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FORBIDDEN TRANSITIONS AND DISCRETE SATURATION IN EPR LINES

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The mechanism of pulse saturation of inhomogeneously broadened EPR lines whose width is due to the nuclei surrounding the paramagnetic center is considered. It is shown that the presence of a complex spectrum of the super-hyperfine structure, when the probabilities for reorientation of nuclear spins in an electronic transition are comparable to probabilities for transitions not involving changes in the nuclear spin projection, may be one of the causes of discrete saturation in EPR lines. As an example discrete saturation in the EPR line of irradiated polyethylene is examined.

1. Discrete saturation (DS) of inhomogeneously broadened EPR lines, consisting of the appearance of several holes in the line during saturation of a small portion of it by short, powerful microwave pulses, has been reported.[1,2] DN has been observed in the EPR lines of paramagnetic ions in monocrystals, free radicals, and also F centers.

As a possible mechanism leading to DS, it has been proposed that a quantum of microwave radiation evokes a simultaneous reorientation of the spin of a magnetic ion and the spin of a nucleus located close to another magnetic ion. For the relative probability of this process (relative to the probability of an ordinary allowed transition of the magnetic ion), it is easy to obtain the expression

$$f = \alpha(\beta / Ar^3)^2, \qquad (1)$$

where β is the Bohr magneton, r is the distance between magnetic ions, A is the hyperfine interaction (HFI) constant of the nucleus with the spin of the magnetic ion, and α is a numerical coefficient. In deriving (1) it is assumed that the interaction of the magnetic ions with each other is dipolar.

According to (1), the averaged value of f should be proportional to the square of the concentration of magnetic ions. Recent measurements we have made on U^{3+} in CaF_2 and on free radicals in irradiated polyethylene have shown that the DS effect is practically unaltered with a change in concentration by approximately 10 times. Thus, it is necessary to seek another mechanism for DS. The independence of DS on concentration indicates that this mechanism must be local[1] (i.e., not associated with the interaction of the magnetic ions with each other).

In the present paper it will be shown that DS can be explained by the presence of "forbidden" transitions. By "forbidden" we mean a transition during which there is a simultaneous change of the projection of the spins of the magnetic ion and of one or several of the nuclei near to it.

2. Clogston et al.[4] have shown that when certain conditions are fulfilled, the probability of a "forbidden" transition can be of the order (and even exceed) the probability of an allowed transition. For greater clarity, we shall first present another explanation of this fact.

Consider a system consisting of one electronic spin (the spin of a magnetic ion) and one nuclear spin coupled to it by HFI. The Hamiltonian of the system is

$$\mathcal{H} = g\beta \mathbf{H}\mathbf{S} + \hbar\gamma \mathbf{H}\mathbf{I} + \mathbf{S}A\mathbf{I}, \qquad (2)$$

where g is the electronic g factor (in the direction of the external field **H**), γ is the nuclear gyromagnetic ratio, **S** and **I** are the electronic and nuclear spin operators, and A is the HFI tensor (dyad). We do not take into account any term due to fine structure. In the presence of fine structure (i.e., if $S > 1/2$), the discussion below will apply to a specific component of this structure.

The external field is assumed so large that the Zeeman energy of the electronic spin is much greater than the remaining terms in the Hamiltonian (2). In the absence of HFI the Hamiltonian (2) is diagonal in m and M (the projections of **S** and **I** on the field), and each stationary state is characterized by definite values of m and M. The term **S**A**I** causes mixing of the states with respect to m and M. We shall symbolize a state by those values m and M that it has in the absence of HFI.

Because of mixing, "forbidden" transitions will occur, the probabilities of which (relative to the probability of an allowed transition) are determined by the squares of the corresponding mixing coefficients. It is easy to see that if A is a scalar, there will be forbidden transitions in a longitudinal alternating field, with a small relative probability of the order $(A/g\beta H)^2$.

