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BEHAVIOR OF A SYSTEM OF SPINS CLOSE IN FREQUENCY AND COUPLED BY CROSS RELAXATION

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The cross-relaxation tendency in a system of spins close in frequency is analyzed by means of kinetic equations for the spin temperatures. It is established that the quasiequilibrium with respect to the cross-relaxation interactions is described by the two temperatures of two energy reservoirs created by the cross-relaxation and similar to the Zeeman and spin-spin reservoirs in the case of identical spins. This confirms and explains the far-reaching similarity previously observed theoretically[2,4] and experimentally[6,7] in the magnetic resonance of systems of spins with close frequencies forming a group of lines or a single inhomogeneous line and systems of equivalent spins forming homogeneous lines. This analogy is extended to non-stationary processes by treating these on the basis of the idea of two reservoirs; this idea has been checked by separate direct calculations.

INTRODUCTION

THE theoretical[1-5] and experimental[6,7] work published in recent years on magnetic resonance in a system of spins that are close in frequency and coupled by cross relation indicates the deep analogy between such systems and an aggregate of identical spins forming a homogeneous magnetic resonance line.

The purpose of our article is to elucidate the origin and physical meaning of this analogy. In the spirit of[8,9], we shall consider for this the quasi-equilibrium with respect to the cross-relaxation interactions. Analyzing the nature and the trend of the cross-relaxation by means of kinetic equations for the spin temperatures, we attempt to determine the integrals of motion in this process and to trace the formation of the energy reservoirs similar to the Zeeman and spin-spin reservoirs in the case of identical spins. We shall also consider non-stationary processes, in order to show that the above analogy can be extended to them too.

1. DESCRIPTION BY MEANS OF TWO TEMPERATURES

Let the spin system under consideration be divided into n sorts of spins, close in frequency and corresponding to n magnetic resonance lines. Taking into account first-order cross-relaxation and assuming that a saturating field of frequency ν_p is applied, we write, starting from the theory of[8,9], the basis system of equations for the Zeeman temperatures T_i of the spins of each sort and for the temperature T_{ss} of the total spin-spin reservoir:

$$\frac{\partial}{\partial t}\frac{\nu_i}{T_i} = -p_i\left(\frac{\nu_i}{T_i}+\frac{\nu_p-\nu_i}{T_{ss}}\right)+\sum_{j\neq i}^{n}\frac{\tilde{N}_j}{\tilde{N}_{ij}}w_{ij}S_{ij} - \frac{1}{\tau_1^{(i)}}\left(\frac{\nu_i}{T_i}-\frac{\nu_i}{T_0}\right), \quad i=1,\ldots n; \tag{1}$$

$$\frac{\partial}{\partial t}\frac{1}{T_{ss}} = -\sum_{i}^{n}\frac{\tilde{N}_i}{\tilde{N}}\frac{\nu_p-\nu_i}{H_L^2}p_i\left(\frac{\nu_i}{T_i}+\frac{\nu_p-\nu_i}{T_{ss}}\right) + \sum_{i<j}^{n}\frac{\tilde{N}_i\tilde{N}_j}{\tilde{N}_{ij}\tilde{N}}\frac{\Delta_{ij}}{H_L^2}w_{ij}S_{ij} - \frac{1}{\tau_1'}\left(\frac{1}{T_{ss}}-\frac{1}{T_0}\right).$$

Here ν_i is the frequency of spins of sort i, $\Delta_{ij} = \nu_j - \nu_i$, H_L is the local field, expressed in frequency units,

$$S_{ij} = \left(\frac{\nu_j}{T_j}-\frac{\nu_i}{T_i}-\frac{\Delta_{ij}}{T_{ss}}\right)$$

is the "cross-relaxation stimulator," p_i is the transition probability under the action of the variable field on the line i, $w_{ij} = w_{ji}$ is the probability of cross-relaxtion between the lines i and j, $\tau_1^{(i)}$ and τ_1' are the spin-lattice relaxation times for the Zeeman and spin-spin reservoirs respectively, $\tilde{N}_i = \frac{1}{3}N_iI_i(I_i+1)$, where N_i and I_i are the number and magnitude of the particle-spins forming the line i, $\tilde{N}_{ij} = \tilde{N}_i + \tilde{N}_j$, $\tilde{N}$ is the sum of $\tilde{N}_i$ over all the particles having a common spin-spin reservoir (the number of sorts of spins is, clearly, $\geq n$) and T_0 is the lattice temperature; the amplitude H_1 of the variable field is assumed to be much smaller than H_L[8,9].

