ESR STUDY OF DIBARIUM COPPER FORMATE TETRAHYDRATE—PART I

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Abstract

ESR investigations on dilute single crystals of dibarium copper formate tetrahydrate, at room temperature and 90° K. have been described. A general method used for the evaluation of the g-tensor in this triclinic crystal, which contains only one ion in the unit cell, has been discussed. A detailed account of the evaluation of the quadrupole interaction is given. Expressions for the positions of the hyperfine levels of the lowest Kramer's doublet of the Cu^{++} ion in the magnetic field have been worked out for the case when B and Q are of similar magnitude.

Introduction

ESR investigations of a number of copper salts have been reported in the literature so far (Bowers and Owen, 1955; Orton, 1959). However, detailed examinations of ionic copper salts have been limited to the Tutton salts (Bleaney *et al.*, 1955 *a*) and some trigonal copper salts (Bleaney *et al.*, 1955 *b*). In the former case the Cu^{++} ion is in a crystal field of considerable rhombic distortion, while the latter showed dynamic Jahn-Teller distortion at room temperature going over to an apparently static distortion at low temperatures. The simple case of a Cu^{++} ion in a tetragonal crystal field was not studied in detail. Dibarium copper formate tetrahydrate, $Ba_2Cu(HCOO)_6.4H_2O$ was therefore taken up for a detailed study of the copper ion in an ionic tetragonal environment. A detailed investigation of this was possible because the isomorphous diamagnetic zinc salt was available and good mixed single crystals could be grown easily in all proportions. The crystal structure of this has been carried out in our laboratory (Sundara Rao *et al.*, 1958). Another simplifying feature is that there is only one ion per unit cell in the crystal, a rare case for a copper salt. This enabled the investigations to be carried out without the complications that arise from overlapping spectra when there are multiple ions in the unit cell.

Most of the copper salts investigated by ESR in single crystals have contained more than one Cu^{++} ion in the unit cell, the ions becoming magnetically equivalent only in certain specific planes or directions. The existence of such symmetry planes or directions has usually made the measurement of the *g*–tensor straight forward (Bleaney and Stevens, 1953; Bowers and Owen, 1955). However, dibarium copper formate tetrahydrate crystallises in the triclinic system with only one ion in the unit cell. Hence a general method has been adopted to find out the principal directions and values for the *g*-tensor for the Cu^{++} ion. This was done by first measuring the *g*-tensor in a particular orthogonal system of axes defined in the crystal and then diagonalising this to obtain the principal *g*-values.

This paper reports the ESR investigation at room and liquid oxygen temperatures on dibarium copper formate tetrahydrate isomorphously diluted with the corresponding zinc compound. The method for deducing the principal *g*-values and the principal directions for the Cu^{++} ion is given in detail. Considerable spin-lattice interaction at room temperature prevented a complete resolution of the spectrum. The spectrum at 90° K. has good resolution and revealed the presence of forbidden lines indicating considerable quadrupole interaction. Analysis of the spectrum at 90° K. for obtaining the spin-Hamiltonian parameters, in particular the hyperfine and quadrupole parameters, is also given in detail. A temperature dependence of the spin-Himiltonian parameters has been noted and a systematic investigation of this has been carried out. These investigations along with the supplementary optical absorption studies are reported in Part II of the paper.

PREPARATION AND CRYSTAL STRUCTURE

Well-developed single crystals of dibarium copper formate tetrahydrate (DBCF) were grown by slow evaporation of a water solution of barium formate and copper formate in 2 : 1 molar ratio, in the presence of formic acid. The pale blue crystals of DBCF belong to the triclinic pinacoidal class, space group $P\bar{1}$ with $z = 1$ and $a = 8{\cdot}75$ Å, $b = 7{\cdot}16$ Å, $c = 6{\cdot}88$ Å, $\alpha = 99° 3'$, $\beta = 109° 2'$, $\gamma = 82° 20'$ (Sundara Rao *et al.*, 1958). The isomorphous zinc compound, dibarium zinc formate tetrahydrate (DBZF) was crystallized likewise. Mixed crystals of DBZ-CF with varying proportions of Cu : Zn have been grown for the ESR studies. The crystals grew either in parallelepipeds elongated along the *c*-axis with the (100) and (010) planes well developed or in plates with the flat face as the *bc*-plane.

Experimental Details

Investigations were carried out using a X-band reflection type ESR spectrometer designed and constructed in our laboratory; it employs 100 kc./s. magnetic field modulation followed by phase sensitive detection. A H_{011} rectangular brass cavity and a H_{111} cylindrical perspex cavity which has been silvered inside, have been used for the investigations at room temperature and 90° K. respectively. The current for the magnet is derived from a motor-generator with externally excited field coils. An electronic current stabilizer employing feed back through the excitor of the generator has been used to regulate as well as to sweep the current through the magnet. The derivatives of the ESR signals could be displayed on one of the beams of a double beam oscilloscope using a large 50 c/s. magnetic field modulation and the line centres measured using a proton resonance meter by simultaneously displaying the proton resonance signal on the second beam of the oscilloscope. The proton resonance frequency is measured using a Signal Corps Frequency meter BC 221–AH. The signals could also be recorded on a strip chart recorder using a slow sweep of the magnetic field. The magnet is mounted on a turn table and can be rotated about the vertical axis. This enables the angular variation of the spectrum to be studied.

Room Temperature Study—Deduction of the Principal *g*-Values

The ESR measurements have been made on single crystals of DBZ-CF with Zn : Cu = 200 : 1 approximately. This reduced the line widths from the spin-spin interaction considerably and helped the resolution of the hyperfine structure from the copper nucleus. However, even with this dilution the hyperfine structure was not fully resolved along any direction; the use of crystals with further dilution did not improve the resolution, but only caused the expected reduction in the intensity. The line widths were of the order of 30 gauss between points of maximum slope. In all directions the spectrum consisted of one set of lines or line as expected, since there is only one ion in the unit cell. A recording of the spectrum along the $g_{max.}$ direction in the *bc*-plane of the crystal of DBZ-CF with Zn : Cu = 200 : 1, is shown in Fig. 1.

