higher temperatures is brought about by the higher excitation of the  $B_{1g}$  mode corresponding to  $\nu = 1, 2$ , etc. Classically, this would mean higher amplitude of vibration in the  $B_{1g}$  mode. It is a similar effect involving odd vibrational modes that causes the variation of the intensity of the optical absorption with temperature, as pointed out earlier.

*g-values.*—Greater mixing of the  $d_{z^2}$  level into the  $d_{x^2-y^2}$  level at higher temperatures causes a variation of  $g$  value in the right direction since the  $g_{\parallel}$  for  $d_{z^2}$  is smaller than the  $g_{\parallel}$  value for  $d_{x^2-y^2}$ . An estimate of the mixing coefficient  $x^2$  could be made from the following expression for the  $g$ -value, viz.,

$$g_{\parallel} = (1 - x^2) (g_{\parallel})_{x^2-y^2} + x^2 (g_{\parallel})_{z^2}$$

where  $(g_{\parallel})_{x^2-y^2}$  and  $(g_{\parallel})_{z^2}$  represent the  $g_{\parallel}$  values for the states  $3d_{x^2-y^2}$  and  $3d_{z^2}$  respectively. The effect of covalency is taken into account, in calculating the  $g_{\parallel}$  values by considering the reduction in spin-orbit coupling as given by Owen (1955), for ionic copper salts. The results indicate that the mixing of the  $3d_{z^2}$  varies from 1.2% at 90° K. to 16.5% at 340° Table (I).

*Hyperfine parameter.*—The observed values of  $A$  at different temperatures have been fitted to the expression

$$A = (1 - x^2) A_{x^2-y^2} + x^2 A_{z^2}$$

where  $A_{x^2-y^2}$  and  $A_{z^2}$  are the hyperfine splitting constants for the pure  $3d_{x^2-y^2}$  and  $3d_{z^2}$  wave functions respectively; these may be calculated from available optical absorption data and a knowledge of  $\kappa$ , the isotropic hyperfine parameter.  $x^2$  is the mixing coefficient which has already been determined by the variation in  $g_{\parallel}$  with temperature. It has been found that to obtain a fit (Table I), the isotropic hyperfine parameters to be used for the two orbitals  $3d_{x^2-y^2}$  and  $3d_{z^2}$  are very different, i.e.,  $\kappa_{x^2-y^2} = 0.334$  and  $\kappa_{z^2} = 0.086$ . While the value of  $\kappa_{x^2-y^2}$  agrees with those encountered in other  $\text{Cu}^{++}$  ionic salts,  $\kappa_{z^2}$  is very low. This is very surprising at first sight as  $\kappa$ , which normally arises from core polarization of the  $1s$ ,  $2s$  and  $3s$  electrons by the unpaired electron in the  $3d$  shell is not expected to depend so strongly on whether the unpaired electron is in a  $3d_{x^2-y^2}$  or  $3d_{z^2}$  orbital. However, the apparent difficulty disappears when we realise that for the case of  $3d_{z^2}$  orbital another mechanism can contribute to the isotropic hyperfine interaction in addition to core polarization. This is the admixture of the  $\text{Cu}^{++}$  ion  $4s$  orbital into the  $3d_{z^2}$  orbital by the static crystalline field, both

orbitals transforming as the  $A_{1g}$  representation of the  $D_{4h}$  point group. It is suggested that the contribution to  $\kappa$  from the 4s electron has the opposite sign to that from core polarization. Since the  $\kappa_{2^2}$  depends only on the static part of the crystalline field the same value for  $\kappa_{2^2}$  fits the results at all the observed temperatures.

The temperature dependence of the spin-Hamiltonian parameters due to the vibronic coupling discussed above, in principle, should be observable in any ionic copper salt. But, the magnitude of the effect might depend on the strength of the tetragonal distortion of the octahedron around the  $Cu^{++}$  ion, which causes the splitting of the  $d_{x^2-y^2}$  and  $d_{z^2}$  levels. Large tetragonal distortion makes this splitting large, thus causing the effect due to vibronic coupling to be less pronounced. However, a closer examination of the temperature dependence of the spin-Hamiltonian parameters in other tetragonal ionic copper salts may show similar effects of vibronic coupling.

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