

## Second-Order Effects and Hyperfine Structure of Nitrogen and Hydrogen in the EPR Spectrum of Glycine Chelate with $^{63}\text{Cu}^{2+}$ in Triglycine Sulphate

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The angular dependence of the electron spin resonance of  $^{63}\text{Cu}^{2+}$  has been measured in triglycine sulphate and the spin-Hamiltonian parameters: *g*-factor, the hyperfine splitting,  $A^{\text{Cu}}$ , and the ligand hyperfine splittings,  $A^N$  and  $A^H$ , have been found.

The angular dependence of spectra is found to obey Bleaney's equation for the energies of the spin states calculated to second order for the magnetic hyperfine interaction.

In addition to the hyperfine structure arising from the nitrogen atoms, extra hyperfine lines produced as a result of the interaction of the unpaired electron with hydrogen atoms have been observed. Deuteration of triglycine sulphate by the replacement of the hydrogen atoms of the amine groups by deuterium proved that these protons are the responsible for the observed hydrogen hyperfine interaction.

### 1. INTRODUCTION

The EPR spectrum of the glycine complex with square structure has been studied in detail by Lösche and Windsch (1), (2) as well as by Stankowski (3-5) in single crystals of triglycine sulphate (TGS) and triglycine fluoroberyllate (TGFB). Copper in these two isomorphous crystals, forms a chelate with two glycine ions, yielding the compound  $(\text{NH}_2\text{CH}_2\text{COO})_2\text{Cu}$ . The coordination neighbourhood of the copper ion forms a slightly distorted square, at the apices of which nitrogen and oxygen atoms are present in trans configuration. From available results, two differently oriented, magnetically equivalent kinds of copper-glycine complexes are known to exist, with principal symmetry axes lying close to the  $YZ$  plane and subtending an angle of about  $35^\circ$  with the  $Y$  axis (Fig. 1).

Previous work dealt with copper of natural isotope composition, so that the EPR was a superposition of spectra from the two isotopes  $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ , which differ slightly in the two magnetic moments of their nuclei. This leads to a poorly resolved and unclear spectrum. By using a sample containing only the  $^{63}\text{Cu}^{2+}$  isotope ( $I = 3/2$ ), a well resolved and easily decipherable EPR spectrum, consisting of four quintets for

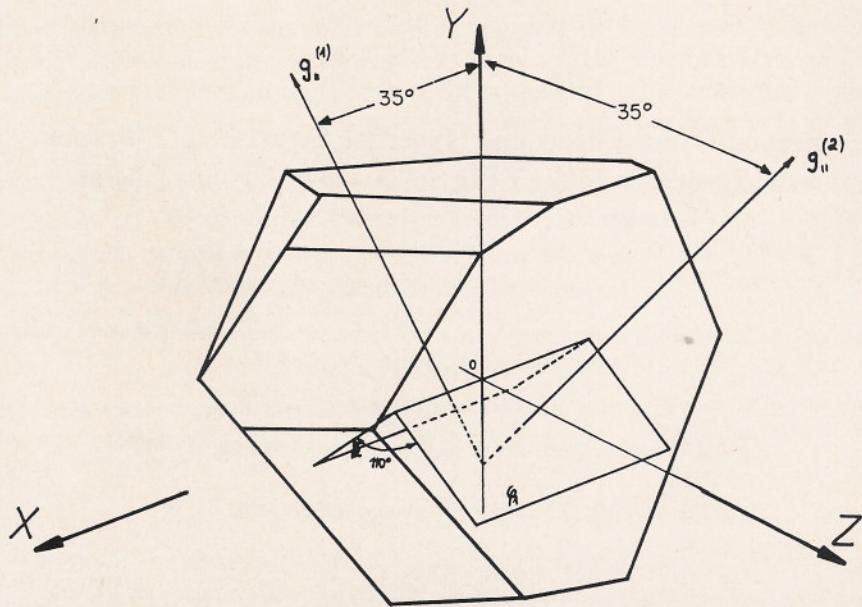


FIG. 1. Diagram showing the coordinate system with regard to the TGS crystal axes. The planes containing the coordination square of the neighbourhood of copper ions formed by the two glycines I and II are also shown.

each of the complexes, was obtained (Fig. 2). It will be remembered that this quartet is due to interaction between the unpaired electron of the  $\text{Cu}^{2+}$  ion and the copper nucleus  $^{63}\text{Cu}$ . Each of the lines of the quartet is a quintet, arising from the interaction with the nuclei of the two nitrogen-14 atoms ( $I = 1$ ).