For the evaluation of the *g*-tensor a set of orthogonal axes a^*, b^*, c^* has been chosen; these are related to the crystallographic axes *a*, *b*, *c* as follows: $c^* \equiv c$-axis, b^* is in the *bc*-plane and perpendicular to the *c*-axis, a^* is perpendicular to the $b^*c^* (\equiv bc)$ plane. The angular variation of the ESR spectrum has been studied in the following planes: $b^*c^* (\equiv bc)$ plane, a^*b^* plane (a plane perpendicular to the *c*-axis) and the *ac*-plane.

Single crystals that grew in the form of a parallelepiped with (100) and (010) faces well developed and elongated along the *c*-axis have been used for the measurements. Use of such a crystal simplified the problem of grinding it into a rectangular parallelepiped, a plane having to be ground perpendicular to a prominent crystallographic axis.

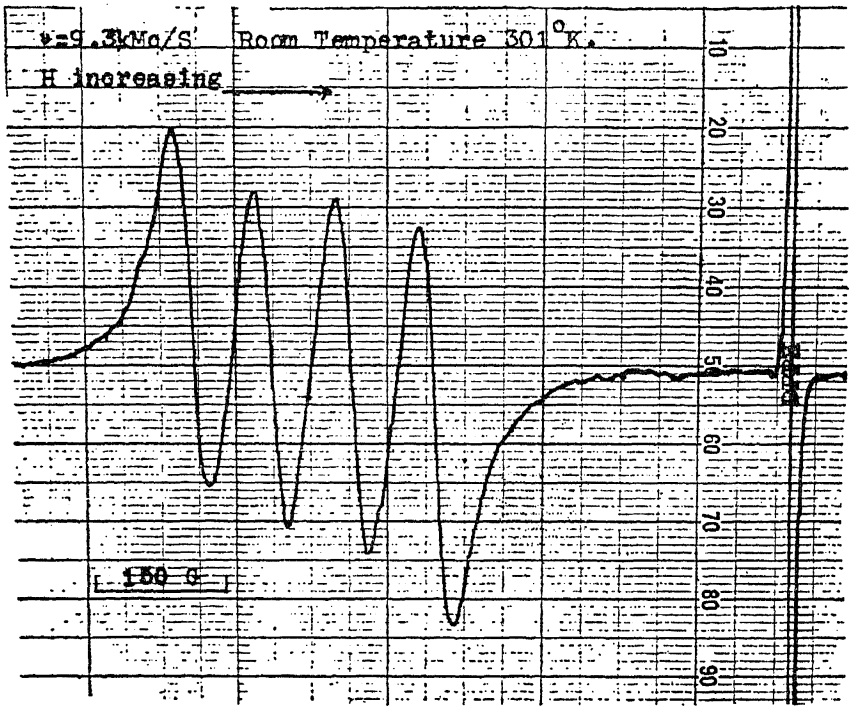

FIG. 1. Recording of the ESR spectrum from DBZ-CF (Zn : Cu = 200 : 1) at room temperature, with magnetic field parallel to the tetragonal axis.

Measurements have been made on the positions of the line centres for every 10° in each of the planes mentioned above. *g*-values have been calculated from the mean positions of the hyperfine lines. DPPH was used as the *g*-marker ($g = 2{\cdot}0036$). The *g*-tensor in the orthogonal basis $a^*b^*c^*$ has then been evaluated as follows.

If l_1, l_2, l_3 are the direction cosines of the magnetic field with respect to the $a^*b^*c^*$ axes, we have

$$g^2 = \sum_{\substack{i,j \\ 1,2,3}} R_{ij} l_i l_j = R_{11} l_1^2 + R_{22} l_2^2 + R_{33} l_3^2 + 2R_{12} l_1 l_2 + 2R_{23} l_2 l_3 + 2R_{13} l_1 l_3 \qquad (1)$$

R_{ij}'s are the components of the g^2 tensor [R] with respect to the $a^*b^*c^*$ system.

In the b^*c^* (bc) plane, if θ is the angle between the magnetic field and the c-axis

$$l_1 = 0,\ l_2 = \sin\theta \quad \text{and} \quad l_3 = \cos\theta$$

then

$$g^2 = R_{22}\sin^2\theta + R_{33}\cos^2\theta + 2R_{23}\sin\theta\cos\theta. \tag{2}$$

The g-values along the c^* ($\equiv c$) axis and the b^* axis give R_{33} and R_{22}. From $g_{max.}$ and $g_{min.}$ in this plane, using Eq. (2), the mean value of R_{23} is evaluated. Using this value and the values of R_{22} and R_{33} in Eq. (2), the angular variation of g^2 versus θ is calculated and by least squares fitting to the experimental g^2 variation, the value of R_{23} is obtained for the best fit. The values obtained were

$$R_{22} = R_{33} = 4{\cdot}95 \quad \text{and} \quad R_{23} = 0{\cdot}5307.$$

In the a^*b^* plane, if ϕ is the angle between the magnetic field and the b^* axis, then $l_1 = \sin\phi$, $l_2 = \cos\phi$ and $l_3 = 0$, so that

$$g^2 = R_{11}\sin^2\phi + R_{22}\cos^2\phi + 2R_{12}\sin\phi\cos\phi. \tag{3}$$

The value of R_{22} is taken from the b^*c^* plane. R_{11} is obtained from the g-value along the a^* axis. As in the b^*c^* plane, the value of R_{12} is obtained by fitting the variation of g^2 in this plane to the Eq. (3). This gave $R_{11} = 4{\cdot}50$, $R_{12} = 0$.

In the ac-plane along a-axis, the expression for g^2 contains all the coefficients, of which five are already known. Further, the direction cosines of the a-axis with respect to $a^*b^*c^*$ axis are known and are given by

$$l_3^a = \cos\beta = -0{\cdot}3313;\ l_2^a = \cos\gamma\cos(\alpha - 90^\circ) = 0{\cdot}1317;$$

$$l_1^a = [1 - (l_3^a)^2 - (l_2^a)^2]^{\frac{1}{2}} = -0{\cdot}9343.$$

Using the value of g^2 along the a-axis the sixth coefficient R_{13} is obtained as 0·0415.

