Low-frequency absorption of a transverse magnetic field in inhomogeneously broadened paramagnetic systems

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(Submitted 17 May 1984)
Zh. Eksp. Teor. Fiz. **87**, 1809–1817 (November 1984)

A systematic theory is derived for the nonresonant absorption of a low-frequency transverse field by paramagnetic systems. How the process is affected by the parameters of the low-frequency field and the nature of the broadening of the ESR line of these systems is analyzed. The fluctuation-dissipation theorem is used to calculate the imaginary part of the magnetic susceptibility of the spin system during linear low-frequency absorption. Depending on the frequency of the low-frequency field, Ω_2, the absorption by inhomogeneous systems differs in nature from that by homogeneous systems. For inhomogeneously broadened systems, a study is also made of irreversible processes associated with nonlinear low-frequency absorption. The behavior of the system in a low-frequency field is studied as a function of the rate of spectral diffusion. During a rapid diffusion, the energy of the low-frequency field goes into the local-field reservoir. If the spectral diffusion is instead limited, the direct absorption of low-frequency energy by the dipole-dipole reservoir may be accompanied by an absorption by Zeeman subsystems of the individual spin packets. If Ω_2 is smaller than the diffusion length $1/K_1$, the absorption is associated with an effective increase in $1/K_1$, but if $\Omega_2 \gg 1/K_1$ the low-frequency field will, by inducing a thermal contact between the packet which is saturated by the microwave field and the packets which are separated from it by a frequency interval $\pm \Omega_2$, cause a heating of the latter packets. Comparison of this theory with experiment reveals a good agreement. The discrepancies found between the experimental results and the theoretical predictions in certain areas are shown to stem from the fact that all the mechanisms which have been offered to explain the low-frequency absorption lack definite terms representing the effective interaction of the spin system with the transverse low-frequency field. The calculations are carried out in second-order perturbation theory.

Interest has recently revived in research on paramagnetic systems by nonresonant methods, particularly after the studies by Atsarkin *et al.*[1,2] Attempts to interpret the corresponding experiments,[3–5] however, have run into certain difficulties which stem from the lack of a systematic theory for the interaction of spin systems with a transverse low-frequency field. We offer such a theory in the present paper.

1. We consider a paramagnetic material containing electron spins S with a gyromagnetic ratio γ in a constant external magnetic field H_0 and in a transverse low-frequency field.

We write the Hamiltonian of the inhomogeneously broadened spin system as follows[1)]:

$$\mathscr{H}=\mathscr{H}_0+V, \quad \mathscr{H}_0=\mathscr{H}_z+\mathscr{H}_d^{sec}, \quad \mathscr{H}_z=\mathscr{H}_\Sigma+\mathscr{H}_\Delta,$$

$$\mathscr{H}_\Sigma=\omega_0\sum_i S_i^z, \quad \mathscr{H}_\Delta=\sum_i(\omega_i-\omega_0)S_i^z,$$

$$V=V_h+V_d, \quad V_h=\omega_2\cos\Omega_2 t\sum_i(S_i^+ + S_i^-), \tag{1}$$

$$V_d=\frac{1}{2}\sum_{i\neq j}\{C_{ij}(S_i^zS_j^+ + S_i^+S_j^z)+D_{ij}(S_i^zS_j^- + S_i^-S_j^z)\};$$

where the operator $\mathscr{H}_z$ represents the Zeeman energy of the spin system, which is split into a "sum part" $\mathscr{H}_\Sigma$ and a "difference part" $\mathscr{H}_\Delta$ (Ref. 6); ω_0 is the frequency of the "center of gravity" of the ESR spectrum; ω_i is the frequency of the ith spin; $\mathscr{H}_d^{\text{sec}}$ is the part of the dipole-dipole interaction which is secular with respect to $\mathscr{H}_\Sigma$; V_h is the interaction of the spin system with the low-frequency field, which has a frequency Ω_2 and an amplitude ω_2; V_d is that part of the nonsecular dipole-dipole interaction which stems from the low-frequency absorption; and C_{ij} and D_{ij} are the dipole-dipole interaction constants of spins i and j.

The nonresonant absorption of the transverse low-frequency field stems from multispin transitions in the system, which are manifested in the higher orders of perturbation theory. To describe these transitions we use therefore the effective-Hamiltonian formalism,[7] in accordance with which we can write, with an accuracy to small terms of second order,

$$\mathscr{H}_{\text{eff}}=\overline{\mathscr{H}(t)}+{}^1/_2\overline{[\widetilde{\mathscr{H}(t)}\mathscr{H}(t)]},$$

$$\mathscr{H}(t)=U(t)\mathscr{H}U^+(t),$$

where $\mathscr{H}_{\text{eff}}$ is the effective Hamiltonian in the rotating coordinate system, the transformation to which is via the unitary operator[8]

$$U(t)=\exp\left(i\omega_0\sum_i S_i^z t\right),$$

the superior bar means an average, and the tilde means an integration.[7] In the course of the integration, $\cos\Omega_2 t$ is taken outside the integral sign since it is a slowly varying function.

