DYNAMIC DISTORTION OF INHOMOGENEOUSLY BROADENED EPR LINE

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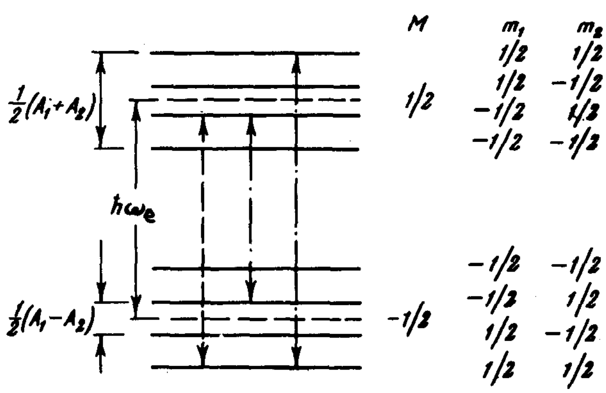
We consider an experimentally observed phenomenon, consisting in the fact that when a certain section ($H = \omega/\gamma_e$) of an inhomogeneously broadened EPR line is saturated there takes place not only the so-called "hole burning" in the field H, but additional dips appear, shifted relative to the field H; we shall call these induced holes (IH). The magnitude and depth of the IH depend on the degree of saturation in the field H, on the line shape, and on the value of H. Similar phenomena were observed in [1,2]. Experiment shows that the formation of the IH takes place within a shorter time than the duration of any relaxation processes in the spin system.

We shall show that the cause of the IH is excitation of forbidden transitions with simultaneous flipping of the electron and nuclear spins under the influence of the saturating pulse (SP). For a qualitative explanation of the phenomenon of dynamic distortion (DD) of the EPR line, we consider the system of energy levels of the electron spin interacting with two non-equivalent protons, the hyperfine interaction (HFI) constants of which are A_1 and A_2 (see Fig. 1). Let the forbidden transition ($M = 1/2$, $m_1 = -1/2$) $\rightleftharpoons$ ($M = -1/2$, $m_k = 1/2$) be saturated (dashed arrow). To this end it is necessary to have $\omega = \omega_e + \omega_n + A_2/2\hbar$, where ω_e and ω_n are the Zeeman frequencies for the electron and the proton. From Fig. 1 it is seen that a simultaneous decrease takes place in the population difference for the forbidden transitions at the frequencies $\omega_e + (A_1 + A_2)/2\hbar$ and $\omega_e + (A_1 - A_2)/2\hbar$ (dash-dot), and consequently dips (IH) will appear at these frequencies following passage of a weak control signal. The frequency difference between the SP and the IH is $\Omega = \omega_n + A_1/2\hbar$. A forbidden transition with the second proton taking part would lead to the appearance of IH at distances $\Omega = \omega_n \pm A_2/2\hbar$.



M, m_1, m_2 - magnetic quantum numbers

Fig. 1

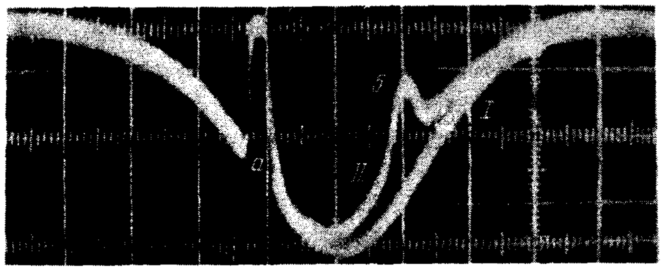


Fig. 2

The effect was observed in phenoxyl radicals produced in ion exchangers of the KU-1 type. The method of preparation and the EPR experimental data for them are given in [3]. The investigations were made with an EPR spectrometer (ν_e = 9340 MHz) [4] by pulsed excitation with simultaneous modulation of the magnetic field. Observation of the dynamic line saturation, as seen from Fig. 2, was made after application of the SP during the same or succeeding passage through the resonance value of the magnetic field. In Fig. 2, curve I is the absorption signal in the absence of the SP, curve II is the signal after the application of the SP, a is the place where the SP was applied, and b is the induced hole.