Solving the system (1) taken without the spin-lattice terms and the terms with the variable field introduces a new time-scale τ_{cr}, which, in order of magnitude, is the time for completion of the cross-relaxation, i.e., the time required for S_{ij} to go to zero for all i and j. Clearly, τ_{cr} is much greater than the spin-spin relaxation time τ_2, during which all the temperatures occurring in (1) are generated. We shall assume the cross-relaxation to be effective, i.e., to predominate over relaxation to the lattice. The detailed condition for this was given in[4] for the stationary solution of Eqs. (1) and here we shall simply assume that $\tau_{cr} \ll \tau_1^{(i)}, \tau_1'$. This means that we can make the assumption, accurate to within a time interval $\sim\tau_{cr}$, that the cross-relaxation tendency is realized, i.e., that "at each moment" all the $S_{ij} = 0$ and all the temperatures can differ from

T_0[1]. This, in its turn, means that for an arbitrary frequency ν the sum $(\nu_i/T_i + (\nu - \nu_i)/T_{ss})$ is independent of the frequency ν_i of the reference line. Then the power $P(\nu)$ absorbed in the display of an aggregate of n lines by a weak signal of frequency ν has the form

$$P(\nu)=\frac{h^2}{k}\nu\sum_i^n p_i(\nu)\left[\frac{\nu_i}{T_i}+\frac{\nu-\nu_i}{T_{ss}}\right] =\frac{h^2}{k}\nu p(\nu)\left[\frac{\nu_i}{T_i}+\frac{\nu-\nu_i}{T_{ss}}\right]. \quad (2)$$

Here $p(\nu) = \sum_i^n p_i(\nu) \propto g(\nu)$, where $g(\nu)$ is the form factor of our system of lines. From (2) follows a relation between the coefficients $K(\nu) = p(\nu)/P_0(\nu)$ at two arbitrary frequencies ν' and ν'', the same relation as that applying within the limits of a single homogeneous line[8,10]:

$$\frac{\nu' K(\nu')-\nu'' K(\nu'')}{T_0}=\frac{\nu'-\nu''}{T_{ss}}, \quad (3)$$

where $P_0(\nu) = h^2\nu^2 p(\nu)/kT_0$. If for an arbitrary frequency ν within the bounds of the original lines we introduce a "Zeeman temperature" $T(\nu)$, defining it in the natural way

$$\frac{\nu}{T(\nu)}=K(\nu)\frac{\nu}{T_0}=\frac{k}{h^2\nu}\frac{P(\nu)}{p(\nu)}=\frac{\nu_i}{T_i}+\frac{\nu-\nu_i}{T_{ss}}, \quad (4)$$

in (2) we can take the reference frequency ν_i to be arbitrary and, in particular, to be the frequency ν_0 of the "center of gravity" of our n lines:

$$\bar{N}^{(n)}\nu_0=\sum_i^n \bar{N}_i\nu_i,\quad \bar{N}^{(n)}=\sum_i^n \bar{N}_i;$$

in this latter case, (2) looks the same as the corresponding formula for a homogeneous line. Thus, magnetic resonance at spins of types close in frequency and coupled by cross-relaxation can, with the indicated degree of exactness, be described, as in the case of identical spins, by two temperatures—by a single temperature T_{ss} and by a Zeeman temperature $T(\nu)$ at arbitrary frequency, for example, at the frequency ν_0 of the center of gravity of their spectrum; the validity of this and, in particular, of the formulas (2) and (3) has also been shown experimentally[7].

2. THE TWO ENERGY RESERVOIRS CREATED BY CROSS-RELAXATION

In order to examine the behavior of the energies in "pure" cross-relaxation, we abbreviate (1) leaving on the right only the terms with S_{ij}. Comparing the first n equations and the last one, it is easily established that $\partial T_{ss}^{-1}/\partial t$ is equal to the expression

$$-\frac{\partial}{\partial t}\mathscr{L}=-\sum_{i<j}^n\frac{\bar{N}_i\bar{N}_j}{\bar{N}^{(n)}\bar{N}}\frac{\Delta_{ij}}{H_L^2}\frac{\partial}{\partial t}\left(\frac{\nu_j}{T_j}-\frac{\nu_i}{T_i}\right),$$

i.e., that the sum $\mathscr{L} + 1/T_{ss}$ is conserved in the cross-relaxation process. Denoting