In the resulting effective Hamiltonian the perturbation

0038-5646/84/111040-06$04.00

with which the absorption of the transverse low-frequency field is associated is

$$V_{\text{eff}} = 2V_1\omega_2 \cos \Omega_2 t,$$

$$V_1 = \frac{1}{4\omega_0}\sum_{i\neq j}(C_{ij}+D_{ij})\{4S_i^zS_j^z-(S_i^+S_j^-+S_i^-S_j^+)\}. \quad (2)$$

We wish to find the imaginary part $\chi''(\Omega_2)$ of the magnetic susceptibility of the spin system. If the low-frequency absorption is linear, i.e., if the spin transitions induced by the low-frequency field occur far more slowly than relaxation processes, we can use the fluctuation-dissipation theorem[9]:

$$\chi''(\Omega_2) = 2\pi \,\text{th}\,({}^1/{}_2\Omega_2\beta_L)\,\Phi(\Omega_2),$$

where

$$\Phi(\Omega_2) = \frac{\gamma^2}{2\pi}\int_{-\infty}^{\infty}\frac{1}{2}e^{-i\Omega_2 t}\{\langle V_1V_1^0(t)\rangle + \langle V_1^0(t)V_1\rangle\}\,dt,$$

$$V_1^0(t) = \exp\,(i\mathscr{H}_0 t)\,V_1 \exp\,(-i\mathscr{H}_0 t),$$

and β_L is the reciprocal of the lattice temperature.

After some straightforward manipulations we find the following expression for the magnetic susceptibility in the high-temperature approximation:

$$\chi''(\Omega_2) = \frac{\pi}{4}\chi_0\frac{V^2\Omega_2}{\omega_0^{\;2}}[\varphi_z(\Omega_2)+g(\Omega_2)], \quad (3)$$

where the function $g(\omega)$ is the shape of the inhomogeneously broadened ESR line, Δ^{*2} is the second moment of this line, and

$$\varphi_z(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\omega t}\left[\frac{\langle S_i^zS_i^z(t)\rangle}{\langle S_i^{z2}\rangle}\right]^2 dt,$$

$$S^z(t) = \exp[i(\mathscr{H}_\Delta+\mathscr{H}_d^{\,sec})t]S^z\exp[-i(\mathscr{H}_\Delta+\mathscr{H}_d^{\,sec})t],$$

$$V^2 = \frac{1}{N}\sum_{i\neq j}(2\,\text{Re}\,C_{ij})^2, \quad \chi_0 = {}^1/{}_3N\gamma^2S(S+1)\beta_L.$$

Here χ_0 is the static susceptibility of the spin system, and N is the number of paramagnetic centers in the sample. That part of susceptibility (3) which corresponds to the function $g(\Omega_2)$ describes the low-frequency-field energy absorption due to the mutual flipping of different spins induced by the low-frequency field. The part which corresponds to the function $\varphi_z(\Omega_2)$ describes the absorption due to the term $S_i^zS_j^z$ in the effective Hamiltonian. In the derivation of $\varphi_z(\omega)$ we made use of the circumstance that under inhomogeneous-broadening conditions the correlation function

$$\langle S_i^z \exp[i(\mathscr{H}_\Delta+\mathscr{H}_d^{\,sec})t]S_i^z\exp[-i(\mathscr{H}_\Delta+\mathscr{H}_d^{\,sec})t]\rangle$$

reduces to

$$\langle S_i^z \exp(i\mathscr{H}_d^{\,sec}t)S_i^z(-i\mathscr{H}_d^{\,sec}t)\rangle,$$

for which an explicit expression is given in Ref. 10.

Omitting the term $\mathscr{H}_\Delta$ from Hamiltonian (1), we can derive in an analogous way an expression for the case of homogeneous broadening of the ESR line:

$$\chi''(\Omega_2) = \frac{\pi}{4}\chi_0\frac{V^2\Omega_2}{\omega_0^{\;2}}[G^z(\Omega_2)+G^{+-}(\Omega_2)], \quad (4)$$

where

$$G^{z,+-}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\omega t}\left[\frac{\langle S_i^{z,+}\tilde{S}_i^{z,-}(t)\rangle}{\langle S_i^{z,+}S_i^{z,-}\rangle}\right]^2 dt,$$

$$\tilde{S}^{z,-}(t) = \exp(i\mathscr{H}_d^{\,sec}t)S^{z,-}\exp(-i\mathscr{H}_d^{\,sec}t).$$

In this case the energy of the low-frequency field goes into a dipole-dipole reservoir, into which the energy of the secular part of the spin-spin interactions of the paramagnetic system is discharged, as usual.[11]

The process by which the energy of a transverse low-frequency field is absorbed by homogeneously broadened spin systems was analyzed in Refs. 12 and 13, but without the interaction component $S_i^zS_j^z$, i.e., without the function $G^z(\Omega_2)$ [cf. (4) and Eq. (25) of Ref. 13].

