

molal. This corresponds to conditions when precipitation is nearly complete. It eliminates Fe^{++} and FeF^{++} as possible poison species and indicates FeF_3 , FeF_4^- , and FeF_5^{2-} are the most likely species responsible for poisoning.

CONCLUSIONS

It has been shown that a ferric fluoride complex ion is a step poison for the growth of lithium fluoride. The growth behavior has been found to correspond qualita-

tively to the expected behavior. Step poisons increase rate of two-dimensional nucleation at fixed supersaturations, but markedly decrease the rate of step motion or of spreading of the newly formed layers.

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Line Shapes of Electron Paramagnetic Resonance Signals Produced by Powders, Glasses, and Viscous Liquids*

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The line shapes arising from randomly oriented particles in a fixed position have been calculated. It has been found that it is possible to determine the three principal g factors with relatively high accuracy and without investigating single crystals. Measurements on powders of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ are used as examples. In addition, the influence of Brownian rotation in viscous liquids on line shapes has been studied. Equations have been derived for the case of high viscosities, supplementing the well-known ones given by McConnell [J. Chem. Phys. **25**, 709 (1956)]. To a first approximation, the effect of decreasing viscosity can be described by an over-all diminishing line width and an unchanged line shape function. The hyperfine splittings are neglected, but can be taken into account.

INTRODUCTION

IN recent papers, Sands,¹ O'Reilly,² and Roberts³ determined experimentally $g_{||}$ and g_{\perp} of unpaired electron spins in fields with axial symmetry of different samples by the consideration of the epr-line shapes produced by the paramagnetic substances dissolved in glasses and highly viscous liquids. Searl, Smith, and Wyard⁴ have carried out a calculation of line shapes for epr-signals caused by two different principal g values including other broadening effects. No treatment of line shapes produced by paramagnetic materials with three different principal g factors has been published. Therefore, the explanation of the absorption lines of powders of $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{Cu}(\text{NH}_3)_4(\text{NO}_3)_2$ measured by Carlson and Spence⁵ has encountered some difficulties.

One purpose of this paper is to present the results of a study of the feasibility of determining the principal

g values from an examination of the epr-line shapes of powders, solutions in glasses, or highly viscous liquids. Such measurements can provide welcome preliminary information for determining the magnetic axes and g factors of single crystals described by Schonland.⁶ In addition, there is some evidence of a difference of the g tensors of a special group of molecules³ measured in single crystals or in solutions.

The second part of this paper deals with the influence on line shapes of Brownian rotation of the paramagnetic particles with anisotropic g factor in viscous liquids.

THEORY

The following assumptions will be made:

- Only systems with $S = \frac{1}{2}$ will be considered.
- The paramagnetic molecules are randomly oriented.
- Hyperfine splitting is neglected.
- Broadening of the absorption lines due only to the anisotropic g factor is taken into account.
- The Brownian motion of the paramagnetic particles in viscous liquids is independent of the magnetic interactions between these particles and their neighbors or the external field. This behavior differs

* This investigation was supported in part by a research grant from the division of General Medical Sciences, Public Health Service, National Institutes of Health.

¹ R. H. Sands, Phys. Rev. **99**, 1222 (1955).

² D. E. O'Reilly, J. Chem. Phys. **29**, 1188 (1958).

³ E. M. Roberts, J. Am. Chem. Soc. (to be published).

⁴ J. W. Searl, R. C. Smith, and S. J. Wyard, Proc. Phys. Soc. (London) **74**, 491 (1959).

⁵ E. H. Carlson and R. D. Spence, J. Chem. Phys. **24**, 471 (1956).

⁶ D. S. Schonland, Proc. Phys. Soc. (London) **73**, 788 (1959).

from Brownian rotation influenced by electric dipole-dipole interaction treated by Debye.⁷