The g^2 tensor [R] with respect to the co-ordinate system $a^*b^*c^*$ is therefore

$$[R] = \begin{bmatrix} R_{11} & R_{12} & R_{13} \\ R_{12} & R_{22} & R_{23} \\ R_{13} & R_{23} & R_{33} \end{bmatrix} = \begin{bmatrix} 4{\cdot}50 & 0 & 0{\cdot}0415 \\ 0 & 4{\cdot}95 & 0{\cdot}5307 \\ 0{\cdot}0415, & 0{\cdot}5307, & 4{\cdot}95 \end{bmatrix}$$

The principal values for the g^2 tensor have been obtained by diagonalising the above tensor [R] by solving $| R - \lambda I | = 0$ for λ. The solutions for λ of the resulting cubic equation give the three principal values for g^2. The principal g-values for the Cu^{++} ion thus obtained are $g_z = 2{\cdot}341$, $g_x = 2{\cdot}123$ and $g_y = 2{\cdot}100$.

The g-values indicate a tetragonal symmetry with a small rhombic component, around the Cu^{++} ion. The difference between g_x and g_y is however only slightly greater than the experimental error, suggesting that the rhombic distortion is not significant. The symmetry around the Cu^{++} ion can therefore be taken to be tetragonal within the experimental errors, with the principal g-values: $g_{\parallel} = 2{\cdot}341 \pm 0{\cdot}005$ and $g_{\perp} = 2{\cdot}11 \pm 0{\cdot}01$. The considerable error along the $g_{\perp}$ direction is due to the large line width along this direction due to unresolved hyperfine structure.

Using the relation: $R_{ii} = g_{\parallel}^2 \cos^2\theta_i + g_{\perp}^2 \sin^2\theta_i$, where $i = 1, 2, 3$ for a^*, b^*, c^* axes, θ_i's the angles the tetragonal axis makes with the three orthogonal axes a^*, b^* and c^* have been found to be 79°, 46° and 46°.

Another interesting feature is that the $g_{gmx.}$ in the bc-plane has been found to be very close to the $g_{\parallel}$ showing that the tetragonal axis lies almost in the bc-plane. In fact the angle α which the tetragonal axis makes with the bc-plane is calculated to be 3° 40′, from the relation $\cos^2\alpha = (g^2_{max.} - g_{\perp}^2)/(g_{11}^2 - g_{\parallel}^2)$. Actually the measurements of the g-values around the $g_{max.}$ direction in the bc-plane by tilting the crystal in a vertical plane (perpendicular to the bc-plane) containing the $g_{max.}$ direction, indicated that the tetragonal axis lies in the bc-plane, within the experimental errors.

In the light of the above result, the hyperfine parameters have been obtained from the measurements in the bc-plane. The mean hyperfine separation with the magnetic field along the tetragonal axis gave the value of A. The value of B could not be obtained likewise, because of lack of resolution in the $g_{\perp}$ direction. So the parameter B was determined by fitting the angular variation of the hyperfine separation K in the plane to the following expression

$$K^2g^2 = A^2g_{\parallel}^2 \cos^2\theta + B^2g_{\perp}^2 \sin^2\theta$$

where θ is the angle from the tetragonal axis. The value of A and B for the best fit are $A = 98 \times 10^{-4}$ cm.$^{-1}$ and $B \sim 30 \times 10^{-4}$ cm.$^{-1}$ This value of B is only an estimate. An accurate determination has been possible only at 90° K. and is described later in this paper.

Summing up, the ESR spectrum from the Cu^{++} ion in dibarium zinc-copper formate tetrahydrate, at room temperature, has been fitted to the following spin-Himiltonian having tetragonal symmetry with $S = \frac{1}{2}$ and $I = 3/2$.

$$\mathcal{H} = g_{\parallel}\beta H_z S_z + g_{\perp}\beta (H_x S_x + H_y S_y) + A S_z I_z + B (S_x I_x + S_y I_y)$$

where

$$g_{\parallel} = 2{\cdot}341 \pm 0{\cdot}005; \qquad A = (98 \pm 2) \times 10^{-4}\ \text{cm.}^{-1}$$

$$g_{\perp} = 2{\cdot}11 \pm 0{\cdot}01; \qquad B = (30 \pm 10) \times 10^{-4}\ \text{cm.}^{-1}$$

It is interesting to compare these ESR results with the X-ray data (Sundara Rao *et al.*, 1958) regarding the symmetry of the co-ordination of the Cu^{++} ion. The Cu^{++} ion in DBCF is octahedrally co-ordinated by six oxygens; four oxygens are from the formate groups and two are water oxygens. The Cu^{++} is at the centre of symmetry. The Cu–O distances are $2{\cdot}18\ (O_{f_1})$; $1{\cdot}97\ (O_{f_2})$ and $2{\cdot}02\ (O_w)$. These distances indicate a slight rhombic symmetry around the Cu^{++} ion. ESR results however show almost tetragonal symmetry. Further the direction $Cu\text{-}O_{f_1}$, along which the octahedron is elongated, appears to correspond to the tetragonal axis. The projection of the $Cu\text{-}O_{f_1}$ direction on the *bc*-plane makes an angle 49° with the *c*-axis, which agrees quite well with the ESR result of 45°. Also the angle α obtained from the X-ray data is 3° which agrees quite well with the ESR result. However, much significance should not be attached to the value of α determined from the *g*-values, since the variation of the *g*-value around $g_{\parallel}$ is very slow and is not very sensitive to the angle. In fact the tetragonal axis has been found to be in the *bc*-plane (within the experimental error) from the measurements around the $g_{max.}$ direction as mentioned earlier.

Low Temperature Study and Quadrupole Interaction

The ultimate resolution in the ESR spectrum of DBZ–CF that could be obtained at room temperature with dilutions greater than Cu : Zn = 1 : 200, was still not sufficient to fully resolve the hyperfine structure in all directions. However, by cooling the crystal to 90° K., the resolution greatly improved and the individual line widths were 5 gauss. This clearly indicates considerable spin-lattice interaction at room temperature, characteristic of ionic copper salts. Fig. 2 shows the recording of the ESR spectrum of a single crystal of DBZ–CF (with Zn : Cu = 200 : 1), along the tetragonal axis, at 90° K. The hyperfine lines from the two isotopes of copper, Cu^{63} and Cu^{65}, have been clearly resolved in the extreme lines. Higher dilutions of

1 : 400 have also been tried out, but further resolution in the spectrum could not be obtained. Deuteration of the sample is not expected to improve the situation much, as only two water molecules are co-ordinating the Cu^{++} ion, the four other positions being occupied by formate groups. Use of still lower temperatures may reduce the line width further, by reducing the spin lattice interaction.