Let us examine the frequency dependence of the low-frequency absorption. Since the functions $G^z(\Omega_2)$ and $G^{+-}(\Omega_2)$ are of the same order of magnitude for all possible values of Ω_2 in the case of homogeneous broadening of the ESR line (the widths of these functions are on the order of V; Ref. 14), the terms $S_i^+S_j^-$ and $S_i^zS_j^z$ of the effective Hamiltonian make identical contributions to the absorption described by (4). The situation is different if the broadening is inhomogeneous. In this case, for sufficiently dilute paramagnetic systems, $\varphi_z(\Omega_2)$ can be written[10]

$$\varphi_z(\Omega_2) = \frac{1}{\pi}\frac{\delta_z}{\delta_z^{\,2}+\Omega_2^{\,2}}. \quad \delta_z \approx \Big\{{\sum_j}' B_{ij}^2\Big\}^{3/2}\Big\{{\sum_j}' B_{ij}^4\Big\}^{-1/2}\frac{\delta}{\Delta^*}f,$$

where δ is the homogeneous line width of the spin packet, B_{ij} is the dipole-dipole interaction constant, and f is the dilution. The prime on the summation symbol means that the sum runs over all the lattice sites.

For $g(\Omega_2)$ we can use the approximation

$$g(\Omega_2) = (2\pi\Delta^{*2})^{-1/2}\exp\,(-\Omega_2^{\,2}/2\Delta^{*2}).$$

At low frequencies of the low-frequency field $\Omega_2 < \delta_z$, we have $\varphi_z(\Omega_2) \sim 1/\delta_z \gg g(\Omega_2) \sim 1/\Delta^*$, while in the frequency range $\delta_z < \Omega_2 < \Delta^*$ we have $\varphi_z(\Omega_2) \sim \delta_z/\Omega_2^2$, so that $\varphi_z(\Omega_2)/g(\Omega_2) \sim \delta_z\Delta^*/\Omega_2^2$. Consequently, if $\Omega_2^2 < \delta_z\Delta^*$ the absorption is caused primarily by the term $S_i^zS_j^z$, which has previously been ignored altogether; only at $\Omega_2^2 > \delta_z\Delta^*$ is the absorption governed by the "cross-relaxation" mechanism discussed in Ref. 13.

Since it is difficult to measure the low-frequency absorption directly, experiments on nonresonant absorption are usually carried out in a microwave field tuned some distance from resonance in order to increase the effect by two or three orders of magnitude.[1] Under these conditions, nonlinear phenomena become important. To analyze them we use the method of a nonequilibrium statistical operator,[15] and we consider separately the cases in which there is a rapid and a limited spectral diffusion in the inhomogeneously broadened spin systems.

2. We first consider the case of a rapid spectral diffusion. We know that under these conditions we can single out from the unperturbed Hamiltonian the total Zeeman subsystem (i.e., the "sum" reservoir) and the local-field reservoir $\mathscr{H}_R$, which is introduced in place of the dipole-dipole reservoir[16,17]:

$$\mathscr{H}_z=\mathscr{H}_\Sigma+\mathscr{H}_R,\quad \mathscr{H}_R=\mathscr{H}_\Delta+\mathscr{H}_d^{sec}$$
$$=\sum_i(\omega_i-\omega_0)S_i^z+\frac{1}{2}\sum_{i\neq j}(A_{ij}S_i^zS_j^z+B_{ij}S_i^+S_j^-),\qquad(5)$$

where A_{ij} is the constant of the dipole-dipole interaction of spins i and j.

Applying the method of a nonequilibrium statistical operator to the effective Hamiltonian in (2) and (5), we find the following equation for the change of the spin temperature β_R^{-1} of the local-field reservoir during low-frequency absorption:

$$d\beta_R/dt=-W_{\rm LF}\beta_R-(\beta_R-\beta_L)/T_{1R},\qquad(6)$$

where the probability $W_{\rm LF}$, which represents the interaction of the local-field reservoir with the transverse low-frequency field, is

$$W_{\rm LF}=\frac{\pi\omega_2^2}{2}\frac{V^2\Omega_2^2}{\omega_0^2(\Delta^{*2}+\omega_d^2)}[\varphi_z(\Omega_2)+g(\Omega_2)],\qquad(7)$$

T_{1R} is the spin-lattice relaxation time of the local-field reservoir, and ω_d is the average frequency of the dipole-dipole reservoir.