Line Shapes Due to Fixed Orientations

First, we calculate line shapes due to particles randomly oriented. Restrictions (a) and (c) lead to the following Hamiltonian:

$$\mathcal{H} = \beta \sum_k H_k' g_k' S_k'$$

for a molecule fixed coordinate system

$$= \beta \sum_k \sum_l H_k G_{kl} S_l$$

for a space fixed coordinate system (1)

where H_k, H_k' are the components of the magnetic field; S_k', S_l the components of the Pauli spin operator; G_{kl} the time dependent g tensor and g_k the principal g values. Taking $H_k = (0, 0, H_z)$ and introducing $g = \hbar\omega/\beta H_z$, we find

$$g^2 = g_1^2 \sin^2\beta \sin^2\gamma + g_2^2 \sin^2\beta \cos^2\gamma + g_3^2 \cos^2\beta$$

or

$$g^2 = g_1^2 + (g_3^2 - g_1^2) \cos^2\beta \quad \text{for} \quad g_1^2 = g_2^2. \quad (2)$$

α, β, γ are the Eulerian angles as defined by Margenau and Murphy.⁸

The normalized shape functions $S(H_z)$ or $S(g^2)$ are determined by the probability of the molecules to absorb in the region H_z to $H_z + dH_z$ or g^2 to $g^2 + d(g^2)$. Therefore we can write

$$S(H_z) = \Omega^{-1} \cdot (dH_z)^{-1} \int_{H_z}^{H_z + dH_z} d\Omega,$$

$$\int_0^\infty S(H_z) dH_z = 1, \quad (3)$$

$$S(g^2) = S(H_z) \cdot 2H_z^3 \cdot \omega^{-2} \beta^2 \hbar^{-2}. \quad (3a)$$

Ω is the phase space. Assumption (b) leads to $d\Omega = \sin\beta d\beta d\gamma = -dz d\gamma$, $\Omega = 4\pi$, where $z = \cos\beta$.

For $g_1 = g_2$, the normalized line shapes can be calculated in a straightforward manner with the aid of Eqs. (2) and (3). They have been evaluated previously by Sands.¹

$$S(H_z) = H_\perp^2 H_\parallel (H_\perp^2 - H_\parallel^2)^{-1/2} H_z^{-2} (H_\perp^2 - H_z^2)^{-1/2}. \quad (4)$$

For three different principal g values, we have to consider in more detail the behavior of g^2 in the phase space. The symmetry of Eq. (2) allows us to reduce the space to an area of $\Omega = \pi/2$. Figure 1 shows the variation of g^2 within this region. For the calculation

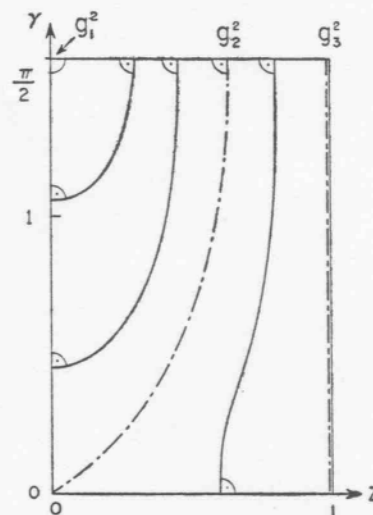


FIG. 1. g^2 as a function of z and γ . g_1, g_2, g_3 are principal g values.

of $S(g^2)$ the following formula is applied:

$$\Omega^{-1} (da)^{-1} \int_a^{a+da} d\Omega(a) = \Omega^{-1} \int_{\Omega'} (d\Omega / |\text{grad}_{\Omega} a|), \quad (5)$$

where a is a function of n dimensions and $d\Omega$ the corresponding volume element. Ω' is Ω reduced by the condition: $a = \text{constant}$. If $d\Omega = dx dy$, this equation becomes

$$(da)^{-1} \int_a^{a+da} dx dy = \int_s (ds / |\text{grad}_a a|) = \int_{a=\text{const}} [dx / a_y(x, a)], \quad (6)$$

where $a_y = \partial a / \partial y$. These expressions can be used to determine shape functions due to Hamiltonians more complicated than (1), e.g., with hyperfine interactions.

The application of (6) leads to the normalized shape functions for $g_3 > g_2 > g_1$: for $H_z \leq H_2$:

$$S(H_z) = 2/\pi \frac{H_1 H_2 H_3 H_z^{-2}}{(H_1^2 - H_z^2)^{1/2} (H_2^2 - H_z^2)^{1/2}} K(k)$$

with

$$k^2 = \frac{(H_1^2 - H_z^2)(H_z^2 - H_3^2)}{(H_1^2 - H_2^2)(H_2^2 - H_3^2)}$$

for $H_z \geq H_2$:

$$S(H_z) = 2/\pi \frac{H_1 H_2 H_3 H_z^{-2}}{(H_1^2 - H_2^2)^{1/2} (H_z^2 - H_3^2)^{1/2}} K(1/k). \quad (7)$$

$K(k)$ is the complete elliptic integral of the first kind, see Jahnke and Emde.⁹

$$K(k) = \int_0^{\pi/2} db / (1 - k^2 \sin^2 b)^{1/2},$$

$$K(0) = \pi/2, \quad K(1) = \infty. \quad (8)$$

⁷ P. Debye, *Polar Molecules* (The Chem. Catalog Company, New York, 1929).