$$\frac{1}{\Delta_{ij}}\left(\frac{\nu_j}{T_j}-\frac{\nu_i}{T_i}\right)=\xi_{ij}$$

and taking into account that the cross-relaxation tends to make all the ξ_{ij} equal to $1/T_{ss}$ and generate some new value $1/T_{ss}^{cr}$, we can write

$$\sum_{i<j}^n\frac{\bar{N}_i\bar{N}_j}{\bar{N}^{(n)}}\Delta_{ij}^2\xi_{ij}(\alpha)+\frac{\bar{N}H_L^2}{T_{ss}(\alpha)}=\text{const} =\frac{1}{T_{ss}^{cr}}\left\{\sum_{i<j}\frac{\bar{N}_i\bar{N}_j}{\bar{N}^{(n)}}\Delta_{ij}^2+\bar{N}H_L^2\right\}, \quad (5)$$

where on the left the argument α denotes an arbitrary state of our spin system when it is isolated from the lattice and from variable fields, while T_{ss}^{cr} on the right refers to the state of completed cross-relaxation. Since $h^2\tilde{N}H_L^2/k$ is the heat capacity c_{ss} of the spin-spin reservoir and $-c_{ss}/T_{ss}$ is its average energy E_{ss}, (5) describes the energy balance and the cross-relaxation can thus be interpreted as a process in which a certain "difference" energy

$$E_\Delta=-\frac{h^2}{k}\sum_{i<j}^n\frac{\bar{N}_i\bar{N}_j}{\bar{N}^{(n)}}\Delta_{ij}^2\xi_{ij}$$

is mixed with the spin-spin energy E_{ss} while their sum is conserved and is an integral of motion in the cross-relaxation, and in which as a result a new reservoir (we shall call it the joint low-frequency reservoir) with a quasi-continuous spectrum in the range $\sim H_L, \Delta_{ij}$, a single temperature T_{ss}^{cr}, a total heat capacity $c_{\Delta ss} = c_\Delta + c_{ss}$, and a total average energy $E_{\Delta ss} = E_\Delta + E_{ss} = -c_{\Delta ss}/T_{ss}^{cr}$, is created. Measuring from $\nu_0(\Delta i = \nu_i - \nu_0)$, we transform E_Δ and c_Δ. Then,

$$E_\Delta=-\frac{h^2}{k}\sum_i^n\bar{N}_i\frac{\Delta_i\nu_i}{T_i},\quad c_\Delta=\frac{h^2}{k}\sum_{i<j}^n\frac{\bar{N}_i\bar{N}_j}{\bar{N}^{(n)}}\Delta_{ij}^2=\frac{h^2}{k}\bar{N}^{(n)}M_2, \quad (6)$$

where

$$M_2=\frac{1}{\bar{N}^{(n)}}\sum_i^n\bar{N}_i\Delta_i^2$$

is the second moment of the lines under consideration about their center of gravity. We now go over to a system of coordinates rotating with frequency ν_0; the spins of sort i acquire there a Zeeman temperature $T_i^{(0)} = \Delta_i T_i/\nu_i$; then

$$E_\Delta=-\frac{h^2}{k}\sum_i^n\bar{N}_i\frac{\Delta_i^2}{T_i^{(0)}},$$

which is equal to the total Zeeman energy $E_Z^{(0)} = \sum_i^n E_{iz}^{(0)}$ of all the spins in the system of coordinates rotating with frequency ν_0. Thus, in accordance with (5), the balance of low-frequency energy in the cross-relaxation has the simple form:

$$E_\Delta(\alpha)+E_{ss}(\alpha)=E_z^{(0)}(\alpha)+E_{ss}(\alpha)=\text{const}=-c_{\Delta ss}/T_{ss}^{cr} \quad (7)$$

Finally, we shall indicate one more expression for E_Δ, by introducing the Zeeman temperature $T_j^{(i)} = T_j(\nu_j - \nu_i)/\nu_j$ of spins of sort j and the Zeeman energy $E_{(j)}^{(i)}$ of all the spins in the system of coordinates rotating with frequency ν_i; then

[1]To realize cross-relaxation at temperatures differing from T_0, it is sufficient that τ_{cr} be shorter than any n of the n + 1 spin-lattice times; the requirement $\tau_{cr} \ll \tau_1'$ is necessary in order that $|T_{ss}^{-1}| \gg T_0^{-1}$ be possible as a result of cross-relaxation. We note that the equalities $S_{ij} = 0$ and the formulas (2)–(4) are conserved in the presence of a saturating field (cf. Sec. 4 below).