We see that in the case of a rapid spectral diffusion the energy of the low-frequency field enters the local-field reservoir as a result of multispin processes which are described by the terms $S_i^zS_j^z$ and $S_i^\pm S_j^\mp$ in the effective Hamiltonian. The absorption resulting from the term $S_i^zS_j^z$ stems from only that part of the local-field reservoir which corresponds to the Hamiltonian $\mathscr{H}_d^{\rm sec}$. As we have already noted, this process is dominant at $\Omega_2^2<\delta_z\Delta^*$. In the absorption due to the mutual flipping of spins (the term $S_i^\pm S_j^\mp$), on the other hand, the energy of the low-frequency field goes primarily into the "difference" reservoir, i.e., into that part of the local-field reservoir ($\mathscr{H}_\Delta$) which is related to the spread in the local fields. This process is dominant at $\Omega_2^2>\delta_z\Delta^*$.

A mechanism for low-frequency absorption involving only the spread of the local fields was analyzed in Ref. 18.

We now assume that a transverse microwave field of frequency Ω_1, which saturates the resonance with a frequency difference $\Delta=\omega_0-\Omega_1$, is applied to the spin system along with the low-frequency field. In this case there will be a contact between the $\mathscr{H}_\Sigma$ and $\mathscr{H}_R$ subsystems,[19] so that the nonresonant low-frequency absorption will now also have an effect on the sum Zeeman reservoir. Supplementing Provotorov's equations[19] with the term (6), we can easily find the steady-state value $\beta_R^{\rm st}$ of the reciprocal temperature of the local-field reservoir. Using (6) and (7), we can then find the low-frequency field power absorbed by the spin system in the steady state.

$$P_{\rm LF}(\omega_2,\Omega_2)=\frac{\pi}{2}\chi_0\frac{\omega_2^2V^2\Omega_2^2}{\gamma^2\omega_0^2}$$
$$\times[\varphi_z(\Omega_2)+g(\Omega_2)]\frac{\omega_0\Delta}{\Delta^2+\alpha\omega_R^2(1+S_{\rm LF})},\qquad(8)$$

where $\alpha=T_{1S}/T_{1R}$, T_{1S} is the scale time of the Zeeman spin-lattice relaxation, $\omega_R^2=\Delta^{*2}+\omega_d^2$ and $S_{\rm LF}=W_{\rm LF}T_{1R}$.

We see that the low-frequency power absorbed by the local field reservoir has a typical "dispersion" behavior: If $\Delta=0$, there is no absorption, and at $\omega_0<\Omega_1$ the absorption is negative; i.e., there is emission instead of absorption. Furthermore, it follows from this expression that the microwave field intensifies the low-frequency absorption, as has been found experimentally.[3-5] The maximum increase occurs at $\Delta=\omega_R[\alpha(1+S_{\rm LF})]^{1/2}$ and is given by

$$\frac{1}{2}\left\{\frac{\omega_0^2}{\alpha\omega_R^2}(1+S_{\rm LF})\right\}^{1/2}\gg1.$$

An optical detection method is frequently used in experiments on low-frequency absorption, because it is the most sensitive method available.[3-5] Since the optical-detection signal is proportional to the magnetization of the system,[20] we will calculate the relative change in the total magnetization due to the low-frequency field:

$$\Delta E_M=(M_z^{\rm MW}-M_z^{\rm MW+LF})/M_{z0},\qquad(9)$$

where M_{z0} is the static magnetization of the sample, $M_z^{\rm MW}$ is the magnetization of the sample during microwave pumping alone, and $M_z^{\rm MW+LF}$ is the magnetization of the sample when subjected to both the microwave and low-frequency fields.

During a rapid spectral diffusion, the relative change in the total magnetization of the spin system will obviously be equal to the relative change in the reciprocal of the spin temperature of the Zeeman subsystem. Using the corresponding expression from Ref. 18, we can write

$$\Delta E_M=S_{\rm LF}\Delta^2\alpha\omega_R^2/(\Delta^2+\alpha\omega_R^2)[\Delta^2+\alpha\omega_R^2(1+S_{\rm LF})].\qquad(10)$$

We see that at $\Delta=\pm\omega_R[\alpha^2(1+S_{\rm LF})]^{1/4}$ the quantity ΔE_M reaches its maximum value

$$\Delta E_{M,\,\max}=S_{\rm LF}/[1+(1+S_{\rm LF})^{1/2}]^2.\qquad(11)$$

We see that in the "double-humped" plot of ΔE_M versus the distance from the resonant frequency, Δ, the distance between the humps is $(1+S_{\rm LF})^{1/4}$ times the width of the inhomogeneous ESR line.

