STRONG SATURATION OF INHOMOGENEOUSLY BROADENED LINES

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Strong stationary saturation of an inhomogeneously broadened EPR line is discussed with allowance for spectral diffusion and the dipole-dipole reservoir. The complex susceptibility of the sample is calculated for conditions of rapid and limited spectral diffusion.

1. In spin systems with inhomogeneous broadening, the cross-relaxation process of energy exchange between spins with different Larmor frequencies is described, under certain conditions, by an equation of the diffusion type in frequency space and is called spectral diffusion (SD)[1]. We denote by T_1 the spin-lattice relaxation time, and introduce the time $T_d = \Delta^{*2}/D$ of the spin-excitation diffusion over the entire inhomogeneous line; D is the SD coefficient and Δ^* is the inhomogeneous width. If $T_d \gg T_1$ then the SD is called limited (LSD), and if $T_d \lesssim T_1$ the SD is called fast (FSD).

Under conditions of LSD, the inhomogeneous line is an aggregate of relatively weak interacting spin packets of width Δ[1] and is described by the Hamiltonian

$$\mathscr{H}_s=\sum_n \mathscr{H}_n+\mathscr{H}_{ss},\quad \mathscr{H}_n=\omega_n\sum_{i=1}^{N_n} S_{ni}^z,\quad \mathscr{H}_{ss}=\mathscr{H}_d+\mathscr{H}_{CR},\tag{1}$$

$$\mathscr{H}_d=\frac{1}{2}\sum_{nn'ij}A_{ij}S_{ni}^zS_{n'j}^z+\sum_{nij}B_{ij}S_{ni}^+S_{nj}^-,$$

$$\mathscr{H}_{CR}=\sum_{n\neq n'ij}B_{ij}S_{ni}^+S_{n'j}^-,$$

where $\mathscr{H}_n$, ω_n, and N_n are the Zeeman energy (it is assumed, that $\hbar = 1$), the resonant frequency, and the number of spins of the n-th packet, S^α_{ni} (α = x, y, z) is the operator of the electron spin located in the i-th point of the lattice and belonging to the n-th packet, $S^\pm_{nj} = S^x_{nj} \pm iS^y_{nj}$, $\mathscr{H}_{ss}$ is the secular part of the dipole-dipole (dd) interaction ($[\mathscr{H}_{ss}, \sum_{in} S^z_{ni}] = 0$), $\mathscr{H}_d$ is the energy of the dd reservoir, ($[\mathscr{H}_d, \mathscr{H}_n] = 0$), and $\mathscr{H}_{CR}$ causes the SD. The coefficients A_{ij} and B_{ij} have a well-known form[2].

The theory of stationary saturation of the magnetic resonance in the case of LSD and with allowance for a single dd reservoir was developed by the authors in[3,4], where it is shown that in LSD, in spite of the appreciable dd-reservoir temperature shift under saturation conditions (it can be observed, for example, by studying the dynamic polarization of the nuclei[3]), the dd reservoir does not play an important role in the calculation of the temperatures of the packets. Consequently, if LSD is realized, the picture of the saturation of the inhomogeneous line and of the SD turns out to be practically the same as without allowance for the heating of the dd reservoir, and such concepts as the coefficient D of spectral diffusion, the "SD length" 1/k $= (DT_1)^{1/2}$[3], etc., retain their previous meaning also in the presence of the dd reservoir.

The situation is different with FSD. We have noted[4] that if $\tilde\Delta \equiv (s + 1)^{1/2}\Delta \sim \Delta^*$ ($\tilde\Delta$ is the width of the hole burned in the absence of the SD and S is the saturation parameter), or else if $1/k \gtrsim \Delta^*$ (this condition corresponds to FSD), then the inhomogeneous line should behave upon saturation like a homogeneous one of width Δ^*. The same result was obtained by Rodak[5].

Equivalent conclusions can be arrived at by recognizing that the FSD causes in final analysis a reduction in the number of the parameters characterizing the spin system with inhomogeneous broadening[6], and leads to the two-temperature model proposed by Clough and Scott[7]. Indeed, under FSD conditions, after the lapse of a time T_d we can get along without introducing spin packets and characterize the spin system by a Hamiltonian

$$\mathscr{H}_s=\omega_0S_z+\sum_i\omega_iS_{iz}+\mathscr{H}_{ss},\quad \mathscr{H}_{ss}=\frac{1}{2}\sum_{ij}A_{ij}S_{iz}S_{jz}+\sum_{ij}B_{ij}S_i^+S_j^-,\tag{2}$$

where $\omega_0 = \gamma H_0$ is the central frequency of the inhomogenoues line[1)] H_0 is the constant magnetic field parallel to the z axis, ω_i/γ is the local field responsible for the inhomogeneous broadening: $\Delta^{*2} = N^{-1}\sum_i \omega_i^2$, where N is the number of spins. Without loss of generality, it can be assumed that $\sum_i\omega_i = 0$. This condition enables us to represent the spin system with Hamiltonian (2) as an aggregate of two subsystems, the Zeeman subsystem ω_0S_z and the local-field reservoir with energy[2)]

$$\mathscr{H}_D=\mathscr{H}_{ss}+\sum_i\omega_iS_{iz}.\tag{3}$$

The theoretical arguments favoring the possibility of describing inhomogeneous broadening in the case of FSD in terms of two temperatures agree with experiments[8], and we shall therefore use the two-temperature model when considering the FSD.

The stationary saturation of an inhomogeneous line was investigated hitherto under the assumption that the probability W of the processes induced by an alternating field is much less than the probability $1/T_2 \sim \Delta$ of the transitions due to dd-interaction of identical spins, i.e.,

1) When there are several allowed lines coupled by effective cross relaxation, ω_0 is the center of gravity of the spectrum: $\omega_0 = N^{-1}\Sigma_m \omega_m N_m$, where $N = \Sigma_m N_m$, ω_m is the center of the m-th line, and N_m is the number of spins producing it.