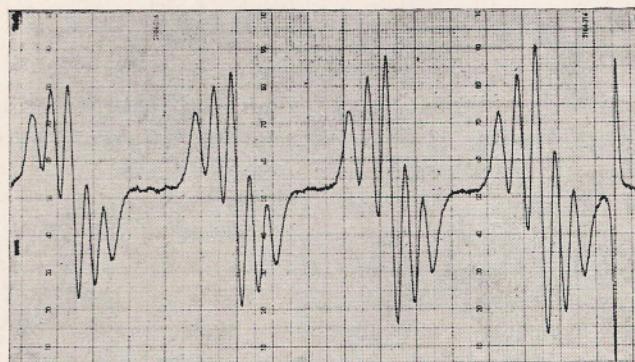


FIG. 2. EPR spectrum of  $(\text{gly})_2\text{Cu}$  chelate in TGS:  $^{63}\text{Cu}^{2+}$ .

## 2. ANGULAR DEPENDENCE OF THE $g$ -FACTOR AND HYPERFINE INTERACTION CONSTANT $A$ FOR THE $^{63}\text{Cu}^{2+}$ ION, AND SECOND-ORDER EFFECTS

Figure 3 shows the angular dependence of the EPR spectra in the  $YZ$  plane. The observed anomaly in angular dependence of EPR spectra, the dip for the line  $M_I = -3/2$

near perpendicular orientation of the magnetic field and principal axis, is very marked here. The anomaly was observed only for the line due to the transition  $\Delta M_s = 1$ ,  $M_I = -3/2$ . The dip near the extremum of angular dependence was the object of our especial attention.

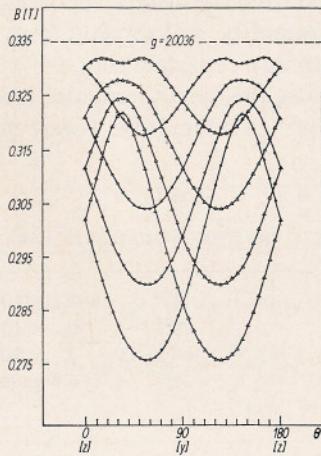


FIG. 3. Angular dependence of the positions of centres of the hyperfine structure lines due to copper  $^{63}\text{Cu}^{2+}$  nuclei in TGS in the  $YZ$  plane.

In the interpretation of the angular dependence obtained for the EPR spectrum, use was made of the expression for spin level energies due to Bleaney (6), for the case of an axially symmetric crystal field, containing terms derived by second-order perturbation calculations:

$$W_{M_s, M_I} = GM_s + AM_I \left\{ M_s + \frac{A_\parallel A_\perp^2}{2A^2G} [M_s^2 - S(S+1)] \right\} + \frac{A_\perp^2(A_\parallel^2 + A^2)}{4A^2G} M_s [I(I+1) - M_I^2] + \left[ \frac{(A_\parallel^2 - A_\perp^2)^2}{8A^2G} \left( \frac{g_\parallel g_\perp}{g^2} \right)^2 \sin^2 2\theta \right] M_s M_I^2. \quad [1]$$

where  $G = g\beta B$  is the Zeeman energy of electron spin,  $A$  and  $g$  are defined by the relations:

$$g^2 A^2 = g_\parallel^2 A_\parallel^2 \cos^2 \theta + g_\perp^2 A_\perp^2 \sin^2 \theta,$$

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

In the horizontal plane of the complex, anisotropy of the  $g$ -factor is very small, and the axial symmetry can be assumed as a good approximation. By Eq. [1], as assuming  $S = M_s = \frac{1}{2}$ ,  $\Delta M_s = 1$ ,  $\Delta M_I = 0$ , one obtains the resonance field values corresponding to the individual lines of hyperfine structure of the EPR spectrum for a given quantum number  $M_I$ :

$$B_m = B_0 - A M_I - \frac{A_\perp^2}{4B_0} \left( \frac{A_\parallel^2 + A^2}{A^2} \right) [I(I+1) - M_I^2] - \frac{1}{2B_0} \left( \frac{A_\parallel^2 - A_\perp^2}{A} \right)^2 \left( \frac{g_\parallel g_\perp}{g^2} \right)^2 M_I^2 \sin^2 \theta \cos^2 \theta. \quad [2]$$

For  $\theta = 0^\circ$ , the fourth term of Eq. [2] vanishes, the third term is negligible, and  $g_{\parallel}$  can be determined directly from the position of the centre of the EPR spectrum. The splitting of the hyperfine structure quartet yields  $A_{\parallel}$ . At this orientation the distance between the hyperfine lines due to the  $^{63}\text{Cu}$  nuclei are almost equal.

At  $\theta = 90^\circ$ ,  $A_{\perp}$  is determined from the distance between the second and third lines of hyperfine structure, but  $g_{\perp}$  cannot be had directly from the spectrum, and the third term in Eq. [2] has to be taken into consideration.