Now let A be non-scalar, and in particular, let the expression **S**A**I** have matrix elements $(m, M) \leftrightarrow (m, M \pm 1)$ that are non-zero. For this, it is necessary that the expression **S**A**I** retain a term proportional to $S_z I_\pm$ (z is the direction of the external field). Then the state $(m, M \pm 1)$ is mixed into the state (m, M) with a coefficient of the order $A/\max(A, \hbar\gamma H)$ (more precisely, the numerator consists of the transverse component of A, i.e., the coefficient of $S_z I_\pm$ in **S**A**I**).

In the case $A \ll \hbar\gamma H$, we find that the relative probability of a forbidden transition $(m, M) \leftrightarrow (m + 1, M \pm 1)$ is of order $(A/\hbar\gamma H)^2$, i.e., it is small.

If A is greater than or of the order of $\hbar\gamma H$, there is strong mixing and the above treatment, which is based on perturbation theory, is inapplicable. However, it can

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[1] The idea that the DS mechanism must be local was expressed in a recent paper by Efremov, Kozushner, and Sokolov. [3]

be shown that if $A \gg \hbar\gamma H$, there is a reduction of large terms in the matrix element of the forbidden transition, and the relative probability is obtained in the order $(\hbar\gamma H/A)^2$, i.e., it is small.

Thus, in order for the probability of a forbidden transition to be comparable to the probability of an allowed one, it is necessary that A be of the order $\hbar\gamma H$ and that the HFI contain non-zero matrix elements that are diagonal in m and non-diagonal in M. Usually, for the nucleus of a magnetic ion we have $A \gg \hbar\gamma H$. For distant nuclei, $A \ll \hbar\gamma H$. The condition $A \sim \hbar\gamma H$ will usually be fulfilled for nuclei close to a magnetic ion.

3. We shall present the gist of the discussion and the results obtained by Clogston et al.[4] relative to the energies and probabilities of forbidden transitions. It should be noted that in the case of the electronic transition $1/2 \leftrightarrow -1/2$, the results they give require correction.

The Hamiltonian of the magnetic ion and the nuclei surrounding it is written in the form

$$\mathscr{H} = g\beta H S n + \sum_i \mathscr{H}_i, \tag{3}$$

$$\mathscr{H}_i = \hbar\gamma H \mathbf{I}^i \mathbf{n} + S A^i \mathbf{I}^i \tag{4}$$

(the subscript i numbers the nucleus, $\mathbf{n}$ is a unit vector along the external field, A^i is the HFI tensor of the i-th nucleus with the electronic spin). Since the electronic Zeeman energy is assumed much greater than all the remaining terms, it is possible in $\mathscr{H}_i$ to replace $\mathbf{S}$ by $(\mathbf{S}\cdot\mathbf{n})\mathbf{n} = m\mathbf{n}$, in other words, we restrict ourselves to matrix elements of $\mathscr{H}$ that are diagonal in m. $\mathscr{H}_i$ takes the form

$$\mathscr{H}_i = (\mathbf{I}^i, \hbar\gamma H\mathbf{n} + mA^i\mathbf{n}) \tag{5}$$

From this we obtain that the i-th nucleus is in an effective field

$$\mathbf{H}_m{}^i = H\mathbf{n} + (m/\hbar\gamma)A^i\mathbf{n}. \tag{6}$$

The direction of this effective field depends, generally speaking, on the projection of the electronic spin on the external field. During an electron transition $m \leftrightarrow m \pm 1$ the direction of the effective field changes, i.e., the direction along which the nuclear spin is quantized changes. Hence during an electronic transition the projection of the nuclear spin can vary in an arbitrary way, and the probability of "forbidden" transitions can become of the order of the probability of an allowed transition.[2)] One can say that during a "forbidden" transition the orientation of nuclear spin does not really change, but before and after the transition the nuclear spin must be projected in different directions (cf.[6]).

