Investigation of the mechanism of dynamic polarization of nuclei by the two-frequency pumping technique

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The effect of two saturating microwave fields with somewhat differing frequencies on the polarization of nuclear spins in a solid paramagnetic substance with inhomogeneous EPR line broadening is analyzed. It is demonstrated that the results of such experiments should depend qualitatively on the dynamic nuclear polarization (DNP) mechanism that acts in the substance, and may serve as a good criterion for its determination. The DNP effect in ethylene glycol with a CrV complex is investigated by the two-frequency pumping method at 1.8°K and 13 kOe. Under these conditions the main DNP mechanism is found to be dynamic cooling of the electron dipole-dipole pool. However, when the remote EPR line wings are saturated this mechanism is superseded by the solid-effect or electron-nuclear cross-relaxation.

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I. INTRODUCTION

Dynamic polarization of nuclear spins (DPN), which is produced when resonant lines of paramagnetic impurities in solids are saturated by a microwave field, has long attracted the interest of researchers (see [1]). Interest in this phenomenon has particularly increased recently, when consistently improved results were obtained on the polarization of proton targets for the needs of nuclear physics. The presently attainable proton polarization (a measure of which is the quantity $p_n = (n^+ - n^-)/(n^+ + n^-)$, where n^+ and n^- are the numbers of nuclear spins oriented parallel and antiparallel to the constant magnetic field H_0) has reached almost 100% (at a temperature $T_0 = 0.2$°K and in a field $H_0 = 25$ kOe[2]), and the host matrices for the paramagnetic impurity are organic compounds, which are convenient for use as polarized targets.[3]

These practical advances are still far from correspondence with the degree of understanding of the physical mechanisms that lead to the DPN effect in the indicated substances. The point is that in most cases one has to cope with strong inhomogeneous broadening of the EPR spectrum of the paramagnetic impurities, and the width of the inhomogeneous EPR line turns out to be commensurate with the NMR frequency of the polarized nuclei of the matrix. In this situation the usual experimental data, such as the value of p_n, its dependence on the microwave frequency and power, etc., turn out to be as a rule insufficient for a reliable choice between one of the three principal theoretical DPN models: the solid effect (SE),[4,1] electron-nuclear cross relaxation (ENC)[5] and dynamic cooling (DC).[6–8]

There is thus a strongly felt need for reliable experimental criteria capable of identifying the DPN mechanism in each concrete case. One such method, which permits assessment of the effectiveness of one of the DPN mechanisms (dynamic cooling), is to register the changes observed in the EPR line shape under conditions of microwave pumping[9] or during a certain time after it is turned off.[10] It is necessary here to measure exactly (without dispersion and nonlinear distortion) the EPR absorption signal, and this is a rather complicated task in DPN experiments.[1)]

Another method, namely the comparison of the values of p_n for different sorts of nuclei that are simultaneously present in the sample lattice,[11] calls for specially introducing additional nuclei (isotopes) into the substance, which is not always possible, and which can furthermore exert by itself an influence on the DPN mechanism (see Sec. II,3 below).

We propose in this paper a relatively simple qualitative method of investigating the DPN mechanism in objects with inhomogeneously broadened EPR lines. In this method, the criterion for choosing any particular theoretical model is the behavior of the quantity p_n when the sample is acted upon simultaneously by two saturating microwave fields with somewhat different frequencies. This method was used by us to ascertain the nature of the DPN in one of the better materials for proton polarization, frozen ethylene glycol (EG) with the paramagnetic complex CrV.

II. DIFFERENT DPN MECHANISMS UNDER CONDITIONS OF TWO-FREQUENCY PUMPING

Consider a solid paramagnetic sample placed in a constant magnetic field H_0 and containing N_n nuclear lattice spins ($I = 1/2$) with Larmor frequency ν_n, as well as N_e electron spins of the paramagnetic impurity ($S = 1/2$). Let the EPR spectrum of the impurity be an inhomogeneously broadened line with central frequency ν_0 and width $\Delta^* \gtrsim \nu_n$; following the usual procedure, we assume that this line consists of a set of homogeneous spin packets with frequencies ν_i and dipole-dipole width $\Delta \ll \Delta^*$, each of which corresponds to N_i identical paramagnetic centers that are randomly distributed over the volume of the sample ($\sum_i n_i = N_e$).