2) Unlike the dd reservoir in Rodak's paper [5], the local-field reservoir contains also terms corresponding to flip-flop spin transitions with different resonant frequencies.

$W \ll 1/T_2$. In the present paper we consider also strong saturation of the inhomogeneous line, when $W \gtrsim 1/T_2$.

2. We assume that two rotating magnetic fields are applied to the sample, one saturating with amplitude H_{1p} and frequency ω_p, and the other detecting with amplitude $H_{1d} \ll H_{1p}$ and with frequency ω_d; ω_d is varied, or, as customarily stated, "one passes through the line," and the corresponding signal is measured. The Hamiltonian of the spin system is expressed in the form

$$\mathscr{H} = \mathscr{H}_s + \mathscr{H}_{sp}(t) + \mathscr{H}_{sd}(t),$$

where $\mathscr{H}_{sp,d}(t) = \frac{1}{2}\omega_{1p,d}\{S^+ \exp(-i\omega_{p,d}t) + S^- \exp(i\omega_{p,d}t)\}$, $\omega_{1p,d} = \gamma H_{1p,d}$, and $\mathscr{H}_s$ is given by formulas (1) or (2). $\mathscr{H}_{sp}$ and $\mathscr{H}_{sd}$ are the interactions of the spin system with the alternating fields. We shall henceforth include $\mathscr{H}_{sp}$ in the main Hamiltonian, and $\mathscr{H}_{sd}$ will be regarded as a small perturbation.

We calculate the imaginary part of the complex susceptibility χ'' of the sample. The behavior of the spin system is described by a statistical operator $\rho(t)$, which is a solution of the Liouville equation

$$i\frac{\partial\rho(t)}{\partial t} = [\mathscr{H}, \rho(t)]. \tag{4}$$

The power absorbed by the spin system from the source of the alternating field H_{1d}, averaged over the period of the field $T_d = 2\pi/\omega_d$, is determined by

$$Q_d = \frac{1}{t_d}\int_0^{t_d} \mathrm{Sp}\,\{\rho(t)D(t)\}\,dt, \tag{5}$$

where

$$D(t) = -\hat{\mathbf{M}}\frac{d\mathbf{H}_d}{dt} = -\tfrac{1}{2}i\,\omega_d\omega_{1d}\,\{S^+\exp(-i\omega_d t) - S^-\exp(i\omega_d t)\},$$

Since in our notation the operator of the total magnetic moment of the system is $\mathbf{M} = -\gamma\mathbf{S}$.

With the aid of the unitary operator $U(t) = \exp(i\omega_p S_z t)$ we change over to a coordinate system that rotates with frequency ω_p about the z axis. Taking into account the relation $[U(t), \mathscr{H}_s] = 0$, Eq. (4) is transformed into

$$i\frac{\partial\rho^*(t)}{\partial t} = [\mathscr{H}^* + \mathscr{H}_1(t), \rho^*(t)], \tag{6}$$

where

$$\rho^*(t) = U(t)\rho(t)U^{-1}(t), \qquad \mathscr{H}^* = \mathscr{H}_s - \omega_p S_z + \omega_{1p}S_x,$$
$$\mathscr{H}_1(t) = \tfrac{1}{2}\omega_{1d}\{S^+\exp[-i(\omega_d - \omega_p)t] + S^-\exp[i(\omega_d - \omega_p)t]\}.$$

The absorbed power (5) can be written in form

$$Q_d = \frac{1}{t_d}\int_0^{t_d} \mathrm{Sp}\,\{\rho^*(t)D^*(t)\}\,dt, \tag{7}$$

$$D^*(t) = -\tfrac{1}{2}i\omega_d\omega_{1d}\{S^+\exp[-i(\omega_d - \omega_p)t] - S^-\exp[i(\omega_d - \omega_p)t]\}.$$

We assume, as is customarily done, that the detecting field is turned on adiabatically at the instant $t = -\infty$, and assume that at this instant the spin system in the rotating coordinate system (RCS) is in a stationary state with a statistical operator $\rho_s^* \equiv \rho^*(-\infty)$. Obviously, ρ_s^* satisfies the condition $[\mathscr{H}^*, \rho_s^*] = 0$. Solving Eq. (6) in an approximation linear in $\mathscr{H}_1(t)$ and substituting the result in (7), we obtain after making simple transformations and using the relation $Q_d = 2\omega_d H_{1d}^2 \chi''$ [2]

$$\chi'' \equiv \chi''(\omega_d, \omega_p) = \frac{1}{4}\gamma^2\,\mathrm{Re}\int_0^\infty \mathrm{Sp}\,\{[S^+, \rho_s^*]S^-(\tau)\}\exp[i(\omega_d - \omega_p)\tau]\,d\tau,$$
$$S^-(\tau) = \exp(i\mathscr{H}^*\tau)S^-\exp(-i\mathscr{H}^*\tau). \tag{8}$$

We present below calculations of χ'' for different limiting cases.

Let FSD be realized, i.e., let $T_d \lesssim T_1$. Then, depending on the amplitude of the saturating field, after the lapse of a time T_d we can characterize the spin system by either one or two spin temperatures.

A. Assume that the probability W of spin reorientation by the saturating field satisfies the inequality $W < 1/T_d$. Physically this condition means that the SD has time to envelope the entire inhomogeneous line before the influence of the saturating field comes into play. It follows therefore that in the course of absorption of the HF energy, the spin system is in a quasi-equilibrium state characterized by a Zeeman temperature β_Z^{-1} and by a local-field reservoir temperature β_D^{-1}. This situation is realized at a sufficiently low amplitude of the saturating alternating field, and corresponds exactly to the Provotorov case in homogeneous broadening[9].