⁸ H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (Van Nostrand Company, New York, 1956), 2nd ed.

⁹ E. Jahnke and F. Emde, *Tables of Functions* (Dover Publications, New York, 1945), 4th ed.

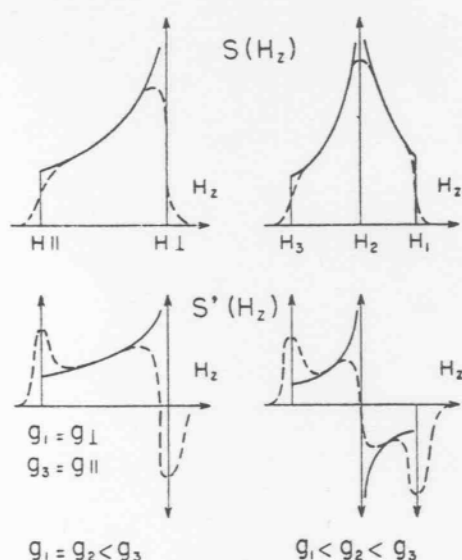


FIG. 2. The shape functions $S(H_z)$ and their derivatives.

Expressions similar to (7) have been found by Bloembergen and Rowland¹⁰ for nmr-line shapes due to anisotropic Knight shift in metals and due to nuclear quadrupole coupling by Cohen and Reif.¹¹

What are the line shapes expected? Figure 2 shows the $S(H_z)$ according to (4) and (7). The continuous lines represent the ideal curves; the broken ones are an approach to the real shapes. This figure indicates: (A) We are able to distinguish between signals due to two and three different principal g values g_k . The derivative of the shape corresponding to two g 's has five points of inflection; the other one has seven. (B) We can determine or estimate all g factors in both cases. $g_{||}$, g_{\perp} , g_1 , and g_3 correspond to maxima, g_2 to a zero point of the derivatives.

With assumption (c), these statements are true in a first approximation. To estimate the errors introduced by Gaussian broadening, we can proceed as follows. For H_z near H_1 , H_3 , $H_{||}$, we superimpose a Gaussian shape with the line width $2H_0$ upon a linear approximation of our ideal curve. H_0 can vary with H_z , but special values of H_0 can be found as indicated in Fig. 2 in experimental curves. The superposition of the two shapes is calculated by taking the convolution⁸ (Faltung) of the shape functions. The effect of additional Gaussian broadening is in a first approximation a shift of the maxima corresponding to g_1 , g_3 and $g_{||}$ of the derivatives. As an example, we write the equation for the position of the maximum near $H_{||}$.

$$H_{z,\max} = H_{||} + H_0^2 \{ [H_{||}/(H_{\perp}^2 - H_{||}^2)] - (2/H_{||}) \}. \quad (9)$$

This is a second-order effect. Similar expressions are valid for the shifts near H_1 and H_3 . But for the cases corresponding to H_2 and H_{\perp} , such equations are difficult

to find. Graphical methods or exact calculations, including all broadening effects from the beginning,⁴ are necessary to determine the theoretical error of the H_2 or H_{\perp} determination.

