(2) We measure the decay time constant of the exponential envelope of the echo in a two-pulse spin-echo experiment to be 1.5 msec. For a Lorentzian line shape, this number implies a peak-to-peak derivative width of 0.22 G, in agreement with Poitrenaud's value. Both measurements are in approximate agreement with Gutowsky and McGarvey's value[2] for the linewidth at 80°K, 0.50 G, if that value is corrected for the T_1 contribution to the linewidth. From our T_1 data, the linewidth contribution at 77°K is 0.20 G. The free-induction decay times in our samples range from 0.60 to 0.75 msec at low temperatures, and are determined by an inhomogeneous broadening mechanism, presumably a distribution of Knight shifts associated with conduction-electron scattering from impurities.

(3) We measure the free-induction decay time for Rb^{87} to be 0.17 msec at 4.2°K. The peak-to-peak derivative width calculated from this value, for a Lorentzian line shape, is 0.78 G. Poitrenaud's value is 0.70 G, and is probably a more reliable number. The earlier measured value[3] of about 1.3 G at 80°K appears to be spurious, since the T_1 contribution to the linewidth at 80°K is only 0.092 G.

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We would like to thank Professor W. G. Clark, whose healthy skepticism about the reality of the anomalous cesium data caused us to carefully investigate the temperature distribution in the samples.

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Forbidden Hyperfine Spectra in Electron Spin Resonance due to Hyperfine Anisotropy and Nuclear Zeeman Interaction*

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Electron spin resonance of Co^{2+} in $Zn(NH_4)_2(SO_4)_2\cdot 6H_2O$ has been studied at 35 and 70 GHz at liquid-helium temperatures. In addition to the usual eight-line hyperfine spectrum from Co^{59} $(I=\frac{7}{2})$, a seven-line "forbidden" hyperfine spectrum was also observed with the applied magnetic field nearly perpendicular to the symmetry axis of the crystalline field. The "forbidden" transitions do not result from nuclear quadrupole coupling, but arise because of the very large anisotropy of the hyperfine interaction, more specifically because $Ag_{\parallel}\gg Bg_{\perp}$. As a consequence of this anisotropy, the axis of spin quantization of the nucleus deviates appreciably from the direction of the applied field, and the nuclear Zeeman interaction contains terms in I_x that at high fields and certain angles can become comparable to the terms in I_z. Since the intensity of the forbidden spectra is a direct measure of the field at the nucleus, it is found that there exists at the cobalt nucleus a pseudo-magnetic-field the same order of magnitude as the applied magnetic field. The measured pseudo-field, which results from the induced magnetization of the electron charge distribution by the external field, is in order-of-magnitude agreement with calculations.

INTRODUCTION

THE electron spin resonance of Co^{2+} in the Tutton salt $Zn(NH_4)_2(SO_4)_2\cdot 6H_2O$ has been extensively studied experimentally by Bleaney and Ingram,[1,2] primarily at 9 GHz, and theoretically by Abragam and Pryce.[3–5] Bleaney and Ingram[2] observed, as x-ray analysis had previously indicated, the existence of two inequivalent sites per unit cell for the Co^{2+} ion, the resonance of each site being related to the other by a simple rotation of the principal axes of the g tensor. For a discussion of crystal structure of the Tutton salts and related details, the reader is referred to the papers of Bleaney and Ingram and references contained therein. The resonance spectra of each site with the eight-line hyperfine structure due to the Co^{59} nucleus, spin $I=\frac{7}{2}$, was satisfactorily explained by a spin Hamiltonian

$$\mathcal{H}=g_{\parallel}\beta H_zS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+AI_zS_z+B(I_xS_x+I_yS_y), \quad (1)$$

with $g_{\parallel}=6.45$, $g_{\perp}=3.06$, $A=2.45\times10^{-2}$ cm^{-1}, and $B=2.0\times10^{-3}$ cm^{-1}.

MEASUREMENTS

Prior to an investigation of spin-spin interactions in the isomorphic concentrated cobalt Tutton salt, we have remeasured the resonance of 0.01% Co^{2+} in zinc ammonium sulfate at 35 GHz. For angles of the applied magnetic field less than 75° from the symmetry axis

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of the g tensor, the measurements were in agreement with those of Bleaney and Ingram. However, for $\theta > 75°$, an additional seven-line "forbidden" hyperfine spectrum was observed (see Fig. 1), the individual forbidden lines being located midway between adjacent pairs of lines of the normal hyperfine structure. The intensity of the forbidden lines as compared to the normal hyperfine spectrum was remarkably sensitive to the angle θ, as can be seen in Fig. 1. By comparing measurements at 35 and 70 GHz at a given angle, the relative intensity of the forbidden lines was found to increase with increasing frequency.

