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Dipole-reservoir cooling and dynamic polarization of nuclei in saturation of inhomogeneous EPR line

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The temperature of the electronic dipole-dipole reservoir (DDR) and of the dynamic polarization of nuclei are calculated under conditions of stationary saturation of an inhomogeneous EPR line. The solution is obtained by two methods: using the model of thermal mixing in a rotating coordinate frame, and in terms of spin packets. In the latter case it is shown that allowance for the DDR leaves the spectral-diffusion valid, but only for a definite combination of the Zeeman and dipole-dipole temperatures. Estimates of the maximum attainable DDR cooling coefficients and of the polarization of the lattice nuclei are presented, and it is shown that they do not depend monotonically on the width of the "hole" produced in the EPR line upon saturation.

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1. INTRODUCTION AND FORMULATION OF PROBLEM

It is known that not-strictly-resonant saturation of a magnetic resonance line in a solid can lower substantially the temperature T_{SS} of the spin-spin interaction reservoir (DDR).[1)] Upon saturation of the EPR line of a paramagnetic impurity in a magnetically dilute paramagnetic crystal, this cooling can be transferred to the Zeeman subsystem of the nuclear spins of the lattice, thus causing dynamic polarization of the nuclei ("dynamic cooling").[2,3] This phenomenon was reliably established in experiment and plays a substantial role in magnetic resonance and its applications, especially at low temperatures.[4-7]

The theory of effects connected with the cooling of the DDR was initially developed for magnetic-resonance lines homogeneously broadened by dipole-dipole interactions.[1-3] In practice, however, the main contribution to the width of paramagnetic-impurity EPR lines are made as a rule by inhomogeneous mechanisms, and it was therefore necessary to extend the theory to cover this case, too. So far this problem could be solved only for two limiting situations: neglecting the spectral diffusion inside the inhomogeneous line, and for very strong spectral diffusion that covers the entire EPR line.[4,8] At the same time, for the more general case (and perhaps of greatest practical importance) of limited spectral diffusion, corresponding to the appearance of a stationary "burned hole" in the inhomogeneous line, only qualitative estimates were proposed.[8,9] These, as will be shown below, do not agree with the true result even in order of magnitude.

In this paper we solve the problem by two methods. The result is first obtained using a simplified model of thermal mixing in a rotating coordinate frame, after which it is generalized within the framework of the description of an inhomogeneous line in the form of an aggregate of spin packets.

The object that we consider is a solid paramagnet at a temperature $T_L \equiv \beta_L^{-1}$, with n_I nuclear spins I and n_S electron spins S per unit volume ($n_I/n_S \gg 1$), and located in a stationary magnetic field $\mathbf{H}_0 \| z$. We assume that $S = \frac{1}{2}$, so that the EPR spectrum consists of a single line, assumed to be inhomogeneously broadened (with width $2\delta_{inh}$), and the distribution of the resonance frequencies of the electron spins does not correlate with their distribution over the crystal volume, so that the electronic DDR is common to all spins S.[8] Let furthermore the sample be acted upon by a high-frequency magnetic field $2H_1 \cos\Omega t (H_1 \perp z)$, that saturates the EPR line with a detuning $\Delta = \Omega - \omega_0$ relative to its "center of gravity" ω_0, determined from the relation

$$\int_{-\infty}^{\infty} \delta G(\delta)\, d\delta = 0, \tag{1}$$

where $\delta = \omega - \omega_0$, and $G(\delta)$ is the form factor, normalized to unity, of the inhomogeneous line.

It is well known that the action of the saturating field leads under the conditions considered above to the appearance of the so-called "burned line" which is observed when the EPR is recorded with a second (unsaturated) high-frequency field. The width $2\delta_h$ of this hold depends on the saturation factor $s(\Omega)$, on the homogeneous width $2\delta_p$ of the spin packet, and on the effectiveness

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of the cross relaxation (spectral diffusion) that leads to propagation of the saturation over the contour of the EPR line. It will be assumed below that $\delta_h \ll \delta_{inh}$.

