SOVIET PHYSICS JETP VOLUME 32, NUMBER 3 MARCH, 1971

FORBIDDEN TRANSITIONS AND DISCRETE SATURATION IN EPR LINES. II

T. I. SANADZE and G. R. KHUTSISHVILI

Tbilisi State University

Submitted April 10, 1970

Zh. Eksp. Teor. Fiz. 59, 753–761 (September, 1970)

The theory of "forbidden" EPR transitions is generalized to include a dilute paramagnetic with g-factor anisotropy. The change in transition energy due to hyperfine interaction and nuclear Zeeman energy is calculated, and expressions are obtained for the transition probabilities. Measurements of the discrete saturation spectra for U^{3+} in CaF_2 are performed for two general orientations of the magnetic field. The experimental data are in good agreement with theory.

1. There has been much theoretical and experimental investigation of hyperfine structure (HFS) in dilute paramagnetic substances. The study of HFS gives the possibility of learning more about the structure of the lattice near the impurity magnetic ion, the character of the covalent bonds in the crystal, the ψ function of the electron on the magnetic ion, etc.

In particular, there is considerable interest in the investigation of the hyperfine interaction (HFI) of the spin of a magnetic ion with those nuclei for which the HFI is of the same order of magnitude as the Zeeman energy.[1-10] The nuclear spin is quantized in an effective field which is the sum of the external field and the field due to the HFI. If the HFI and the Zeeman energy are of the same order, the direction of this effective field will change significantly during an electron spin transition. Hence the probability of a "forbidden" transition, in which the projection of the nuclear spin (in the effective field) changes simultaneously with the electron spin projection, will be of the same order as the probability of an "allowed" transition, in which only the electron spin projection changes.

In an earlier paper[10] we showed that by taking forbidden transitions into account it is possible to explain the discrete saturation (DS) of an inhomogeneously broadened EPR line, a phenomenon observed earlier by the Tbilisi group.[11]

The theory of forbidden EPR transitions developed in[2,3,6,8,10] is valid in the case of a magnetic ion whose spin has an isotropic g factor. The results are also applicable to the case of an anisotropic g factor if the applied field H is oriented along a principal axis of the g tensor. But in the general case one has to assume that the direction along which the electron spins are quantized does not coincide with the direction of the external field.[12-14]

The purpose of the present paper is to generalize the theory of forbidden EPR transitions to the case of an anisotropic g factor of the magnetic ion and to compare the results of the theory with the experimental data on DS of U^{3+} ions in CaF_2.

2. The Hamiltonian of the magnetic ion and its surrounding nuclei has the form

$$\mathscr{H} = \beta g_{ik} S_i H_k + \sum_\alpha \mathscr{H}^\alpha, \qquad (1)$$

where the Hamiltonian of the α-th nucleus is

$$\mathscr{H}^\alpha = -\hbar\gamma^\alpha I_i^\alpha H_i + A_{ik}{}^\alpha I_i^\alpha S_k, \qquad (2)$$

S and I^α are the spin operators of the magnetic ion and the α-th nucleus, β is the Bohr magneton, γ^α is the gyromagnetic ratio of the α-th nucleus, g_{ik} is the g tensor of the magnetic ion, and A_{ik}^α is the tensor of the HFI between the α-th nucleus and the magnetic ion. Repeated Latin subscripts indicate summation.

We shall not consider effects due to fine structure and to the quadrupole interaction, since we are mainly interested in the case $S = I^\alpha = 1/2$. We also neglect the effect of nuclear pseudomagnetic moment,[9,14] This effect is often important for the nucleus of a magnetic ion, but not for other nuclei. Note also that, unlike[2,10], we choose the minus sign in front of the nuclear Zeeman term in Eq. (2); this is justified physically.