Using the method of constructing the nonequilibrium statistical operator[10] and considering strong saturation $2WT_{ZL} \gg 1$, we can obtain the following values of the stationary reciprocal temperatures in the RCS:

$$\beta_z = \beta_D = \beta_L\frac{\omega_0(\omega_0 - \omega_p) + \Delta^{*2} + \alpha\omega_{ss}^2}{(\omega_p - \omega_0)^2 + \Delta^{*2} + \alpha\omega_{ss}^2}$$
$$\omega_{ss}^2 = \mathrm{Sp}\,\mathscr{H}_{ss}^2/\mathrm{Sp}\,S_z^2, \quad \alpha = T_{zL}/T_{dL}, \tag{9}$$

where T_{zL} and T_{dL} are the spin-lattice relaxation times of the Zeeman subsystem and of the dd reservoir. Formula (9) agrees with the result of[5,11].

Equation (9) leads to an interesting feature. Even in this case when $\Delta^{*2} \gg \omega_{ss}^2$ (ω_{ss} itself is much larger than Δ in strongly diluted samples[12]) it may turn out that $\Delta^{*2} \ll \omega_{ss}^2$ (owing to the fast relaxation of the dd reservoir through the lattice), and the inhomogeneous broadening will not play any role in the saturation.

The local-equilibrium part of the non-equilibrium statistical operator, which is of importance for the absorption, is given by

$$\rho_s^* = \{1 - \beta_z\mathscr{H}_z - \beta_D\mathscr{H}_D\}/\mathrm{Sp}\,1, \quad \mathscr{H}_z = (\omega_0 - \omega_p)S_z. \tag{10}$$

Substituting (9) and (10) in (8) and assuming that $\omega_0|\omega_0 - \omega_p| \gg \Delta^{*2} + \alpha\omega_{ss}^2$, we obtain

$$\chi'' = \frac{\pi}{2}\chi_0\omega_0 f(\omega_d - \omega_p)\frac{(\omega_d - \omega_p)(\omega_0 - \omega_p)}{(\omega_p - \omega_0)^2 + \Delta^{*2} + \alpha\omega_{ss}^2}, \tag{11}$$

where $\chi_0 = \frac{1}{3}N\gamma^2 S(S+1)\beta_L$ is the static susceptibility of the spin system. Thus, the entire difference from the homogeneous broadening reduces to the appearance of Δ^{*2} and replacement of the homogeneous line shape $\varphi(\omega)$ by the correlator $f(\omega)$. When $M_2 \gg \Delta^{*2}$ (M_2 is the second moment due to the interaction of $\mathscr{H}_{ss}$ from (2)), $f(\omega)$ coincides with $\varphi(\omega)$, and in the opposite case it coincides with the inhomogeneous shape of the line $g(\omega)$. It follows from (11) that, just as in homogeneous broadening, we have $\chi'' < 0$, i.e., stimulated emission takes place at $\omega_d > \omega_p > \omega_0$ or $\omega_d < \omega_p < \omega_0$.

Let us assume that $1/T_d < W < 1/T_2$. The saturating field can still be regarded as a small perturbation, but unlike the preceding case, it has time to act on the resonant packet before the SD encompasses the entire inhomogeneous line, and makes the temperature of this packet equal to the temperature of the single dd reservoir. In such a situation, the result of the SD reduces to the fact that the entire spin system as a whole is characterized in the RCS after a time T_d, by a single spin temperature $\beta_s^{-1}(t)$ and by a statistical operator

$$\rho_s^*(t) = \{1 - \beta_s(t)(\mathcal{H}_z + \mathcal{H}_D)\}/\operatorname{Sp} 1.$$

The dependence of β_s on the time is determined by the spin-lattice interaction. It is easy to show that the stationary value of β_s is determined by formula (9), so that we obtain for χ'' the result (11), just as in Rodak's paper[5].

The reason for this circumstance is that the form of the stationary absorption does not depend on the manner in which the single spin temperature is established in the spin system. Nonetheless, there is a difference between the indicated two possibilities. When $W < 1/T_d$ it is possible to describe the process of equalization of the temperatures β_z^{-1} and β_D^{-1}, whereas at $1/T_d < W < 1/T_2$ these temperatures are assumed to be different from the very beginning. In the latter case it is possible to have hole burning in nonstationary saturation of the inhomogeneous line after a time $t < T_d$, and the hole can gradually vanish within a time T_d.

B. We assume that $1/T_2 \lesssim W \lesssim \Delta^*$. In this case the situation is made complicated by the fact that the saturating field changes the SD coefficient. If the FSD is nevertheless realized, we obtain the following picture. The alternating field must be included in the main Hamiltonian

$$\mathcal{H}^* = \mathcal{H}_z^* + \mathcal{H}_D, \quad \mathcal{H}_z^* = (\omega_0 - \omega_p)S_z + \omega_{1p}S_x.$$

The spin system in the RCS after a time T_d can be characterized as before by a single temperature $\beta_s^{-1}(t)$ and by a statistical operator

$$\rho^*(t) = \{1 - \beta_s(t)\mathcal{H}^*\}/\operatorname{Sp} 1.$$

Let us find the stationary value of the spin temperature β_0^{-1}. The mean values of

$$\overline{\mathcal{H}_z^*}(t) = \operatorname{Sp}\rho^*(t)\mathcal{H}_z^*, \quad \overline{\mathcal{H}_D}(t) = \operatorname{Sp}\rho^*(t)\mathcal{H}_D$$

are equal to

$$\begin{aligned}\overline{\mathcal{H}_z^*}(t) &= -\beta_s(t)[(\omega_0-\omega_p)^2 + \omega_{1p}^2]\langle S_z^2\rangle,\\ \overline{\mathcal{H}_D}(t) &= -\beta_s(t)(\Delta^{*2} + \omega_{ss}^2)\langle S_z^2\rangle,\end{aligned} \tag{12}$$

where $\langle\ldots\rangle \equiv \operatorname{Sp}(\ldots)/\operatorname{Sp} 1$. It is known[13,14] that the relaxation equations for the mean values are

$$\frac{\partial \bar{S}_z(t)}{\partial t} = -\frac{\bar{S}_z(t) - S_0}{T_{zL}}, \quad \frac{\partial S_x(t)}{\partial t} = -\frac{\bar{S}_x(t) - S_{x0}}{T_{xL}'} - \frac{\bar{S}_x(t)}{T_{xL}''} \tag{13}$$

$$\frac{\partial \overline{\mathcal{H}_D}(t)}{\partial t} = -\frac{\overline{\mathcal{H}_D}(t) - \overline{\mathcal{H}_D}^0}{T_{DL}},$$

where $S_0 = -\beta_L\omega_0\langle S_z^2\rangle$, $\overline{\mathcal{H}}_D^0 = -\beta_L(\Delta^{*2} + \omega_{ss}^2)\langle S_z^2\rangle$ are the equilibrium values of the corresponding quantities, $S_{x0} = -\beta_L\omega_{1p}\langle S_z^2\rangle$, and T'_{xL} and T''_{xL} are the relaxation times due to the secular and nonsecular parts of the spin-lattice interaction in the RCS[14].