The Effect of Brownian Rotation

For epr measurements dealing with viscous solutions, we must consider the effects of Brownian rotation on the line shapes. We use two probability densities to describe this movement, P_0 and P_{τ} . They are functions of the orientations determined by the Eulerian angles α , $z = \cos\beta$, γ of the molecules containing unpaired spins. $P_0(\alpha, z, \gamma)$ is the probability density to find such a molecule with an orientation in the interval between α, z, γ and $\alpha + d\alpha, z + dz, \gamma + d\gamma$ at a certain time t_0 . P_0 is independent of the time t_0 and with assumption (e), we can easily prove

$$P_0(\alpha, z, \gamma) = 1/4\pi. \quad (10)$$

P_{τ} is the probability density of finding a molecule in the interval at α, z, γ at time $t_0 \pm \tau$, if it was or will be in the interval α_0, z_0, γ_0 at time t_0 . P_{τ} is independent of t_0 , and it represents a solution of the equation

$$\partial P_{\tau} / \partial \tau = D \Delta_{(\alpha, z, \gamma)} P_{\tau}. \quad (11)$$

The initial condition for time t_0 or $\tau = 0$ is

$$P_{\tau}(\alpha_0, z_0, \gamma_0, \tau, \alpha, z, \gamma)_{\tau=0} = \delta(\alpha - \alpha_0, z - z_0, \gamma - \gamma_0). \quad (12)$$

Equation (18) follows from assumption (e) and it is related to the laws ruling heat transfer and diffusion. Debye⁷ calculated D for spherical particles of volume V in a liquid with a viscosity η at temperature T :

$$D = kT/6V\eta, \quad \tau_c = 1/6D = V\eta/kT. \quad (13)$$

In epr and nmr literature D is usually replaced by τ_c . Because we will deal with averages of functions of z and γ only, we take the following solution of (11) and (12) as P_{τ} :

$$P_{\tau}(z_0, \gamma_0, \tau, z, \gamma) = \sum_n \exp\{-[n(n+1)\tau]/6\tau_c\} \times \sum_m Y_n^{*m}(z_0, \gamma_0) Y_n^m(z, \gamma). \quad (14)$$

Y_n^m are normalized spherical functions. Averaging any function of the form

$$f(z, \gamma) = \sum_m a_m Y_n^m(z, \gamma)$$

by the aid of P_{τ} we find

$$\iint f(z, \gamma) P_{\tau} dz d\gamma = \exp\{-[n(n+1)\tau]/6\tau_c\} \cdot f(z_0, \gamma_0). \quad (15)$$

The effect of Brownian rotation on the absorption curves can be described by a contribution to the spin-

¹⁰ N. Bloembergen and T. J. Rowland, *Acta Met.* **1**, 731 (1953).

¹¹ M. Cohen and F. Reif, in *Solid State Physics* (Academic Press, Inc., New York, 1957), Suppl. to Vol. 5.

lattice relaxation and one to the spin-spin interaction. The former decreases with growing viscosity; the latter increases and causes an asymmetric line shape.

McConnell¹² has given a first approximation for these two effects in slightly viscous liquids, using the relaxation times T_1 and T_2' . Assuming $g_1 = g_2$, he found a good formula for the broadening due to spin-lattice relaxation, but his expression for the spin-spin interaction neglects the asymmetry of the line shapes. Therefore, an approximation of the spin-spin effect for high viscosities is needed.

The square of the Hamiltonian (1) as function of time t can be written

$$\mathcal{H}^2(t) = \frac{1}{4}(\beta H_z)^2 g^2(t) U = \frac{1}{4}\hbar^2 \omega^2(t) U. \quad (16)$$

U is the two-dimensional unity matrix. Assuming a high viscosity and $|g_1 - g_3| \ll g_1$, we neglect the spin-lattice contribution and calculate averages of $\omega^2(t)$ or $g^2(t)$ as follows: We consider the paramagnetic particles with an orientation in the region α_0, z_0, γ_0 at about time t_0 . Some of their unpaired spins undergo transitions; we call the group of these spins $E(\alpha_0, z_0, \gamma_0)$. Because of our assumptions, the number of particles in such a group is independent of α_0, z_0, γ_0 and t_0 . The uncertainty of t_0 is determined by Heisenberg's principle: $\Delta t \approx 1/\omega$. To calculate the shape functions due to Brownian rotation, we replace g^2 of (2) by the averages of g^2 over all particles of a group E and over the time interval $t_0 \pm \Delta t$. We introduce the spin-spin relaxation, taking¹³ only the interval $|\nu| \leq 1/\pi T_2'$ of the Fourier spectrum. The relaxation time T_2' is much larger than Δt , because $|g_1 - g_3| \ll g_1$. g^2 of (2) is a linear combination of Y_0^0 and Y_2^m . Therefore, we have to consider only Y_2^m . Averaging Y_2^m over E leads to

$$\begin{aligned} \langle Y_2^m \rangle_{Av}^E &= \iint P_\tau Y_2^m d\alpha d\gamma = Y_2^m(z_0, \gamma_0) \exp[-|\tau|/\tau_c] \\ &= \int_{-\infty}^{+\infty} a(z_0, \gamma_0, \nu) \exp(i2\pi\nu\tau) d\nu. \end{aligned} \quad (17)$$