We are interested in the strong-field case, $g\beta H \gg A$. Then we must first diagonalize the first term of Eq. (1), and then each nucleus can be considered independently of the others (since $\mathscr{H}$ has no matrix elements corresponding to the simultaneous change of the spin projections of several nuclei). From the expression for $\mathscr{H}^\alpha$ we can determine the energy and transition probabilities for the system "magnetic ion + α-th nucleus." Then one can go on to calculate the probabilities of all kinds of transitions for the entire system (magnetic ion and its surrounding nuclei).[2,10]

Note the following important circumstance. The tensors g and A, generally speaking, can be asymmetrical.[14,15] Usually, however, the g tensor is symmetrical because of the rather high symmetry of the site of the magnetic ion in the crystal. For the nucleus of the magnetic ion the symmetry of the A tensor coincides with that of the g tensor.[14] For another nucleus, however, the symmetry of the surroundings relative to the line joining it to the magnetic ion may be low, and the A tensor can be asymmetrical.

As an example, consider CaF_2 with a trivalent magnetic impurity (cf.[15]). In CaF_2 the F^- ions are situated on a simple cubic lattice, and the Ca^{2+} ions occupy the centers of alternate cubes. A trivalent ion (Ce^{3+}, Yb^{3+}, U^{3+}) replaces a Ca^{2+} ion, but then there is the problem of charge compensation. In the case of the so-called tetragonal center, there is a F^- ion in the center of a neighboring cube (see Fig. 1). Since the magnetic ion is in an intracrystalline field of tetragonal symmetry, its g factor will be axially symmetric. The eight fluoride ions surrounding the magnetic ion will be situated in a crystalline field possessing only the sym-

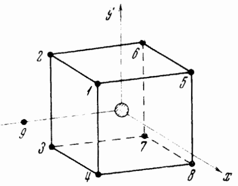

FIG. 1. Model of the immediate vicinity of U^{3+} in CaF_2.

metry of a reflection plane. Thus the HFI tensor for the eight fluorides in the immediate vicinity of the paramagnetic ion will not be symmetric.[1] But the ninth fluoride will be in a crystalline field of tetragonal symmetry and is therefore described by an axially symmetric HFI tensor.

Note that the presence of the impurity ion and the ninth fluoride ion causes a shift of the equilibrium positions of the eight fluorides, which, however, does not affect the above conclusions.

The aim of a complete experiment is the determination of the components of the g tensor of the magnetic ion and of the HFI tensors for nuclei located close to the magnetic ion. In[15] this problem was solved for CaF_2 with a trace of Ce^{3+} and Yb^{3+} by using the method of electron-nuclear double resonance. In[16] this same problem was solved for $CaF_2 - U^{3+}$ by the DS method.

We shall henceforth consider the g tensor to be symmetric.

The correction to the energy due to HFI, with account taken of the effects of anisotropy, was calculated in[12-14] (see also[5,9]). However, these papers took the symmetries of the g and A tensors to be identical and $A \gg \hbar\gamma H$. In[15] the energy correction was calculated for arbitrary values of the ratio $\hbar\gamma H/A$, but for the case of axial symmetry of the g tensor. Below we shall obtain expressions for the energy correction and for the transition probabilities without these limitations.

3. Consider the general case of unequal principal values of the g tensor, g_x, g_y, g_z. We place the coordinate axes x, y, z along the principal directions of the g tensor. We place the axis ζ' along the external field H and denote the direction cosines of the field relative to the x, y, z axes by l_x, l_y, l_z. The Zeeman Hamiltonian of the electron spin is written in the form

$$\beta H(g_x l_x S_x + g_y l_y S_y + g_z l_z S_z). \tag{3}$$

The electron spin is quantized on the ζ axis with direction cosines $g_x l_x/g$, $g_y l_y/g$, $g_z l_z/g$.[12-14] Then

$$g = [g_x^2 l_x^2 + g_y^2 l_y^2 + g_z^2 l_z^2]^{1/2}, \tag{4}$$

$$gS_\zeta = g_x l_x S_x + g_y l_y S_y + g_z l_z S_z. \tag{5}$$

For the eigenvalues of the electronic Zeeman energy we obtain the expression $mg\beta H$, where $m = S_\zeta$.

We introduce the axes ξ and η perpendicular to each other and to the ζ axis (otherwise arbitrary). In the nuclear Hamiltonian (2) we may omit terms containing S_ξ, and S_η, since they evoke a mixing of states with given $m = S_\zeta$ with states with other values of m, with mixing coefficients of the order $A/g\beta H$ and $\hbar\gamma/g\beta$ (these terms can be handled by perturbation theory).