CALCULATION AND RESULTS

A. The Hamiltonian

The mechanism usually responsible for forbidden transitions in ESR spectra is the interaction of a nuclear quadrupole moment with an electric field gradient. Although Co^{59} possesses a reasonably large quadrupole moment, the quadrupole interaction cannot possibly be the cause of the observed forbidden structure for several reasons. Bleaney and Ingram[2] did not observe any influence of a quadrupole interaction on the spacings of the hyperfine lines at 9 GHz and concluded from their measurements that the quadrupole-coupling constant must be less than 5×10^{-4} cm^{-1}, in agreement with the calculations of Abragam and Pryce.[5] The intensity of forbidden transitions calculated for such an interaction is two orders of magnitude smaller than that measured. Also, the relative intensity of one

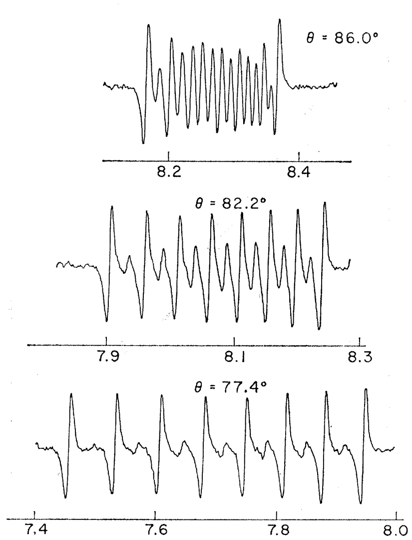

FIG. 1. The field derivative of the electron-spin-resonance spectrum of Co^{2+} in $Zn(NH_4)_2(SO_4)_2\cdot 6H_2O$ is illustrated at several different angles of the magnetic field with respect to the tetragonal axis. In addition to the usual eight "allowed" hyperfine lines associated with the $I=\frac{7}{2}$ Co^{59} nucleus, the spectra exhibit seven "forbidden" lines. The measurements were performed at $\nu=35.7$ GHz, $T=1.2$°K.

forbidden line as compared to another is not that predicted by a quadrupole interaction, nor can the angular dependence or the frequency dependence be explained by such an interaction.[6]

The fact that the intensity of the forbidden lines increases with increasing frequency and field indicates that the transitions do not arise from terms off diagonal in the electron spin, such as S_x. Since such terms admix states having different eigenvalues M of S_z, the energy separation of which increases with field, the forbidden intensity arising from such a perturbation would decrease with increasing magnetic field and level separation. At the field used in these measurements, the calculated forbidden intensity resulting from terms in S_x is four orders of magnitude less than the observations.

The forbidden transitions are explained, however, by including in the Hamiltonian the interaction of the nuclear spin with magnetic field. In addition to the hyperfine and electronic Zeeman interaction terms of Eq. (1) we consider

$$\mathcal{H}_N = -\gamma\beta_N \mathbf{H}\cdot\mathbf{I} - \mathbf{H}\cdot\mathbf{R}\cdot\mathbf{I}, \tag{2}$$

where the first term on the right is the usual Zeeman interaction of the nuclear moment with the applied field, and the second term is the interaction of the nucleus with a field produced by the induced magnetization of the electronic charge distribution by the external field. As discussed by Elliott[7] and Low,[8] this interaction results from the coupling of the electrons both to the external field $\beta\mathbf{H}(\mathbf{L}+2\mathbf{S})$ and to the nuclear spin $(2\gamma\beta_N\beta/\langle r^3\rangle)\mathbf{N}\cdot\mathbf{I}$. Here $\mathbf{N}$ is a function of both the electronic spin and angular momentum operators.[7,9] In second-order perturbation theory, the interaction takes the form of Eq. (2). An order-of-magnitude estimate of R for Co^{2+} is given by the expression

$$R \approx 2\gamma\beta_N\beta/\langle r^3\rangle\lambda, \tag{3}$$

where λ is the spin-orbit splitting of the orbitally degenerate ground state in the approximately tetragonal symmetry of the crystalline field. With $\lambda\approx200$ cm^{-1}, Eq. (3) gives $R\approx10^{-8}$ cm^{-1}/G, a number the same order of magnitude as $\gamma\beta_N=3\times10^{-8}$ cm^{-1}/G. For tetragonal symmetry, the nuclear Hamiltonian is written

$$\mathcal{H}_N = -(\gamma\beta_N + R_{||})H_zI_z - (\gamma\beta_N + R_\perp)(H_xI_x + H_yI_y). \tag{4}$$