According to (12)

$$\frac{\partial\overline{\mathcal{H}^*}(t)}{\partial t} = \frac{\partial\overline{\mathcal{H}_z^*}(t)}{\partial t} + \frac{\partial\overline{\mathcal{H}_D}(t)}{\partial t} =$$

$$= -[(\omega_0-\omega_p)^2 + \omega_{1p}^2 + \Delta^{*2} + \omega_{ss}^2]\frac{\partial\beta_s}{\partial t}\langle S_z^2\rangle,$$

and with the aid of (13) we obtain

$$\frac{\partial\beta_s}{\partial t} = -\frac{\beta_s(t) - \beta_0}{T_{1\rho}} \tag{14}$$

where

$$\beta_0 = \beta_L\frac{\omega_0(\omega_0-\omega_p) + \omega_{1p}^2 T_{zL}/T_{xL}' + \Delta^{*2} + \alpha\omega_{ss}^2}{(\omega_0-\omega_p)^2 + \omega_{1p}^2 T_{zL}/T_{xL} + \Delta^{*2} + \alpha\omega_{ss}^2},$$

$$\frac{1}{T_{1\rho}} = \frac{1}{T_{zL}}\frac{(\omega_0-\omega_p)^2 + \Delta^{*2} + \alpha\omega_{ss}^2 + \omega_{1p}^2 T_{zL}/T_{xL}}{(\omega_0-\omega_p)^2 + \Delta^{*2} + \omega_{ss}^2 + \omega_{1p}^2},$$

$$\frac{1}{T_{xL}} = \frac{1}{T_{xL}'} + \frac{1}{T_{xL}''}.$$

As a result we get for χ'' the expression (it is assumed that $\omega_0|\omega_0 - \omega_p| \gg \Delta^{*2} + \alpha\omega_{ss}^2 + \omega_{1p}^2 T_{zL}/T_{xL}$)

$$\chi'' = \frac{\pi}{2}\chi_0\omega_0 f^*(\omega_d - \omega_p)\frac{(\omega_d-\omega_p)(\omega_0-\omega_p)}{(\omega_0-\omega_p)^2 + \Delta^{*2} + \alpha\omega_{ss}^2 + \omega_{1p}^2 T_{zL}/T_{xL}}. \tag{15}$$

Here $f^*(\omega)$ is the Fourier transform of the correlator

$$f^*(t) = \frac{1}{\langle S^+S^-\rangle}\langle S^+\exp(i\mathcal{H}^*t)S^-\exp(-i\mathcal{H}^*t)\rangle,$$

whose second moment is $M_2^* = M_2 + \Delta^{*2} + \omega_{1p}^2$.

Formula (15) differs from (11) in the presence of the form $\omega_{1p}^2 T_{zL}/T_{xL}$ in the denominator, and in the fact that the absorption line $f^*(\omega)$ has a different width in comparison with $f(\omega)$.

C. Let now $\omega_{1p} \gg \Delta^*$. In this limit, it is convenient to apply to the Liouville equation (6) with Hamiltonian

$$\mathcal{H}^* = (\omega_0 - \omega_p)S_z + \omega_{1p}S_x + \mathcal{H}_D$$

the canonical transformation

$$U_y = \exp(i\theta S_y), \quad \operatorname{tg}\theta = \frac{\omega_{1p}}{\omega_0 - \omega_p},$$

which is equivalent to introduction of an inclined RCS with z axis directed along the effective field $H_e = \omega_e/\gamma = \gamma^{-1}[(\omega_0 - \omega_p)^2 + \omega_{1p}^2]^{1/2}$. Neglecting in the transformed Hamiltonian $U_y\mathcal{H}^*U_y^{-1}$ the nonsecular terms (i.e., those not commuting with $S_z = \sum_i S_{iz}$), which can be done because $\omega_{1p} \gg \Delta^*$, we obtain the equation

$$\frac{\partial\tilde{\rho}(t)}{\partial t} = \frac{1}{i}[\tilde{\mathcal{H}}, \tilde{\rho}(t)], \tag{16}$$

where

$$\tilde{\rho}(t) = U_y\rho^*(t)U_y^{-1}, \quad \tilde{\mathcal{H}} = \tilde{\mathcal{H}}_z + \tilde{\mathcal{H}}_D, \quad \tilde{\mathcal{H}}_z = \omega_e S_z,$$

$$\tilde{\mathcal{H}}_D = {}^1/_2(3\cos^2\theta - 1)\mathcal{H}_{ss} + \cos\theta\sum_i\omega_i S_{iz}.$$