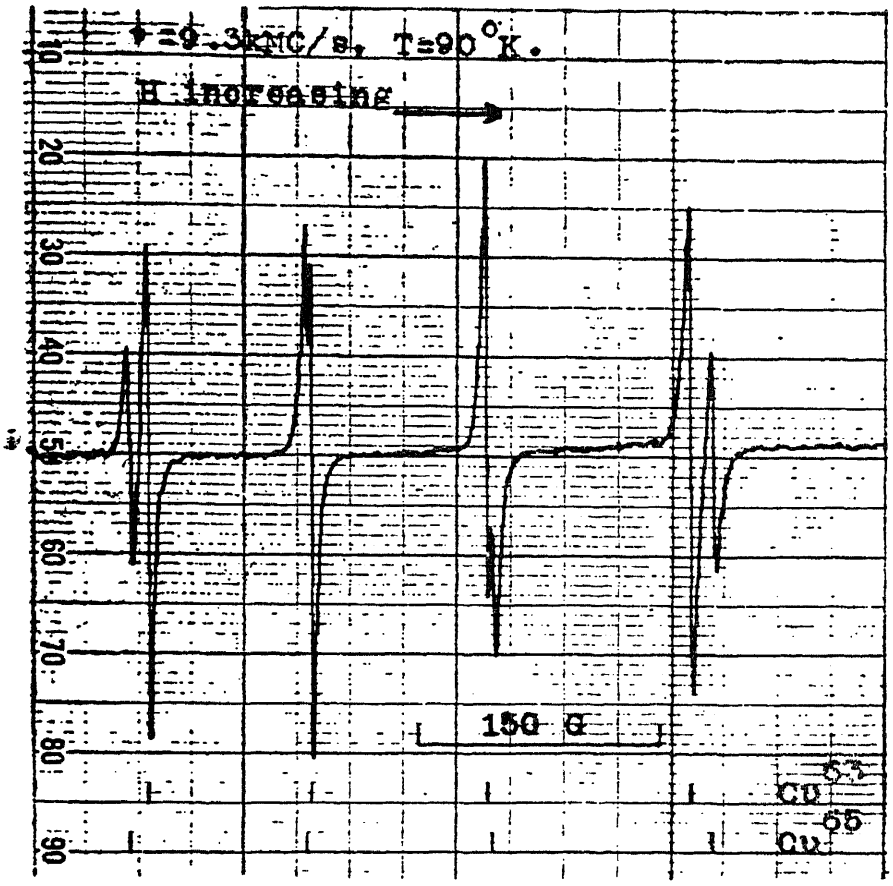

FIG. 2. Recording of ESR spectrum from DBZ-CF (Zn : Cu = 200 : 1) at 90°K, with magnetic field along the tetragonal axis.

Investigations at room temperature indicated that the symmetry around the Cu^{++} ion, inside the crystal is almost tetragonal with the symmetry axis lying in the *bc*-plane. The ESR investigations at 90° K. have therefore been confined to the *bc*-plane. In this plane, the line positions were measured for every 10° over a range of 160° in a single mounting, since the signal to noise ratio was quite good.

As the angle θ between the magnetic field direction and the tetragonal axis is increased, the nature of the spectrum remained the same until about 70°, except for a change in the mean position of the spectrum and a decrease in the hyperfine separation. Around 70° extra lines started appearing between the $m = \frac{1}{2}$ and 3/2 lines and $m = -\frac{1}{2}$ and $-3/2$ lines. They grew rapidly in intensity as the $g_\perp$ direction was approached and in fact became more intense than the allowed transitions near the $g_\perp$ direction. These

lines have been identified as the forbidden $\Delta M = \pm 1$, $\Delta m = \pm 1$ transitions which are caused by the quadrupole interaction of the unpaired electron with the copper nucleus (Ingram, 1949; Bleaney, 1951; Bleaney *et al.*, 1955*a*, *b*). For angles very near the $g_\perp$ direction and along it the spectrum became very complicated and the poor resolution at these angles prevented indexing of all the lines in the spectrum. Fig. 3 shows some typical recordings of the spectra of a single crystal of DBZ-CF (Zn : Cu = 200 : 1) at 90° K. for $\theta = 64°$ to 90°.

As Fig. 3 shows, the ESR spectrum changes rapidly between 70° and 90° and hence between these angles the measurements of all the lines in the spectrum, *i.e.*, allowed as well as forbidden lines have been made for every 2°. The line positions of the forbidden lines have been used for the evaluation of the quadrupole parameter Q.

The observed spectrum was fitted to the following spin-Hamiltonian, characteristic of tetragonal symmetry with $S = \frac{1}{2}$ and $I = 3/2$.

$$\mathcal{H} = \beta [g_\parallel S_z H_z + g_\perp (S_x H_x + S_y I_y)] + A S_z I_z + B (S_x I_x + S_y I_y) + Q [I_z^2 - (\tfrac{1}{3}) I (I + 1)]. \quad (4)$$

The values of the parameters in the spin-Hamiltonian have been evaluated as follows:

g-values.—*g*-values have been calculated from the mean positions of the hyperfine lines. $g_\parallel$ and $g_\perp$ values have been obtained from the measurements along and perpendicular to the tetragonal axis. The correction to the *g*-values due to the second order effects (less than 0·1%) are smaller than the experimental errors and so have not been taken into account. Fig. 4 shows the fitting of the experimental g^2 variation with θ to the expression

$$g^2 = g^2_\parallel \cos^2\theta + g_\perp^2 \sin^2\theta$$

with $g_\parallel = 2{\cdot}39 \pm 0{\cdot}002$ and $g_\perp = 2{\cdot}08 \pm 0{\cdot}005$, where θ is measured from the tetragonal axis.