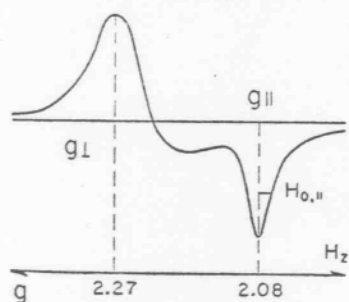


FIG. 3. Derivative presentation of the electron paramagnetic resonance spectrum of polycrystalline $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with two principal g values. Measured at room temperature at a frequency of about 9.2 kMc/sec with a Varian 100 kc spectrometer, model V-4500.

¹² H. M. McConnell, J. Chem. Phys. **25**, 709 (1956).

¹³ N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. **73**, 679 (1948).

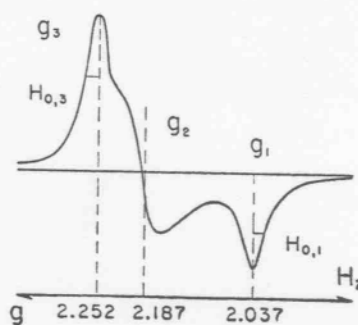


FIG. 4. The same as Fig. 3, but for $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with three different g factors.

Introducing T_2' and taking the average over the time interval $t_0 \pm \Delta t$, we find

$$\begin{aligned} \langle Y_2^m \rangle_{Av} &= \frac{1}{2} \Delta t^{-1} \int_{-\Delta t}^{+\Delta t} d\tau \int_{-1/\pi T_2'}^{+1/\pi T_2'} a(z_0, \gamma_0, \nu) \exp(2\pi i \nu \tau) d\nu \\ \langle Y_2^m \rangle_{Av} &= Y_2^m(z_0, \gamma_0) (2/\pi) \tan^{-1}(\tau_c/T_2'). \end{aligned} \quad (18)$$

Using this result, we can determine $\langle g^2 \rangle_{Av}$.

$$\begin{aligned} \langle g^2 \rangle_{Av} &= \sin^2 \beta_0 \sin^2 \gamma_0 [s + (g_1^2 - s) (2/\pi) \tan^{-1}(\tau_c/T_2')] \\ &\quad + \sin^2 \beta_0 \cos^2 \gamma_0 [s + (g_2^2 - s) (2/\pi) \tan^{-1}(\tau_c/T_2')] \\ &\quad + \cos^2 \beta_0 [s + (g_3^2 - s) (2/\pi) \tan^{-1}(\tau_c/T_2')] \\ s &= (g_1^2 + g_2^2 + g_3^2)/3. \end{aligned} \quad (19)$$

Concerning the angular dependence, this equation is similar to (2). Only the g_k 's of (2) must be replaced by $s + 2/\pi \cdot (g_k^2 - s) \cdot \tan^{-1} \tau_c/T_2'$. Therefore, the shape functions $S(g^2)$ and $S(\langle g^2 \rangle_{Av})$ are equal. With the assumption $|g_1 - g_3| \ll g_1$, we can use the transformation (3a) to determine the first approximation of $S(\langle H_z \rangle_{Av})$. The difference between s and g_0^2 , where $g_0 = \frac{1}{3}(g_1 + g_2 + g_3)$, is very small. Therefore the Brownian rotation reduces the over-all width of the absorption line, but it does not affect its shape as long as T_2'/τ_c is small. The points corresponding to $g_{||}$, g_{\perp} or g_1, g_2, g_3 move with increasing T_2'/τ_c towards g_0 .

EXPERIMENTS

Fixed Orientations

In order to demonstrate the line shapes arising from arbitrarily oriented molecules, the first derivatives of the absorptions due to crystalline powders of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ have been measured at room temperature and a frequency of about 9.2 kMc/sec. In spite of exchange effects,¹⁴ these powders show the expected curves, as is evident from Figs. 3 and 4.