2. THERMAL MIXING

By "thermal mixing" is meant the process of establishment of a single spin temperature β^{-1} in a spin system consisting of quasi-equilibrium subsystems with Hamiltonians $\mathcal{H}_j$ and temperatures β_j^{-1}, between which resonant energy exchange is possible. The exceptional convenience of the thermal-mixing model lies in the fact that its result can be obtained without solving the corresponding rate equations for β_j, using only the simple heat-balance principle. In the stationary regime, the common temperature is given by[7]

$$\beta = \sum_j c_j \tau_{jL}^{-1} \beta_j \Big/ \sum_j c_j \tau_{jL}^{-1}, \tag{2}$$

where $c_j = -\langle \mathcal{H}_j \rangle / \beta_j$ is the "specific heat" of the j-th subsystem, τ_{jL} is the time of its spin-lattice relaxation, and β_j^0 is the value of β_j when the j-th subsystem is at equilibrium with the lattice (we emphasize that all the β_j^0 are the same and are equal to the reciprocal of the lattice temperature β_L only in the laboratory reference frame).

We now apply this approach to this problem and recall, to start, the results for the case when the spectral diffusion is effective over the entire contour of a saturable inhomogeneous EPR line (such a line can be called quasi-homogeneous).[4-8] In this situation, the thermal mixing is possible in a rotating coordinate frame (RCF), the transformation to which is effected by the unitary operator

$$U = \exp\left(-i\Omega \sum_i S_i^z t\right),$$

where S_i^z is the operator of the z-th component of the i-th electron spin, and the participants in the mixing are the following subsystems.

The summary electronic Zeeman subsystem $\mathcal{H}_\rho$ in the RCF, for which

$$\mathcal{H}_\rho = -\Delta \sum_i S_i^z, \quad c_\rho = \frac{\hbar^2}{4k} n_S \Delta^2, \quad \beta_\rho^0 = -\frac{\omega_0 \beta_L}{\Delta} \tag{3}$$

(the Hamiltonian corresponding to it in the laboratory frame was $\mathcal{H}_\Sigma = \omega_0 \sum_i S_i^z$).

The aggregate of the difference electronic Zeeman subsystems $\mathcal{H}_\Delta$ with parameters

$$\mathcal{H}_\Delta = \sum_i \Delta_i S_i^z, \quad c_\Delta = \frac{\hbar^2}{4k} n_S M_2^0, \quad \beta_\Delta^0 = \beta_L. \tag{4}$$

The electronic DDR, whose Hamiltonain $\mathcal{H}_{SS}$ is well known, and

$$c_{SS} = \frac{\hbar^2}{4k} n_S \omega_{SS}^2, \quad \beta_{SS}^0 = \beta_L. \tag{5}$$

Finally, the nuclear Zeeman subsystem, for which

$$\mathcal{H}_{IZ} = -\omega_I \sum_i I_i^z, \quad c_{IZ} = \frac{\hbar^2}{4k} n_I \omega_I^2, \quad \beta_{IZ}^0 = \beta_L. \tag{6}$$

Here M_2^0 is the second moment of the distribution of the resonant frequencies relative to ω_0, ω_{SS} is the average DDR frequency, and ω_I is the NMR frequency.

We note that independently of the presence of a saturating field (i.e., even in the laboratory frame) the cross relaxation between the spin packets leads to a mixing of the subsystems $\mathcal{H}_\Delta$ and $\mathcal{H}_{SS}$ with formation of the so-called low-frequency reservoir[4] (or in other words, the reservoir of local fields[10]), and the direct thermal contact $\mathcal{H}_{SS} - \mathcal{H}_{IZ}$ connects to them also the nuclear subsystem. At the same time, a connection between these reservoirs and the $\mathcal{H}_\rho$ subsystem occurs only in the RCF, and the effectiveness of this connection is determined by the saturation factor at the frequency Ω.

