Saturation of inhomogeneously broadened EPR line at low temperatures

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(Submitted October 12, 1973)
Zh. Eksp. Teor. Fiz. **67**, 161–167 (July 1974)

Strong saturation of an inhomogeneously broadened EPR line at low temperatures is considered under conditions when the spectral diffusion rate exceeds the spin-lattice relaxation rate. Under these conditions the spin system can be described by a single temperature in the rotating coordinate system. An equation is obtained for the stationary spin temperature and approximate solutions of the equation are found. The power absorbed at the detecting-field frequency is calculated and the corresponding curves are plotted.

As is well known, the dynamics of a spin system saturated by a not-strictly-resonant alternating magnetic field can be described sufficiently well in the high-temperature approximation by means of the two-temperature theory[1-2]. Within the framework of this theory, the spin system is represented after the lapse of the spin-spin relaxation time in the form of an aggregate of two statistically independent systems, the Zeeman pool (ZP) and the dipole dipole pool (DDP), each of which is assigned its own temperature. As to the low-temperature region, a consistent quasithermodynamic description encounters here difficulties connected with the subdivision of the spin system into statistically independent subsystems[3].

On the other hand, in experiments on magnetic-resonance saturation and dynamic polarization of nuclei (DPN) one uses rather strong saturating fields, under the influence of which the equilibrium within the spin system in a rotating coordinate system (RCS) is established more rapidly than between the spin system and the lattice. Under these conditions, the spin system in the RCS is described by a single temperature, and the problem of separating statistically-independent subsystems does not arise. The case of strong saturation in a spin system with dipole-dipole interaction was considered by Kozhushner[4]. The particular results obtained by Kochelaev and Nigmatulin[5] also pertain to this case. At the same time, the low-temperature approximation is easier to realize in EPR experiments, since the EPR line is usually inhomogeneously broadened. It is therefore of practical interest to consider strong saturation of an inhomogeneously broadened EPR line in the low-temperature limit.

The complete Hamiltonian of a spin system placed in a dc and rf magnetic field and interacting with the lattice (thermostat) is given by

$$\begin{gathered}\mathscr{H}=\mathscr{H}_z+\mathscr{H}_d+\mathscr{H}_L+\mathscr{H}_{sh}+\mathscr{H}_{sL},\\ \mathscr{H}_z=\sum_n(\omega_0+\omega_n)S_n^z,\qquad \mathscr{H}_L=\sum_{\mathbf{k}j}\omega_{kj}a_{\mathbf{k}j}^+a_{\mathbf{k}j},\\ \mathscr{H}_{sh}=\frac{\omega_1}{2}(S^+e^{-i\Omega_pt}+S^-e^{i\Omega_pt}),\qquad \mathscr{H}_{sL}=\frac{1}{2}(S^+L^-+S^-L^+),\\ h_p^\pm=(\omega_{1p}/\gamma)\exp(\pm i\Omega_pt).\end{gathered}\tag{1}$$

Here $\mathscr{H}_Z$ is the total Zeeman energy of the spin system (with respect to the scatter of the local Zeeman frequency it is assumed here, as usual, that $\Sigma\omega_n = 0$), $\mathscr{H}_d$ is the secular part of the dipole-dipole interaction, $\mathscr{H}_L$ is the Hamiltonian of the phonons considered in the harmonic approximation, H_{sh} is the energy of interaction of the spin system with the radio frequency field $h_p^\pm$, which is considered classically from the very outset, and finally $\mathscr{H}_{SL}$ is the Hamiltonian of the spin-lattice interaction. We confine ourselves henceforth to the single-phonon relaxation mechanism, which plays the decisive role at sufficiently low temperatures. In this case the lattice operators $L^\pm$ can be represented in the form

$$L^\pm=\sum_{\mathbf{k}j}L_{\mathbf{k}j}^\pm,\quad L_{\mathbf{k}j}^+=(A\omega_{kj})^{1/2}a_{\mathbf{k}j}^+,\quad L_{\mathbf{k}j}^-=(L_{\mathbf{k}j}^+)^+,\tag{2}$$

where A is the spin-phonon coupling constant[1)].