Hyperfine parameters A, B and quadrupole parameter Q.—The mean hyperfine separation along the tetragonal axis straightaway gave the parameter A. Since the lines from both isotopes have been resolved the values of A for both the isotopes have been obtained. The parameter B however could not be obtained in a similar way, because of the second order effects due to quadrupole interaction which are very pronounced along the $g_\perp$ direction. The expression for the hyperfine line positions was given by Bleaney (1951) by solving the spin-Hamiltonian in the Eq. (4) to second order for the case

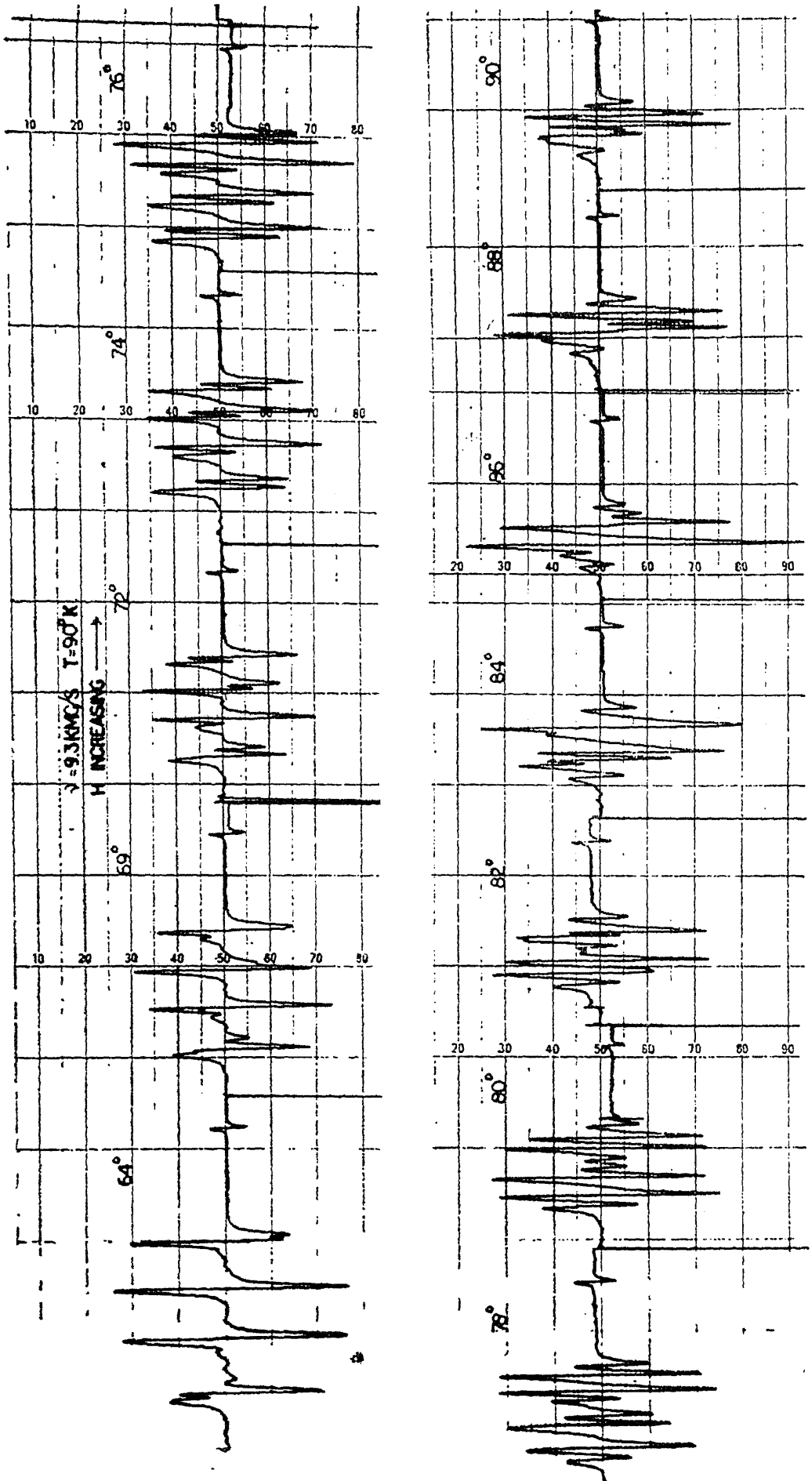

FIG. 3. Recording of the ESR spectra from DBZ-CF at 90° K for various values θ from 64-90°

when A, $B \gg Q$. The observation of the lines corresponding to the forbidden transitions, along directions around $g_\perp$, indicates that Q is comparable to B. Actually the quadrupole parameter Q, calculated from the line positions of the forbidden transitions, as described later, using the uncorrected hyperfine separations K, has been found to be 15×10^{-4} cm.$^{-1}$ and this is comparable to the value of $B = 18 \times 10^{-4}$ cm.$^{-1}$ obtained from the hyperfine line positions corresponding to $m = \pm 3/2$, without taking into account the second order corrections. For the case of $Q \approx B$ the energy levels have therefore been worked out, by solving the secular determinant for the spin-Hamiltonian in the representation for $S = 1/2$ and $I = 3/2$. In the high field approximation, the zero order wave functions in the representation for S and I can be taken to be $|M, m\rangle$ where M and m are the electron and nuclear spin magnetic quantum numbers. In solving the determinant, the off-diagonal terms connecting the $M = \pm \frac{1}{2}$ states are neglected while those in Q, that connect states having the same M value are retained. In this approximation the 8×8 determinant factorizes into four blocks of 2×2. If $E(M, m)$ denotes the energy of the state which corresponds to $|M, m\rangle$ in the zero order, we have

$$E(\pm \tfrac{1}{2}, \tfrac{3}{2}) = \tfrac{1}{2}[\pm G \pm \tfrac{1}{2}B + \tfrac{5}{2}Q \pm (B^2 \mp 2BQ + 4Q^2)^{\frac{1}{2}}]$$

$$E(\pm \tfrac{1}{2}, \tfrac{1}{2}) = \tfrac{1}{2}[\pm G \mp \tfrac{1}{2}B + \tfrac{5}{2}Q \pm (B^2 \pm 2BQ + 4Q^2)^{\frac{1}{2}}]$$