Substituting the indicated parameters in (2) and neglecting quantities of order Δ/ω_0, we obtain the well known formula

$$E = \beta/\beta_L = -\Delta\omega_0/(M_2^0 + a\omega_{SS}^2 + f\omega_I^2), \tag{7}$$

in which $a = \tau_{SZL}/\tau_{SSL}$, $f = n_I \tau_{SZL}/n_S \tau_{IZL}$, with τ_{SZL}, τ_{SSL}, and τ_{IZL} the partial times of the spin-lattice relaxation of the corresponding subsystems. The quantity E introduced here determines, obviously, the degree of cooling of the DDR and the coefficient of the enhancement of the nuclear polarization.

We apply now this approach to the case $\delta_h \ll \delta_{inh}$. We make a simplifying assumption wherein all the spins whose frequencies lie inside an interval of width $2\delta_h$ with center at the point $\omega = \Omega$ are in a state of strong saturation (either directly by a microwave field or with participation of cross relaxation), and the all the remainder of the EPR line is at equilibrium with the lattice (see the figure). We note that the rectangular hole shown in the figure does not necessarily correspond to the observed form of the absorption signal, since the latter is determined not only by the degree of saturation of the line, but also by the state of the DDR.

We assume first that the spectral diffusion is negligibly weak, so that the width of the hole is determined only by the saturation. Then all the arguments presented above concerning the thermal mixing must be applied to the "burned" section of the EPR line, and the role of the remaining electron spins reduces only to their contribution to the common DDR and to the nuclear spin-lattice relaxation. Applying to the line section contained in the frequency interval $\Omega \pm \delta_h$ the relations (3)–(6) and substituting them in (2), we get

$$E = -\frac{\Delta_h \omega_h^0}{M_2^h + \Delta_h^2 + \alpha^{-1}(a\omega_{SS}^2 + f\omega_I^2)}. \tag{8}$$

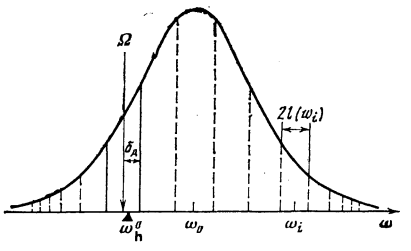

FIG. 1. Inhomogeneously broadened EPR line. Solid vertical lines—boundaries of the burned hole, dashed—boundaries of quasi-homogenous sections. The saturation frequency is marked by the arrow.

Here ω_h^0 is the center of the gravity of the indicated section of the line (see the figure), $M_2^h = \delta_h^2/3$ is its normalized second moment relative to ω_h^0, $\Delta_h = \Omega - \omega_h^0$ and $\alpha = n_h/n_S$, where $n_h \approx 2\delta_h G(\Delta) n_S$ is the number of electron spins that land in the burned hole.

The quantity ω_h^0 can be easily obtained by using the definition of the center of gravity (1) as applied to the frequency interval $\Omega \pm \delta_h$, with allowance for the fact that $\delta_h \ll \delta_{inh}$. As a result we have

$$\Delta_h = M_2^h G'(\Delta)/G(\Delta). \tag{9}$$

Substituting (9) in (8) and neglecting the quantity $\Delta_h^2/M_2^h \sim (\delta_h/\delta_{inh})^2$ compared with unity, we obtain ultimately

$$E = \frac{\omega_0 G'(\Delta)}{G(\Delta)} \left(1 + \frac{a\omega_{ss}^2 + f\omega_I^2}{\alpha M_2^h}\right)^{-1}. \tag{10}$$

We now take into account the spectral diffusion and assume that the half-width of the burned hole (which we continue to assume to be rectangular) is determined no longer by the saturation factor, but by the characteristic diffusion length $l(\Omega)$, with $\delta_h \ll l(\Omega) \ll \delta_{inh}$ (under this condition the diffusion length is not very sensitive to the state of the DDR and can be estimated without taking the latter into account[8]). We note that the diffusion length is in general not the same for different sections of the homogeneous line, a fact emphasized by using the notation $l(\Omega)$.