It follows from (11) that under the condition $S_{\rm LF}\ll1$ the maximum relative change in the total magnetization of the system is proportional to the squared amplitude of the low-frequency field, while at $S_{\rm LF}\gg1$ it approaches unity. As for the frequency dependence of ΔE_M we note that, as can be seen from (7) and (10), it is quadratic if $\Omega_2\ll\delta_z$: $\Delta E_M\sim\Omega_2^2$. With increasing frequency Ω_2, however, the functional dependence becomes progressively weaker, and in the interval $\delta_z^2\ll\Omega_2^2\ll\delta_z\Delta^*$ the quantity ΔE_M becomes essentially independent of Ω_2.

3. We now consider the case of a limited spectral diffusion. We know that the spin system under these conditions is

a set of individual homogeneously broadened spin packets, with frequencies ω_n and Zeeman temperatures β_n^{-1}, and a common dipole-dipole reservoir.[21,22]

For simplicity we ignore the effects of the dipole-dipole reservoir. In this case the part of the effective Hamiltonian which is responsible for the low-frequency absorption is

$$V'_{\text{eff}} = -\frac{\omega_2}{2\omega_0}\cos\Omega_2 t \sum_{mn}\sum_{i\neq j} (C_{ij}+D_{ij})(S_{ni}^{+}S_{mj}^{-}+S_{ni}^{-}S_{mj}^{+}), \tag{12}$$

where m and n are the indices of the packets, and i and j are the indices of the spins in the packets.

Using the method of a nonequilibrium statistical operator, we can easily derive the following kinetic equations:

$$\frac{d\beta_n}{dt} = -\sum_m g_m W(\omega_m-\omega_n+\Omega_2)\left(\beta_n - \frac{\omega_m}{\omega_n}\beta_m\right) - \sum_m g_m W(\omega_m-\omega_n-\Omega_2)\left(\beta_n - \frac{\omega_m}{\omega_n}\beta_m\right) - \frac{\beta_n-\beta_L}{T_{1S}}, \tag{13}$$

where

$$W(\omega) = \frac{\pi\omega_2^2}{2}\frac{V^2}{\omega_0^2}\varphi(\omega)$$

is the probability of spin transitions induced by the low-frequency field; $g_m = N_m/N$, where N_m is the number of paramagnetic centers in packet m; and $\varphi(\omega)$ is the Fourier transform of the correlation function

$$\varphi(t) = \langle \tilde{S}_{ni}^{+}(t)\tilde{S}_{mj}^{-}(t)S_{ni}^{-}S_{mj}^{+}\rangle / \langle S_{ni}^{+}S_{ni}^{-}\rangle\langle S_{mj}^{+}S_{mj}^{-}\rangle,$$
$$\tilde{S}^{\pm}(t) = \exp(i\mathscr{H}_d t)S^{\pm}\exp(-i\mathscr{H}_d t).$$

The function $\varphi(t)$ does not depend on m or n, since the A term makes the predominant contribution to the correlation function. [sic!]

We thus see that the multispin absorption of energy of the transverse low-frequency field is due in this case exclusively to a change in the Zeeman energies of the individual spin packets. The absorption of a photon of the low-frequency field in accompanied by mutual flips of the spins belonging to different packets.

If spectral diffusion occurs in an inhomogeneous broadened ESR line, and the system is subjected to low-frequency and microwave fields simultaneously, we should supplement Eq. (13) with some corresponding terms.[23] In the limit of a continuous packet frequency distribution we would then have[2)]

$$\frac{d\beta(\omega)}{dt} = \frac{1}{\omega}\int_{-\infty}^{\infty} d\omega' g(\omega'-\omega_0)W_2^{cr}(\omega-\omega') \times[\omega'\beta(\omega')-\omega\beta(\omega)] - W_2(\omega-\omega_0+\Omega_2)[\beta(\omega)-\beta(\omega+\Omega_2)] - W_2(\omega-\omega_0-\Omega_2) \times[\beta(\omega)-\beta(\omega-\Omega_2)] - 2W_1(\Omega_1-\omega)\beta(\omega) - (\beta(\omega)-\beta_L)/T_{1S}. \tag{14}$$

Here

$$W_2(\omega) = \frac{\pi\omega_2^2}{2}\frac{V^2}{\omega_0^2}g(\omega),$$

$W_2^{\text{cr}}(\omega)$ is the probability for cross-relaxation transitions, and $W_1(\omega)$ is the probability for transitions induced by the microwave field.