The nuclear Hamiltonian (2) takes the form (leaving out the α)

$$-\hbar\gamma H I_{\zeta'} + mA_{i\zeta} I_i.$$

For the components (along the axes ξ, η, ζ) of the effective field H_m acting on a nucleus in the state $S_\zeta = m$, we obtain (we equate the last expression to $-\hbar\gamma H_m I$ and express $I_{\zeta'}$ in terms of I_ξ, I_η, I_ζ):

$$\mathbf{H}_m\left(Hl_\xi - \frac{m}{\hbar\gamma}A_{\xi\zeta},\quad Hl_\eta - \frac{m}{\hbar\gamma}A_{\eta\zeta},\quad Hl_\zeta - \frac{m}{\hbar\gamma}A_{\zeta\zeta}\right), \tag{6}$$

where l_ξ, l_η, l_ζ are the direction cosines of the field H relative to the axes ξ, η, ζ. Let M be the projection of the nuclear spin in the direction of H_m. The energy correction due to HFI and the nuclear Zeeman energy equals $-M\epsilon_m$, where

$$\varepsilon_m = \hbar\gamma H_m = [(\hbar\gamma Hl_\xi - mA_{\xi\zeta})^2 + (\hbar\gamma Hl_\eta - mA_{\eta\zeta})^2 + (\hbar\gamma Hl_\zeta - mA_{\zeta\zeta})^2]^{1/2}, \tag{7}$$

(positive root always implied).

For the angle $\chi_{m,m+1}$ between H_m and H_{m+1} we obtain easily

$$\begin{aligned}\cos\chi_{m,m+1} = (\varepsilon_m\varepsilon_{m+1})^{-1}\{&[\hbar\gamma Hl_\xi - mA_{\xi\zeta}][\hbar\gamma Hl_\xi - (m+1)A_{\xi\zeta}]\\ &+ [\hbar\gamma Hl_\eta - mA_{\eta\zeta}][\hbar\gamma Hl_\eta - (m+1)A_{\eta\zeta}]\\ &+ [\hbar\gamma Hl_\zeta - mA_{\zeta\zeta}][\hbar\gamma Hl_\zeta - (m+1)A_{\zeta\zeta}]\}.\end{aligned} \tag{8}$$

The quantities $A_\|$, $A_\perp$, and $\bar{A}$ are defined as follows

$$A_\| = A_{\zeta\zeta},\quad A_\perp^2 = A_{\xi\zeta}^2 + A_{\eta\zeta}^2,\quad \bar{A} = A_{\zeta'\zeta} = l_\xi A_{\xi\zeta} + l_\eta A_{\eta\zeta} + l_\zeta A_{\zeta\zeta}. \tag{9}$$

Equations (7) and (8) are easily given a more convenient form:

$$\varepsilon_m = [(\hbar\gamma H)^2 + m^2(A_\|^2 + A_\perp^2) - 2m\hbar\gamma H\bar{A}]^{1/2}, \tag{10}$$

$$\begin{aligned}\cos\chi_{m,m+1} = (\varepsilon_m\varepsilon_{m+1})^{-1}[&(\hbar\gamma H)^2 + m(m+1)(A_\|^2 + A_\perp^2)\\ &-(2m+1)\hbar\gamma H\bar{A}].\end{aligned} \tag{11}$$

Making use of the formulas for the transformation of the components of a second-rank tensor following rotation of the coordinate axes, we find easily

$$A_\| = \alpha_{\zeta i}\alpha_{\zeta k}A_{ik},\quad A_\|^2 + A_\perp^2 = \alpha_{\zeta i}\alpha_{\zeta k}A_{pi}A_{pk},\quad \bar{A} = \alpha_{\zeta' i}\alpha_{\zeta k}A_{ik}, \tag{12}$$

where i, k, and p assume the values x, y, z; $\alpha_{\zeta i}$ ($\alpha_{\zeta' i}$) is the cosine of the angle between the axis ζ (ζ') and the axis i; A_{ik} is a component of the tensor A in any orthogonal coordinate system fixed in the crystal. If, in particular, we let the directions of x, y, and z be those of the principal directions of the g tensor, we have $\alpha_{\zeta' x} = l_x$, $\alpha_{\zeta x} = g_x l_x/g$, etc.