The EPR line was broadened by the HFI of the electron spin with the spins of the neighboring protons. The line width is much larger than the width of the individual spin packet ($2\Delta\omega_0 \gg 2\delta$). In this case the influence-layer model can be successfully employed. The spin Hamiltonian of the system is

$$\hat{\mathcal{H}} = \hbar\omega_e \hat{S}^z - \hbar\omega_n \sum_i \hat{I}_i^z + \hat{S}^z \sum_i A_i \hat{I}_i^z + \hat{S}^z \sum_i (B_i \hat{I}_i^+ + B_i^* \hat{I}_i^-) + 2\hbar\gamma_e H_1 \hat{S}^x \cos\omega t. \qquad (1)$$

Here $\hat{S}$ and $\hat{I}_i$ are the spin operators of the electron and of the i-th proton, and $2H_1$ is the amplitude of the alternating field.

A forbidden transition with the k-th proton is possible only if

$$\omega \simeq \omega_e \pm \omega_n \pm \Delta_k/\hbar, \qquad (2)$$

where Δ_k/γ_e is the local field produced by all the protons excepth the k-th. The saturation of the forbidden transition with the k-th nucleus, as shown above, leads to a change of the populations of the electronic spin levels in the local fields $(\Delta_k \pm A_k/2\hbar)/\gamma_e$. This change of the populations depends both on the degree of saturation of the forbidden transition, and on the probability of finding in the system a Δ_k satisfying condition (2).

We introduce $P_{M,m_k}(\Delta_k)$, which is the population of the level defined by the indices M and m_k, when the field of all the remaining protons is equal to Δ_k/γ_e, referred to a unity frequency interval:

$$P_{M,m_k}(\Delta_k) = P^0_{M,m_k} \phi_k(\Delta_k), \qquad (3)$$

where $\varphi_k(\Delta_k)$ is the distribution function of Δ_k normalized to unity, and P^0_{M,m_k} is the total population of the corresponding level independently of the value of Δ_k.

The shape function of the EPR line is defined by the expression

$$\Phi(\Delta) = \sum_{k,m_k} \iint [P_{1/2,m_k}(\Delta_k) - P_{-1/2,m_k}(\Delta_k)] \rho(A_k) \delta \times (\Delta_k - \Delta + m_k A_k/\hbar) d\Delta_k dA_k, \qquad (4)$$

where $\rho(A_k)$ is the probability density of the field distribution produced by the k-th nucleus. Without allowance for the relaxation processes (the time of action t of the SP is much shorter than the relaxation time) we get

$$P_{M,m_k}(\Delta_k, t) = \frac{1}{4} [P^0_{1/2} + P^0_{1/2} + (P_M - P_M) \exp(-2W^{(i)}_k t)] \phi_k(\Delta_k) \qquad (5)$$

following the flip of the k-th proton. (We disregard the simultaneous flip of several protons, since we assume that $|B_i| < \hbar\omega_n$.) Here $W^{(i)}_k$ is the probability of the forbidden transition; $i = 1$ for the transition $(M = -1/2, m_k = 1/2) \rightleftharpoons (M = 1/2, m_k = -1/2)$ and $i = 2$ for the transition $(M = -1/2, m_k = -1/2) \rightleftharpoons (M = 1/2, m_k = 1/2)$; P^0_M is the total population of the level corresponding to the index. Then, taking (3) - (5) into account, we obtain a general expression for the description of the dynamic distortion of the EPR line shape, due to the presence of the forbidden transitions:

$$\Phi(\Delta) = \frac{1}{4}(P^0_{1/2} - P^0_{-1/2}) \sum_{i,k,m_k} \int dA_k \rho(A_k) \phi_k(\Delta - m_k A_k/\hbar) \times \exp(-2W^{(i)}_k t). \qquad (6)$$

In this formula we took into account the DD due to: (i) the different types of forbidden transitions (summation over i and m_k) and (ii) the part played in the forbidden transitions by all protons, which determine the EPR line shape (summation over k).