We discuss the DPN effect produced when the EPR line wing is saturated by a microwave field of fixed frequency ν_1, and investigate the dependence of p_n on the frequency ν_2 of a second microwave field which saturates the EPR line on the same wing ($\Delta_1 = \nu_1 - \nu_0$ and $\Delta_2 = \nu_2 - \nu_0$ have the same sign). As will be shown below, from the form of the function $p_n(\Delta_{12})$, where $\Delta_{12} = \nu_2 - \nu_1$, we can identify the DPN mechanism that operates in the given substance.

For simplicity we shall use throughout the "high-temperature approximation" $\tanh(h\nu_0/2kT) \approx h\nu_0/2kT$; nonetheless, the main features of the method should remain the same also at lower temperatures.

We proceed now to consider the various DPN mechanisms.

1. The Solid Effect (SE)

The elementary act of the SE[4,1] consists of simultaneous flipping of one electron and one nuclear spin with Larmor frequencies ν_i and ν_n under the influence of a microwave field that induces a "forbidden" electron-nuclear transition at one of the frequencies $\nu_i \pm \nu_n$. If the "forbidden" transition is strongly saturated, this process tends to establish the equality

$$p_n = \pm p_i, \tag{1}$$

where p_i is the electron polarization.

In the case of inhomogeneous broadening of the EPR line, the action of the microwave field at a certain frequency $\nu_1 = \nu_\beta$ causes simultaneous saturation of the "forbidden" transitions of opposite sign for the packets α and γ ($\nu_\alpha = \nu_1 + \nu_n$; $\nu_\gamma = \nu_1 - \nu_n$), and also saturation of the pure electronic ("allowed") transition, which does not lead to DPN, at the frequency ν_β (see Fig. 1a). In the model of the "ideal" SE it is assumed that in this case the "allowed" and "forbidden" transitions do not overlap for each of the packets, i.e., $\Delta \ll \nu_n$, and in addition there is no cross relaxation.

The resultant value of p_n depends on the extent to which the distribution of the nuclear polarization is homogeneous over the volume of the sample. We consider two limiting cases that differ in the rate of the spatial diffusion of p_n ("spin diffusion"[12]).

A. Isolated spheres of influence. At a moderate rate of spin diffusion, each paramagnetic center determines completely the polarization of the nuclei in its own sphere of influence, which contains N_n/N_e nuclear spins. In this case the value of p_n is determined by simple arithmetic averaging of the polarizations p_{ni} pertaining to the spheres of influence of the corresponding spin packets ν_i, with allowance for their relative weight N_i/N_e.[1] For pumping at the frequency $\nu_1 = \nu_\beta$ this yields

$$p_n = (N_\alpha p_{n\alpha}^- + N_\gamma p_{n\gamma}^+)/N_e, \tag{2}$$

where $p_{n\alpha}^-$ and $p_{n\gamma}^+$, which have opposite signs ("differential SE") are given, in the case of strong stationary saturation of the "forbidden" transitions, by the formula[1]

$$p_{ni} = \frac{+p_i^0}{1+f_i}, \quad f_i = \frac{\tau_{1e}}{\tau_{1n}}\frac{N_n}{N_i}. \tag{3}$$

Here p_i^0 is the equilibrium value of p_i, while f_i is the "leakage factor" and τ_{1e} and τ_{1n} are the electron and nuclear spin-lattice relaxation times.

If we now turn on the other saturating microwave field with frequency $\nu_2 \neq \nu_1 \pm \nu_n$, then two additional spin packets enter in the action: $\nu_{\alpha'} = \nu_2 + \nu_n$ and $\nu_{\gamma'} = \nu_2 - \nu_n$; their spheres of influence also become "regions of high polarization" and make a contribution $N_{\alpha'} p_{n\alpha'}^- + N_{\gamma'} p_{n\gamma'}^+$ to the numerator of (2). Since, by assumption, both pumps act on one wing of the EPR line, this will cause an additive growth of the quantity $|p_n|$.