To eliminate the explicit time dependence of the Hamiltonian (1), we carry out the unitary transformation[8]

$$\Psi^\bullet=U\Psi,\qquad U=\exp\Big\{i\Omega_p\Big(S^z+\sum_{\mathbf{k}j}\omega_{kj}a_{\mathbf{k}j}^+a_{\mathbf{k}j}\Big)t\Big\},\tag{3}$$

which represents, with respect to the spin system, a transition to a coordinate system that rotates with frequency Ω_p around the direction of the constant magnetic field (z axis), and signifies with respect to the phonons a shift in energy space by an amount equal to the frequency Ω_p.

It is easily seen that in the new reference frame, which we call the rotating coordinate system (RCS), the Hamiltonian of the coupled spin-phonon system takes the form[2)]

$$\begin{gathered}\mathscr{H}^\bullet=\mathscr{H}_s^*+\sum_j\int_0^{k_j}dk\,\mathscr{H}_{kj}^*+\frac{1}{2}\sum_j\int_0^{k_j}dk\,(L_{kj}^+S^-+L_{kj}^-S^+),\\ \mathscr{H}_s^*=\sum_n(\omega_0+\omega_n-\Omega_p)S_n^z+\omega_1S^x+\mathscr{H}_d,\\ \mathscr{H}_{kj}^*=\int\frac{d\Omega}{4\pi}\frac{k^2}{2\pi^2}\mathscr{H}_{\mathbf{k}j}^*,\quad \mathscr{H}_{\mathbf{k}j}^*=(\omega_{kj}-\Omega_p)a_{\mathbf{k}j}^+a_{\mathbf{k}j},\quad L_{kj}^\pm=\int\frac{d\Omega}{4\pi}\frac{k^2}{2\pi^2}L_{\mathbf{k}j}^\pm.\end{gathered}\tag{4}$$

We assume that the saturation field and the spectral diffusion due to the cross-relaxation interaction ensure establishment, within the spin system, of an equilibrium state (characterized by a reciprocal temperature β_S^*) within times shorter than the spin-lattice relaxation time. At low temperatures, when the spin-lattice relaxation processes are slow, this situation can be easily realized in experiment. Since the specific heat corresponding to the secular part of the dipole-dipole interaction is small in comparison with the specific heat corresponding to the local Zeeman energy, and since the width of the inhomogeneously broadened EPR line greatly exceeds[3)] ω_1, the last two terms of $\mathscr{H}_S^*$ can be neglected, with assurance of establishment of a unified spin temperature[4)].

We assume furthermore that the internal equilibrium in the phonon packets $dk\mathscr{H}_{kj}$ is also effective within a time much shorter than the spin-lattice relaxation time. Then, after the lapse of this time, the phonons with frequency $\omega = kc$ are characterized by a reciprocal temperature $\beta^*(\omega)$, and in accord with[8] we have

$$\beta^*(\omega)=\frac{\omega}{\omega-\Omega_p}\beta_L, \tag{5}$$

where β_L is the reciprocal lattice temperature in the laboratory frame.

The spin-lattice relaxation process now corresponds to the macroscopic stage of evolution of the quasi-equilibrium spin-phonon system—to an aggregate of a weakly interacting statistically-independent the spin and phonon subsystems, and can be described by a nonequilibrium statistical operator (NSO) in the form

$$\begin{gathered}\rho^*=Q\exp\Big\{-\beta_s^*\mathscr{H}_s^*-\sum_j\int_0^{k_j}dk\,\beta_{kj}^*\mathscr{H}_{kj}^*\\+\int_{-\infty}^{0}dt\,e^{\varepsilon t}\Big[\beta_s^*K_s^*(t)+\sum_j\int_0^{k_j}dk\,\beta_{kj}^*K_{kj}^*(t)\Big]\Big\},\end{gathered} \tag{6}$$