$$\xi_{ij}=\frac{1}{T_i^{(i)}}+\frac{1}{T_j^{(i)}},\quad E_\Delta=\frac{1}{\tilde N^{(n)}}\sum_i^n \tilde N_i E_z^{(i)}.$$

We turn now to the remainder of the Zeeman energy $E_Z - E_\Delta$. We shall again consider the abbreviated Eqs. (1) for "pure" cross-relaxation. Comparing the first n equations with each other, we obtain

$$\frac{\partial}{\partial t}\sum_i^n \tilde N_i\frac{\nu_i}{T_i}=0,$$

i.e., I_Z, the component along the constant field of the total spin of the particles involved in the cross-relaxation, is conserved. By writing the relation (4) for all i, taking as ν the frequency ν_0 and summing, we obtain

$$\frac{k}{h^2}I_z(\alpha)=\sum_i^n \tilde N_i\frac{\nu_i}{T_i(\alpha)}=\text{const}=\tilde N^{(n)}\frac{\nu_0}{T^{cr}(\nu_0)}. \tag{8}$$

Since

$$E_z-E_\Delta=-\frac{h^2}{k}\sum_i^n \tilde N_i\frac{\nu_i^2}{T_i}-E_\Delta=-\frac{h^2}{k}\nu_0\sum_i^n \tilde N_i\frac{\nu_i}{T_i}=-\nu_0 I_z,$$

we have thereby distinguished, according to (8), one more energy, this time high-frequency, E_0, that is an integral of motion in the cross-relaxation:

$$\begin{aligned}E_0(\alpha)&=E_z(\alpha)-E_\Delta(\alpha)=-\nu_0 I_z(\alpha)=\text{const}\\&=-h^2k^{-1}\tilde N^{(n)}\nu_0^2/T^{cr}(\nu_0).\end{aligned} \tag{9}$$

We can interpret the relation (9) as the separating out, by the cross-relaxation, of some conserved part E_0 from the total Zeeman average energy E_Z and the formation of a reservoir (we shall call it the central reservoir) with frequency ν_0, temperature $T^{cr}(\nu_0)$, heat capacity $c_0 = h^2\tilde N^{(n)}\nu_0^2/k$ and, consequently, average energy $E_0 = -c_0/T^{cr}(\nu_0)$; naturally,

$$c_0+c_\Delta=c_z=\frac{h^2}{k}\sum_i^n \tilde N_i\nu_i^2.$$

Thus, the cross-relaxation coupling the n Zeeman reservoirs with each other and with the total spin-spin reservoir at constant total spin energy $E = E_Z + E_{SS}$, transforms them, irrespective of n, into two reservoirs: the central (high-frequency) and the joint low-frequency reservoirs with heat capacities c_0 and $c_{\Delta SS}$ and temperatures $T^{cr}(\nu_0)$ and T_{SS}^{cr} respectively. Such an interpretation is in agreement with the analysis of the cross-relaxation in $NaNO_3$ carried out in[11], and will be confirmed below in our treatment of the relaxation to the lattice and saturation: a direct calculation shows that in these processes our spin system does indeed behave as a system consisting of the two reservoirs, created in a time $\sim\tau_{cr}$. In this respect also, it is to a considerable extent analogous to a system of identical spins, in which the two reservoirs, the Zeeman (high-frequency) and the spin-spin (low-frequency), are formed much more rapidly, in a time $\sim\tau_2$. Also, by analogy with the density matrix ρ describing the quasi-equilibrium with respect to the spin-spin interactions between identical spins, we write the density matrix $\hat\rho_{cr}$ for the quasi-equilibrium with respect to the slower cross-relaxational interactions. The correct density matrix, in the linear approximation for the general case of spins of n sorts possessing a single spin-spin reservoir,[8,11]

$$\hat\rho\approx C\left[1-\sum_i^n\frac{\hat{\mathscr H}_z^{(i)}}{kT_i}-\frac{\hat{\mathscr H}_{ss}}{kT_{ss}}\right]$$

is transformed for the case of effective cross-relaxtion into

$$\hat\rho_{cr}\approx C_{cr}\left[1-\frac{\hat{\mathscr H}_0}{kT^{cr}(\nu_0)}-\frac{\hat{\mathscr H}_\Delta+\hat{\mathscr H}_{ss}}{kT_{ss}^{cr}}\right]\cdots, \tag{10}$$