If the magnetic field makes an angle θ with respect to the tetragonal axis, the complete Hamiltonian, the

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sum of Eqs. (1) and (4) becomes

$$\mathcal{H}=g\beta HS_z+KS_zI_z+\left(\frac{AB}{K}S_xI_x+BS_yI_y\right)+\frac{B^2-A^2}{K}\times\frac{g_{\parallel}g_{\perp}}{g^2}\sin\theta\cos\theta S_xI_z$$
$$-\frac{H\{Ag_{\parallel}(\gamma\beta_N+R_{\parallel})\cos^2\theta+Bg_{\perp}(\gamma\beta_N+R_{\perp})\sin^2\theta\}}{Kg}I_z$$
$$-\frac{H\{Ag_{\parallel}(\gamma\beta_N+R_{\perp})-Bg_{\perp}(\gamma\beta_N+R_{\parallel})\}\sin\theta\cos\theta}{Kg}I_x. \quad (5)$$

The z axis is taken parallel to the applied field while the x axis is perpendicular to the z axis in the plane formed by the tetragonal axis and the field. The quantities g and K have the usual definitions,

$$g^2=g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta,$$
$$K^2g^2=A^2g_{\parallel}^2\cos^2\theta+B^2g_{\perp}^2\sin^2\theta. \quad (6)$$

B. Position of Allowed Transitions

When the calculation of the states of the Hamiltonian given by Eq. (5) is carried to second order, the energy of the allowed transitions $\Delta M=\pm1$, $\Delta m=0$ is found to be

$$h\nu=g\beta H+Km+\frac{B^2}{4g\beta H}\left(\frac{A^2+K^2}{K^2}\right)\{I(I+1)-m^2\}$$
$$+(2g\beta H)^{-1}\left(\frac{B^2-A^2}{K}\right)^2\left(\frac{g_{\parallel}g_{\perp}}{g^2}\right)^2\sin^2\theta\cos^2\theta m^2+\frac{2F^2m}{K-4G^2/K}, \quad (7)$$

where

$$F=-\frac{H\{Ag_{\parallel}(\gamma\beta_N+R_{\perp})-Bg_{\perp}(\gamma\beta_N+R_{\parallel})\}}{Kg}\sin\theta\cos\theta,$$
$$G=-\frac{H\{Ag_{\parallel}(\gamma\beta_N+R_{\parallel})\cos^2\theta+Bg_{\perp}(\gamma\beta_N+R_{\perp})\sin^2\theta\}}{Kg}. \quad (8)$$

Equation (7) is that derived by Bleaney,[6] neglecting quadrupole terms for the case $S=\frac{1}{2}$ with the addition of the small second-order term $2F^2m/(K-4G^2/K)$.

The field spacing between adjacent allowed hyperfine lines can be calculated from Eq. (7). For a fixed angle the separations are not the same, the differences arising from the off-diagonal terms of the electron spin in the Hamiltonian, not from the terms off diagonal in the nuclear spin. The term $2F^2m/(K-4G^2/K)$ is small and can be neglected in computing the positions of the allowed lines. In Fig. 2, the experimental results are shown to be in satisfactory agreement with the calculations for angles at which the forbidden lines have appreciable intensity. For angles less than 4° from the perpendicular ($\theta=90°$), the structure could not be unambiguously resolved.