$$E(\pm \tfrac{1}{2}, -\tfrac{1}{2}) = \tfrac{1}{2}[\pm G \pm \tfrac{1}{2}B + \tfrac{5}{2}Q \mp (B^2 \mp 2BQ + 4Q^2)^{\frac{1}{2}})$$

$$E(\pm \tfrac{1}{2}, -\tfrac{3}{2}) = \tfrac{1}{2}[\pm G \mp \tfrac{1}{2}B + \tfrac{5}{2}Q \mp (B^2 \pm 2BQ + 4Q^2)^{\frac{1}{2}}]$$

where

$$G = g_\perp \beta H. \tag{5}$$

The positions of the $m = \pm 3/2$ lines, corresponding to the allowed transitions $\Delta M = \pm 1$, $\Delta m = 0$ are given by

$$H_{3/2} = H_0 - \frac{B}{2g_\perp\beta} - \frac{1}{2g_\perp\beta}[(B^2 - 2BQ + 4Q^2)^{\frac{1}{2}} + (B^2 + 2BQ + 4Q^2)^{\frac{1}{2}}]$$

$$H_{-3/2} = H_0 + \frac{B}{2g_\perp\beta} + \frac{1}{2g_\perp\beta}[(B^2 - 2BQ + 4Q^2)^{\frac{1}{2}} + (B^2 + 2BQ + 4Q^2)^{\frac{1}{2}}]$$

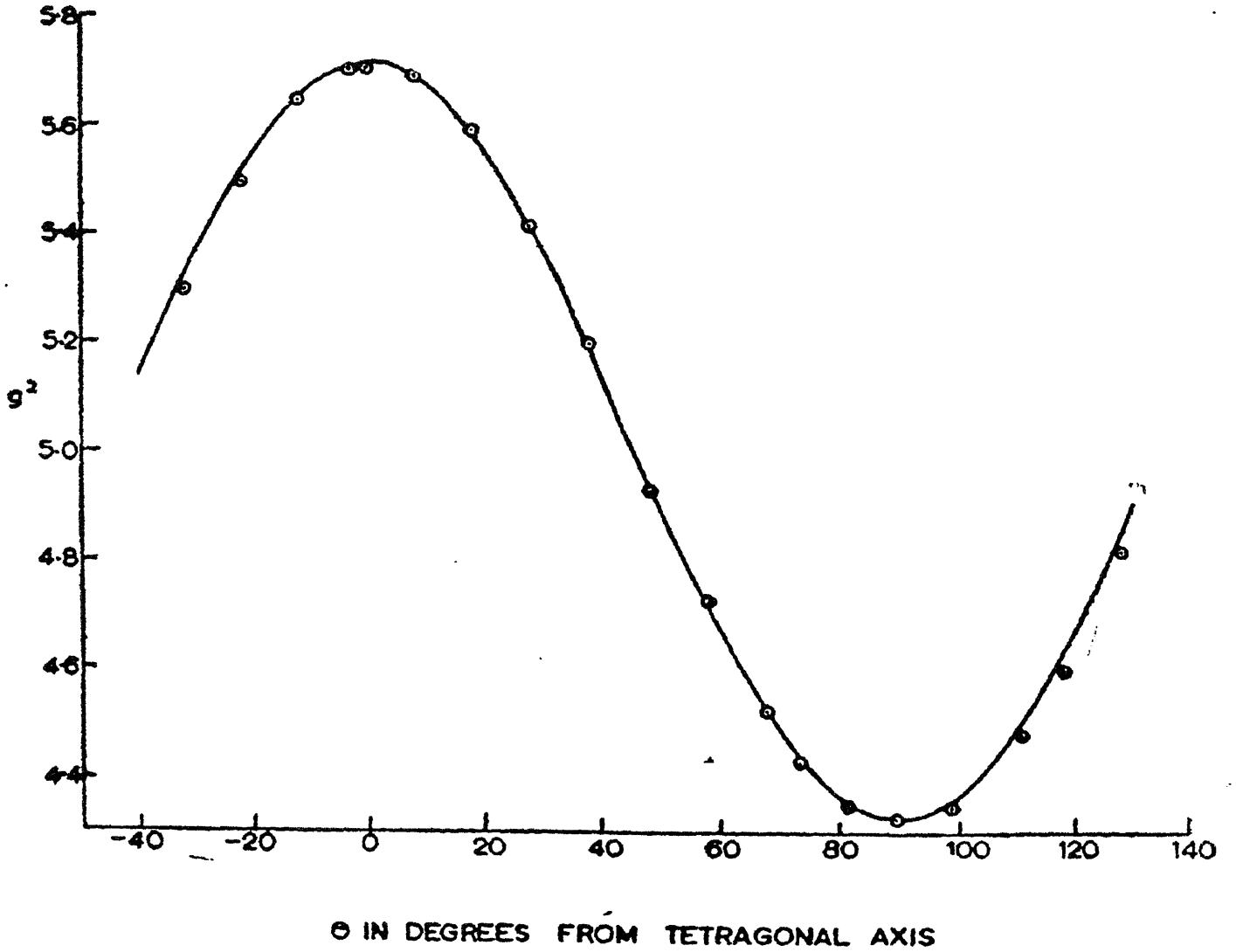

FIG. 4. Fitting of the observed g^2 variation in the *bc*-plane of DBZ-CF at 90° K. Points ⊙ represent the experimental g^2 values, the curve represents the equation

$$g^2 = g_{\parallel}{}^2 \cos^2\theta + g_{\perp}{}^2 \sin^2\theta \text{ with}$$

$g_{\parallel} = 2{\cdot}39$ and $g_{\perp} = 2{\cdot}08$.

where

$$h\nu = g_{\perp}\beta H_0.$$

Hence we have

$$H_{-3/2} - H_{3/2} = \frac{B}{g_{\perp}\beta} + \frac{1}{g_{\perp}\beta}[(B^2 - 2BQ + 4Q^2)^{\frac{1}{2}} + (B^2 + 2BQ + 4Q^2)^{\frac{1}{2}}]. \quad (6)$$

where $H_{-3/2}$, $H_{3/2}$ are in gauss, B, Q are in cm.$^{-1}$ β Bohr magneton in cm.$^{-1}$ gauss.$^{-1}$