The equations in (12) connect the fundamental quantities A_{ik}, which describe the HFI, with the quantities $A_\|$, $A_\perp$, and $\bar{A}$, which depend on the orientation of the applied field relative to the crystal axes.

In the case $S = 1/2$, Eqs. (10) and (11) give ($\epsilon_{\pm 1/2}$ is symbolized by $\epsilon_{1/2}$, $\chi_{-1/2,+1/2}$ by χ)

$$\varepsilon_\pm = [(\hbar\gamma H)^2 + 1/4(A_\|^2 + A_\perp^2) \mp \hbar\gamma H\bar{A}]^{1/2}, \tag{13}$$

$$\cos\chi = (\varepsilon_+\varepsilon_-)^{-1}[(\hbar\gamma H)^2 - 1/4(A_\|^2 + A_\perp^2)]. \tag{14}$$

In the case $I = 1/2$ it is easy to find expressions for $p_{m,m+1}$ and $q_{m,m+1}$, the relative probabilities of the electronic transition $m \longleftrightarrow m+1$, accompanied and not accompanied by a change in the nuclear spin projection (on the direction of the effective field)

$$\begin{aligned} p_{m,m+1} &= \cos^2\frac{\chi_{m,m+1}}{2} = \frac{1+\cos\chi_{m,m+1}}{2},\\ q_{m,m+1} &= \sin^2\frac{\chi_{m,m+1}}{2} = \frac{1-\cos\chi_{m,m+1}}{2}, \end{aligned} \tag{15}$$

---

[1] For more details see [15], where it is shown that for these fluorine nuclei the HFI tensor reduces to five independent components.

Note that when $\hbar\gamma H \ll A$, (6) gives $H_{-m} \approx -H_m$. Hence in the electronic transition $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$ we have, according to (15), $p \approx 0$, $q \approx 1$. If in the state $m = -\frac{1}{2}$ the nuclear spin is quantized not along the direction $H_{-1/2}$, but in the opposite sense, we have $p \approx 1$, $q \approx 0$, and we go over to the usual terminology in the weak-field case.[13] However, for the sake of uniformity in the formulas, we shall prefer always to quantize the nuclear spin in the direction of H_m. Besides, replacement of the direction of quantization by the opposite one, in states with $m < 0$, is completely unjustified in the case of a strong applied field.

For arbitrary I, the relative probability of the electronic transition $m \longleftrightarrow m+1$ accompanied by a nuclear transition $M \longleftrightarrow M'$, is given by the square of the Wigner D coefficient[17]

$$D^{I}_{M'M}[0, \chi_{m,m+1}, 0] = \sum_{\varkappa} (-1)^{\varkappa} \frac{[(I+M)!(I-M)!(I+M')!(I-M')!]^{1/2}}{(I-M'-\varkappa)!(I+M-\varkappa)!\varkappa!(\varkappa+M'-M)!} \cdot \times \left(\cos\frac{\chi_{m,m+1}}{2}\right)^{2I+M-M'-2\varkappa} \left(\sin\frac{\chi_{m,m+1}}{2}\right)^{2\varkappa+M'-M} \quad (16)$$

(κ varies from $\max(0, M - M')$ to $\min(I - M', I + M)$).

4. If the g factor is isotropic, or the applied field is along one of the principal directions of the g tensor, the results are greatly simplified. In this case the axes ζ' and ζ coincide, $\overline{A} = A_{\parallel}$, and we obtain

$$\varepsilon_m = [(\hbar\gamma H - mA_{\parallel})^2 + m^2 A_{\perp}^2]^{1/2}, \quad (17)$$

$$\cos\chi_{m,m+1} = (\varepsilon_m \varepsilon_{m+1})^{-1}\{[\hbar\gamma H - mA_{\parallel}][\hbar\gamma H - (m+1)A_{\parallel}] + m(m+1)A_{\perp}^2\}. \quad (18)$$