C. Position of Forbidden Transitions

The terms off diagonal in the nuclear spin admix the various nuclear states and give rise to forbidden transitions $\Delta M=\pm1$, $\Delta m=\pm1$. Inspection of Eq. (5) shows that the magnitude of the I_x terms responsible for the admixture is dependent upon the difference in energy between $Ag_{\parallel}$ and $Bg_{\perp}$. When the hyperfine interaction is anisotropic, it tends to align the nucleus along a direction considerably different than that of the applied field, and consequently there is a large off-diagonal coupling of the field with the nuclear spin. The energy of the forbidden transitions is given by

$$h\nu=g\beta H+Kk+\frac{B^2}{4g\beta H}\left(\frac{A^2+K^2}{K^2}\right)\times\{I(I+1)-\tfrac{1}{2}[(k+\tfrac{1}{2})^2+(k-\tfrac{1}{2})^2]\}$$
$$+(2g\beta H)^{-1}\left(\frac{B^2-A^2}{K}\right)^2\left(\frac{g_{\parallel}g_{\perp}}{g^2}\right)^2\times\sin^2\theta\cos^2\theta\tfrac{1}{2}[(k+\tfrac{1}{2})^2+(k-\tfrac{1}{2})^2]$$
$$+\frac{2F^2k}{K-4G^2/K}\pm G\pm\frac{B^2}{4g\beta H}\frac{A}{K}\pm\frac{2F^2G/K}{K-4G^2/K}, \quad (9)$$

where k takes on the $2I$ possible values from $(I-\frac{1}{2})$ to $-(I-\frac{1}{2})$. In the last three terms, the upper and lower signs are associated with the transitions $\Delta M=+1$,

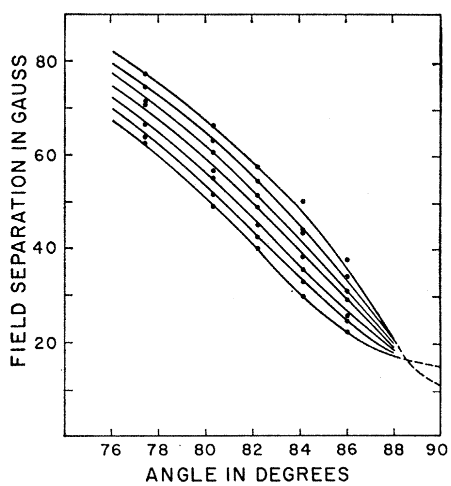

FIG. 2. The magnetic field separation of adjacent pairs of lines of the allowed spectrum is plotted as a function of angle of the applied field with respect to the tetragonal axis. The curves are calculated from Eq. (7) while the points are taken from experimental measurements. The largest field separation is associated with the difference in position of the hyperfine lines associated with $m=+\frac{7}{2}$ and $m=+\frac{5}{2}$, the next largest separation with $m=+\frac{5}{2}$ and $m=+\frac{3}{2}$, etc.

$\Delta m = \mp 1$, i.e., $m \to m-1$, $m-1 \to m$ (or, similarly, $\Delta M = -1$, $\Delta m = \pm 1$). Since the last three terms are small, the order of gauss when divided by $g\beta$, the two transitions have approximately the same energy and pairs of forbidden lines are coincident, equidistant between adjacent allowed lines. The positions of the forbidden lines as predicted by Eq. (9) are in accord with observations as illustrated in Fig. 1, and quantitative measurements are in agreement with calculations within experimental error.

D. Intensities of Allowed and Forbidden Spectra

While the term in I_x of Eq. (5) has little effect in determining the position of either the allowed or forbidden transitions [the $2F^2/(K-4G^2/K)$ term in Eqs. (7) and (9)], it contributes a very considerable admisture of the nuclear states. If terms of order $[F/(K-4G^2/K)]^2$ are kept in the wave functions and in the relative transition probabilities for a harmonic perturbation, the relative intensities of the allowed and forbidden transitions are

$$\mathcal{I}_a = 1 - 2(2F/K - 4G^2/K)^2\{I(I+1) - m^2\}, \qquad m = I, I-1, \cdots, -I, \quad (10)$$

$$\mathcal{I}_f = 2(2F/K - 4G^2/K)^2\{I(I+1) - (k-\tfrac{1}{2})(k+\tfrac{1}{2})\}, \qquad k = I-\tfrac{1}{2}, I-\tfrac{3}{2}, \cdots, -(I-\tfrac{1}{2}). \quad (11)$$