The situation is formally analogous to that considered in item A. Consequently, after the lapse of a time $\tilde{T}_d$, the SD on the entire inhomogeneous line (we assume that $\tilde{T}_d \lesssim T_1$), the state of the spin system can be described by the following non-equilibrium statistical operator:

$$\tilde{\rho}(t) = \{1 - \tilde{\beta}_z\tilde{\mathcal{H}}_z - \tilde{\beta}_D\tilde{\mathcal{H}}_D\}/\operatorname{Sp} 1,$$

where $\tilde{\beta}_z$ and $\tilde{\beta}_D$ are the reciprocal temperatures of the subsystems with Hamiltonians $\tilde{\mathcal{H}}_z$ and $\tilde{\mathcal{H}}_D$, respectively, and the time dependence is determined by the spin-lattice interaction. Since we are not interested in the "rotational saturation"[2,15] by the field H_{1d}, the subsystem $\tilde{\mathcal{H}}_D$, owing to the small specific heat, does not play any role in the absorption and we can use a statistical operator in the form

$$\tilde{\rho}_s = \{1 - \tilde{\beta}_z\tilde{\mathcal{H}}_z\}/\operatorname{Sp} 1 \equiv U_y\rho_s^*U_y^{-1}. \tag{17}$$

The stationary value of $\widetilde{\beta}_z$ is given by the formula

$$\beta_z = \beta_L \frac{\omega_0(\omega_0-\omega_p)+\omega_{1p}^2 T_{zL}/T_{xL}'}{(\omega_0-\omega_p)^2+\omega_{1p}^2 T_{zL}/T_{xL}}, \quad (18)$$

which is obtained from (14) under the assumption

$$\Delta^{*2}+\alpha\omega_{ss}^2 \ll \omega_{1p}^2 T_{zL}/T_{xL}.$$

Using the invariance of the trace relative to cyclic permutation of the operators in (8), we obtain after simple transformations and using formulas (17) and (18)

$$\chi'' = \frac{\pi}{8}\chi_0\omega_e \frac{\omega_0(\omega_0-\omega_p)+\omega_{1p}^2 T_{zL}/T_{xL}'}{(\omega_0-\omega_p)^2+\omega_{1p}^2 T_{zL}/T_{xL}} \quad (19)$$
$$\times\{(1+\cos\theta)^2\widetilde{f}(\omega_d-\omega_p-\omega_e)-(1-\cos\theta)^2\widetilde{f}(\omega_p-\omega_d-\omega_e)\},$$

from which it follows that the form of the absorption is determined by the Fourier transform of the correlator

$$\widetilde{f}(t) = \langle S^+ \exp(i\widetilde{\mathscr{H}}_D t) S^- \exp(-i\widetilde{\mathscr{H}}_D t)\rangle / \langle S^+S^-\rangle.$$

The second moment of the function $\widetilde{f}(\omega)$ is equal to

$$\widetilde{M}_2 = {}^1/_4(3\cos^2\theta-1)^2 M_2 + \Delta^{*2}\cos^2\theta. \quad (20)$$

Formula (20) shows that the absorption line width varies in a very wide range, depending on the ratio of the amplitude of the alternating field H_{1p} to the detuning $|H_0-\omega_p/\gamma|$. In particular, at $\omega_p \approx \omega_0$ (i.e., $\theta = \pi/2$) we can observe an appreciable narrowing of the inhomogeneous line in the RCS[3)].

Expression (19) determines the energy absorbed by the spin system from the source of the non-saturating transverse alternating field H_{1d} under conditions when the spin system is strongly saturated by another transverse field $H_{1p} \gg \Delta^*$ (the field H_{1p} corresponds to the so-called "Redfield case"[15]). The absorption has a resonant character and is observed in the vicinity of two frequencies $\omega_d = \omega_p \pm \omega_e$, with absorption at one of these frequencies ($\chi'' > 0$) and stimulated emission at the other ($\chi'' < 0$).

A simple calculation shows that for the frequently employed[2] longitudinal detecting field $H_{1d}\cos\omega_d t$ parallel to the constant field we obtain in place of (19) the formula

$$\chi'' = \frac{\pi}{2}\chi_0\omega_e \frac{\omega_0(\omega_0-\omega_p)+\omega_{1p}^2 T_{zL}/T_{xL}'}{(\omega_0-\omega_p)^2+\omega_{1p}^2 T_{zL}/T_{xL}}\widetilde{f}(\omega_d-\omega_e)\sin^2\theta; \quad (21)$$

resonance in the RCS is observed at one frequency $\omega_d = \omega_e$ and there is an appreciable deviation from the situation with two transverse fields when, as noted above, the absorption line consists of two resolved resonances. This feature obviously is not connected with the inhomogeneity of the broadening and is observed also in homogeneous broadening.

4. Assume that LSD is realized, i.e., $T_d \gg 1$. There are several possibilities.

a) $W < 1/T_2$. This case was investigated in detail earlier[3,4].

b) $1/T_2 < W \lesssim \Delta^*$. The effective Hamiltonian of the spin system in the RCS is

$$\mathscr{H}^* = \sum_{ni}(\omega_n-\omega_p)S_{ni}^z + \omega_{1p}S_x + \mathscr{H}_{ss}.$$

We apply to equation (6) the canonical transformation

$$U_y = \exp\left(i\sum_{nj}\theta_n S_{nj}^y\right), \quad \mathrm{tg}\,\theta_n = \frac{\omega_{1p}}{\omega_n-\omega_p},$$

which is equivalent to introducing for each packet a separate local system of coordinates with axis z_n directed along the corresponding effective field $H_{en} = \Lambda_n/\gamma \equiv \gamma^{-1}[(\omega_n-\omega_p)^2+\omega_{1p}^2]^{1/2}$. Neglecting in the transformed Hamiltonian $U_y\mathscr{H}^*U_y^{-1}$ the terms that do not commute with $S_z = \sum_{ni} S_{ni}^z$, we obtain Eq. (16) with Hamiltonian

$$\widetilde{\mathscr{H}} = \sum_n \widetilde{\mathscr{H}}_n + \widetilde{\mathscr{H}}_d + \widetilde{\mathscr{H}}_{CR}, \quad (22)$$

$$\widetilde{\mathscr{H}}_n = \Lambda_n \sum_i S_{ni}^z, \quad \widetilde{\mathscr{H}}_{CR} = \sum_{n\neq n'ij} B_{ij,nn'}S_{ni}^+S_{n'j}^-,$$

$$\widetilde{\mathscr{H}}_d = \frac{1}{2}\sum_{nn'ij} A_{ij,nn'}S_{ni}^zS_{n'j}^z + \sum_{nij} B_{ij,nn}S_{ni}^+S_{nj}^-,$$

$$A_{ij,nn'} = A_{ij}\cos\theta_n\cos\theta_{n'} + 2B_{ij}\sin\theta_n\sin\theta_{n'},$$

$$B_{ij,nn'} = {}^1/_2\{{}^1/_2 A_{ij}\sin\theta_n\sin\theta_{n'} + B_{ij}(1+\cos\theta_n\cos\theta_{n'})\}.$$