Further, it is easy to get

$$p_{m,m+1} = \cos^2\frac{\vartheta_m \mp \vartheta_{m+1}}{2}, \quad q_{m,m+1} = \sin^2\frac{\vartheta_m \mp \vartheta_{m+1}}{2}, \quad (19)$$

where the upper sign is chosen if $m \neq -\frac{1}{2}$, and the lower sign for the transition $-\frac{1}{2} \longleftrightarrow +\frac{1}{2}$. If ϑ_m is the angle between the effective field H_m and the applied field

$$\operatorname{tg}\vartheta_m = |mA_{\perp}| \,/\, (\hbar\gamma H - mA_{\parallel}). \quad (20)$$

Thus, we arrive at the results of[10].

5. We consider also the important special case of axial symmetry of the g tensor. It is known that the z axis (the axis of symmetry), ζ' and ζ are in one plane.[12-14] Let φ and ψ be the angles between the z axis and the ζ' and ζ axes, respectively. We have

$$\cos\psi = \frac{g_{\parallel}}{g}\cos\varphi, \quad \sin\psi = \frac{g_{\perp}}{g}\sin\varphi, \quad \operatorname{tg}\psi = \frac{g_{\perp}}{g_{\parallel}}\operatorname{tg}\varphi, \quad (21)$$

and

$$g = [g_{\parallel}^2\cos^2\varphi + g_{\perp}^2\sin^2\varphi]^{1/2}. \quad (22)$$

Choosing the ξ axis in the $\zeta'\zeta$ plane, we make the following replacements in Eqs. (7) and (8)2)

$$l_{\xi} \to \pm\sin(\varphi - \psi) = \pm\frac{g_{\parallel} - g_{\perp}}{g}\sin\varphi\cos\varphi, \quad l_{\eta} \to 0,$$
$$l_{\zeta} \to \cos(\varphi - \psi) = \frac{1}{g}(g_{\parallel}\cos^2\varphi + g_{\perp}\sin^2\varphi). \quad (23)$$

A formula for the total probability of the electronic transition $m \longleftrightarrow m+1$ in the case of an axially symmetric g tensor is given in[18].

6. We now turn to the general case of anisotropic g factor. In[2,10] is given a rule from which one can determine the position of all EPR transitions and their relative intensities in terms of the quantities ϵ_m, $p_{m,m+1}$, and $q_{m,m+1}$.

From the data on DS it is possible to determine for a given nucleus the quantity ϵ_m. Thus, the experimental data together with Eq. (10) make it possible to determine, for a given orientation of the external field, the quantities $A_{\parallel}^2 + A_{\perp}^2$ and $\overline{A}$3). By carrying out the DS experiment in several orientation of the external field, it is possible, through the use of Eqs. (12), to determine the quantities A_{ik}, i.e., to obtain complete information about the HFI tensor.

In the presence of a large number of nuclei in the immediate vicinity of the magnetic center the determination of the HFI tensor components by making observations of DS spectra in several miscellaneous orientations is practically impossible, because of the huge number of transitions that overlap. It makes more sense to use orientations of H along principal directions of the g tensor; then the nuclear groups become equivalent, which greatly simplifies the DS spectra.

But if there are only a few nuclei in the immediate vicinity of the magnetic center (two, for example), then it is possible to use just a few miscellaneous orientations of H to establish the HFI tensor. This may be useful for determining the signs of some of the HFI tensor components.

It should also be observed that after the HFI tensor components for the closest nuclei have been determined, one can calculate ϵ_m, p, and q for each nucleus using Eqs. (12)–(15), and then use Eq. (14) of[10] to construct the expected shape of the EPR line for an arbitrary orientation of the applied field.

7. Above we gave a picture of the surroundings of the U^{3+} ion in CaF_2 (see Fig. 1). The EPR spectrum of U^{3+} in CaF_2 is well explained by the presence of three inequivalent ions with marked g-factor anisotropy[19] ($g_{\parallel} = 3.501$, $g_{\perp} = 1.866$).

The DS spectra of $CaF_2 - U^{3+}$ have been investigated recently.[16] By performing the experiment in three orientations for which g equals its principal values ($g_{\parallel}$ once, $g_{\perp}$ twice), it was found possible to completely establish the HFI tensors for the nine closest fluorine nuclei.