Two limiting cases

A. Diffusion limit ($\Omega_2 < 1/K_l$, where $1/K_l$ is the spectral diffusion length). Expanding $\beta(\omega \pm \Omega_2)$ in (14) in a series about the point ω, and using the standard procedure for transforming from an integral equation to a differential one,[23] we find the following diffusion equation in the approximation $W(\omega - \omega_0 \pm \Omega_2) = W(\omega - \omega_0)$:

$$d^2\beta(\omega)/d\omega^2 - K^2\beta(\omega) = -K^2\beta_L + K^2 S_1\pi\delta\varphi(\omega-\Omega_1)\beta(\omega), \tag{15}$$

where $K^{-1} = (DT_{1S})^{1/2}$, $D = D_1 + D_u$, $S_1 = \omega_1^2 T_{1S}/\delta$, ω_1 is the amplitude of the microwave field, D_1 is the coefficient of the spectral diffusion caused by the cross-relaxation terms $S_{ni}^{+}S_{mj}^{-}$, and $D_u = \Omega_2^2 W_2(\omega - \omega_0)$ is the coefficient of the diffusion induced by the low-frequency field.

A solution of Eq. (15) is [the solution is valid for small values of Δ, such that $K(\Delta^*/2 - |\Delta|) \gg 1$); Ref. 23]

$$\beta^{\text{MW+LF}}(\omega) = \frac{\beta_L}{1+S'}\{1+S'[1-\exp(-K|\omega-\Omega_1|)\}, \tag{16}$$

where $S' = (1/2)S_1\pi K\delta$.

Comparison of this result with the corresponding expression for the case without a low-frequency field [expression (32) in Ref. 23] shows that the effect of the low-frequency field is to cause an effective increase in the spectral diffusion length. This increase leads to an intensification of the microwave absorption, since the microwave energy absorbed by a resonant spin packet propagates into a broader spectral region.

Expanding S' and K in (16) in the small parameter $D_u/D_1 \sim \omega_2^2\Omega_2^2/\omega_0^2 M_2^{\text{cr}} \ll 1$ (M_2^{cr} is the second moment of the cross-relaxational line shape), and using the solution of the diffusion equation derived without consideration of low-frequency absorption, we find the following expression for the relative change in the reciprocal of the Zeeman temperature:

$$\Delta E_S(\omega) = \frac{\beta^{\text{MW}}(\omega) - \beta^{\text{MW+LF}}(\omega)}{\beta_L} = \frac{S_1'}{1+S_1'}\frac{\pi\omega_2^2}{2}\frac{V^2\Omega_2^2}{\omega_0^2 W^{cr} M_2^{cr}} \times\left[K_1|\omega-\Omega_1| - \frac{1}{1+S_1'}\right]\exp[-K_1|\omega-\Omega_1|], \tag{17}$$

where

$$W^{cr} = 2\pi\sum_j |B_{ij}|^2, \quad S_1' = {}^1/_2 S_1\pi K_1\delta, \quad K_1^{-1} = (D_1 T_{1S})^{1/2},$$

$\beta^{\text{MW}}(\omega)$ is the reciprocal of the Zeeman temperature of the packet of frequency ω during microwave pumping alone, and $\beta^{\text{MW+LF}}(\omega)$ is the corresponding reciprocal temperature for the case in which microwave and low-frequency fields are applied simultaneously.

We thus see that in the case of a weak microwave saturation ($S_1' \ll 1$) the quantity $\Delta E_S(\omega)$ is positive if $|\omega - \Omega_1| > 1/K_1$ and changes sign at $\Omega_1 - 1/K_1 < \omega < \Omega_1 + 1/K_1$; i.e., the low-frequency field promotes a cooling of the packets from the interval $[\Omega_1 - 1/K_1; \Omega_1 + 1/K_1]$, by transferring heat from these packets to packets with frequencies $\Omega_1 - 1/K \leqslant \omega < \Omega_1 - 1/K_1$; $\Omega_1 + 1/K_1 < \omega \leqslant \Omega_1 + 1/K$.

We easily find the relative change in the total magnetization of the sample to be

$$\Delta E_M = \frac{1}{\omega_0} \int_{-\infty}^{\infty} \omega g(\omega - \omega_0) \Delta E_S(\omega)\, d\omega \approx \left(\frac{S_1'}{1+S_1'}\right)^2 \frac{\pi V^2 \omega_2{}^2 \Omega_2{}^2}{K_1 \omega_0{}^2 W^{cr} M_2{}^{cr}} g(\omega_0 - \Omega_1). \tag{18}$$

B. If the frequency Ω_2 exceeds the diffusion length ($1/K_1 \ll \Omega_2 \ll \Delta^*$), the terms in (14) which correspond to the transitions induced by the low-frequency field cannot be written in diffusion form. In this case, combining (13) and (14), we find a system of equations for $\beta(\omega)$ and $\beta(\omega \pm \Omega_2)$. Ignoring the small terms in the equation for $\beta(\omega)$ (under the condition $W_2 \ll W_1$, $1/T_{1S}$), we find

$$\Delta E_S(\omega \pm \Omega_2) = \frac{S_2(\omega)}{2} \frac{S_1'}{1+S_1'} \exp(-K_1|\omega - \Omega_1|), \tag{19}$$

where $S_2(\omega) = 2W_2(\omega - \omega_0)T_{1S}$.