Following[4] we symbolize by $A_p^i = \mathbf{n}A^i\mathbf{n}$ and A_n^i the components of the vector $A^i\mathbf{n}$ respectively along $\mathbf{n}$ and in a plane perpendicular to $\mathbf{n}$. We further introduce a unit vector $\mathbf{t}_m^i$ along the component of the vector $\mathbf{H}_m^i$ in the plane perpendicular to $\mathbf{n}$:

$$\mathbf{t}_m{}^i = \frac{A^i\mathbf{n} - A_p{}^i\mathbf{n}}{|A^i\mathbf{n} - A_p{}^i\mathbf{n}|}\operatorname{sign} m. \tag{7}$$

The angle ϑ_m^i between $\mathbf{H}_m^i$ and $\mathbf{H}$ is given by the formula

$$\operatorname{tg}\vartheta_m{}^i = |mA_n{}^i| \,/\, (mA_p{}^i + \hbar\gamma H); \tag{8}$$

and the azimuth φ_m^i of the vector $\mathbf{H}_m^i$ is the same as the azimuth of $\mathbf{t}_m^i$.

We limit ourselves to the case $I^i = 1/2$. For the energies of the states with spin projections of the i-th nucleus $\pm 1/2$ in the effective field $\mathbf{H}_m^i$ we have $\pm \frac{1}{2}\epsilon_m^i$, where

$$\varepsilon_m{}^i = [(A_p{}^i m + \hbar\gamma H)^2 + m^2|A_n{}^i|^2]^{1/2}. \tag{9}$$

The relative probabilities of the transitions $(m, \pm 1/2) \leftrightarrow (m+1, \pm 1/2)$ and $(m, \pm 1/2) \leftrightarrow (m+1, \pm 1/2)$ (relative to the probability of the transition $(m, \pm 1/2) \leftrightarrow (m+1, \pm 1/2)$ in the absence of HFI) are symbolized respectively by $p_{m,m+1}^i$ and $q_{m,m+1}^i$. We find easily

$$p_{m,m+1}^i = \cos^2\frac{\vartheta_m{}^i - \vartheta_{m+1}^i}{2}\cos^2\frac{\varphi_m{}^i - \varphi_{m+1}^i}{2} + \cos^2\frac{\vartheta_m{}^i + \vartheta_{m+1}^i}{2}\sin^2\frac{\varphi_m{}^i - \varphi_{m+1}^i}{2}.$$

$$q_{m,m+1}^i = \sin^2\frac{\vartheta_m{}^i - \vartheta_{m+1}^i}{2}\cos^2\frac{\varphi_m{}^i - \varphi_{m+1}^i}{2} + \sin^2\frac{\vartheta_m{}^i + \vartheta_{m+1}^i}{2}\sin^2\frac{\varphi_m{}^i - \varphi_{m+1}^i}{2}. \tag{10}$$

For all electronic transitions except $+1/2 \leftrightarrow -1/2$ we have, in accordance with (7), that $\varphi_m = \varphi_{m+1}$. Hence[3)]

$$p_{m,m+1}^i = \cos^2\frac{\vartheta_m{}^i - \vartheta_{m+1}^i}{2}, \qquad q_{m,m+1}^i = \sin^2\frac{\vartheta_m{}^i - \vartheta_{m+1}^i}{2}. \tag{11}$$

In the case of the transition $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$, according to (7), $\varphi_{-1/2} - \varphi_{+1/2} = \pi$ (this circumstance was not taken into account in[4]), which leads to

$$p_{-1/2,+1/2}^i = \cos^2\frac{\vartheta_{+1/2}^i + \vartheta_{-1/2}^i}{2}, \qquad q_{-1/2,+1/2}^i = \sin^2\frac{\vartheta_{+1/2}^i + \vartheta_{-1/2}}{2}. \tag{12}$$

If $|A_p^i|, |A_n^i| \ll \hbar\gamma H$, then, according to (8) we will have $\vartheta_m^i \ll 1$ for all m. In this case $q^i \approx 0$, i.e., there are no forbidden transitions. This kind of spectrum is called simple.