The principal g values of these salts have been determined by single crystal measurements¹⁴ as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$: $g_{\perp} = 2.27$, $g_{||} = 2.08$; $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$: $g_1 = 2.037$, $g_2 = 2.187$, $g_3 = 2.252$. To calculate the positions of the peaks of our derivatives, we determine first the half-

¹⁴ K. D. Bowers and J. Owen, Repts. Progr. in Phys. **18**, 304-373 (1955).

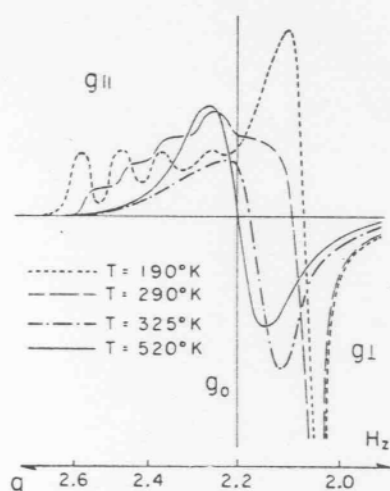


FIG. 5. Derivative presentation of the electron paramagnetic resonance absorption of a solution of $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ ($x=0-5$), in glycerol at different temperatures. The microwave frequency is about 9.2 kMc/sec. The intensity scale is different for each curve.

line widths H_0 from the experimental curves. We find $H_{0,11}/H_{11}=6.6 \cdot 10^{-3}$, $H_{01}/H_1=7.0 \cdot 10^{-3}$; $H_{03}/H_3=7.8 \cdot 10^{-3}$. Using Eq. (9) and related ones, we evaluate theoretical errors of the g determination; $\delta g_{11}/g_{11}=0.36 \cdot 10^{-3}$, $\delta g_1/g_1=0.43 \cdot 10^{-3}$, $\delta g_3/g_3=1.1 \cdot 10^{-3}$.

These estimated errors or corrections are comparable with those of single crystal work, $2 \cdot 10^{-3}$. Our results are plotted in Figs. 3 and 4. There is a good agreement with our theory. The position of the peak corresponding to g_1 seems to undergo a shift of the same order of magnitude as those just mentioned, whereas the zero point belonging to g_2 moves more.

Effect of Brownian Rotation

To demonstrate the change of the line shapes caused by Brownian rotation, we measured the epr absorption of a solution of $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$ ($x=0-5$) in glycerol at temperatures from -140°C to 250°C . The absorption patterns do not depend on the initial water content (x) of the sulfate. The influence of the concentration of the solute on the shapes can be neglected for our considerations. The viscosity of glycerol is a complex

function of the amount of impurities and solutes and varies considerably with temperature. Lutze and Bösnecker¹⁵ have recently investigated the system CuSO_4 -glycerol by epr. They have related the spectra from 90°K to room temperature to two different paramagnetic centers.

For our measurements, we have varied the temperature in steps of about 5°C and have found a continuous change with increasing temperature of the entire line shape toward a Gaussian or Lorentzian shape. This behavior can be explained by a Hamiltonian slightly different from (1) and a modified Eq. (19). Figure 5 shows four of the measured curves and demonstrates the shift of the peaks toward g_0 predicted by (19).

If we take an anisotropic g factor with axial symmetry and a nuclear-spin coupling with the same properties, we can relate our absorption pattern to a single type of paramagnetic centers. The Hamiltonian is

$$\mathcal{H} = \beta \sum_k \sum_l H_k G_{kl} S_l + \sum_k \sum_l A_{kl} I_k S_l \quad (20)$$

where A_{kl} and G_{kl} are tensors with the same axis of symmetry. We find from our measurement $g_{\perp} \approx 2.08$, $g_{11} \approx 2.40$, $A_{11} \approx 130$ gauss, A_{\perp} small, in accordance with the low-temperature results of Lutze and Bösnecker.¹⁵ The assignment of g_{\perp} and g_{11} is justified by the ratio of their differences from g_0 and the line shapes. To study the relaxation effects of the system CuSO_4 -glycerol quantitatively, we need additional information on the influence of impurities on the viscosity as well as detailed knowledge on how the viscosity changes with temperature.

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¹⁵ E. Lutze and D. Bösnecker, Z. Naturforsch. **14a**, 755-58 (1959).