This, however, is far from a complete description of the role of the spectral diffusion. The point is that the cross relaxation is now effective not only on the burned out section of the line, but also outside this section, provided only that the spins that participate in it are separated by a frequency interval that does not exceed the diffusion length. This leads to thermal mixing of the corresponding difference subsystems and the common DDR, and this should manifest itself in the total thermal balance.

This circumstance can be approximately taken into account by breaking up the entire EPR line into spectral sections of width $2l(\omega_i)$, each of which is set in correspondence to a different subsystem (we neglect the cross relaxation between these sections). The specific heats of the newly introduced subsystems $\mathcal{H}_\Delta^i$ are defined, obviously, as

$$c_\Delta^i = \frac{\hbar^2}{4k} n_S^i M_2^i, \tag{11}$$

where $n_S^i \approx 2l(\omega_i) n_S G(\omega_i - \omega_0)$ is the number of the spins in the i-th section, and $M_2^i \equiv M_2(\omega_i - \omega_0) = l^2(\omega_i)/3$ is its second moment. Adding the terms corresponding to the subsystems $\mathcal{H}_\Delta^i$ in (2) and replacing the sum over i by an integral, we have

$$E = \alpha \frac{\omega_0 G'(\Delta)}{G(\Delta)} \left(\alpha + J + \frac{a\omega_{ss}^2 + f\omega_I^2}{M_2^h}\right)^{-1}, \tag{12}$$

where

$$J = \frac{1}{M_2^h} \int_{-\infty}^{\infty} G(\delta) M_2(\delta)\, d\delta.$$

3. THE SPIN-PACKET MODEL

We now represent, as is customary, the inhomogeneously broadened EPR line in the form of a continuous set of homogeneous spin packets with resonant frequencies ω' and with form factors $g(\omega - \omega')$ normalized to unity and with a cross relaxation with probability $W_{CR}(\omega' - \omega'')$ (for which an explicit expression is given, e.g., in Ref. 11) acting between them. Neglecting the influence of the nuclear spins (their role, as is clear from (10) and (12), reduces only to the appearance in the final formulas of terms proportional to f), we can write down a system of equations for the Zeeman temperature $[\beta_S(\omega')]^{-1}$ of the packets and for the common spin-spin temperature β_{SS}^{-1} under conditions of stationary saturation at the frequency Ω, in the form[9]

$$[\beta_S(\omega') - \beta_L] + \pi s \delta_p g(\omega' - \Omega) \left[\beta_S(\omega') - \frac{\omega' - \Omega}{\omega'} \beta_{ss}\right] + \tau_{SL} \int W_{CR}(\omega' - \omega'') G(\omega'' - \omega_0) \left[\beta_S(\omega') - \frac{\omega''}{\omega'} \beta_S(\omega'') - \frac{\omega' - \omega''}{\omega'} \beta_{ss}\right] d\omega'' = 0, \tag{13a}$$

$$(\beta_{ss} - \beta_L) + \frac{\pi s \delta_p}{a\omega_{ss}^2} \int \omega' (\Omega - \omega') g(\omega' - \Omega) G(\omega' - \omega_0) \times \left[\beta_S(\omega') - \frac{\omega' - \Omega}{\omega'} \beta_{ss}\right] d\omega' - \frac{\tau_{SSL}}{\omega_{ss}^2} \iint \omega' (\omega' - \omega'') W_{CR}(\omega' - \omega'') G(\omega'' - \omega_0) G(\omega' - \omega_0) \times \left[\beta_S(\omega') - \frac{\omega''}{\omega'} \beta_S(\omega'') - \frac{\omega' - \omega''}{\omega'} \beta_{ss}\right] d\omega' d\omega'' = 0, \tag{13b}$$

where $S = (\gamma_S H_1)^2 \tau_{SL}/\delta_p$ (γ_S is the spectroscopic-splitting factor for the electron spins); all the integrals here and below are taken between infinite limits.