Now let $|A_p^i| \gg \hbar\gamma H$. According to (8), for all transitions except the transition $+1/2 \leftrightarrow -1/2$, we have $\vartheta_m^i \approx \vartheta_{m+1}^i$ and (12) gives $q^i \approx 0$, i.e., we again obtain a simple spectrum. But in the case of the transition $+1/2 \leftrightarrow -1/2$ we obtain from (8) that $\vartheta_{+1/2}^i + \vartheta_{-1/2}^i \approx \pi$, hence $p^i \approx 0$, $q^i \approx 1$. In this case the direction of the effective field reverses. Therefore the projection of the nuclear spin (on the effective field) changes sign. A simple spectrum is again obtained.

In order to obtain the total change of energy of the transition due to the nuclei, it is necessary to sum the expression $\pm \frac{1}{2}\epsilon_m^i$ over all the nuclei. Nuclei for which

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[2)] Bir and Sochava have shown [5] that an analogous situation arises for a nucleus of a magnetic ion in the case of a strong intracrystalline field. If the parameters D and E of this field are comparable with $g\beta H$, the direction of the effective field action on the nucleus depends on the orientation of the vector S. Hence in an electronic transition the orientation of the effective field changes and there will be "forbidden" transitions. This effect is absent in case S = ½.

[3)] It is easy to verify that Eq. (11) is applicable also for electronic transitions $0 \leftrightarrow 1$ and $-1 \leftrightarrow 0$.

$A \gg \hbar\gamma H$ evoke a hyperfine structure (hfs) in which there are only allowed transitions. This pertains, in the first place, to the nucleus of the magnetic ion, as well as, possibly, to the nuclei of the host lattice that are closest to the magnetic ion. Distant nuclei, for which $A \ll \hbar\gamma H$ will not produce observable splittings and may in general be neglected.

Thus in the sum over i it is possible to limit the calculation to those nuclei for which $A \sim \hbar\gamma H$. The number of these nuclei (per magnetic ion) we shall call l. The expression

$$\sum_{i=1}^{l}\left(\pm\frac{1}{2}\varepsilon_m{}^i\right)$$

with all possible combinations of sign gives 2^l levels of super-hfs into which a given hfs level (due to nuclei with $A \gg \hbar\gamma H$) is split. We remark that for the validity of the above considerations it is required that the nuclei for which $A \sim \hbar\gamma H$ have a spin equal to 1/2; there is no restriction on the spins of the other nuclei, however. We also remark that if $S > 1/2$, the entire splitting pattern presented above pertains to a given component of the fine structure (in this we neglect complications that arise if the constants of the crystal field are comparable with $g\beta H$[5]).

It follows from all of this that the system of l nuclei gives in the general case 4^l lines of super-hfs, whereas in the case of a simple spectrum the number of lines is 2^l. In the usual experiment, however, the number of lines will be much less, since among the l nuclei there will be some that are in equivalent positions (both in the sense of position relative to the magnetic ion and relative to the magnetic field). For example, a system of 1 equivalent nuclei has, as is well known, $l + 1$ levels. Hence in the general case one obtains $(l + 1)^2$ lines of super-hfs. In the case of a simple spectrum, on the other hand, there are at most $l + 1$ lines.

Forbidden transitions are absent if the external field is directed along one of the principal directions of the tensor A^i. However, for different nuclei these principal directions will in general be different. Hence for an appropriate choice of the orientation of H one can count on obtaining a simple spectrum of super-hfs only for very high symmetry of arrangement of these nuclei.

Clogston et al.[4] give a recipe for obtaining the energies of transition and the intensities of all lines of the super-hfs. For this we introduce two variables

$${}_i = {}^1/_2(\varepsilon_m{}^i + \varepsilon_{m+1}^{i}) \qquad s_i = {}^1/_2(\varepsilon_m{}^i - \varepsilon_{m+1}^{i}) \tag{13}$$

and calculate the expression

$$2^{-l}\prod_{i=1}^{l}[p_{m,\,m+1}^{i}(x^{s_i} + x^{-s_i}) + q_{m,\,m+1}^{i}(x^{r_i} + x^{-r_i})]. \tag{14}$$

Each term of this expression, after reduction of like terms, corresponds to a certain line of the super-hfs (i.e., to all transitions of the super-hfs with identical energy): the exponent gives the energy of the transition and the coefficient the relative intensity of the corresponding line.