For intermediate orientations, the fourth term also has to be included. In this way, the principal values of  $g$  and  $A^{\text{Cu}}$  listed in Table 1 were determined.

TABLE 1  
VALUES OF THE SPIN-HAMILTONIAN PARAMETERS

|                   |                                       |                             |  |
|-------------------|---------------------------------------|-----------------------------|--|
| $g_{\parallel}$   | 2.261                                 | $A_{\parallel}^{\text{Cu}}$ | $150.1 \times 10^{-4} \text{ cm}^{-1}$ |
| $g_{\perp}$       | 2.054                                 | $A_{\perp}^{\text{Cu}}$     | $30 \times 10^{-4} \text{ cm}^{-1}$    |
| $g_{\perp}(X)$    | 2.064                                 | $A_{\perp}^{\text{Cu}}(X)$  | $5 \times 10^{-4} \text{ cm}^{-1}$     |
| $A_{\parallel}^N$ | $7.4 \times 10^{-4} \text{ cm}^{-1}$  | $A^H$                       | 4.6 gauss                              |
| $A_{\perp}^N$     | $11.4 \times 10^{-4} \text{ cm}^{-1}$ |                             |  |

The anomalous shape of the angular dependence of the line position for  $M_I = -3/2$  was analysed in detail. The quantitative analysis was aimed at deciding which of the terms of Eq. [2] is responsible for the occurrence of the double extremum close to the orientation  $\theta = 90^\circ \pm 20^\circ$ . The derivative  $dB_m/d\theta$  in Eq. [2] was calculated and equated to zero  $dB_m/d\theta = 0$ , yielding the following expression for those angles at which an extremum occurs:

$$\cos^2 \theta_{\max} = \left[ 1 + \frac{g_{\parallel}^2}{g_{\perp}^2} \cdot \frac{A_{\parallel}^2 - A^2}{A^2 - A_{\perp}^2} \right]^{-1}, \quad [3]$$

where:

$$A = \frac{hv}{4M_I} + \frac{1}{4} \left[ \left( \frac{hv}{M_I} \right)^2 + \frac{8(A_{\parallel}^2 g_{\parallel}^2 - A_{\perp}^2 g_{\perp}^2)}{g_{\parallel}^2 - g_{\perp}^2} \right]^{1/2}. \quad [4]$$

Computation with the values of Table 1 led to a double extremum only for the hyperfine component with  $M_I = -3/2$  at angles of  $\theta = 70^\circ$ . Assuming some anisotropic character of the hyperfine interaction constant  $A$  in the plane of the complex, the value  $A_{\perp} = 26 \times 10^{-4} \text{ cm}^{-1}$ , i.e. the value of  $A_{\perp}$  in the  $YZ$  plane, was assumed for the computations. This value corresponds to a direction in the plane of the complex forming an angle of  $\varphi = 25^\circ$  with the  $Y$  axis of the latter. Calculations were also performed to verify that the lines for  $M_I = -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$  exhibit no double extremum (Fig. 4). However, for complete consistency of the size of the dip observed near  $\theta = 90^\circ \pm 20^\circ$ , it is not sufficient to take only the term  $AM_I$ , and the subsequent terms also have to be taken into consideration, as is also shown in Fig. 4 in enlarged scale. The good agreement achieved between the calculations and experimental results (Fig. 5) permits the conclusion that quadrupole interactions, which presumably exist for  $^{63}\text{Cu}^{2+}$  in TGS, are very weak and are not accessible to experimental determination from the angular dependence of the spectrum.