It is of interest to make a measurement of the DS spectrum for a general orientation of H and then compare the experimental data with the theoretical results of this paper, using the known values of the HFI tensor components. We have done this for two orientations of H.

Recall that for U^{3+} in CaF_2, we have $S = I = \frac{1}{2}$. Using Eqs. (12) and (13) we find the quantities $\epsilon_{\pm}$ for each of the nine fluorine nuclei.

It is known that when H is directed along x, y, or z, the eight closest fluorines divide into two groups of four equivalent nuclei.[15,16] It follows that when H is located in the zx plane (or zy), these eight nuclei fall into four pairs of equivalent nuclei. For such an orientation the ninth fluorine nucleus also participates in the

---

2) The double sign is associated with the two possibilities for choice in the direction of the ξ axis in the $\zeta'\zeta$ plane, which is reflected also in the sign of $A_{\xi\zeta}$.

3) In the case of a scalar g factor or H directed along a principal direction of the g tensor, the quantities $A_{\parallel}$ and $|A_{\perp}|$ are determined.

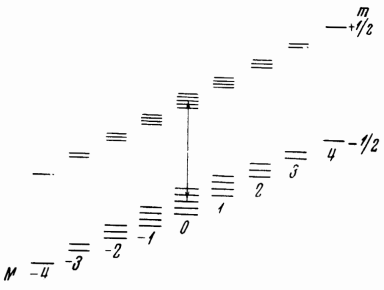

FIG. 2. Level scheme for the two groups of four equivalent nuclei with spin ½ (m and M are the projections of the electronic and total nuclear spins). The arrow indicates the transition saturated by a pulse.

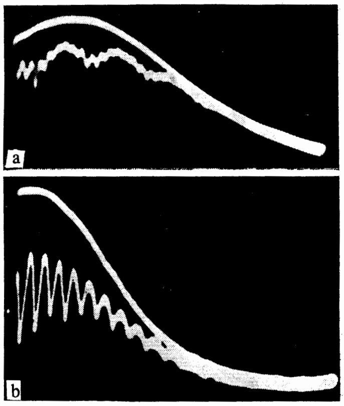

FIG. 3. Oscillograms of DS spectra and the true shape of the same portions of the line without saturation: a—orientation of the magnetic field corresponds to φ = 85°30′ and b—φ = 76° in the zx plane.

DS (it falls out of the DS when H is directed along x, y, or z[16]).

However, as shown in[16], in orientations of the external field along x, y, or z, the DS spectra are explained to a very good approximation by eight equivalent closest nuclei. In this same approximation, for an external field located in the zx (or zy) plane, we obtain two groups of four equivalent nuclei, namely the groups 1, 4, 6, 7 and 2, 3, 5, 8 (see Fig. 1), and the ninth nucleus. The inequivalence of the nuclei inside each group is weak (less than 0.5 Oe) and is not resolved in the DS spectrum in these samples.

We analyze first the DS spectrum yielded by the eight fluorine nuclei. The level scheme for the two groups of four equivalent nuclei is shown in Fig. 2, where the levels are arranged in the following order:

$$\begin{array}{ccccccccc}
 & & & & -2\varepsilon+2\varepsilon' & -\varepsilon+2\varepsilon' & 2\varepsilon' & \varepsilon+2\varepsilon' & 2\varepsilon+2\varepsilon' \\
 & & & -2\varepsilon+\varepsilon' & -\varepsilon+\varepsilon' & \varepsilon' & \varepsilon+\varepsilon' & 2\varepsilon+\varepsilon' & \\
 & & -2\varepsilon & -\varepsilon & 0 & \varepsilon & 2\varepsilon & & \\
 & -2\varepsilon-\varepsilon' & -\varepsilon-\varepsilon' & -\varepsilon' & \varepsilon-\varepsilon' & 2\varepsilon-\varepsilon' & & & \\
-2\varepsilon-2\varepsilon' & -\varepsilon-2\varepsilon' & -2\varepsilon' & \varepsilon-2\varepsilon' & 2\varepsilon-2\varepsilon' & & & &
\end{array}$$

where $\epsilon = \epsilon_+$, $\epsilon' = \epsilon'_+$ for the upper ($m = +\frac{1}{2}$) and $\epsilon = \epsilon_-$, $\epsilon' = \epsilon'_-$ for the lower levels ($m = -\frac{1}{2}$). The parameters $\epsilon_\pm$ and $\epsilon'_\pm$ correspond to the two groups of equivalent nuclei.