where the Zeeman energy $\hat{\mathscr H}_Z^{(i)} = \nu_i\hat I_{iz}$, $\hat I_{iz}$ is the spin component along the constant field for particles of sort i, and $I_Z = \sum_i^n I_{iz}$; $\hat{\mathscr H}_0 = h\nu_0\hat I_Z$ and $\hat{\mathscr H}_\Delta = h\sum_i^n\Delta_i\hat I_{iz}$ are respectively the energies of the central and joint low-frequency reservoirs, and $\hat{\mathscr H}_{SS}$ is the spin-spin energy. It is easily checked that the requirement $E = \mathrm{Tr}(\hat\rho_{cr}\hat{\mathscr H})$ is fulfilled for the average energies E_0, E_Δ and E_{SS}.

We note that (10) is essentially the same as formula (21) of[2] in which an inhomogeneously broadened line that clearly does not consist of homogeneous parts is considered. This agreement, despite the difference in the approaches, is not surprising: we should naturally expect that in a spin system with a certain spread of resonance frequencies the spin-spin interactions should lead to analogous results irrespective of the possibility of separating the spins into equivalent groups ("packets") and thereby introducing two markedly different time-scales τ_2 and τ_{cr}.

3. SPIN-LATTICE RELAXATION

By means of the concept of reservoirs created by the cross-relaxation, it is not difficult to establish the nature of the relaxation of our spin system to the lattice. Let $\tau_1^{(i)} = \tau_1^{(j)} = \tau_1$, i, j = 1, . . . , n. Since the joint low-frequency reservoir consists of two reservoirs, the difference and spin-spin reservoirs, with heat capacities c_Δ and c_{SS} respectively, such that the first of these would relax independently to the lattice with a rate τ_1^{-1}, and the second with a rate $\tau_1'^{-1}$, the required rate $\tau_1''^{-1}$ for the joint reservoir is obtained by simple averaging:

$$\tau_1''^{-1}=\frac{c_\Delta\tau_1^{-1}+c_{ss}\tau_1'^{-1}}{c_\Delta+c_{ss}}. \tag{11}$$

This result is confirmed by direct solution of the system of n equations for T_{SS}^{-1} and the n − 1 independent differences ξ_{ij}.

Since n − 1 of the n roots of the corresponding characteristic equation $f(\lambda) = 0$ necessarily describe the cross-relaxation, we can seek the relatively small rate λ_1 of relaxation to the lattice by means of an expansion of $f(\lambda)$ in the vicinity of zero; the condition for effective cross-relaxation, as in the calculation of the stationary saturation[4], also requires that the leading terms in $\omega_{ij}\tau_1^{(j)}\tilde N_i/\tilde N_{ij}$ predominate over the sum of all the remaining terms. With these assumptions, formula (11) is obtained for $\lambda_1\equiv\tau_1''^{-1}$. As regards the central reservoir, by expressing the time derivative of $\nu_0/T^{cr}(\nu_0)$ in terms of $\partial\nu_i T_i^{-1}/\partial t$ for all i in accordance with[8] and using the first n equations of the system (1) without the variable field, we obtain

$$\frac{\partial}{\partial t}\frac{1}{T^{cr}(\nu_0)}=-\frac{1}{\tau_1}\left[\frac{1}{T^{cr}(\nu_0)}-\frac{1}{T_0}\right]$$

and the same equation, naturally, for the energy E_0. This result is also confirmed by a direct calculation: the characteristic equation for the system (1) without the variable field has, along with λ_1, a second small root $\lambda_0 = \tau_1^{-1}$.

Thus, for $\tau_1^{(i)} = \tau_1^{(j)} = \tau_1$, each of the two reservoirs, the central and joint low-frequency, relaxes to the lattice like a single exponential with times τ_1 and τ_1'' respectively, and the relaxation strongly resembles the case of identical spins: as in the latter, the resonance absorption signal $p(\nu)$, according to[2], recovers its equilibrium value as the sum of two exponential parts $p(\nu)\nu_0/T^{cr}(\nu_0)$ and $p(\nu)(\nu - \nu_0)/T_{ss}^{st}$, which for symmetric $p(\nu)$ will be symmetric and antisymmetric respectively, as in the case of a homogeneous line; the second part usually attains equilibrium (i.e., practically disappears) earlier since, according to (11), $\tau_1'' < \tau_1$ because $\tau_1' < \tau_1$ (incidentally, in this case $\tau_1'' > \tau_1'$). In the case of different $\tau_1^{(i)}$, the two reservoirs each relax to the lattice like two exponentials, and the similarity to the relaxation of a homogeneous line is to some extent impaired.