where the flux operators are defined by the relations

$$\begin{gathered}K_s^*=\frac{1}{2i}\sum_n\sum_{\mathbf{k}j}(A\omega_{kj})^{1/2}(\omega_0+\omega_n-\Omega_p)(a_{\mathbf{k}j}S^+-a_{\mathbf{k}j}^+S^-),\\K_{kj}^*=-\frac{1}{2i}\int\frac{d\Omega}{4\pi}\frac{k^2}{2\pi^2}(A\omega_{kj})^{1/2}(\omega_{kj}-\Omega_p)(a_{\mathbf{k}j}S^+-a_{\mathbf{k}j}^+S^-)\end{gathered} \tag{7}$$

and satisfy the energy conservation law

$$K_s^*+\sum_j\int_0^{k_j}dk\,K_{kj}^*=0.$$

Using this relation, expanding the NSO in terms of thermodynamic flux containing a weak spin-lattice interaction, and confining ourselves for simplicity to the case $S = 1/2$, we obtain after some calculation[5)]

$$\begin{gathered}\overline{\mathscr{H}}_s^*=\operatorname{Sp}\rho^*\mathscr{H}_s^*=-\frac{1}{2}\sum_n(\omega_0+\omega_n-\Omega_p)\operatorname{th}\beta_s^*(\omega_0+\omega_n-\Omega_p)/2,\\\overline{K}_s^*=\operatorname{Sp}\rho^*K_s^*=-\frac{\pi}{2}\sum_n(\omega_0+\omega_n-\Omega_p)L^{+-}(\omega_0+\omega_n)\varphi(\omega_n),\end{gathered} \tag{8}$$

where

$$\varphi(\omega)=\frac{\exp\{(\omega_0+\omega)\beta_L-(\omega_0+\omega-\Omega_p)\beta_s^*\}-1}{\exp\{-(\omega_0+\omega-\Omega_p)\beta_s^*\}+1}$$

$$L^{+-}(\omega)=\frac{3A\omega^3}{2\pi^2c^3}n(\omega),\qquad n(\omega)=(e^{\beta_L\omega}-1)^{-1}.$$

Recognizing now that

$$d\overline{\mathscr{H}}_s^*/dt=\overline{d\mathscr{H}_s^*/dt}=\overline{K}_s^*,$$

assuming the condition for quasistatic behavior[9], and changing to a continuous description of the inhomogeneously broadened EPR line (i.e., changing from summation over the local Zeeman frequencies to integration), by means of the substitution

$$\sum_n(\ldots)\to N\int d\omega g(\omega)(\ldots),$$

we obtain an equation that describes the time variation of the reciprocal spin temperature in the RCS during the macroscopic stage of development

$$d\beta_s^*/dt=G/F, \tag{9}$$

where

$$F=\frac{1}{2}\int d\omega\,g(\omega)(\omega_0+\omega-\Omega_p)^2\sec^{-2}\beta_s^*(\omega_0+\omega-\Omega_p)/2,$$

$$G=\int d\omega\,g(\omega)(\omega_0+\omega-\Omega_p)L^{+-}(\omega_0+\omega)\varphi(\omega),$$

and in accordance with the data on EPR in solids we have

$$g(\omega)=(1/\sqrt{2\pi}\Delta)\exp(-\omega^2/2\Delta^2).$$

It follows therefore that in the stationary state, to which we confine ourselves, β_S^* satisfies the equation

$$\int d\omega\,g(\omega)(\omega_0+\omega-\Omega_p)\varphi(\omega)=0. \tag{10}$$

It can be shown that in the frequency interval bounded by the inequality

$$|\omega_0-\Omega_p|\ll\Delta/\operatorname{th}\frac{\beta_L\omega_0}{2} \tag{11}$$

this equation has an approximate analytic solution

$$\beta_s^*=\beta_L\frac{\omega_0(\omega_0-\Omega_p)}{(\omega_0-\Omega_p)^2+\Delta^2}\left(\operatorname{th}\frac{\beta_L\omega_0}{2}\Big/\frac{\beta_L\omega_0}{2}\right). \tag{12}$$