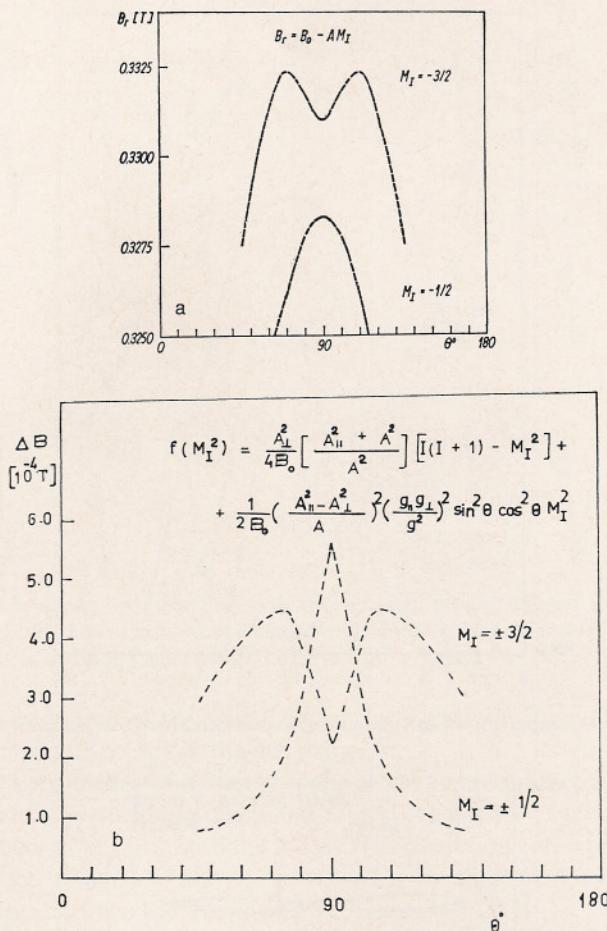


FIG. 4. (a) Graph of both resonance field values derived from Bleaney formula in the first-order approximation for the lines  $M_I = -3/2$  and  $M_I = -1/2$ . (b) Contributions from the second-order terms in Bleaney's formula for the region of angles near  $\theta = 90^\circ \pm 20^\circ$ .

### 3. ANISOTROPY OF THE NITROGEN HYPERFINE STRUCTURE

Each of the lines of the quartet due to  $^{63}\text{Cu}^{2+}$  is, in turn, split into quintet due to interaction of the unpaired electron and the two equivalent  $^{14}\text{N}$  nuclei of  $\text{NH}_2$  amine groups of the ligands. This type of interaction leads to five lines of hyperfine structure with the intensity ratios 1:2:3:2:1 (Fig. 2). At certain orientations, these lines undergo a further splitting by interaction with protons.

The angular dependence of the splitting constant  $A^N$  with regard to rotation of the crystal about the  $X$  axis and about the  $Y$  axis was investigated. The largest anisotropy was observed in the  $YZ$  plane during rotation about the  $X$  axis of the orthogonal coordinates. The hyperfine interaction constants, in this plane, vary from  $7.4 \times 10^{-4} \text{ cm}^{-1}$  in the direction parallel to the principal  $z$  axis of the complex to  $10.6 \times 10^{-4} \text{ cm}^{-1}$  in the plane of the complex (Fig. 6). In Fig. 7, one of the quintets obtained at this orientation is shown. Moreover, Fig. 7 shows simulated spectra, obtained with a JRA-1

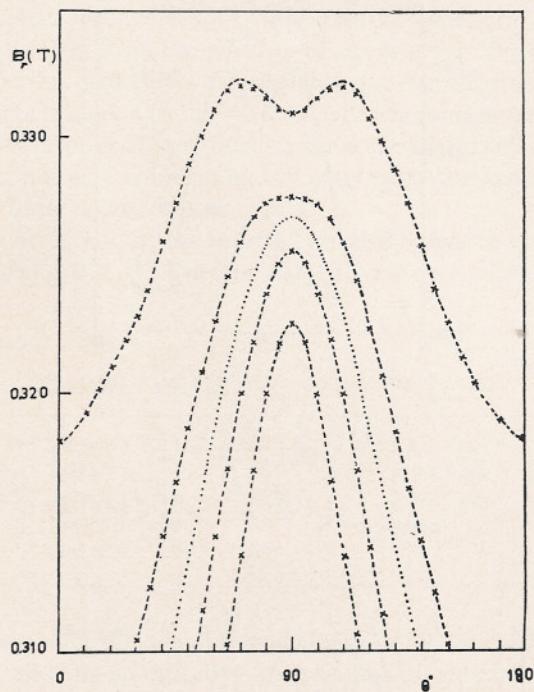


FIG. 5. Comparison of calculated and experimental angular dependence.

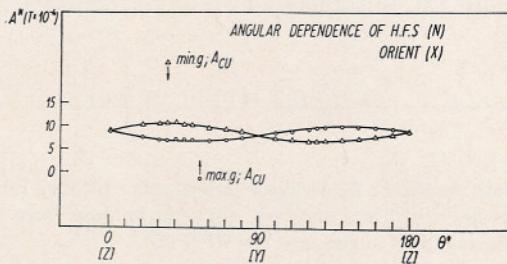


FIG. 6. Angular dependence of splitting from  $^{14}\text{N}$  in the  $YZ$  plane.

spectrum accumulator on the assumption of an individual hyperfine component of the Lorentzian and Gaussian shapes.