The most important, however, is the case $\nu_2 = \nu_1 \pm \nu_n$ (e.g., $\nu_2 + \nu_\gamma$, Fig. 1a). Now two spin packets (β and γ) go out of the action, inasmuch as we have for them $p_{n\beta} = p_\beta = p_{n\gamma} = 0$ by virtue of (1), so that we are left in the numerator of (2) only with $N_\alpha p_{n\alpha}^- + N_\delta p_{n\delta}^+$, where $\nu_\delta = \nu_\gamma - \nu_n$. As a result, a characteristic resonant dip should appear in the experimental plot of $p_n(\nu_2)$, with depth $N_\beta p_{n\beta}^- + N_\gamma p_{n\gamma}^+$; here, too, however, the value of $|p_n|$ remains larger than under the action of pump (2) alone, since $N_\delta < N_\gamma$.

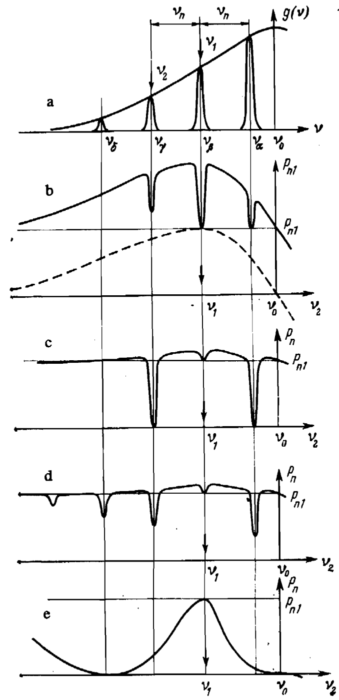

FIG. 1. a—Scheme of two-frequency saturation of the wing of an inhomogeneous EPR line. The arrows indicate the microwave pump frequencies. b—Approximate dependence of the nuclear polarization on the second pump frequency (ν_2) at a fixed first-pump frequency (ν_1, marked by the arrow) for the SE mechanism in the model of isolated spheres of influence. c—The same for the SE mechanism in the model of fast nuclear spin diffusion. d—The same for the ENC mechanism. e—The same for the DC mechanism. The value p_{n1} corresponds to $\nu_2 = \nu_1$. The dashed curve in Fig. b shows a plot for $p_n(\nu_2)$ in the absence of the first pump.

Of course, an analogous dip appears also at $\nu_2 = \nu_1 + \nu_n$ (see Fig. 1b).

B. Fast spin diffusion. In this limiting case the nuclear spin-spin interaction ensures establishment of a single value p_n in the entire volume of the sample (with the exception of small inclusions around the magnetic centers that serve as sources or sinks of the polarization)[13,14] In this situation, the stationary value of the nuclear polarization can be obtained approximately from the simple rate equations for p_n and the polarizations of the electron spin packets p_i, which are affected by the microwave pumping, assuming that the role of the remaining packets consists only of the shortened time τ_{1n}, and that the rates of change of p_i and p_n as a result of the "forbidden" induced transition are in the ratio $N_n : N_i$.

At $\nu_1 = \nu_\beta$, $p_\beta = 0$, and strong saturation of the "forbidden" transitions we have for the packets α and γ (see, e.g., [15])

$$p_n = -p_e^0 \frac{N_\alpha - N_\gamma}{N_\alpha + N_\gamma + \tau_{1e} N_n/\tau_{1n}}.$$

In this formula, just as in (2), there enters a difference ("differential") effect due to the opposing polarizing actions of packets α and γ; but now the sample no longer contains regions with different nuclear polarizations (including equilibrium regions), and therefore turning on of the second pump can not lead simply to an additive increase of p_n. If $\nu_2 \neq \nu_1 \pm \nu_n$, then the influence of the second pump will in general not be very appreciable, even though an increase due to the growth in the relative number of polarization sources is possible even now. The most interesting, however, is again the case $\nu_2 = \nu_1 \pm \nu_n$.

In the same concrete example of two-frequency pumping $\nu_1 = \nu_\beta$, $\nu_2 = \nu_\gamma$ (Fig. 1a), the stationary solution of the SE rate equations for p_α and p_n under strong saturation of the "allowed" transitions ($p_\beta = p_\gamma = 0$) takes the form

$$p_n = -p_e^0 \{1 + [f_\alpha + (S_\alpha^-)^{-1}](1 + S_\beta^- + S_\gamma^+)\}^{-1}, \tag{4}$$

where $S_i^{\pm} = \tau_{1n} W_i^{\pm}(N_i/N_n)$ are the saturation factors of the "forbidden" transitions at the frequencies $\nu_i \pm \nu_n$, the probabilities $W_i^{\pm}$ of which are proportional to the powers of the corresponding microwave pumps[2)] (the influence of the weak packet δ will be neglected for simplicity).