It follows from inequality (11) that at low thermostat temperatures, $\beta_L\omega_0 \gtrsim 1$, relation (12) is valid only for saturation near the center. With increasing thermostat temperature, the frequency interval in which this relation remains in force broadens and encompasses practically the entire line in the high-temperature limit, $\beta_L\omega_0 \ll 1$. Relation (12) then reduces to the well known result[2]

$$\beta_s^*=\beta_L\omega_0(\omega_0-\Omega_p)/[(\omega_0-\Omega_p)^2+\Delta^2]. \tag{13}$$

It is of interest to consider the behavior of the spin-system temperature $1/\beta_S^*$ under conditions of EPR saturation close to the center, when relation (12) remains valid in a wide temperature interval. In the high-temperature region, the spin temperature decreases in proportion to the lattice temperature. When the low-temperature region is approached, $\tanh(\beta_L\omega_0/2)$ becomes close to unity and the spin-system temperature becomes independent of the lattice temperature, i.e., saturation sets in. This means that the degree β_L/β_S^* of spin-system heating increases in comparison with the results of the low-temperature analysis by a factor $(\beta_L\omega_0/2)/\tanh(\beta_L\omega_0/2)$.

Since the degree of nuclear polarization for the DPN is determined by the electron spin-system temperature in the RCS, this means that starting with temperatures $1/\beta_L \lesssim \omega_0$ further cooling of the thermostat should not lead to an increase in the degree of polarization of the nuclei.

We shall show below that the conclusions drawn on the basis of (12) remain in force, generally speaking, also in the case of saturation far from the center, where this relation ceases to hold in the low-temperature region.

Another approximate solution can be obtained for saturation of inhomogeneously broadened EPR lines on the wings ($|\omega_0 - \Omega_p| \gg \Delta$). It is easy to show that this solution is

$$\beta_s^*=\beta_L\frac{\omega_0}{\omega_0-\Omega_p}\left[1-\frac{\Delta^2}{(\omega_0-\Omega_p)^2}-\frac{\beta_L\omega_0}{2}\left(1-\operatorname{th}\frac{\beta_L\omega_0}{2}\right)\right]. \tag{14}$$

As expected, $\beta_S^* \approx \beta_L\omega_0/(\omega_0 - \Omega_p)$ regardless of the value of β_L.

Finally, for arbitrary values of the resonance detuning $\delta_p = (\omega_0 - \Omega_p)/\sqrt{2}\Delta$ and the thermostat temperature $1/\beta_L$, Eq. (10) can be solved numerically. The results of these calculations are given in Figs. 1 and 2. It is seen from Fig. 2 that the saturation of the spin-system temperature takes place at any detuning from resonance. With increasing detuning, the point at which

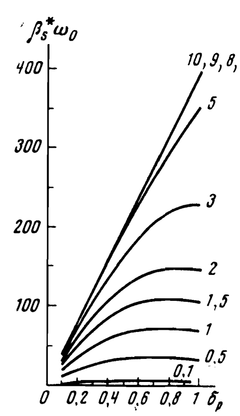

FIG. 1

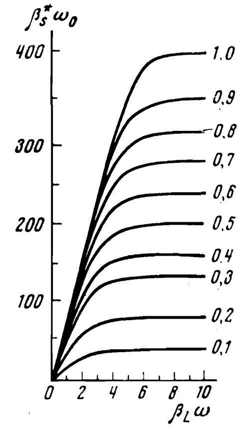

FIG. 2

FIG. 1. Dependence of the reciprocal spin-system temperature on the detuning δ_p of the saturating field at various values of $\beta_L\omega_0$ (marked on curves).

FIG. 2. Dependence of the reciprocal spin-system temperature on the reciprocal thermostat temperature at various values of the detuning δ_p of the saturating field (marked on the curves).