Using the approximate value of Q and the line positions $H_{3/2}$, $H_{-3/2}$, the Eq. (6) was solved for B to give a corrected B, consisent with the value of Q used. This value of B was then used to calculate the values of K from the expression:

$$K^2g^2 = A^2g_{\parallel}^2 \cos^2\theta + B^2g_{\perp}^2 \sin^2\theta. \tag{7}$$

These values of K were in turn used in the place of the uncorrected K's to calculate a better value of Q. The whole cycle was then repeated till we arrived at a stationary value for $B = (12.3 \pm 2)\ 10^{-4}$ cm.$^{-1}$

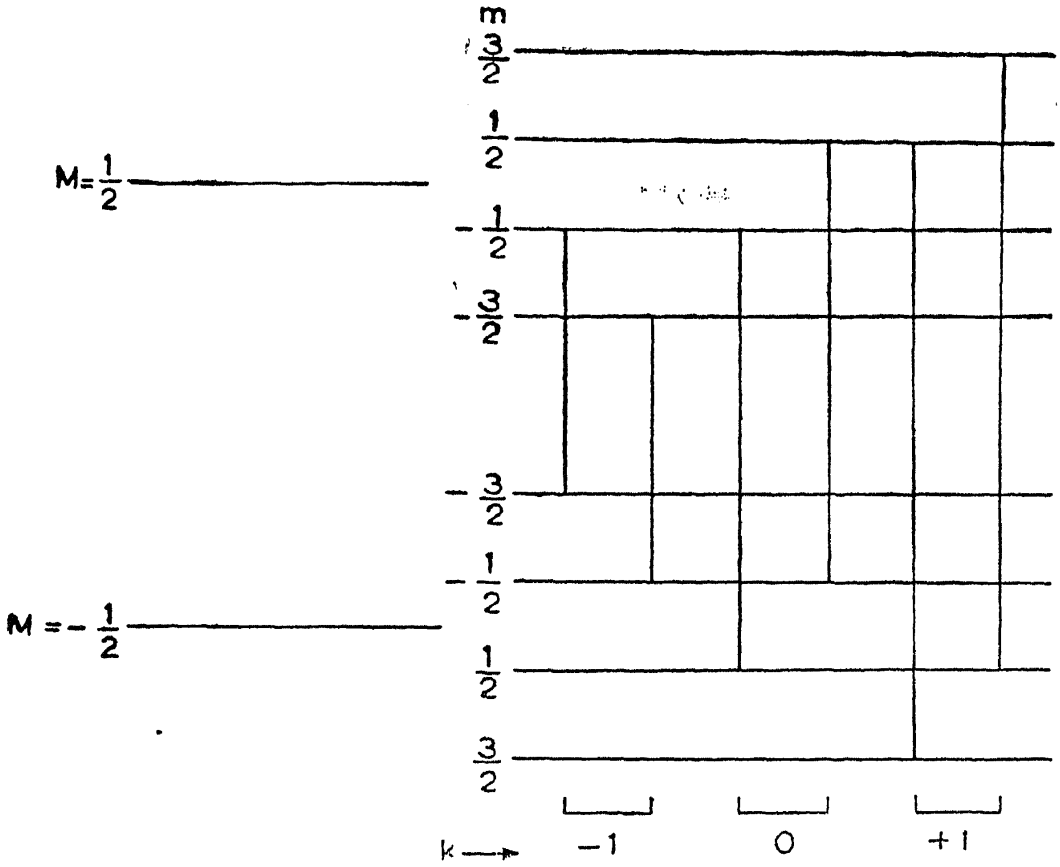

FIG. 5. Possible transitions corresponding to the selection rule $\Delta M = \pm 1$, $\Delta m = \pm 1$ for the case of $S = \frac{1}{2}$ and $I = 3/2$.

The value of Q has been calculated from the positions of the lines corresponding to the forbidden transtions $\Delta M = \pm 1$, $\Delta m = \pm 1$. The expression for the positions of these lines was given by Bleaney (1951) and it involves only the first power of Q. Higher order terms like Q^2/K contributing small shifts in the lines were neglected. But when Q is comparable to K this is not a good approximation in general. However, calculating the line positions for the forbidden transitions using Eq. (5) along the $g_{\perp}$ direction and analysing the forbidden line positions as described below to get a value of Q, we find that the error involved in neglecting the higher

order terms would be less than 13% if B were greater than 3Q. Extending the argument for directions away from 90° where expressions would involve angular dependence through some functions of cos θ and sin θ, the approximation can be taken to be reasonably good for directions along which $K > 3Q$. The value of Q was therefore evaluated from measurements along the directions which satisfied this condition.

The positions of the lines corresponding to the forbidden transitions $(\frac{1}{2}, k \pm \frac{1}{2}) \rightarrow (-\frac{1}{2}, k \mp \frac{1}{2})$, *i.e.*, $\Delta M = \pm 1$, $\Delta m = \pm 1$ are given by (Bleaney 1951)

$$H = H_0 - \left(\frac{K}{g\beta}\right) k \pm \left\{\left(\frac{Q'}{g\beta}\right) k - \left(\frac{\gamma'}{g\beta}\right)\right\} \tag{8}$$

where k takes the values 1, 0, -1 for the case of $I = 3/2$ and

$$Q' = Q\left(3\frac{A^2 g_{\parallel}^{\ 2}}{K^2 g^2}\cos^2\theta - 1\right) \tag{9}$$

$$\gamma' = \frac{\gamma\beta_N H\,(Ag_{\parallel}\cos^2\theta + Bg_{\perp}\sin^2\theta)}{Kg}.$$