For times t that exceed the small time scale $\widetilde{T}_q$ due to the interaction $\widetilde{\mathscr{H}}_d$, we can separate in the spin system with Hamiltonian (22), as subsystems, the Zeeman energies of the individual spin packets $\widetilde{\mathscr{H}}_n$ and the single dd reservoir $\widetilde{\mathscr{H}}_d$, assigning to them the reciprocal temperatures $\widetilde{\beta}_n$ and $\widetilde{\beta}_d$. $\mathscr{H}_{CR}$ realizes the interaction between the subsystems and leads to the SD between the packets in the RCS. The non-equilibrium statistical operator describing the system at times $t \gg \widetilde{T}_2$, takes the form

$$\widetilde{\rho}(t) = \frac{1}{\mathrm{Sp}\,1}\left\{1-\sum_n\widetilde{\beta}_n\widetilde{\mathscr{H}}_n - \widetilde{\beta}_d\widetilde{\mathscr{H}}_d + \sum_n(\widetilde{\beta}_n-\widetilde{\beta}_d)\int_{-\infty}^{0} e^{\varepsilon t}\widetilde{K}_n(t)\,dt\right\}, \quad (23)$$

where the flux operator is

$$\widetilde{K}_n(t) = -i[\widetilde{\mathscr{H}}_n(t), \quad \widetilde{\mathscr{H}}_{CR}(t)] = e^{i\widetilde{\mathscr{H}}t}\widetilde{K}_n e^{-i\widetilde{\mathscr{H}}t}, \quad \widetilde{K}_n = -i[\widetilde{\mathscr{H}}_n, \widetilde{\mathscr{H}}_{CR}]$$

and the time dependence of the temperature is determined by the SD and by the spin-lattice interaction, which is not taken into account explicitly.

In analogy with the procedure used in[3], we can derive with the aid of (23) equations for $\widetilde{\beta}_n$ and $\widetilde{\beta}_d$ and obtain the diffusion approximation an explicit equation for the SD coefficient $\widetilde{D}(\omega)$ for a packet with frequency ω in the RCS. We shall not do this, and confine ourselves to an examination of two limiting cases, in one of which the SD plays no role whatever, and in the other the influence of the rotating field H_{1p} on the SD does not appear. Disregarding, as before, the "rotational saturation," that part of the nonequilibrium statistical operator which is of importance in the calculation of the absorption can be expressed in the form

$$\widetilde{\rho}_s = \frac{1}{\mathrm{Sp}\,1}\left\{1-\sum_n\widetilde{\beta}_{n0}\widetilde{\mathscr{H}}_n\right\}, \quad (24)$$

where $\widetilde{\beta}_{n0}$ is the stationary value of $\widetilde{\beta}_n(t)$. Calculation of χ'' yields

$$\chi'' = \frac{\pi}{8}\chi_0\frac{1}{\beta_L}\sum_n g_n\Lambda_n\widetilde{\beta}_{n0}\{(1+\cos\theta_n)^2 f_n(\omega_d-\omega_p-\Lambda_n) - \quad (25)$$
$$-(1-\cos\theta)^2 f_n(\omega_p-\omega_d-\Lambda_n)\}.$$

Here $g_n = N_n/N$, $N = \Sigma_n N_n$, $f_n(\omega)$ is the Fourier transform of the correlator

$$f_n(\tau) = \langle S_{ni}^+\exp(i\widetilde{\mathscr{H}}_d\tau)S_{ni}^-\exp(-i\widetilde{\mathscr{H}}_d\tau)\rangle/\langle S_{ni}^+S_{ni}^-\rangle.$$

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3)Unlike this result, "rotational" narrowing of an inhomogeneously broadened line [2] is observed in the vicinity of the magic angle θ_M defined by the condition $\cos^2\theta_M = 1/3$.

The second moment of the function $f_n(\omega)$ is equal to

$$M_2^{(n)}=\frac{1}{9}M_2\left\{\frac{5}{4}(3\cos^2\theta_n-1)^2 g_n+\cos\theta_n\sum_{n'(\neq n)} g_{n'}\cos\theta_{n'}\right\}. \quad (26)$$

$g_n \ll 1$, and therefore at frequencies ω_n not too close to ω_p the main contribution to $M_2^{(n)}$ will be made by the second term in the curly brackets of (26). Changing over in (25) to a continuous distribution of the spin packets, in accordance with the rule

$$\sum g_n\varphi_n \to \int g(\omega-\omega_0)\varphi(\omega)d\omega,$$

we obtain

$$\chi''=\frac{\pi}{8}\chi_0\frac{1}{\beta_L}\int_{-\infty} g(\omega-\omega_0)\Lambda(\omega)\beta_0(\omega)\{(1+\cos\theta(\omega))^2 f_\omega(\omega_d-\omega_p-\Lambda(\omega)) -[1-\cos\theta(\omega)]^2 f_\omega(\omega_p-\omega_d-\Lambda(\omega))\}\,d\omega, \quad (27)$$

where

$$M_2(\omega)=\frac{1}{9}M_2\cos\theta(\omega)\int_{-\infty}^{\infty} g(\omega'-\omega_0)\cos\theta(\omega')d\omega',$$

$$\cos\theta(\omega)=\frac{\omega-\omega_p}{\Lambda(\omega)},\quad \Lambda(\omega)=[(\omega-\omega_p)^2+\omega_{1p}^2]^{1/2}$$

and the notation $f_\omega(x)$ indicates that the second moment of the correlator $f(x)$ depends on the frequency ω.