4. BEHAVIOR OF THE SYSTEM UNDER SATURATION CONDITIONS

Now let a field be applied at frequency ν_p, saturating at least one of the n lines. We shall start with the case when the coupling with the lattice does not have time to develop during the course of the saturation and cross-relaxation processes. Comparing Eqs. (1) with each other, without the spin-lattice terms, we obtain an integral of motion of the form

$$-\frac{h^2}{k}\sum_i^n \tilde{N}_i \frac{\nu_i(\nu_p - \nu_i)}{T_i(\alpha)} + E_{ss}(\alpha) = E_z^{(p)}(\alpha) + E_{ss}(\alpha) = \text{const}, \quad (12)$$

where

$$E_z^{(p)} = -\frac{h^2}{k}\sum \tilde{N}_i \frac{(\nu_p - \nu_i)^2}{T_i^{(p)}}$$

is the Zeeman energy of all the spins in a system of coordinates rotating with frequency ν_p, $T_i^{(p)}$ is the Zeeman temperature of spins of sort i in the same coordinates, and the argument α denotes an arbitrary state of our spin system when it is isolated from the lattice. Thus, for the combined process of saturation of at least one line and general cross-relaxation, the energy balance is of the same time as that for simultaneous direct saturation of all n lines at the frequency ν_p, because of their overlap: this is simply thermal mixing in the system of coordinates rotating with frequency ν_p. Since $E_Z^{(p)} = E_Z^{(0)} + \Delta_p I_z$, where $\Delta_p = \nu_p - \nu_0$, taking (7) into account, it is clear, for example, that saturation exactly at the center of gravity adds nothing to the low-frequency balance during cross-relaxation: such saturation has no effect on T_{ss}, as in the case of saturation exactly at the center of a homogeneous line. The result of the combined saturation and cross-relaxation process can be derived from (12), if we take into account that saturation of spins of sort i has a tendency to give $T_i^{(p)} = T_{ss}$[12], while cross-relaxation tends to give $s_{ij} = 0$ for all i, j. Since

$$s_{ij} = (\nu_p - \nu_i)\left[\frac{1}{T_i^{(p)}} - \frac{1}{T_{ss}}\right] - (\nu_p - \nu_j)\left[\frac{1}{T_j^{(p)}} - \frac{1}{T_{ss}}\right]$$

cross-relaxation taken separately implies the equalization of all values of $(\nu_p - \nu_i)[1/T_i^{(p)} - 1/T_{ss}]$ (degrees of "unsaturation"), while combined with the saturation of at least one sort of spin, it leads to the equalization of all the $T_i^{(p)}$ and T_{ss}. An important point is that, as in any thermal mixing, the result of the combined saturation and cross-relaxation does not depend on the rate of these two processes taken separately, i.e., on the quantity $\sim(\max p_i)\tau_{cr}$[2)]. Therefore, we are always justified in imagining the cross-relaxation to be completed first, before the saturation; it will then look as if the combined process were one in which the two reservoirs, with heat capacities c_0 and $c_{\Delta ss}$ and created by the cross-relaxation, were subjected to saturation. Thus, irrespective of the actual value of $(\max p_i)\tau_{cr}$, we obtain the quantity T_{ss} after the completion of both processes by substituting into (12) the energy $-(c_Z^{(p)} + c_{ss})/T_{ss}$ resulting from the mixing:

$$\frac{1}{T_{ss}} = \left[\sum_i^n \tilde{N}_i \frac{(\nu_i - \nu_p)\nu_i}{T_i(\alpha)} + \tilde{N}H_L^2 \frac{1}{T_{ss}(\alpha)}\right] \times \left[\sum_i^n \tilde{N}_i(\nu_i - \nu_p)^2 + \tilde{N}H_L^2\right]^{-1} = \left[-\frac{\nu_0}{\Delta_p}\frac{c_0^{(p)}}{T^{cr}(\nu_0)} + \frac{c_{\Delta ss}}{T_{ss}^{cr}}\right](c_0^{(p)} + c_{\Delta ss})^{-1}, \quad (13)$$

where T_{ss}^{cr} and $T^{cr}(\nu_0)$ are determined from (5) and (8). In particular, if the initial state is equilibrium with the lattice $(T_i(\alpha) = T_{ss}(\alpha) = T_0,\ i = 1, \ldots, n)$, then it follows from (13) that