No general solution has been obtained so far for the system (13a), (13b), and the main difficulty lies in the fact that these are integral equations. To get around this difficulty, we introduce a new characteristic of the spin packet, namely the quantity

$$\gamma(\omega') = \beta_S(\omega') - \frac{\omega' - \Omega}{\omega'} \beta_{ss}, \tag{14}$$

which is the deviation of the reciprocal Zeeman temperature of the packet from the limiting value $\beta_\rho(\omega') = -\Delta' \beta_{SS}/\omega'$ reached in the case of strong saturation of this packet with a detuning Δ' and (or) effective cross relaxation on the frequency interval $\omega' - \Omega$. We note that $[\beta_\rho(\omega')]^{-1}$ is the value of the single spin temperature under conditions of thermal mixing in the RCF. We note also that for packets not affected by saturation (i.e., located far enough from the center of the burned hole), the parameter $\gamma(\omega')$ becomes

$$\gamma_L(\omega') = \beta_L - \frac{\omega' - \Omega}{\omega'} \beta_{ss}. \tag{15}$$

Using (14) and (15), Eq. (13a) takes the form

$$[\gamma(\omega') - \gamma_L(\omega')] + \pi s \delta_p g(\omega' - \Omega) \gamma(\omega') + \tau_{SL} \int W_{CR}(\omega' - \omega'') G(\omega'' - \omega_0) \left[\gamma(\omega') - \frac{\omega''}{\omega'} \gamma(\omega'')\right] d\omega'' = 0. \tag{16}$$

Thus, in place of Eq. (13a), which contains two unknown parameters—the function $\beta_S(\omega')$ and the quantity β_{SS}—we have obtained an equation for a single unknown function $\gamma(\omega')$. Moreover, as can be readily seen Eq. (16) has practically the same form as the equation that describes the behavior of the Zeeman temperature of the packets without allowance for the DDR, and obtained from (13a) by excluding the terms that contain β_{SS} (the

only difference is that the "lattice term $\gamma_L(\omega')$ in (16) depends on the frequency, whereas β_L in (13a) is a constant). This fortunate circumstance enables us to express immediately the sought function $\gamma(\omega')$ in terms of the well known[11] solution of the truncated equation (13a). In fact, if we express the Zeeman-temperature distribution obtained without allowance for the DDR in the form

$$\tilde{\beta}_s(\omega')=\beta_L[1-F(\Omega-\omega',\ s)],$$

where $F(\Omega-\omega', s)$ characterizes the shape of the burned hole under the condition $\beta_{SS}=0$ (the explicit form of $F(\Omega-\omega', s)$ is given, for example, in Ref. 11), then the solution of Eq. (16) is

$$\gamma(\omega')=\gamma_L(\omega')[1-F(\Omega-\omega',\ s)]. \tag{17}$$

If the cross relaxation between the packets can be neglected, the validity of (17) can be directly proved by substituting it in (16); in the opposite case it is necessary to use the usual procedure of going from the integral equation (16) to the differential equation of spectral diffusion[11]; this yields

$$l_{CR}^2\frac{d^2\gamma(\omega')}{d\omega'^2}-\gamma(\omega')=-\gamma_L(\omega')+\pi s\delta_p g(\omega'-\Omega)\gamma(\omega'), \tag{18}$$

where

$$l_{CR}^2=\tfrac{1}{2}\tau_{sL}G(\Delta)\int x^2W_{CR}(x)\,dx \tag{19}$$

is the square of the spectral-diffusion length. Recognizing that $\tilde{\beta}_S(\omega')$ satisfies the usual equation of spectral diffusion (without allowance for the DDR),[11] it is easy to show that (17) is a solution of (18) if $l_{CR}\gg\delta_p$.