The linewidth was assumed to be of order of the nitrogen hyperfine interaction constant:

$$2\Delta B_{1/2}^x = aA^N,$$

where  $2\Delta B_{1/2}^x$  is the width at half maximum intensity for Lorentzian ( $\propto = L$ ) or Gaussian ( $\propto = G$ ) shapes and  $a$  is a dimensionless constant. The spectrum in the center of Fig. 7a simulated with  $a = 1.25$  for Lorentzian shape appears to be nearest to the experimental one. This procedure failed to yield full agreement between the shapes of the original and simulated lines. Better agreement was obtained after taking into consideration the interaction with four hydrogens of the two amine groups, with  $n^H = 4$  and  $A^H:A^N = 0.25$

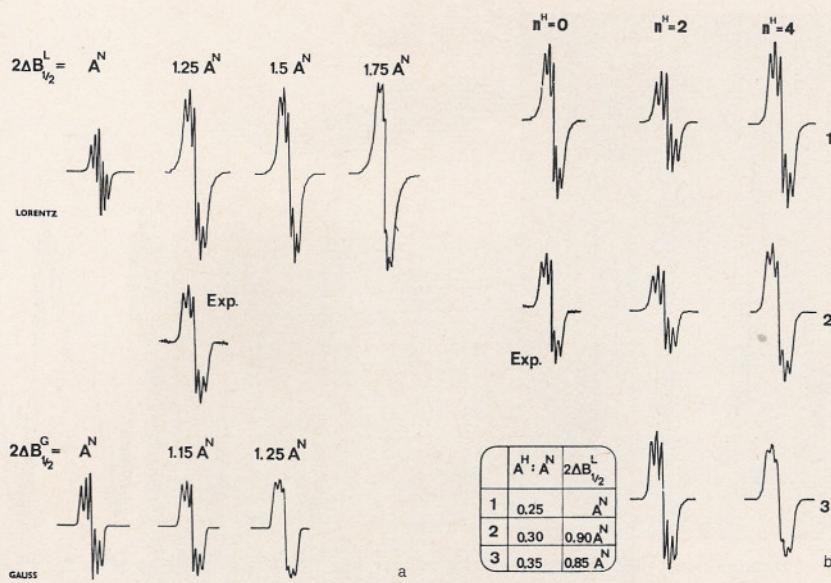


FIG. 7. (a) Quintet due to interaction with two nitrogen atoms, original and simulated spectra obtained on the assumption of Lorentz and Gauss line shapes for the individual hyperfine components. (b) Taking into consideration the interaction with two ( $n^H = 2$ ) and four ( $n^H = 4$ ) protons.

(Fig. 7b). Upon rotation of the crystal about the  $Y$  axis, the angular behaviour of  $A^N$  pointed to a small anisotropy in the  $XZ$  plane.

The angular dependence of  $A^N$  in the plane of the complex was also studied (Fig. 8). Although anisotropy was low, a maximum of  $A^N = 11.4 \times 10^{-4} \text{ cm}^{-1}$  was found for the direction subtending  $65^\circ \pm 5^\circ$  with the  $X$  axis. This direction corresponds to that of the N—Cu—N bond ( $y$ -axis) of the complex and is in agreement with the previously determined angle between the  $Y$  axis and  $YZ$  plane ( $\varphi = 25^\circ$ ).

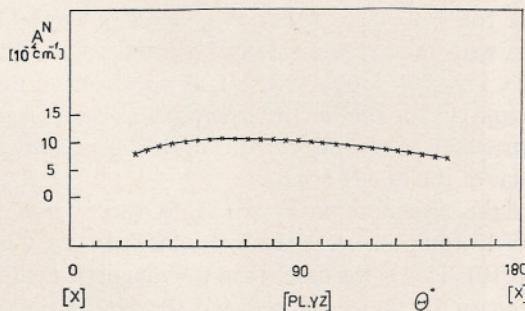


FIG. 8. Angular dependence of splitting from nitrogen in the plane of the complex.

#### 4. HYPERFINE STRUCTURE DUE TO THE HYDROGENS

As already stated, due to the use of  $^{63}\text{Cu}$  isotope, for certain orientations a well resolved EPR spectrum was observed pointing to interaction between the unpaired electron and hydrogens as well (Fig. 9). In Fig. 9, moreover, a simulated spectrum