$$\frac{T_0}{T_{ss}} = \frac{-\nu_0 c_0^{(p)}/\Delta_p + c_{\Delta ss}}{c_0^{(p)} + c_{\Delta ss}} = -\frac{\tilde{N}^{(n)}(\Delta_p\nu_0 - M_2) - \tilde{N}H_L^2}{\tilde{N}^{(n)}(\Delta_p^2 + M_2) + \tilde{N}H_L^2} \approx -\frac{\tilde{N}^{(n)}\Delta_p\nu_0}{\tilde{N}^{(n)}(\Delta_p^2 + M_2) + \tilde{N}H_L^2} \quad (14)$$

The dependence of T_{ss} on Δ_p from (14) is of the same type as the dependence on the detuning in the saturation of a homogeneous line; the shape $P(\nu)$ of the signal displaying a group of our lines, as given by (2)—(4), is also the same as for a homogeneous line: on one side of the center of gravity, beyond the saturation point, all the lines are found to be inverted (this has already been discovered experimentally[6,7]), while on the other side, starting from a well-defined line, the absorption signal is greater than the equilibrium signal. An essential point is that the detunings of the saturating field are now reckoned from the center of gravity of the whole aggregate and are not bounded by the width of an individual line; thus the increase of $|T_{ss}^{-1}|$ and all the consequences of this are usually found to be of no lesser order than in the saturation of a single homogeneous line of the same shape as our aggregate. The quantity $|T_{ss}^{-1}|$ attains a maximum when

$$|\Delta_p| = |\Delta_p^*| = \left(M_2 + \frac{\tilde{N}}{\tilde{N}^{(n)}}H_L^2\right)^{1/2}$$

and $|T_{ss}^{-1}|^{\max} = \nu_0/2|\Delta_p^*|$. An increase of $|T_{ss}^{-1}|$ twice as large is obtained in the analog of adiabatic demagnetization in the rotating frame (isentropic passage

2) We recall that we have $H_1 \ll H_L$ even for $(\max p_i)\tau_{cr} \gg 1$, i.e., the energy of the variable fields does not take part in the heat balance, but is only a medium facilitating the mixing. It is in this that the difference from the case of identical spins at $H_1 \gtrsim H_L$ lies.

of the saturating field from the far wing of the line to its center), but now the scanning, starting from a "wing" of the aggregate of lines, must terminate at its center and must, while outstripping the relaxation to the lattice, proceed slowly enough for both the saturation and the cross-relaxation to have time to be completed at each moment, i.e., for a single temperature to be established in the system of coordinates rotating with frequency ν_p.

We shall now take into account the relaxation to the lattice and obtain the stationary solution of the complete Eqs. (1). We shall start from the fact that the total energy flux R passing out to the lattice from the single reservoir formed by thermal mixing in the system of coordinates rotating with frequency ν_p is equal to zero in the stationary regime; the temperature of this reservoir is $T^{(p)} = T_{ss}^{(p)} = T_{ss}$, and it consists of two parts with heat capacities $c_0^{(p)}$ and $c_{\Delta ss}$ and spin-lattice times τ_1 and τ_1'' (we take $\tau_1^{(i)} = \tau_1^{(j)}$) respectively, Since

$$R = \sum_{\beta} \eta_\beta \left[\frac{1}{T^{(p)}} - \frac{1}{T_{0\beta}^{(p)}} \right],$$

where the sum is taken over the parts of the reservoir, i.e., over the coupling channels with the lattice (we have $\beta = 1, 2$), $T_{0\beta}^{(p)}$ is the lattice temperature for the part β in the frame rotating with frequency ν_p and the thermal conductivity η_β of channel β is $c_\beta^{(p)} \tau_{1\beta}^{-1}$, from $R = 0$ we obtain the stationary value $T^{(p)} = T_{ss}$:

$$T_{ss}^{-1} = \frac{c_0^{(p)} \tau_1^{-1} / T_0^{(p)} + c_{\Delta ss} \tau_1''^{-1} / T_0}{c_0^{(p)} \tau_1^{-1} + c_{\Delta ss} \tau_1''^{-1}} = -\frac{1}{T_0} \frac{\tilde{N}^{(n)} (\Delta_p \nu_0 - M_2) \tau_1^{-1} - \tilde{N} H_L^2 \tau_1'^{-1}}{\tilde{N}^{(n)} (\Delta_p^2 + M_2) \tau_1^{-1} + \tilde{N} H_L^2 \tau_1'^{-1}}; \qquad (15)$$

The simplification for large $|\Delta_p| \nu_0$ is obvious.