In the case of a disordered distribution of the protons about the paramagnetic center, the IH due to different protons overlap and are therefore not resolved by the control signal. In the case of a regular proton spin arrangement, the IH from the non-equivalent protons can be observed separately [2].

For comparison with experiment, let us consider a model close to that of our case, of a random distribution of protons about an electron, the EPR line being broadened as a result of anisotropic HFI. Calculation yields for the distance between the SP and the IH a value $\sim\omega_n \pm \delta$, which agrees with experiment within the limits of errors. As seen from (6), the shape and depth of the IH are determined by the energy delivered by the SP $(\hbar\gamma_e^2 H_1^2 t)$. When $H_1 = 0.15$ Oe and $t = 80$ μsec, the experimentally measured change of the signal at the center of the IH is $C = 60\%$. Calculation yields $C = 35\%$, which in our opinion is in satisfactory agreement for the model assumed. The experimental dependence of the depth of the IH on t for one of the samples is

$$V = V_1 \exp(-t/\tau_1) + V_2 \exp(-t/\tau_2), \qquad (7)$$

where $\tau_1 = 80$ μsec and $\tau_2 = 330$ μsec. From (6) it follows that in our model

$$V = V_0 \exp(-t/\tau_0), \tag{8}$$

where $\tau_0 \approx [1.2\sqrt{\pi}(\gamma_e H_1/\omega_n)^2\delta]^{-1} \approx 100 - 300$ μsec. We emphasize that the difference between (7) and (8) is due to the assumed model of random homogeneous distribution of the proton spins about the paramagnetic center.

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DIRECT DETERMINATION OF THE STRUCTURE FORMED BY CRYSTAL MAGNETIC FIELDS AT NUCLEI HAVING MOSSBAUER ISOTOPES

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We show in this paper that the character of the interference in Mossbauer scattering of γ quanta by a crystal depends on the structure formed by the crystal magnetic fields at the nuclei of the Mossbauer isotope, and depends by the same token on the magnetic structure of the crystal. An analysis of the picture of the diffraction and polarization of the Mossbauer radiation at the Bragg maxima makes it possible to determine the structure formed by the magnetic fields at the crystal lattice sites containing the Mossbauer nuclei. The physical cause of the influence of the magnetic structure on the character of the Mossbauer scattering lies in the dependence of the amplitude of the Mossbauer scattering on the direction of the magnetic field at the scattering nucleus.

Assume that a monochromatic γ-quantum beam is resonantly scattered by a single crystal containing a Mossbauer isotope, and let the magnetic ordering in the crystal produce at the nuclei magnetic fields sufficiently strong to split the Mossbauer radiation into individual Zeeman components. We shall assume that the crystal is ideal, the content of the Mossbauer isotope is 100%, and the nuclei have zero spin in the ground state and are rigidly secured at the crystal sites. These assumptions signify that the elastic scattering is fully coherent and that the Mossbauer factor is f = 1. Assuming also that the crystal is sufficiently thin, we neglect extinction. In the case of a fully polarized beam of primary γ quanta, the polarization of which is defined by a polarization vector $\vec{n}$, the cross section for elastic resonant scattering corresponding to a finite polarization defined by a polarization vector $\vec{n}'$ is of the form

$$\frac{d\sigma(\mathbf{k}, \mathbf{n}; \mathbf{k}'\mathbf{n}')}{d\Omega_{\mathbf{k}'}} = A\left|\sum_m f_m(\mathbf{k}, \mathbf{n}; \mathbf{H}_m; \mathbf{k}', \mathbf{n}')e^{i(\mathbf{k}-\mathbf{k}')\mathbf{r}_m}\right|^2, \tag{1}$$

where $\vec{k}$ and $\vec{k}'$ are the wave vectors of the initial and scattered γ quanta, respectively,