In pulse saturation of a specific pair of levels, for example, the one shown by the arrow in Fig. 2, there will be observed a system of dips in the EPR line, since all transitions which are associated with the levels of the saturated pair will be found in a state of partial saturation. More exactly, there will be two subsystems of dips which are superposed on one another. One of the subsystems is due to transitions associated with the saturated level $m = +\frac{1}{2}$, the other with transitions associated with the saturated level $m = -\frac{1}{2}$.

Figure 3 shows oscillograms of DS spectra corresponding to directions of the field H in the plane zx and making angles of φ = 85°30′ and 76° with the axis of symmetry z (see Fig. 1). In these orientations well resolved and regular DS spectra are observed.

In the DS spectrum observed at φ = 85°30′ (Fig. 3a), it is possible to extract the parameters 1.1 Oe and 6.4 Oe. The first of these coincides with the calculated value of the spacings in the upper levels ($m = +\frac{1}{2}$). The spacings in the lower levels ($m = -\frac{1}{2}$) are about twice as great and amount to 2 Oe. The two subsystems of dips we referred to above are superposed in a way so as to enhance the observed DS pattern. The large parameter (6.4 Oe) in the DS spectrum is the same as the calculated value of $\frac{1}{2}(\overline{\epsilon}_+ + \overline{\epsilon}_-)$, where $\overline{\epsilon}_\pm = \frac{1}{2}(\epsilon_\pm + \epsilon'_\pm)$. Actually, by neglecting the non-equivalence of the nuclei in the level scheme in Fig. 2, we will find two subsystems of dips with parameters $\overline{\epsilon}_+$ = 7.2 Oe and $\overline{\epsilon}_-$ = 5.6 Oe. Taking the non-equivalence of the nuclei into account gives a "fine" structure which causes these two subsystems to overlap. As a result we get a system of dips with a large parameter $\frac{1}{2}(\overline{\epsilon}_+ + \overline{\epsilon}_-)$ = 6.4 Oe and a small parameter $|\epsilon_+ - \epsilon'_+|$ = 1.1 Oe. Note that for this orientation of H the role of the ninth fluorine nucleus in the DS spectrum is negligible, since H makes a small angle with the x axis (4°30′).

In the orientation φ = 76° the splitting in the upper levels due to the inequivalence of the nuclei increases to 3 Oe, and in the lower levels to 5.5 Oe. A structure with a parameter of about 3 Oe is thereby resolved in the DS spectrum (Fig. 3b).

It is necessary to note that in the given orientation of the magnetic field, the ninth fluorine nucleus also participates in the DS spectrum. The interaction of the paramagnetic center with this nucleus produces a splitting equal to 8.5 Oe in the upper levels and 5.5 Oe in the lower. Two subsystems of levels are formed for $m = \pm\frac{1}{2}$ and two for $m = -\frac{1}{2}$. Hence there will be four groups of transitions between these subsystems. The DS pattern for one such group of transitions was considered above. Thus, accounting for the effect of the ninth nucleus gives a superposition of four identical DS spectra. However, a feature of this orientation (φ = 76°) is that the displacements of the superposed DS spectra are multiples of the observed parameter 3 Oe. Actually, these shifts will equal 8.5 − 5.5 = 3 Oe, $8.5 \approx 3 \times 3$ and $5.5 \approx 2 \times 3$. The inexact multiplicity of the shifts causes only an additional broadening of the DS dips (see Fig. 2b).

Thus, the expected DS spectra in inclined orientations of H, the parameters of which are calculated according to Eqs. (12) and (13), are found to be in good agreement with the experimentally observed spectrum.