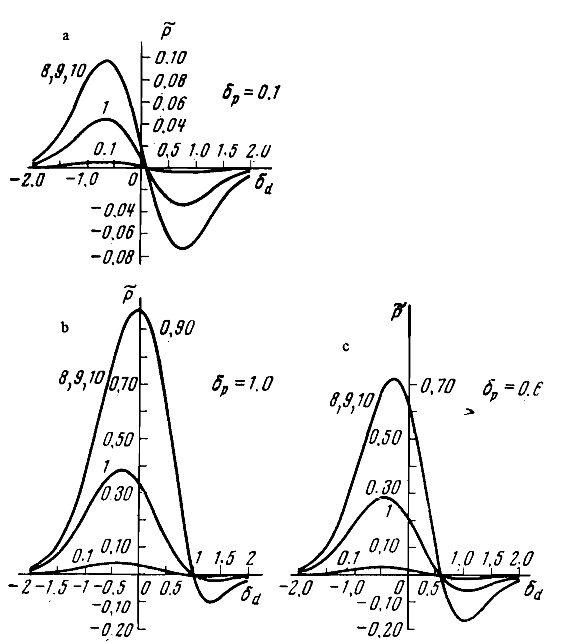

FIG. 3. Plots of the absorption line

$$\tilde{P} = \left[\frac{\sqrt{\pi}}{2}\left(\frac{\omega_0}{\sqrt{2}\,\Delta}\right)N\omega_{1d}^2\right]^{-1} P$$

at fixed saturation detunings δ_p for various values of $\beta_L\omega_0$ (marked on the curves).

the proportionality of β_S^* to β_L gives way to the saturation stage shifts towards lower temperatures.

In conclusion, we consider the absorption line shape in the so called experiments of the second type. In these experiments, as is well known, the inhomogeneously broadened EPR line saturated by a strong radio-frequency field at a frequency Ω_p is scanned by a nonsaturating radio frequency field, and the absorption of the latter is measured. Using the results of[11], it can be shown that the power absorbed at the frequency Ω_d of the detecting field is determined, when the EPR line is saturated at the frequency Ω_p, by the expression

$$P = \frac{\sqrt{\pi}}{2}\left(\frac{\omega_0}{\sqrt{2}\,\Delta}\right)N\omega_{1d}^2 \exp(-\delta_d^2)\,\mathrm{th}\left[\frac{\beta_s^*\omega_0}{2}\left(\frac{\sqrt{2}\,\Delta}{\omega_0}\right)(\delta_p-\delta_d)\right], \quad (15)$$

where $h_{1d} = \omega_{1d}/\gamma$ is the amplitude of the detecting field. It follows from this expression that all the qualitative features of the indication signal (the asymmetry of the absorption curve, the shift of its top in a direction opposite to the point of application of the saturating field, the presence of a region of induced radiation as determined by the condition $\beta_S^*(\delta_p - \delta_d) < 0$) are preserved also in the low-temperature limit. A characteristic feature is that starting with a certain value of β_L further cooling of the lattice exerts no influence (as is clearly seen from Fig. 3) on the indication signal. This is the result of the saturation referred to above.

The authors are grateful to Yu. G. Mamaladze and N. A. Lapauri for the computer solution of Eq. (10) and for plotting the absorption curves.

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1)We discard here from the very beginning that term of $L_{kj}^{\pm}$ which leads subsequently to time-oscillating terms that are ineffective from the point of view of the relaxation, and assume also the long-wave approximation ($\exp(\pm i\mathbf{k}\cdot\mathbf{r}_n) \sim 1$), without loss of generality.

2)From now on we assume the continuous description for the phonons.

3)We do not consider the case of superstrong saturation.

4)As is well known, the spin-lattice relaxation time, which is indeed the small time scale, increases with decreasing temperature. The analysis that follows is therefore valid only down to temperatures at which this time still remains much shorter than the time scales that characterize the macroscopic stage of the evolution.

5)These calculations are analogous in many respects to those performed in [7], where they are reported in sufficient detail. Relation (5) was used to eliminate $\beta^*(\omega)$.

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Translated by J. G. Adashko
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