The intensities given by Eqs. (10) and (11) are normalized in such a way that the intensity of each allowed hyperfine line is equal to unity in the absence of the forbidden transitions. The forbidden intensity Eq. (11) had included in it both of the lines ($m \to m-1$, $m-1 \to m$) that overlap between a pair of adjacent allowed lines. Substituting Eqs. (8) into Eq. (11) yields

$$\mathcal{I}_f = \{I(I+1) - (k-\tfrac{1}{2})(k+\tfrac{1}{2})\}\{Ag_{\parallel}(\gamma\beta_N + R_{\perp}) - Bg_{\perp}(\gamma\beta_N + R_{\parallel})\}^2 \times \frac{8H^2 \sin^2\theta \cos^2\theta}{[K^2 g - (4H^2/K^2 g)\{Ag_{\parallel}(\gamma\beta_N + R_{\parallel})\cos^2\theta + Bg_{\perp}(\gamma\beta_N + R_{\perp})\sin^2\theta\}^2]^2}. \quad (12)$$

It need hardly be mentioned that Eqs. (10)–(12) are good approximations only when the perturbation is small. This is, in fact, not the case at 35 GHz and $\theta = 86°$, as can be seen in Fig. 1. The "forbidden" spectrum is more intense than the allowed spectrum, a situation for which the above equations are not applicable. In the discussion that follows, it should be understood that the comparisons between theory and experiment are limited to conditions for which the perturbation calculations are valid. The little additional information that can be obtained by a more rigorous calculation, such as diagonalizing an 8×8 matrix, does not seem to warrant the effort.

There are several aspects of Eqs. (10)–(12) that are subject to experimental test: (i) the relative intensities of the forbidden and allowed components with respect to one another at fixed angle and field, (ii) the relative intensity of the forbidden spectrum to the allowed spectrum at a given angle as a function of field, (iii) the intensity of the forbidden hyperfine components as a function of angle, and (iv) the absolute magnitude of the forbidden intensity.

(i) The relative intensities of both the allowed and forbidden lines are illustrated in Fig. 3 for several different angles. The data are in reasonable agreement with the predictions of Eqs. (10) and (11).

(ii) Since $A, B \gg \gamma\beta_N H$ for all reasonable values of H, the largest term in the denominator of Eq. (12) is $K^2 g$. Thus the intensity of the forbidden spectra is predicted to vary approximately as H^2. This dependence is presumably the reason why Bleaney and Ingram did not observe the forbidden lines of Co^{2+} at 9 GHz in the Tutton salts whereas the spectrum is immediately apparent at 35 GHz. The ratio of the intensity of the forbidden to the allowed spectra at 70 GHz was determined to be considerably larger than at 35 GHz, but because of poor signal to noise at the higher frequency no quantitative comparison with theory could be made. The increase of the forbidden intensity with magnetic field is evidence of the nature of the terms responsible for the phenomenon.

(iii) The angular dependence of the forbidden intensity as expressed by Eq. (12) arises from several factors, the two main contributions being the $\cos^2\theta \sin^2\theta$ in the numerator and the K^2 in the denominator. A plot of the angular dependence of $\mathcal{I}_f$, namely, the function $2[2F/(K-4G^2/K)]^2$, is illustrated in Fig. 4. For angles very close to 90° such that

$$Ag_{\parallel}\cos\theta < Bg_{\perp}\sin\theta,$$

$\mathcal{I}_f$ is approximately

$$\mathcal{I}_f \propto \cos^2\theta,$$

but for

$$Ag_{\parallel}\cos\theta > Bg_{\perp}\sin\theta,$$

we have

$$\mathcal{I}_f \propto \frac{\sin^2\theta}{\cos^2\theta}.$$

The measurements of the angular dependence of $\mathcal{I}_f$ are in agreement with Eq. (12) over the region $\mathcal{I}_f < \mathcal{I}_a$.

(iv) The magnitude of $2[2F/(K-4G^2/K)]^2$ is plotted in Fig. 5 as a function of angle for two different