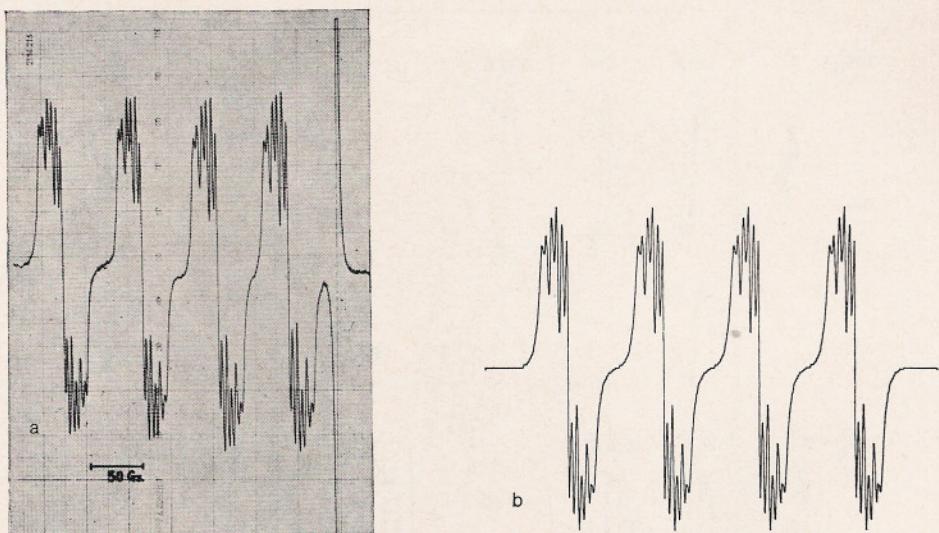


FIG. 9. 11-component EPR spectrum of the copper ion  $^{63}\text{Cu}^{2+}$  in TGS at  $n^{\text{H}} = 2$ ,  $A^{\text{H}} = \frac{1}{2} A^{\text{N}}$ ; (a) original spectrum; (b) simulated spectrum with a JRA-1 spectrum accumulator  $2\Delta B_{1/2}^{\text{L}} = 0.7 A^{\text{N}}$ ,  $A^{\text{H}} = 0.45 A^{\text{N}}$ .

obtained with a JRA-1 spectrum accumulator on the assumption of interaction with two hydrogen nuclei, in addition to interaction with copper and two nitrogens, is shown. On assuming the ratio:

$$\eta = \frac{A^{\text{N}}}{A^{\text{H}}} = 2,$$

and the number of nitrogen and hydrogen atoms  $n^{\text{N}} = 2$ ,  $n^{\text{H}} = 2$ , respectively, the number of lines  $N$  was calculated from the formula

$$N = 2I^{\text{N}}n^{\text{N}}\eta + 2I^{\text{H}}n^{\text{H}} + 1. \quad [5]$$

This formula is true for  $N \leq N_{\text{max}}$ , where  $N_{\text{max}} = (2I^{\text{N}}n^{\text{N}} + 1) \cdot (2I^{\text{H}}n^{\text{H}} + 1)$  yielding  $N = 11$ , in agreement with the experimentally observed value. The intensities of the individual lines are as 1:2:3:4:5:6:5:4:3:2:1. A spectrum of this type arises when the interaction constant  $A^{\text{H}}$  for one of the hydrogen nuclei of each glycine is larger than that for the other which can be neglected. This is the case when the magnetic field direction lies close to that of the N—H bond.

During rotation of the crystal about  $X$  axis, EPR spectra are observed in the  $YZ$  plane which consist of 13 components of the hyperfine structure due to four equivalent hydrogen nuclei (Fig. 10). This is the case when the magnetic field is directed approximately along the bisector of the angle between the N—H bonds in the



group.