Formula (15) was obtained previously by a direct calculation[4], and this confirms once more the concept of the reservoirs created by the cross-relaxation, and all the consequences of this. It is clear that (15) gives the same dependence $T_{ss}(\Delta_p)$ and the same signal shape $P(\nu)$ as (14); however, as in the case of a homogeneous line, the stationary growth of $|T_{ss}^{-1}|$ is somewhat smaller than for isolation from the lattice, since usually $\tau_1' < \tau_1$. From (15) one can, obviously, obtain (14) by putting $\tau_1' = \tau_1$. It is clear also that the effects predicted[13] by means of a direct calculation of the combined action of cross-relaxation between two lines and saturation in the "wing" of one of them, in particular the limitation on the transfer of the saturation to a second line and even the "cooling" of this line, follow from (14) or (15) together with (2)–(4). Finally, by simple averaging over the two parts of the reservoir formed by thermal mixing in the system of coordinates rotating with frequency ν_p, we can obtain the rate θ^{-1} of the exponential relaxation to the lattice of the single temperature $T^{(p)} = T_{ss}$ of this reservoir (i.e., the rate at which the stationary solution (15) is established, starting from (14)):

$$\theta^{-1} = \frac{c_0^{(p)} \tau_1^{-1} + c_{\Delta ss} \tau_1''^{-1}}{c_0^{(p)} + c_{\Delta ss}} = \frac{\tilde{N}^{(n)} (\Delta_p^2 + M_2) \tau_1^{-1} + \tilde{N} H_L^2 \tau_1'^{-1}}{\tilde{N}^{(n)} (\Delta_p^2 + M_2) + \tilde{N} H_L^2}.$$

CONCLUSION

An analysis of the quasi-equilibrium with respect to the cross-relaxational interactions in a system of sorts of spins close in frequency has led to the concept of two energy reservoirs, created by the cross-relaxation and analogous to the Zeeman and spin-spin reservoirs in the case of identical spins. The treatment of magnetic-resonance saturation and spin-lattice relaxtion on the basis of this idea is in agreement both with separate direct calculations performed as a check or previously[4], and with experiments on EPR in crystals[6,7], confirming and explaining the observed similarity in the magnetic resonance of a system of identical spins forming a homogeneous line and of a system of spins, close in frequency, forming an aggregate of individual homogeneous lines or one inhomogeneous line. It is possibly true that an inhomogeneous line does not always consist of homogeneous parts[2] and, when there is cross-relaxation in it, it is not always possible to guarantee the fulfilment of the condition $\tau_2 \ll \tau_{cr}$ assumed in Eqs. (1). However, in this case, it can, evidently, be considered to be intermediate between a single homogeneous line and a group of lines spanned by cross-relaxation.

Moreover, it is natural to assume, taking into account paper[2] also, that in an arbitrary system of spins with close frequencies, the quasi-equilibrium with respect to the spin-spin interactions can always be described by two temperatures of two reservoirs, similar to those obtained above. All systems of spins with nearby frequencies in which the spin-spin interactions are effective (i.e., predominate over the spin-lattice interactions) are thereby linked up with a system of identical spins, and therefore quasi-equilibrium between these systems is realized. In magnetic resonance they all behave analogously, differing only in the time required to establish the quasi-equilibrium and the character of this process: there is either a single-step process in a time $\sim\tau_2$ between identical spins, or a two-step process in a time $\sim\tau_{cr} \gg \tau_2$ between sorts of spins close in frequency, or more complicated cases. The magnetic-resonance lines formed by such systems may be called quasi-homogeneous, whereas in the opposite case of ineffective spin-spin interactions, when quasi-equilibrium between them is not established because of the interaction with the lattice, the lines are essentially inhomogeneous and consist of independent parts. The experimentally investigated EPR lines of[6,14], which are clearly inhomogeneous in the traditional classification, must now, along with the systems of separate lines coupled by effective cross-relaxation[7], be considered to be quasi-homogeneous, and the fact that it has been possible to interpret[14] a number of experiments on them by means of the theory of homogeneous broadening need not seem surprising. We remark, finally, that all the results obtained are easily generalized to the case of cross-relaxation in a system of EPR lines when the electron spin-spin reservoir is strongly coupled to the nuclear Zeeman reservoir[14,15].

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84