Returning now to the old unknowns $\beta_S(\omega')$ and β_{SS}, we get from (14), (15), and (17)

$$\beta_s(\omega')=\beta_L[1-F(\Omega-\omega',s)]+\beta_{ss}\frac{\omega'-\Omega}{\omega'}F(\Omega-\omega',s). \tag{20}$$

Thus, in place of the integral equation (13a) we have obtained the simple algebraic equation (20), which furthermore does not contain any explicit connection between the Zeeman temperatures of the different packets. Substituting (20) in (13b) and recognizing that $G(x)$ varies much more slowly than $W_{CR}(x)$, $g(x)$, and $F(x, s)$, we obtain

$$\frac{\beta_{ss}}{\beta_L}=\frac{\Omega G'(\Delta)}{G(\Delta)}\frac{\pi s\delta_p G(\Delta)J_F+2l_{CR}^2\alpha_{CR}}{a\omega_{ss}^2+\pi s\delta_p G(\Delta)J_F+2l_{CR}^2[G(\Delta)]^{-1}J_G} \tag{21}$$

where

$$J_F=\int x^2g(x)[1-F(x,s)]\,dx,\quad J_G=\int G^2(x)\,dx,$$

$$\alpha_{CR}=2G(\Delta)\int F(x,s)\,dx.$$

We consider now the concrete form of (21) for two limiting cases.

a) If spectral diffusion can be neglected, then according to Ref. 11

$$F(\Omega-\omega',s)=\frac{\pi s\delta_p g(\omega-\omega')}{1+\pi s\delta_p g(\omega-\omega')}.$$

Using the notation

$$\bar{M}_2^h=\frac{1}{2\delta_p\sqrt{s+1}}\int x^2F(x,s)\,dx$$

and

$$\alpha_{sat}=2\pi G(\Delta)\delta_p\sqrt{s+1},$$

we have

$$\frac{\beta_{ss}}{\beta_L}=\frac{\Omega G'(\Delta)}{G(\Delta)}\left(1+\frac{a\omega_{ss}^2}{\alpha_{sat}\bar{M}_2^h}\right)^{-1}. \tag{22}$$

b) If the width of the burned hole is determined mainly by spectral diffusion, then according to Ref. 11

$$F(\Omega-\omega',s)=\frac{s'}{1+s'}\exp\left(-\frac{|\Omega-\omega'|}{l_{CR}}\right),$$

where

$$s'=\tfrac{1}{2}s\pi\delta_p/l_{CR}\ll s.$$

Then

$$\frac{\beta_{ss}}{\beta_L}=\alpha_{CR}\frac{\Omega G'(\Delta)}{G(\Delta)}\left[\frac{J_G}{G(\Delta)}+\frac{a\omega_{ss}^2}{\bar{M}_2^h(\infty)}\right]^{-1}, \tag{23}$$

where $\bar{M}_2^h(\infty)$ is the value of $\bar{M}_2^h$ in the case of strong saturation ($s'\gg1$) (but formula (23) itself is valid for all s').

4. DISCUSSION OF RESULTS

We compare first the results obtained in Secs. 2 and 3. It is easily seen that in the case of strong saturation and for a hole of rectangular shape (i.e., under the conditions assumed in Sec. 2) the quantities α_{sat} and α_{CR} go over into α, and $\bar{M}_2^h$ and $\bar{M}_2^h(\infty)$ go over into M_2^h; next, at $\delta_h=l_{CR}\propto[G(\Delta)]^{1/2}$ [see (19)] we have $J(\Delta)=J_G/G(\Delta)$. As a result it turns out that formulas (22) and (23) go over exactly into (10) and (12) (without allowance for the nuclear spins). This agreement reveals clearly the physical meaning of the results and attests to the usefulness of the model of thermal mixing in the RCF as applied to problems of spin dynamics.

We now stop to obtain a quantitative estimate of the results, assuming for the sake of argument that $G(\delta)$ is described by a Gaussian curve with parameter σ, so that $G'(\Delta)/G(\Delta)=-\Delta/\sigma^2$, and $J_G=(2\pi^{1/2}\sigma)^{-1}$. As seen from (10) and (22), the maximum cooling of the DDR which can be obtained in the absence of spectral diffusion is reached at detunings $\Delta\sim\pm\sigma$ under the condition that $(a\omega_{SS}^2+f\omega_I^2)/\alpha M_2^h\lesssim1$, which yields $E_{max}\sim\omega_0/\delta_{inh}$. We note, however, that $\alpha\ll1$, and therefore the foregoing condition will in no way be always satisfied in practice.