It is seen from (4) that an increase of any of the factors S_β^- or S_γ^+ leads in the limit to complete depolarization of the nuclei, $p_n \to 0$. The physical meaning of this "resonant quenching" of the nuclear polarization is quite clear: the effect is due to simultaneous saturation of the "allowed" and "forbidden" transitions for each of the packets β and γ, so that at $p_\beta = p_\gamma = 0$ it follows immediately from (1) that $p_n = 0$. Whereas in the model of isolated spheres of influence the situation was limited only to depolarization of the nuclei in the spheres of influence of packets β and γ, now these packets, owing to the fast spin diffusion, provide a powerful additional leakage for the polarization of the entire sample, and this is indeed reflected in the appearance of the coefficient of f_α in the denominator of (4).

Thus, an attribute of the SE mechanism in conjunction with fast spin diffusion is the appearance in the function $p_n(\nu_2)$, at $\nu_2 = \nu_1 \pm \nu_n$, of narrow resonant dips, the depth of which is completely determined by the pump power and tends to zero when the saturation is strengthened (Fig. 1c).

2. Electron-Nuclear Cross Relaxation (ENC)

In this DPN mechanism, first described in [5] (see also [13,16]), the elementary act of polarization consists of a flipping, in opposite directions, of two electron spins i and j, accompanied by simultaneous flipping of one nuclear spin, with the total Zeeman energy conserved: $\nu_i - \nu_j = \pm\nu_n$. This process is also "forbidden" (because of angular-momentum nonconservation), but unlike the SE it does not require participation of a microwave field, being due only to dipole spin-spin interactions. If the probability of the ENC is large in comparison with the spin-lattice relaxation rate, then the process will tend to establish the equality

$$p_j - p_i = \pm p_n. \tag{5}$$

When one of the "allowed" EPR lines at the frequency ν_i or ν_j is saturated, Eq. (5) goes over into (1) and a DPN effect is produced differing from the SE only in that it does not require saturation of "forbidden" transitions.

Let us proceed to an inhomogeneous EPR line and again put $\nu_1 = \nu_\beta$ and $p_\beta = 0$. In contrast to the SE case, we can no longer confine ourselves to only two packets α and γ, since all the packets k, having frequencies

$$\nu_k = \nu_\beta \pm k\nu_n, \tag{6}$$

where k is an integer, now take part in the polarization process. Applying in succession the relation (5) for each pair of the spin packets satisfying the condition (6), we arrive at the equality[3)]

$$p_k = \mp k p_n. \tag{7}$$

It is easily seen that saturation, by the second pump field, of any spin packet k (i.e., $\nu_2 = \nu_1 \pm k\nu_n$; $p_k \to 0$) leads, according to (7), to a decrease in the value of p_n, which is more appreciable the more effective the ENC process is in comparison with the spin-lattice relaxation. Estimates show that for an "ideal" ENC effect (without pure electronic cross relaxation and saturation of "forbidden" transitions) the stationary value will be determined in this case by an expression similar to (4), with S_i replaced by $(\tau_{1n} W_{ij})^{-1}$, where W_{ij} is the probability of the ENC per nuclear spin.

Thus, the criterion for the effectiveness of the ENC mechanism can be the presence of a number of dips in the experimental $p_n(\nu_2)$ plot at the multiple detunings $\Delta_{12} = \pm k\nu_n$, and also independence of the maximum depth of these dips of the pump power (see Fig. 1d).