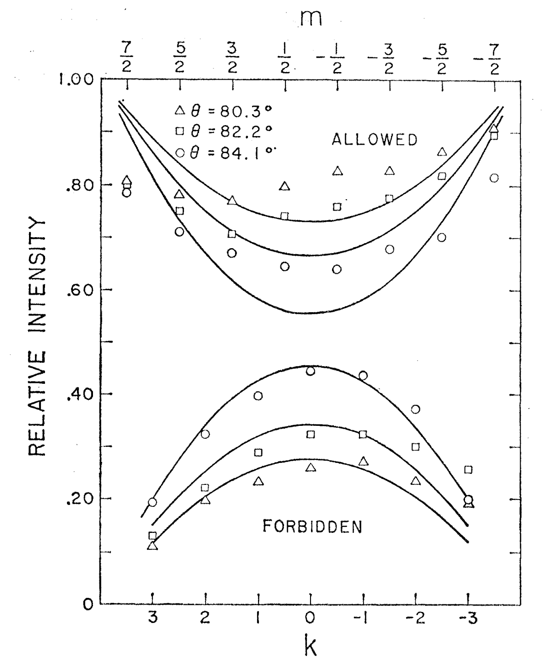

FIG. 3. The relative intensity of the "forbidden" and "allowed" lines is plotted as a function of k and m at three different values of θ. The points are experimental results while the solid curves are drawn through the values calculated from Eqs. (10) and (11). For each angle the curves are scaled at one point.

values of the unknown parameter $R_\perp$. (The curves are insensitive to $R_{\parallel}$ for $R_{\parallel}<\gamma\beta_N$ in that $Ag_{\parallel}\gg Bg_\perp$.) The measurements for which $\theta<84°$ support the conclusion that $R_\perp\approx 0.5\gamma\beta_N$, i.e., there exists an additional field at the cobalt nucleus of the same sign as, but half the magnitude of the applied field. The measurements for

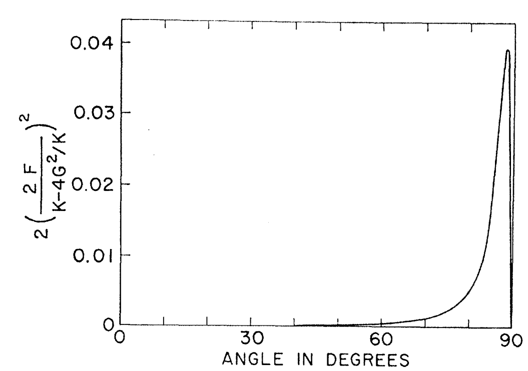

FIG. 4. The angular dependence of the relative forbidden intensity as calculated from $[2F/(K-4G^2/K)]^2$ is plotted as a function of the angle from the tetragonal axis. $R_\parallel=R_\perp=0$, $\nu=35.7$ GHz.

$\theta>84°$ cannot be directly compared with Eq. (12) because the admixture of the wave functions becomes too large to be treated in perturbation theory. The measured value of $R_\perp$ is in agreement with the order-of-magnitude estimate given by Eq. (3). However, detailed calculations to be reported elsewhere of the induced magnetic field yield $R_\perp=0.1\gamma\beta_N$ for Co^{2+} in the zinc ammonium sulfate. The nature of this discrepancy between experiment and theory, details of the calculations, and additional experimental evidence will be presented in a later publication.

SUMMARY

The forbidden hyperfine transitions observed in the resonance of Co^{2+} can be satisfactorily explained by the

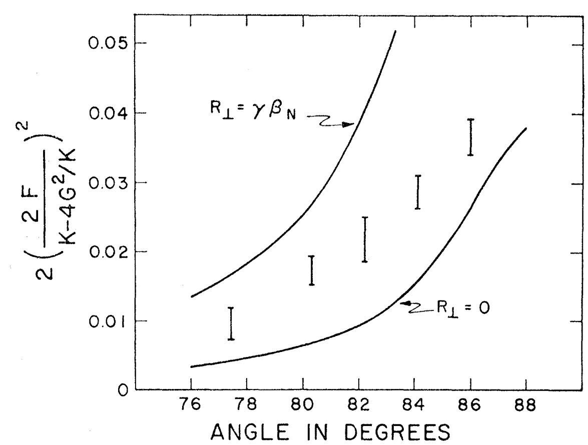

FIG. 5. The value of $2[2F/(K-4G^2/K)]^2$ is plotted as a function of angle. The error bars indicate the results of measurements at 35.7 GHz while the curves are theoretical calculations for $R_\perp=0$ and $R_\perp=\gamma\beta_N$.

combination of a very anisotropic hyperfine interaction and the nuclear Zeeman coupling. A pseudo-magnetic field at the nucleus, which can be thought of as having an origin similar to the Van Vleck temperature-independent paramagnetism, has been estimated from the measurements.

ACKNOWLEDGMENTS

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