The possible transitions $\Delta M = \pm 1$, $\Delta m = \pm 1$ for the case of $S = \frac{1}{2}$ $I = 3/2$ are shown in Fig. 5. Of the six transitions, the lines corresponding to $k = 0$ have vanishing intensity (Bleaney, 1951). So only four lines corresponding to the above selection rule are observed. Their positions with respect to main hyperfine lines are shown in Fig. 6. If H_{1a}, H_{2a}, etc., give the positions of the forbidden lines as shown in the figure it can be proved from Eq. (8) that

$$(H_{2a} - H_{1a}) + (H_{4a} - H_{3a}) = 4\,(Q'/g\beta). \tag{10}$$

The values of $(Q'/g\beta)$ were thus found experimentally from the positions of the forbidden lines, for different values of θ using Eq. (10). The angular variation of $(Q'/g\beta)$ was then fitted to the theoretical Eq. (9). The values of K^2g^2 were obtained from Eq. (7) using the corrected value for B. Repeating the process as explained before, the value of Q consistent with the value of B was found to be $Q = (9 \pm 2)\ 10^{-4}$ cm.$^{-1}$

Accurate values for the quadrupole parameter could be obtained more easily from measurements on the forbidden $\Delta m = \pm 1$ transitions, at angles closer to tetragonal axis, since the overlap of the allowed hyperfine lines would be less and there would be greater resolution in the spectrum. Further the Eq. (8) could be used conveniently with sufficient accuracy. However,

the intensity of these lines is very small at these angles and they could not be detected in the spectrum. In fact they start appearing only at angles near 65° and grew rapidly in intensity as the $g_\perp$ direction is approached.

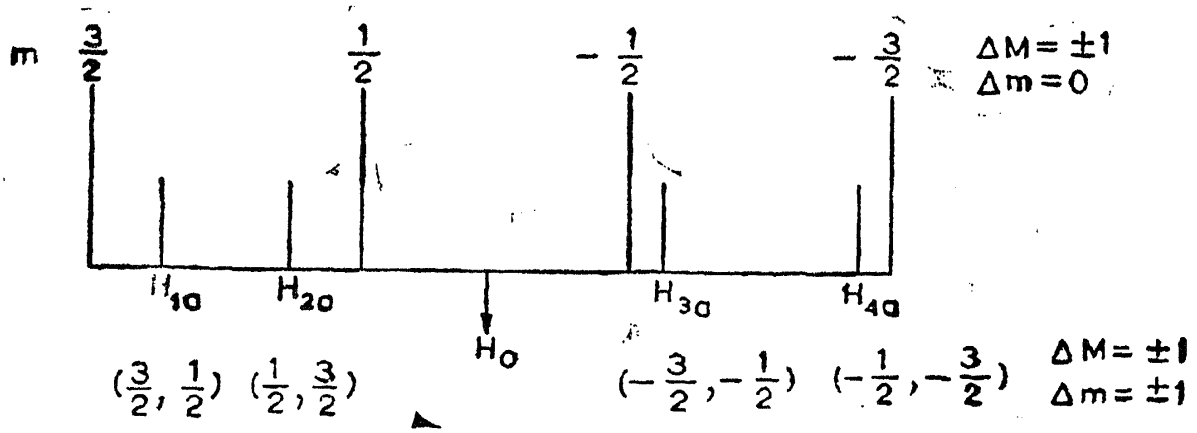

FIG. 6. Positions of the forbidden transitions corresponding to $\Delta m = \pm 1$ relative to the allowed hyperfine lines corresponding $\Delta m = 0$.

Attempts have not been made to derive expressions for the energy levels for the case $Q \approx K$, since the expressions become very complicated; in any case the errors in the measurements of the line positions due to lack of good resolution make such exact calculations unnecessary. However, if the resolution in the spectrum were good and enabled accurate measurements such calculations could be used, and an accurate value of Q obtained.

The lines corresponding to the forbidden transitions $\Delta M = \pm 1$, $\Delta m = \pm 2$ have appreciable intensity for values of θ, very close to 90°. Even though such lines have been observed in the spectrum, they could not be analysed due to lack of resolution in the spectrum in those directions.

Summing up, the spin-Hamiltonian parameters for the Cu^{++} ion in DBZ–CF at 90° K. are

$$g_\parallel = 2{\cdot}39 \pm 0{\cdot}002$$
$$g_\perp = 2{\cdot}08 \pm 0{\cdot}005$$
$$A^{63} = (131 \pm 2) \times 10^{-4}\ \text{cm.}^{-1}$$
$$A^{65} = (140 \pm 2) \times 10^{-4}\ \text{cm.}^{-1} \qquad A^{63}/A^{65} = 0{\cdot}93\,(6).$$
$$B = (12\,(\cdot 3) \pm 2) \times 10^{-4}\ \text{cm.}^{-1}$$
$$Q = (9 \pm 2) \times 10^{-4}\ \text{cm.}^{-1}.$$

DISCUSSION

The values for the spin-Hamiltonian parameters indicate that the Cu^{++} ion binding to the oxygen ligands in DBZ–CF is predominantly ionic with

the unpaired electron in the $3d_{x^2-y^2}$ orbital (Bowers and Owen, 1955). The strong spin-lattice interaction observed at room temperature is also typical of ionic copper salts.

The EPR results at room and liquid oxygen temperatures show an interesting temperature dependence of the spin-Hamiltonian parameters. The difference in the parameters at the two temperatures is much larger than the experimental error. Particularly the changes in the parameters $g_{\parallel}$ and A are significant. A systematic investigation of the temperature variation of the spin-Hamiltonian parameters and a model to explain this are described in detail in Part II of the paper. A detailed description of the optical absorption studies on single crystals of DBCF is also given.

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REFERENCES

Bowers, K. D. and Owen, J. — *Repts. Prog. Phys.*, 1955, **18**, 304.

Orton, J. W. .. — *Ibid.*, 1959, **22**, 204.

Bleaney, B., Bowers, K. D. and Ingram, D. J. E. — *Proc. Roy Soc.*, 1955 *a*, **228 A**, 147.

——, —— and Trenam, R. S. — *Ibid.*, 1955 *b*, **228 A**: 157.

Sundara Rao, R. V. G., Sundaramma, K. and Sivasankara Rao, G. — *Z. Kristallogr.*, 1958, **111**, 231.

Bleaney, B. and Stevens, K. W. H. — *Repts. Prog. Phys.*, 1953, **16**, 108.

Ingram, D. J. E. .. — *Proc. Phys. Soc.*, 1949, **62 A**, 664.

Bleaney, B. .. — *Phil. Mag.*, 1951, **42**, 441.

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