In the other case, when the shape of the hole is determined by spectral diffusion (a situation that seems to be the most realistic), it follows from (12) and (23) that the maximum attainable value is $E_{max}\sim\omega_0\delta_h/\delta_{inh}^2$, i.e., it turns out to be smaller by a factor δ_{inh}/δ_h than in the absence of spectral diffusion. The physical meaning of this effect is quite clear: as indicated in Sec. 2, the cross relaxation between the "idle" spin packets (those not landing in the burned hole) increases the specific heat of the low-frequency energy reservoir, and it is this which leads to the decrease of E. We note that with further enhancement of the spectral diffusion, the fraction of the idle packet s in the total balance decreases gradually and at $\delta_h\sim\delta_{ihn}$, when none are left, E_{max} reaches a value $\omega_0/2\delta_{inh}$ [see (7)]. Thus, the dependence of E_{max} on the diffusion length is quite unusual:

both at small and at large l_{CR} the enhancement reaches values of the order δ_0/δ_{inh}, whereas in the intermediate region there is a slight decrease, reaching a minimum near $l_{CR} \approx \delta_{inh}\sqrt{1+s}$.

We compare now our results with the data of Refs. 8 and 9. In the absence of spectral diffusion the formulas are almost the same (we note that our Eq. (10), in contrast to Refs. 8 and 9, takes the influence of the nuclei into account). At the same time the estimate proposed in Refs. 8 and 9 for the case $\delta_h \approx l_{CR}$ yields $E_{max} \gg \omega_0/\delta_{inh}$, which deviates greatly with the results of the present article and apparently does not agree with the physical arguments advanced above.

We note finally that Eqs. (10), (12) and (22), (23) are quite similar in structure with the result obtained for the "solid-effect" under conditions of inhomogeneous broadening of EPR.[7,12] In particular, in both case, with increasing $|\Delta|$, the quantity $|E|$ first increases in proportion to $\omega_0 G'(\Delta)/G(\Delta)$, and then decreases in accord with the decrease of the fraction of the active electron spins (the factor α in the notation of Sec. 2). This similarity emphasizes once more the common physical bases of the two dynamic-polarization mechanism, which is connected with thermal mixing in a rotating coordinate system.[7]

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[1]We use the traditional abbreviation DDR—dipole-dipole reservoir—although it can include also other spin-spin interactions (sey, exchange interactions).

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Experimental dependence of the volume of solid normal hydrogen on the pressure up to 30 kbar at a temperature 77 K

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The piston-displacement method was used to measure the dependence of the molar volume of n-H_2 on the pressure at liquid-nitrogen temperature in the pressure range 4–29 kbar. The results are presented in analytic form that approximates the experimental data with accuracy 0.03 cm^3/mol. The relative jump of the volume at melting amounts to $(4.7 \pm 0.4)\%$.

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Notwithstanding recent interest in hydrogen, both scientific and applied, the number of experimental investigations of the equation of state of solid hydrogen at high pressures is quite limited. There are particularly few investigations of the $P - V - T$ dependence at high static pressures, i.e., studies that would permit the calculation of the equation of state and of the thermodynamic functions with sufficient accuracy. In fact, at 4.2 K measurement of the $P - V$ dependence were made up to 20 kbar[1] and 25 kbar.[2] On the other hand, at temperatures higher than 4.2 K, the region in which experimental research was performed does not exceed several hundred bars.[3,4]

We present here experimental $P - V$ data for solid normal (75% ortho, 25% para) hydrogen ($n - H_2$) at liquid-nitrogen temperature. The measurements were made with a low-temperature press by the piston-displacement method. The apparatus and the experimental procedure are described in detail in the preceding papers.[5,6] The high-pressure chambers had inside diameters 6–7 mm and were made of steels ÉI958 and ÉP637, of high-strength manganese–nickel steel, and of beryllium bronze. The maximum pressures were 11 kbar in beryllium–bronze chambers and 17–29 kbar in steel chambers. From two to five experiments were performed with each of the four chambers. The volume of

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