Figure 10 also shows the simulated spectrum. On assuming as previously

$$\eta = \frac{A^{\text{N}}}{A^{\text{H}}} = 2,$$

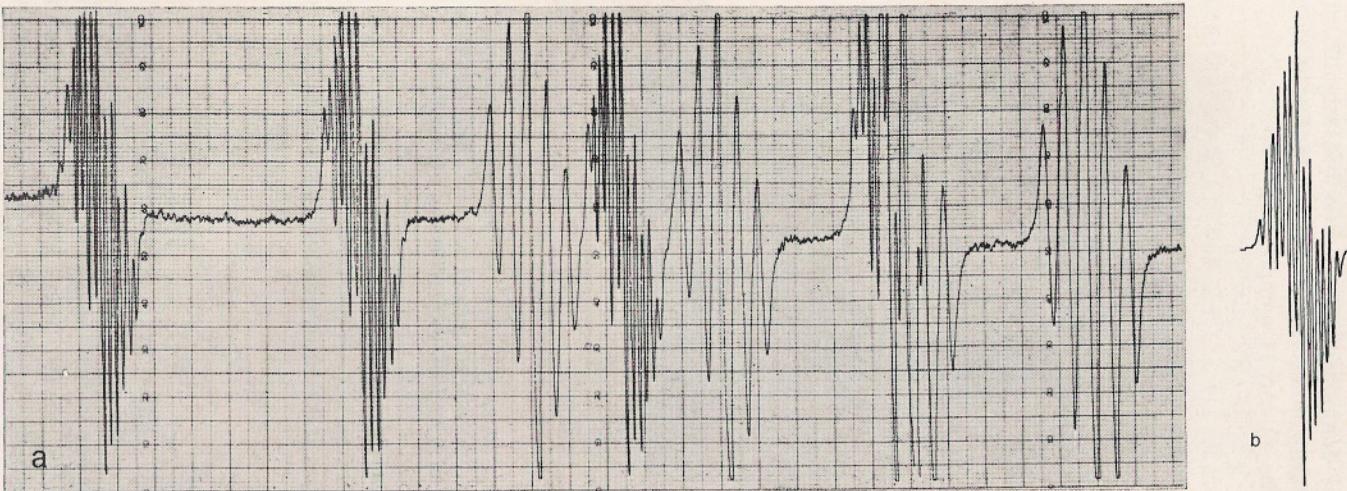


FIG. 10. 13-component EPR spectrum of the copper ion  $^{63}\text{Cu}^{2+}$  in TGS at  $n^{\text{H}} = 4$ ,  $A^{\text{H}} = \frac{1}{2}A^{\text{N}}$ : (a) original spectrum, (b) simulated spectrum  $2\Delta B_{1/2}^{\text{L}} = 0.42A^{\text{N}}$ ,  $A^{\text{H}} = 0.6A^{\text{N}}$ .

with  $n^N = 2$ ,  $n^H = 4$ , and on calculating the number of lines  $N$  from Eq. [5], we obtain  $N = 13$ . The intensity ratios of the lines now are 1:4:8:12:16:20:22:20:16:12:8:4:1. The 13-component and 11-component spectra differ but insignificantly. This is obvious if one considers their intensity ratios. Thus, on reduction to scale by dividing the former by 4, we obtained for the 13 and 11 components, respectively:

$$\frac{1}{4}:1:2:3:4:5:5\frac{1}{2}:5:4:3:2:1:\frac{1}{4}, \text{ and } 1:2:3:4:5:6:5:4:3:2:1.$$

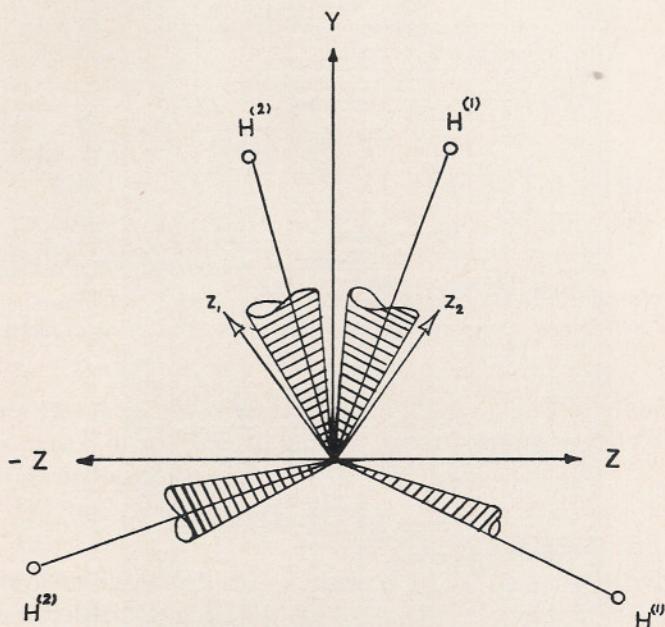
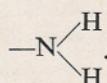


FIG. 11. Regions of maximal values of the hyperfine interaction constants  $A^H$  in the  $YZ$  plane. The angles between the  $-N-H$  directions are seen to equal  $95^\circ$ , their bisector is perpendicular to the principal  $z$  axis of the complex. ■ Regions where proton HFS is resolved.

Figure 11 shows the intervals of hyperfine splitting in the  $YZ$  plane due to hydrogen nuclei. Four splitting maxima are seen to occur, two for each of the two complexes, subtending pairwise angles of  $95^\circ$  corresponding to the angle between the  $N-H$  bonds in



The splitting constants  $A^H$  assume maximal values amounting to 3.5 and 4.3 Gauss.

Now, if the crystal is rotated about the  $Y$  axis at a certain orientation, the magnetic field becomes parallel to one of the  $N-H$  bonds leading to effective interaction with only two hydrogen nuclei of the two amine groups belonging to the complex. At  $50^\circ$  with respect to the  $X$  axis, the constant of hyperfine interaction with the hydrogens exhibits a maximum value of 4.6 gauss.