8. In the DS experiments carried out by the Tbilisi group ([10,11,16] and this paper), microwave pulses with length $\tau \gg T_2$ ($\tau \approx 10^{-5}$ s, the electron transverse relaxation time $T_2 < 10^{-6}$ s). Hence during a pulse a transverse component of the magnetization does not arise, the pulse will be purely saturating, and coherent effects are not evoked by it. The degree of saturation of a pair of levels (between which the pulse induces

transitions) should be determined by the quantity $P\tau \propto H_1^2\tau$, where P is the power, H_1 the half-amplitude of the saturating pulse. And this same quantity $P\tau$ should determine the depth of the DS dips. In fact, according to experiment, the depths of the DS dips do not change if P and τ change in such a way that their product remains constant. But if $P\tau$ increases, so do the depths of the DS dips.[11]

On the other hand, if $\tau \ll T_2$, one has a completely different picture. Such a pulse is coherent, and it evokes not saturation, but a rotation of the magnetization by an angle $\gamma_S H_1\tau$ (γ_S is the gyromagnetic ratio of the electron spin) in a rotating system of coordinates about the direction of H_1. As a result of a rapid (in comparison with cross-relaxation and spin-lattice relaxation) passage over the line, one will observe a central dip at the field corresponding to the frequency of the pulse. Then the resonance signal will be positive in the dip, if the angle $\gamma_S H_1 \tau$ (after reduction to the interval $0-2\pi$) is less than $\pi/2$ or greater than $3\pi/2$; otherwise the signal in the central dip will be negative. On either side of the central dip, one should observe (positive) DS dips, the depths of which will be determined by the angle of rotation, i.e., the quantity $H_1\tau$.[4)] However, the possible presence of transient effects may strongly complicate the observed pattern.

[4)] The pattern which should occur in the case of a coherent pulse was elucidated as a result of a conversation with Prof. K. W. H. Stevens, to whom we express our thanks.

[1] G. T. Trammel, H. Zeldes, and R. Livingston, Phys. Rev. 110, 630 (1958).

[2] A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, Phys. Rev. 117, 1222 (1960).

[3] H. M. McConnell, C. Heller, T. Cole, and R. W. Fessenden, J. Am. Chem. Soc. 82, 766 (1960).

[4] J. M. Baker, W. Hayes, and M. C. M. O'Brien, Proc. Roy. Soc. (London) A254, 273 (1960).

[5] H. H. Woodbury and G. W. Ludwig, Phys. Rev. 124, 1083 (1961).

[6] J. L. Hall and R. T. Schumacher, Phys. Rev. 127, 1892 (1962).

[7] B. Welber, Phys. Rev. 136, A1408 (1964).

[8] U. Ranon and J. S. Hyde, Phys. Rev. 141, 259 (1966).

[9] S. H. Choh and G. Seidel, Phys. Rev. 164, 412 (1967).

[10] T. I. Sanadze and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. 56, 454 (1969) [Sov. Phys.-JETP 29, 248 (1969)].

[11] P. I. Bekauri, B. G. Berulava, T. I. Sanadze, and O. G. Khakhanashvili, Zh. Eksp. Teor. Fiz. 52, 447 (1967) [Sov. Phys.-JETP 25, 292 (1967)].

[12] M. H. L. Pryce, Nature 164, 116 (1949).

[13] B. Bleaney, Phil. Mag. 42, 441 (1951).

[14] B. Bleaney, Hyperfine Interactions (ed. by A. J. Freeman and R. B. Frankel), Academic Press, N.Y., 1967, p. 1.

[15] J. M. Baker, E. R. Davies, and J. P. Hurrell, Proc. Roy. Soc. (London) A308, 403 (1968).

[16] P. I. Bekauri, B. G. Berulava, T. I. Sanadze, O. G. Khakhanashvili, and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. 59, 368 (1970) [Sov. Phys.-JETP 32, 200 (1971)].

[17] E. P. Wigner, Group Theory and its Application to the Quantum Mechanics of Atomic Spectra, Academic Press, NY, 1959 (Russ. Transl., IIL, Moscow, 1961).

[18] B. Bleaney, Proc. Phys. Soc. (London) 75, 621 (1960).

[19] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) B69, 858 (1956).

Translated by L. M. Matarrese
87