3. Dynamic Cooling (DC)

If the pure electronic cross relaxation between the spin packets ("spectral diffusion") prevails over the spin-lattice interaction, the behavior of the electron spin system under saturation condition can be described with practically no changes by the Provotorov theory,[18] which was developed originally for homogeneous dipole-dipole broadening (see [19-21]). As applied to our case, this means that when the packet β is saturated ($\nu_1 = \nu_\beta$; $p_\beta = 0$) there should be produced a characteristic linear distribution of the electronic polarization along the EPR line:

$$p_i = -\frac{h}{2kT_D}(\nu_i - \nu_1), \tag{8}$$

where T_D is the dipole temperature, which characterizes the internal equilibrium in the electron dipole-dipole-interactions pool (DDP). We note that the same result is obtained also without spectral diffusion, if simultaneous saturation of all the spin packets is ensured by the action of the pump ν_1 on their wings;[22] this situation is however unlikely if $\Delta \ll \Delta^*$.

Applying relation (8) to the packets α and γ (Fig. 1a), we see that any of the DPN mechanisms considered above (SE or ENC) leads by virtue of (1) or (5) to the equation

$$p_n = h\nu_n / 2kT_D. \tag{9}$$

Since, on the other hand, $p_n = h\nu_n/2kT_{zn}$, where T_{zn} is the Zeeman spin temperature of the nuclei, this means equalization of the spin temperatures T_{zn} and T_D (the DC mechanism)[6-8,23].[4)]

Thus, in this case the only difference between the DC mechanism and the "ideal" SE and ENC is the presence of an effective electron cross relaxation over the entire EPR line (or at least in a frequency interval of order ν_n). This difference, however, leads to important consequences.

First, the establishment of a single value of p_n over the entire volume of the sample is now ensured by the distribution (8) itself, i.e., by the electron cross relaxation, and does not depend on the rate of nuclear spin diffusion between the different spheres of influence.

Second, it becomes possible to calculate p_n in simple fashion, since the value of T_D is known from the solution of the Provotorov equations. In the case of strong stationary saturation at the frequency ν_1 we have (see, e.g., [20,21])

$$p_n = p_e^0 \frac{\nu_n}{\Delta_1}\left[1 + \left(\frac{\Delta_0}{\Delta_1}\right)^2\right]^{-1}, \tag{10}$$

where $\Delta_0^2 = D^2\tau_{1e}/\tau_{1D} + M_2^* + \nu_n^2 N_n \tau_{1e}/N_e \tau_{1n}^*$, D^2 is the mean squared local field for the electron spins, τ_{1D} is the DDP spin-lattice relaxation time, τ_{1n}^* is the time of parasitic nuclear spin-lattice relaxation, and M_2^* is the second moment of the inhomogeneous EPR line.

Finally, an essential distinguishing feature of the DC mechanism, which follows directly from (8) and (9), is the equalization of the spin temperatures of all types of nuclei present in the substance (provided only that their frequencies do not exceed Δ^*). This phenomenon, known as "thermal mixing of the nuclei via the DDP,"[24-26] was used in [2,11] to identify the DC mechanism in partly deuterated frozen alcohols. It should be noted, however, that this result should be approached with certain caution, since the distribution (8) can become established also as a result of the ENC process, provided only that $\nu_n \ll \Delta^*$[27] (this is directly evident from the fact that Eq. (7) goes over into (8) with T_D replaced by T_{zn} as $\nu_n \to 0$). Since the NMR frequency of the deuterons was low enough in [2,11], the addition of deuterium could in principle accelerate the spectral diffusion in the EPR line and change the DPN mechanism for protons.

We proceed now to two-frequency pumping. The stationary solution of the Provotorov equation for saturation at the frequencies ν_1 and ν_2 yields (see [28,29])

$$p_n = \frac{p_e^0 \nu_n \Delta_0 (S_1\Delta_1 + S_2\Delta_2)}{\Delta_0^2 + S_1(\Delta_1^2+\Delta_0^2) + S_2(\Delta_2^2+\Delta_0^2) + S_1S_2\Delta_{12}^2}, \qquad (11)$$

where $S_1 = W_1\tau_{1e}$ and $S_2 = W_2\tau_{1e}$ are the saturation factors at the frequencies ν_1 and ν_2, while W_1 and W_2 are the corresponding probabilities of the "allowed" induced transitions and are proportional to the pump powers.

It is seen from (11) that for arbitrary $\Delta_{12} \neq 0$ it follows from $S_1 \to \infty$ and $S_2 \to \infty$ that $p_n \to 0$, and if the powers of both pumps are given and Δ_1 is fixed (with the condition $S_1, S_2 > 1$), then the depolarizing action of the second pump increases with increasing Δ_{12} until the frequency ν_2 is located on the far wing of the EPR line (Fig. 1e).