In our case $M_2(\omega) \ll \omega_{1p}^2$, so that for all values of the detuning $\Delta_d \equiv \omega_d - \omega_p$ we obtain $f_\omega(\Lambda(\omega) + |\Delta_d|) \approx 0$. Consequently, at $\omega_d \neq \omega_p$ we can represent (27) in the form

$$\chi''=\frac{\pi}{8}\chi_0\frac{1}{\beta_L}\frac{\Delta_d}{|\Delta_d|}\int_{-\infty}^{\infty} g(\omega-\omega_0)\Lambda(\omega)\beta_0(\omega)\left[1+\frac{\Delta_d}{|\Delta_d|}\cos\theta(\omega)\right]^2 \times f_\omega(|\Delta_d|-\Lambda(\omega))d\omega. \quad (28)$$

In the region of detecting-field frequencies satisfying the condition $|\Delta_d| < \omega_{1p}$ we have $f_\omega(|\Delta_d| - \Lambda(\omega)) \approx 0$, and there is practically no absorption of energy from this field by the spin system. Noticeable absorption takes place in the region $|\Delta_d| > \omega_{1p}$. In this case the argument of the correlation function in (28) vanishes at two frequencies ω_1 and ω_2, which are determined from the condition $|\Delta_d| - \Lambda(\omega) = 0$ and are equal to $\omega_{1,2} = \omega_p \pm (\Delta_d^2 - \omega_{1p}^2)^{1/2}$. Using the approximation

$$f_\omega(|\Delta_d|-\Lambda(\omega))\approx\delta(|\Delta_d|-\Lambda(\omega)) =\frac{|\Delta_d|}{(\Delta_d^2-\omega_{1p}^2)^{1/2}}\{\delta(\omega-\omega_1)+\delta(\omega-\omega_2)\}$$

in formula (28), we obtain

$$\chi''=\frac{\pi}{8}\chi_0\frac{\Delta_d}{|\Delta_d|}(\Delta_d^2-\omega_{1p}^2)^{1/2}\frac{1}{\beta_L}\left\{g(\omega_1-\omega_0)\left[1+\frac{\Delta_d}{(\Delta_d^2-\omega_{1p}^2)^{1/2}}\right]^2\beta_0(\omega_1) + g(\omega_2-\omega_0)\left[1-\frac{\Delta_d}{(\Delta_d^2-\omega_{1p}^2)^{1/2}}\right]^2\beta_0(\omega_2)\right\}. \quad (29)$$

Let $\omega_{1p} \gg 1/k$, i.e., let the amplitude of the saturating field be much larger than the SD length. Then the SD does not play any role, and the values of the stationary reciprocal temperatures $\tilde{\beta}_0(\omega_1)$ and $\tilde{\beta}_0(\omega_2)$ are determined by the saturating field and by the spin-lattice relaxation in the RCS. Using in place of (13) the relaxation equations

$$\frac{\partial\overline{S_{ni}^z}}{\partial t}=-\frac{\overline{S_{ni}^z}-S_0/N}{T_{zL}},\quad \frac{\partial\overline{S_{ni}^x}}{\partial t}=-\frac{\overline{S_{ni}^x}-S_{x0}/N}{T_{xL}'}-\frac{\overline{S_{ni}^x}}{T_{xL}''}$$

and recognizing that, in accordance with (24),

$$\rho_s^*=\exp\left(-i\sum_{nj}\theta_n S_{nj}^y\right)\tilde{\rho}_s\exp\left(i\sum_{nj}\theta_n S_{nj}^y\right)=\frac{1}{\mathrm{Sp}\,1}\left\{1-\sum_n\beta_{n0}\mathscr{H}_n^*\right\},$$

we obtain after a number of calculations that are similar to those given above in the derivation of (14),

$$\beta_0(\omega)=\beta_L\frac{\omega(\omega-\omega_p)}{(\omega-\omega_p)^2+\omega_{1p}^2 T_{zL}/T_{xL}}.$$

Assuming that in (29) $|\Delta_d| \gg \omega_{1p}$, we get

$$\chi''\approx {}^1\!/_2\pi\chi_0\omega_0 g(\omega_d-\omega_0)\equiv\chi_0''(\omega_d). \quad (30)$$

As expected, far from the frequency of the saturating field we observe an undistorted inhomogeneous line shape. On the other hand, if $|\Delta_d| \ll \Delta^*$, then $\omega_p \approx \omega_d \approx \omega_0$, $g(\omega_{1,2} - \omega_0) \approx g(\omega_d - \omega_0)$ and

$$\chi''=\chi_0''(\omega_d)\frac{|\Delta_d|(\Delta_d^2-\omega_{1p}^2)^{1/2}}{\Delta_d^2-\omega_{1p}^2+\omega_{1p}^2 T_{zL}/T_{xL}}. \quad (31)$$

In particular, for the isotropic mechanism of the spin-lattice relaxation $T_{zL} = T_{xL}$ and

$$\chi''=\chi_0''(\omega_d)(\Delta_d^2-\omega_{1p}^2)^{1/2}/|\Delta_d|.$$

Thus, in our case, in an interval $|\Delta_d| < \omega_{1p}$ with widths $2\omega_{1p}$ and with a center at the point $\omega_d = \omega_p$, there is practically no absorption, and when $|\Delta_d|$ increases from the value $|\Delta_d| = \omega_{1p}$ it increases to its unsaturated value (30). Consequently, the width of the burned hole is of the order of $2\omega_{1p}$, and the shape of its edges is determined by the function

$$g(\omega_d-\omega_0)\frac{|\Delta_d|(\Delta_d^2-\omega_{1p}^2)^{1/2}}{\Delta_d^2-\omega_{1p}^2+\omega_{1p}^2 T_{zL}/T_{xL}}, \quad (32)$$

which approaches rapidly the form $g(\omega_d - \omega_0)$ with increasing $|\Delta_d|$, so that the hole is almost rectangular in shape.