We thus see that the result of the low-frequency field, which induces a thermal contact between the packets from the interval $[\Omega_1 - 1/K_1; \Omega_1 + 1/K_1]$ and the packets separated from them by a frequency interval $\pm\Omega_2$, is to heat the latter packets.

For ΔE_M we have

$$\Delta E_M = S_2(\Omega_1) \frac{S_1'}{1+S_1'} \frac{1}{K_1} g(\omega_0 - \Omega_1). \tag{20}$$

We thus see that the functional dependence of ΔE_M on the frequency and amplitude in the case of a limited spectral diffusion is of the same nature as in the case of a rapid spectral diffusion (for frequencies $\Omega_2^2 < \delta_z \Delta^*$): For relatively small values of these parameters we have $E_M \sim \omega_2^2$, Ω_2^2, while the frequency dependence fades away with increasing Ω_2. As for the functional dependence on the deviation of the microwave frequency from the resonant frequency, we note that there is an important difference: There is no dip at the center of the line in the case of a limited spectral diffusion. If, however, we take the dipole-dipole reservoir into account under these conditions,[24] we find that such a dip appears, although it does not extend all the way to zero.

It is interesting to compare these theoretical conclusions with experimental results. As an example we consider the results of Refs. 4 and 5, where a study was made of the ESR signal as a function of the amplitude and frequency of a low-frequency field with optical detection and also as a function of the deviation of the microwave pump from the resonant frequency. We recall that in the qualitative analysis of Ref. 5 several experimental results went unexplained. It can be suggested that the "anomalies" which were observed stemmed primarily from the terms $S_i^z S_j^z$ in effective Hamiltonian (2), i.e., from an additional source of "forbidden" low-frequency transitions which was ignored in the previous studies. The frequency dependence of the effect was apparently studied in the range $\Omega_2^2 < \delta_z \Delta^*$ in Refs. 4 and 5 (since we have

$$f\left\{\sum_j{}' B_{ij}{}^2\right\}^{3/2} \left\{\sum_j{}' B_{ij}{}^4\right\}^{-1/2} \sim \delta$$

in order of magnitude,[14] we have an expression for δ_z: $\delta_z \sim \delta^2/\Delta^*$). As mentioned earlier, in this case it is the terms $S_i^z S_j^z$ which are responsible for the low-frequency absorption; at $\delta_z^2 < \Omega_2^2 < \delta_z \Delta^*$, the frequency dependence $\Delta E_M(\Omega_2)$ becomes much weaker. This is the behavior which was observed in experiments[5] with $CaF_2{:}Tm^{2+}$. If $\Omega_2^2 > \delta_z \Delta^*$, on the other hand, the frequency dependence becomes quadratic again, apparently in accordance with the results found for ruby (Fig. 5 in Ref. 5).

In the case of a rapid spectral diffusion we also find an explanation for the double-humped plot of ΔE_M versus the difference between the microwave frequency and the resonant frequency, Δ [expression (10)]. The discrepancy between the peaks on the theoretical and experimental curves (Fig. 1 in Ref. 5) can also be attributed to the effect of terms $S_i^z S_j^z$ (the experiments were carried out under the condition $\Omega_2^2 \lesssim \delta_z \Delta^*$). As for the nonzero magnitude of the effect at $\Delta = 0$, we note that this result is evidently due to the finite rate of spectral diffusion, i.e., the contribution of the mechanism of limited spectral diffusion [see (18)].

We wish to thank V. A. Atsarkin for useful advice and discussions.

1)We are using a system of units with $\hbar = 1$ and $k_B = 1$.

2)In the coefficients of $\beta(\omega \pm \Omega_2)$ we are ignoring Ω_2 in comparison with ω.

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[1] V. A. Atsarkin, Zh. Eksp. Teor. Fiz. **64**, 1087 (1973) [Sov. Phys. JETP **37**, 552 (1973)].

[2] V. A. Atsarkin and O. A. Ryabushkin, Pis'ma Zh. Eksp. Teor. Fiz. **17**, 103 (1973) [JETP Lett. **17**, 71 (1973)]; V. A. Atsarkin, O. A. Ryabushkin, and V. A. Skidanov, Zh. Eksp. Teor. Fiz. **72**, 1118 (1977) [Sov. Phys. JETP **45**, 584 (1977)].