This characteristic result, which differs strongly from the picture of the resonant dips in the SE and ENC cases (cf. Figs. 1b–1d), can serve as a good experimental criterion for the separation of the DC mechanism.

III. EXPERIMENT AND DISCUSSION OF RESULTS

The experiment was performed on samples of frozen ethylene glycol (EG) with the paramagnetic complex CrV as an impurity.[30,31] The nature of the DPN effect in this substance, which is successfully used in polarized targets,[2] was recently discussed in the literature[32-35] (in this discussion we favored the SE model and our opponents the DC model), but owing to the lack of reliable criteria the question remained open. To be sure, most recently, evidence appeared favoring the predominance of the DC mechanism in partly deuterated material,[26] but this evidence concerned samples with extremely high CrV concentration (2×10^{20} cm^{-3}), and furthermore, did not take into account the possible influence of deuterium on the proton polarization mechanism (see Sec. II,3).

The EG-CrV samples for our investigations were prepared by a photochemical method (samples "C" of [33]); the concentration was $N_e \approx 3 \times 10^{19}$ cm^{-3} and corresponded to the maximum DPN effect at $T_0 = 1.8$°K and $H_0 = 13$ kOe. Under these conditions we have $\nu_n = 54.5$ MHz, $\nu_0 = 35.4$ GHz, $\Delta^*/2 = 65$ MHz, $\tau_{1n} \approx 5$ to 10 sec, and $\tau_{1e}/\tau_{1n} \approx 10^{-3}$.[33] We used the apparatus described in [33], with addition of a second pump generator. The Q of the microwave resonator with the sample was chosen low enough to ensure simultaneous saturation of the EPR at the two frequencies and at $|\Delta_{12}| \lesssim 150$ MHz.

During the course of the experiment, the frequency of the first pump generator was set at a certain fixed value $\nu_1 = \nu_0 + \Delta_1$ and the proton polarization gain in comparison with the equilibrium value, $E = p_n/p_n^0$, was measured as a function of the frequency of the second pump, $\nu_2 = \nu_0 + \Delta_2$ (Δ_1 and Δ_2 had the same sign). At the employed microwave powers, the action of each pump separately was enough to ensure saturation of the DPN effect, i.e., to attain a maximum of $|E|$ at the given Δ_1 or Δ_2.

Figure 2 shows typical measurement results for four values of Δ_1. The figure shows also the shape of the low-frequency wing of the EPR line in EG-CrV and the usual dependence of E on the pump frequency when one microwave generator is in operation. The main features of the results reduce to the following:

1. At relatively small detunings $|\Delta_1|$ (within the limits of the main part of the EPR line contour) the $E(\Delta_2)$ curves reveal broad nonresonant dips (their widths reach 90 and 75 MHz for curves 1 and 2 of Fig. 2).

2. With increasing Δ_1, the width of the dips decreases, and at $\Delta_1 = -89$ MHz (curve 4) a well pronounced resonance is observed (with width about 30 MHz) at $\nu_1 - \nu_2 = (52 \pm 5)$ MHz, which practically coincides with ν_n.

3. In no case does turning on the second pump lead to an increase of $|E|$.

For curves 2 and 4 of Fig. 2 we investigated also the dependence on the power of the second pump (P_2). It turned out that a twofold decrease of P_2 raises the entire central part of curve 2 by 10–15%, and the depth of the resonance peak on curve 4 is decreased (by approximately 30%). A comparison of these data with the conclusions of Sec. II and with Figs. 1b to 1e shows that in the case of EPR saturation in the main part of the line contour the principal DPN mechanism is dynamic cooling. At the same time, on going to the far wing of the line, the DC gradually gives way to one of the resonant mechanisms (SE or ENC); we cannot distinguish between the two in this case, since the width of the EPR line is insufficient for the observation of the possible series of dips at $\Delta_{12} = k\nu_n$ (Fig. 1d), and the pump-generator power is insufficient to obtain maximum depth of the dip on curve 4. We note that a similar change of the DPN mechanism on going from the center of the EPR line to the periphery was observed in [36].