With the aim of deciding whether the hyperfine structure is really due to hydrogens

of the  $-\text{NH}_2$  group and not the  $-\text{CH}_2-$ , we studied the EPR spectrum of single crystals with deuterated glycines  $^+\text{ND}_3\text{CH}_2\text{COO}^-$ . The spectra previous and subsequent to deuteration are shown in Figs. 9 and 12, respectively. One notes a splitting into a quintet, due solely to interaction with the two nitrogen nuclei. Spectrum simulation

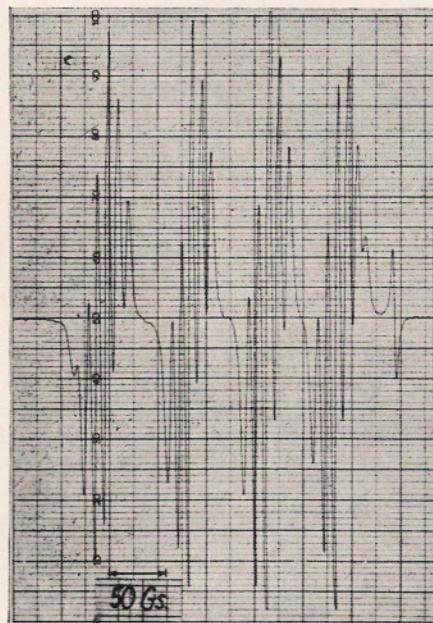


FIG. 12. Spectrum of deuterated TGS:  $\text{Cu}^{2+}$ .

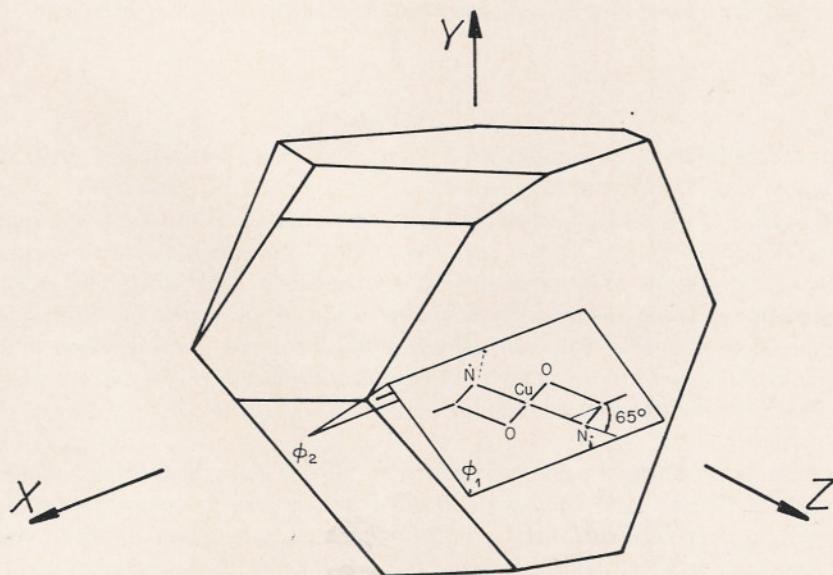


Fig. 13. Disposition of the glycine-copper complex in TGS crystal.

yielded a lesser width for the individual components of the quintet amounting to  $2\Delta B_{1/2}^L = 0.9A^N$ . In the study of deuterated TGS crystal, copper of natural abundance was used. Also EPR spectra were obtained for protonated TGS, containing copper at natural isotope composition. The last spectrum resembled the one from TGS with  $^{63}\text{Cu}$  isotope. Hence, the absence of further splitting of the quintets for TGS: $\text{Cu}^{2+}$  is not a result of using copper ions at natural composition. The lack of splitting due to hydrogen in the deuterated TGS: $\text{Cu}^{2+}$  spectrum proves that the hydrogens of amine groups, and not those of the methylene groups, are responsible for the hyperfine splitting. Fig. 13 shows the disposition of the glycine-copper complex in TGS as well as the direction of —N—Cu—N bond with respect to the X axis ( $65^\circ \pm 5^\circ$ ).

#### ACKNOWLEDGMENTS

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#### REFERENCES

1. A. LÖSCHE AND W. WINDSCH, *Physica Status Solidi* **11**, K55 (1965).
2. W. WINDSCH AND M. WELTER, *Z. Naturforsch.*, **22a**, 1 (1967).
3. J. STANKOWSKI, *Proc. Internat. Meeting on Ferroelectricity*, Prague 1966, Vol. II, pp. 364–368.
4. J. STANKOWSKI, *Acta Phys. Polon.* **33**, 387 (1968).
5. J. STANKOWSKI, *Physica Status Solidi* **24**, 451 (1967).
6. A. ABRAGAM AND B. BLEANEY, "Electron Paramagnetic Resonance of Transition Ions", Clarendon Press, Oxford 1970, p. 175.