If $S = 1/2$, there is only one electronic transition, $+1/2 \leftrightarrow -1/2$. In this case we may leave out the subscripts on p^i and q^i.

4. As was pointed out above, in the general case the number of lines of super-hfs equals 4^l. The parameters of the super-hfs A^i are usually small, since for a complex spectrum they ought to be of the order $\hbar\gamma H$, which for a magnetic field of magnitude 3×10^3 Oe gives $(1-10) \times 10^{-4}$ cm^{-1}. Hence a high density of transitions in a small energy interval inevitably leads to a superposition of many transitions in frequency. Saturation of a small portion of an EPR line by a short, powerful microwave pulse in general will lead to saturation of a broad region, and instead of a narrow hole in the line there will appear a wide gap (independently of the concentration of paramagnetic centers). It may often happen, particularly in the presence of a group of equivalent nuclei, that the portion of the EPR line corresponds principally to a small number of transitions, and in this case one will observe saturation consisting of several narrow gaps, since in the saturated state there will be hfs components adjacent to the saturated portion. For an unresolved spectrum this will appear as a resolution of the structure.

We shall clarify the above by means of a simple example of four equivalent nuclei in the vicinity of a magnetic center with effective spin $S = 1/2$. Such a situation occurs, for example, for the paramagnetic center in irradiated polyethylene $-CH_2-CH_2-\dot{C}H-CH_2-CH_2-$. The unpaired electrons interact with the five nearest, almost equivalent protons and, as is well known, yield a spectrum with hfs of six lines with binomial intensity ratios 1:5:10. The spacing between the components of this spectrum in isotropic polyethylene is approximately equal to 30 Oe. In an oriented sample, obtained by stretching polyethylene with a stringy structure, this parameter is 33 Oe with the magnetic field oriented along the stetching axis (along the polymer chains). At X-band, the observed spectrum for the five nearest protons is a simple one, since $A \gg \hbar\gamma H$. This spectrum at 4.2°K is shown in Fig. 1.

The large width of the components of this spectrum is due to the interaction of the unpaired electron with the next four protons, for which one expects a complex super-hfs spectrum. The level scheme for these four protons is shown in Fig. 2. The total number of expected components inside each of the six lines of the simple spectrum is $5^2 = 25$, according to (14), which in this particular case takes the form

$$2^{-4}[p(x^s + x^{-s}) + q(x^r + x^{-r})]^4. \tag{15}$$

In the general case, pulse saturation of the central

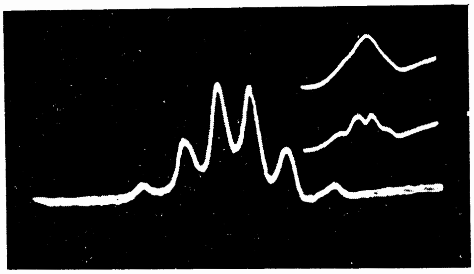

FIG. 1. Oscillogram of the super-hfs spectrum in irradiated oriented polyethylene at 4.2°K. The dc magnetic field was applied along the polymer chains. Modulation of the magnetic field was sinusoidal (50 Hz). To the right is shown the characteristic shape of one of the components and DS by the application of a microwave pulse at the center of this component.

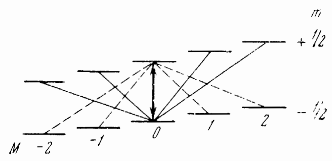

FIG. 2. Level scheme for four equivalent nuclei. m and M are respectively the projections of the electronic and the total nuclear spin. The arrow indicates the saturated transition.