Finally, the failure of $|E|$ to increase under the in-

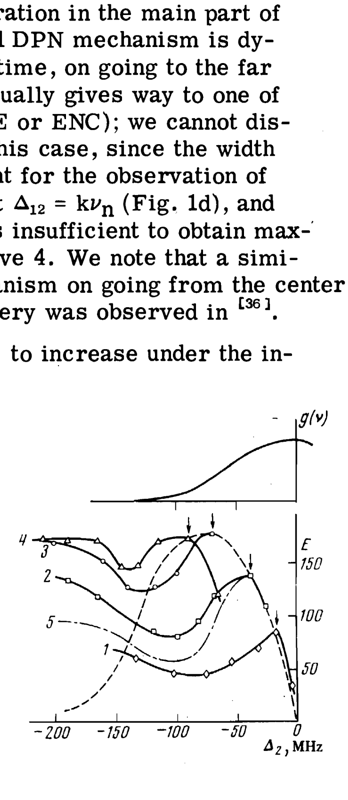

FIG. 2. Dependence of the enhancement of the proton polarization in EG-CrV on the detuning Δ_2 of the second pump relative to the center of the EPR line at fixed detunings of the first pump Δ_1 (indicated by arrows); curves 1–4—experiment, 5—result of calculation by formula (11) for $\Delta_1 = 39$ MHz. Dashed—plot of $E(\Delta_2)$ in the absence of the first pump. Top—form of the EPR line wing.

fluence of the second pump at $\nu_2 \neq \nu_1 - \nu_n$ (curve 4) indicates that nuclear spin diffusion is effective in this substance (see Sec. II,1).

Figure 2 shows also one of the results of the calculation of E by formula (11) (S_1 and S_2 were determined from the experimental dependence of E on the power of each generator in the one-frequency pumping mode, and the value of Δ_0 was set equal to $|\Delta_{max}| = 70$ MHz, where Δ_{max} is the detuning at which the maximum $|E|$ is reached (see (10)). A comparison of curves 2 and 5 in Fig. 2 shows that the agreement between the experimental data and the DC model is only qualitative, and we are obviously dealing in fact with an intermediate case, when the rate of spectral diffusion in the EPR line is still not large enough to ensure exact satisfaction of the distribution (8).

This conclusion agrees well with the presence of a gradual transition to another DPN mechanism on the far wing of the EPR line; this is apparently due to the further weakening of the spectral diffusion on the wing, owing to the decrease in the paramagnetic-center concentration (thus, in the region of the dip on curve 4, the intensity of the EPR line is only about 3% of the maximum, see Fig. 2). We note also that already in the region $\Delta_{max} = 70$ MHz we observe a deviation of the experimental value $|E_{max}| = 180$ from the DC theory (10), which calls for $|E_{max}| = \nu_0/2\Delta_{max} \approx 250$ (the error of the high-temperature approximation does not exceed 7% here).

Thus, the method of investigating DPN with the aid of two-frequency pumping has proved to be effective. It was possible to solve with its aid the problem of the DPN mechanism in EG-CrV in a field $H_0 = 13$ kOe and to observe directly the transition from the DC to the SE (or ENC) when the number of paramagnetic centers affected by the pump is decreased. An attractive feature of the method, in our opinion, is its qualitative character, which makes it possible to dispense with extremely accurate measurements or with the fitting of some free parameters. We note that the same method yields incidentally valuable information on the effectiveness of spectral diffusion in an EPR line and of nuclear spin diffusion.

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[1)]We note that no such quantitative measurements were made in the well known study [10], so that the conclusion of its authors that the spin temperatures of the nuclei and of the electron dipole pool are equal have remained not fully justified (the EPR line asymmetry observed in [10] can be attributed also to the contribution of "forbidden" electron-nuclear transitions.

[2)]The values of $S_i^{\pm}$ can be significantly smaller than the saturation factors of the "allowed" EPR transitions, owing to the appreciable leakage produced by the remaining spin packets.

[3)]We note that Eq. (7) reflects the appearance in the EPR line of a number of "dips" at the frequencies ν_k, of the type of the "discrete saturation" effect. [17]

[4)]In [7], where the "DC" term was first introduced, it was used in a narrower sense, only for a homogeneous EPR line and without saturation of "forbidden" transitions.

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