At $\omega_{1p} \ll 1/k$, the width and shape of the burned hole, with the exception of a region $|\Delta_d| < \omega_{1p}$ that is small in comparison with $1/k$, are determined mainly by the SD that is not perturbed by the saturating field and by spin-lattice relaxation. We shall henceforth neglect the dimensions of the region $|\Delta_d| < \omega_{1p}$. Such an approximation is equivalent to assuming the alternating field to act at only one frequency $\omega_d = \omega_p$ and that the field can be regarded as a perturbation[9]. This circumstance can be easily understood, since in the considered limiting case the SD reduces, as it were, to an effective increase of the width of the packet, from a value $\omega_{ss} \ll \omega_{1p}$ to a value $1/k \gg \omega_{1p}$, which is equivalent to regarding the alternating field as a perturbation.

Putting $|\Delta_d| \gg \omega_{1p}$ we obtain in accord with (29)

$$\chi''=\frac{\pi}{8}\chi_0\Delta_d g(\omega_d-\omega_0)\frac{1}{\beta_L}\left\{\left(1+\frac{\Delta_d}{|\Delta_d|}\right)^2\beta_0(\omega_1)+\left(1-\frac{\Delta_d}{|\Delta_d|}\right)^2\beta_0(\omega_2)\right\}. \quad (33)$$

Since we are interested in the region $|\omega_{1,2} - \omega_p| \approx |\Delta_d| \gg 2\omega_{1p}$, the Zeeman energy of the packet with frequency ω_n in the RCS can be taken in the form $(\omega_n - \omega_p)S_{ni}^z$. It follows therefore that the packet temperature $\tilde{\beta}_0^{-1}(\omega)$ in the RCS can be expressed in terms of the temperature of the same packet $\tilde{\beta}_0^{-1}(\omega)$ in the laboratory frame, by using the known relation[2],

$$\beta_0(\omega)=\frac{\omega}{\omega-\omega_p}\beta_0(\omega),$$

Therefore (33) yields

$$\chi'' = \chi_0''(\omega_d)\frac{1}{4\beta_L}\left\{\left(1+\frac{\Delta_d}{|\Delta_d|}\right)^2\beta_0(\omega_1)+\left(1-\frac{\Delta_d}{|\Delta_d|}\right)^2\beta_0(\omega_2)\right\}. \quad (34)$$

$\beta_0(\omega)$ is a solution of the free SD equation

$$\frac{d^2\beta_0(\omega)}{d\omega^2} - k^2[\beta_0(\omega)-\beta_L]=0$$

with boundary condition $\beta_0(\omega_p) = 0$ and $\beta_0(\omega) \to \beta_L$ at $\omega \to \pm\infty$ and was obtained in[4] in the form

$$\beta_0(\omega) = \beta_L(1-\exp(-k|\omega-\omega_p|)),$$

so that

$$\chi'' = \chi_0''(\omega_d)(1-\exp(-k|\Delta_d|)), \quad (35)$$

which, as expected, coincides with the result of[4]. It follows from (35) that the width of the burned hole is of the order of $1/k$, and the shape of its edges, unlike (32), is determined by the function $g(\omega_d - \omega_0)(1 - \exp(-k|\Delta_d|))$, which slowly approaches the value $g(\omega_d - \omega_0)$ with increasing $|\Delta_d|$, so that the hole has in this case an almost triangular form.

c) $\omega_{1p} \gg \Delta^*$. Obviously, in this limiting case there is no difference between the FSD and the LSD, and the saturation of the inhomogeneously broadened line is described by (19) or (21).

[1] A. M. Portis, Phys. Rev. **91**, 1070, 1953; **104**, 584, 1956; A. Kiel, Phys. Rev. **125**, 1451, 1956.

[2] M. Goldman, Spin Temperature and NMR in Solids, Clarendon Press, Oxford, 1970.

[3] L. Buishvili, M. D. Zviadadze, and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. **54**, 876 (1968) [Sov. Phys.-JETP **27**, 469 (1968)].

[4] L. L. Buishvili, M. D. Zviadadze, and G. R. Khutsishvili, ibid. **56**, 290 (1969) [**29**, 159 (1969)].

[5] M. I. Rodak, Fiz. Tverd. Tela **12**, 478 (1970) [Sov. Phys.-Solid State **12**, 371 (1970)]. Zh. Eksp. Teor. Fiz. **61**, 832 (1971) [Sov. Phys.-JETP **34**, 443 (1972)].

[6] N. S. Bendiashvili, L. L. Buishvili, and M. D. Zviadadze, Zh. Eksp. Teor. Fiz. **58**, 597 (1970) [Sov. Phys.-JETP **31**, 321 (1970)].

[7] S. Clough and C. A. Scott, Proc. Phys. Soc., ser. 2, **1**, 919, 1968.

[8] V. A. Atsarkin, Zh. Eksp. Teor. Fiz. **59**, 769 (1970) [Sov. Phys.-JETP **32**, 421 (1971)].

[9] B. N. Provotorov, ibid. **41**, 1582 (1961) [**14**, 1126 (1962)]; Fiz. Tverd. Tela **4**, 2940 (1962) [Sov. Phys.-Solid State **4**, 2155 (1963)].

[10] D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Non-equilibrium Statistical Thermodynamics), Nauka, 1971.

[11] A. Abragam and M. Borghini, Progress in Low Temperature Physics, C. J. Gorter, ed., Vol. IV, Amsterdam, 1964, p. 384.

[12] C. Kittel and E. Abrahams, Phys. Rev. **90**, 238, 1953.

[13] I. Solomon and T. Ezratty, Phys. Rev. **127**, 78, 1962.

[14] N. S. Bendiashvili, L. L. Buishvili, and M. D. Zviadadze, Fiz. Tverd. Tela **11**, 726 (1969) [Sov. Phys.-Solid State **11**, 579 (1969)].

[15] A. G. Redfield, Phys. Rev. **98**, 1787, 1955.

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