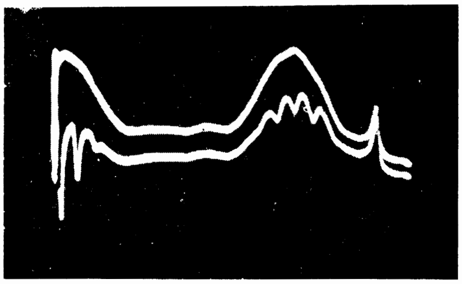

FIG. 3. Pattern of discrete saturation in one of the six components of the hfs, observed in irradiated isotropic polyethylene and due to more distant protons in the polymer chain. The spacing between gaps is 6 Oe. The upper trace is the same portion of the spectrum, traversed twice during the modulation period, without saturation. To the right is an anthracite reference line.

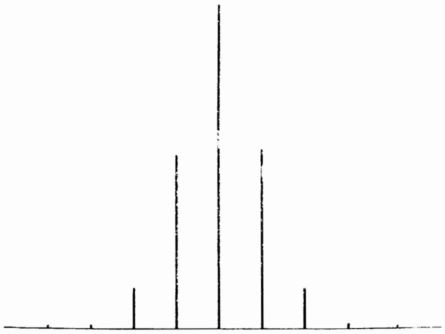

FIG. 4. Calculated super-hfs spectrum for one of the six components of the spectrum shown in Fig. 1. The plot is of relative intensity vs. magnetic field. The number of components is nine, with spacing 6 Oe.

transition indicated by the arrow in Fig. 2 should lead to the appearance of two subsystems of gaps in the EPR line with spacings $\epsilon_{+1/2}$ and $\epsilon_{-1/2}$, since in the state of partial saturation there are the forbidden transitions indicated by the solid and dashed lines. The number of gaps in each subsystem is five. But the total number of gaps is nine, since the central gaps overlap and correspond to the saturated portion of the EPR line.

In particular, for small values of the components of the HFI tensor, and particularly A_p, the spacings $\epsilon_{+1/2}$ in the upper ($m = +1/2$) levels will approximate the spacings $\epsilon_{-1/2}$ in the lower ($m = -1/2$) levels. In other words, we have $s \ll r$. In this case, the two subsystems of gaps will coincide with respect to the parameter ϵ. Saturation of the central transition, indicated by the arrow in Fig. 2, will lead in this case to saturation of five vertical transitions in the level scheme. In the portions of the EPR line corresponding to the forbidden transitions, there will be gaps with spacings equal to $\frac{1}{2}(\epsilon_{+1/2} + \epsilon_{-1/2})$. From the width of the central transition we may estimate the magnitude of $2(\epsilon_{+1/2} - \epsilon_{-1/2})$. From these data we can determine the parameters $|A_p|$, $|A_n|$, p, and q.

Figure 3 shows DS in irradiated isotropic polyethylene, which obviously occurs according to the second scheme described above. From the DS pattern we have been able to determine the values of the parameters

$$|A_p| = 0.5 \pm 0.2 \text{ Oe}, \ |A_n| = 6 \pm 1\text{Oe}, \ p = 0.75, \quad q = 0.25.$$

With the aid of (15) it is possible to calculate the expected spectrum of EPR lines shown in Fig. 4.

For various reasons, the main one of which is evidently anisotropy of the spectrum (as well as anisotropy of the basic spectrum due to the protons nearest to the paramagnetic center), the individual components of this EPR spectrum are barely resolved even in an oriented sample (see Fig. 1). This spectrum is well resolved by means of DS. In fact, it is not hard to see that DS in this case is the inverted pattern of the spectrum represented in Fig. 4, since the intensities of the individual gaps should be related as the intensities of the individual components of the spectrum, namely

$$(16p^4 + 48p^2q^2 + 6q^4) : (32p^3q + 24pq^3) : (24p^2q^2 + 4q^4) \approx 6.7 : 3.6 : 0.8. \tag{16}$$

These relations are easy to obtain from (15) by combining the intensities for the closely spaced transitions (the four outer gaps in the DS pattern are not observed because of their low intensities).

The relations in (16), together with $p + q = 1$, give the possibility of independently determining the values of p and q from the observed intensity ratios in the DS pattern. These data can be used for estimating the parameters $|A_p|$ and $|A_n|$.

It is clear from this example that the simple DS method can greatly simplify the decipherment of complex super-hfs spectra.

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