[3] V. A. Atsarkin and S. A. Kazanskiĭ, Zh. Eksp. Teor. Fiz. **84**, 2306 (1983) [Sov. Phys. JETP **57**, 1345 (1983)]; S. A. Kaganskiĭ, Zh. Eksp. Teor. Fiz. **80**, 1469 (1981) [Sov. Phys. JETP **53**, 753 (1981)]; S. A. Kaganskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **30**, 296 (1979) [JETP Lett. **30**, 274 (1979)].

[4] S. A. Kaganskiĭ, Opt. Spektrosk. **52**, 588 (1982) [Opt. Spectrosc. (USSR) **52**, 353 (1982)].

[5] S. A. Kaganskiĭ, Zh. Eksp. Teor. Fiz. **84**, 1202 (1983) [Sov. Phys. JETP **57**, 697 (1983)].

[6] M. I. Rodak, Zh. Eksp. Teor. Fiz. **61**, 832 (1971) [Sov. Phys. JETP **34**, 443 (1971)]; V. A. Atsarkin, Usp. Fiz. Nauk **126**, 3 (1978) [Sov. Phys. Usp. **21**, 725 (1978)].

[7] L. L. Buishvili, G. V. Kobakhidze, and M. G. Menabde, Zh. Eksp. Teor. Fiz. **84**, 138 (1983) [Sov. Phys. JETP **57**, 80 (1983)].

[8] A. Abragam, The Principles of Nuclear Magnetism, Clarendon Press, Oxford (1961) (Russ. transl. IIL, Moscow, Ch. 2, 1963).

[9] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika, Part I, Ch. 12, Nauka, Moscow, 1976 (Statistical Physics, Pergamon Press, New York).

[10] L. L. Buishvili, I. M. Metreveli, and N. P. Fokina, Zh. Eksp. Teor. Fiz. **80**, 678 (1981) [Sov. Phys. JETP **53**, 341 (1981)].

[11] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Clarendon Press, Oxford (1970) (Russ. transl. Mir, Moscow, 1972; V. A. Atsarkin and M. I. Rodak, Usp. Fiz. Nauk **107**, 3 (1972) [Sov. Phys. Usp. **15**, 251 (1972)].

[12] L. S. Brown, IBM J. Res. Dev. **6**, 338 (1962).
[13] A. G. Anderson and S. R. Hartman, Phys. Rev. **128**, 2023 (1962).
[14] S. A. Al'tshuler and B. M. Kozyrev, Élektronnyĭ paramagnitnyĭ rezonans (Electron Paramagnetic Resonance), Nauka, Moscow, Ch. 4, 1972.
[15] D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Nonequilibrium Statistical Thermodynamics), Nauka, Moscow, Ch. 4, 1971.
[16] N. S. Bendiashvili, L. L. Buishvili, and M. D. Zviadadze, Zh. Eksp. Teor. Fiz. **58**, 597 (1970) [Sov. Phys. JETP **31**, 321 (1970)].
[17] S. Clough and C. A. Scott, Proc. Phys. Soc. **1**, 919 (1968).
[18] T. Sh. Abesadze and Z. I. Mosashvili, Radiofizika **7**, 903 (1984).
[19] B. N. Provotorov, Zh. Eksp. Teor. Fiz. **41**, 1582 (1961) [Sov. Phys. JETP **14**, 1126 (1962)] Fiz. Tverd. Tela (Leningrad) **4**, 2940 (1962) [Sov. Phys. Solid State **4**, 2155 (1962)].
[20] I. V. Starostin and P. P. Feofilov, Usp. Fiz. Nauk **97**, 621 (1969) [Sov. Phys. Usp. **12**, 252 (1969)]; E. B. Aleksandrov and V. S. Zapasskiĭ, Opt. Spektrosk. **41**, 855 (1976) [Opt. Spectrosc. (USSR) **41**, 502 (1976)].
[21] A. M. Portis, Phys. Rev. **91**, 1070 (1953).
[22] L. L. Buishvili, M. D. Zviadadze, and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. **56**, 290 (1969) [Sov. Phys. JETP **29**, 159 (1969)].
[23] L. L. Buishvili, M. D. Zviadadze, and G. R. Khutsishvili, Zh. Eksp. Teor. Fiz. **54**, 876 (1968) [Sov. Phys. JETP **27**, 469 (1968)].
[24] V. A. Atsarkin and V. V. Demidov, Zh. Eksp. Teor. Fiz. **76**, 2185 (1979) [Sov. Phys. JETP **49**, 1104 (1979)].

Translated by Dave Parsons