# Cross relaxation in weak magnetic fields at ultralow spin temperatures

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The cross relaxation between two kinds of spins caused by the part of the nonsecular dipole-dipole interaction that produces single spin flips (flip-stops) has been theoretically investigated at ultralow spin temperatures (less than the nuclear Zeeman energies). It has been shown that such cross relaxation (which has a fairly high probability in weak constant magnetic fields) results in thermal mixing of the averaged Zeeman subsystem with the local-field reservoir. The rate of cross relaxation by means of flip-stops increases with increasing initial polarizations of the spins, in agreement with experimental data.

Cross relaxation has been investigated in spin systems for several decades, but new aspects of this problem have recently become evident. Before proceeding to them, let us recount the essence of the phenomenon. Let there be two kinds of spins with slightly differing Larmor frequencies $\omega_a$ and $\omega_b$. The corresponding Zeeman Hamiltonians are $\mathscr{H}_a = -\omega_a I_a^z$ and $\mathscr{H}_b = -\omega_b I_b^z$. (Here and in the following we set $\hbar = k_B = 1$.)

We consider the hierarchy of times in this spin system. Flip-flops of identical spins, which are caused by the secular parts of the dipole-dipole ($dd$) interaction of the forms $B_{ij} I_{ai}^{\pm} I_{aj}^{\mp}$ and $B_{ij} I_{bi}^{\pm} I_{bj}^{\mp}$, conserve the Zeeman energies; therefore, they cause a very rapid process characterized by the spin-spin relaxation time $T_2$. This process results in the establishment of internal equilibrium in the partial Zeeman subsystems. Flip-flops of spins with different frequencies, which are caused by the nonsecular part of the $dd$ interaction of the form $B_{ij} I_{ai}^{\pm} I_{bj}^{\mp}$, take place without exact conservation of the Zeeman energies; therefore, the inverse probability of such a process (if it is still more rapid than spin-lattice relaxation) will be greater than $T_2$. This process was termed cross relaxation,[1,2] and it was assumed that it results in the establishment of thermal equilibrium between Zeeman subsystems $\mathscr{H}_a$ and $\mathscr{H}_b$, which, as we know from thermodynamics, marks the establishment of a single temperature for them. This is actually the case if the difference $|\omega_a - \omega_b|$ is far smaller than the magnetic resonance linewidths of the spins under consideration. However, there is interest in the case in which the difference between the frequencies of the spins is of the order of this width or exceeds it. Then spin flip-flops can occur only if the difference $|\omega_a - \omega_b|$ enters a third subsystem or comes from one. As Provotorov[3] showed, such a subsystem is a reservoir of secular spin-spin interactions, which, like partial Zeeman subsystems, forms within a time of order $T_2$. Due to the participation of the third subsystem in the cross-relaxation process, it no longer results in the establishment of a common temperature for the two Zeeman subsystems. If the cross-relaxation time $T_{x2}$ is far smaller than the spin-lattice relaxation time, then, as was shown in Refs. 4 and 5, cross relaxation will result in the establishment of internal equilibrium in two spin subsystems, one of which is an averaged Zeeman subsystem with the Hamiltonian

$$\mathscr{H}_z = \bar{\omega}(I_a^z + I_b^z), \tag{1}$$

where $\bar{\omega} = x_a \omega_a + x_b \omega_b$ is the frequency of the center of gravity of the spectrum, $x_a$ and $x_b$ are the relative concentrations of the two kinds of spins, and $x_a + x_b = 1$. The second subsystem formed, which is called the local-field reservoir (LFR),[4] consists of the secular spin-spin interactions $\mathscr{H}'_{ss}$ and so-called "difference subsystems,"[5] which are caused by the difference between the partial frequencies of the spins and the frequency of the center of gravity of the spectrum. The corresponding Hamiltonian has the form

$$\begin{aligned} \mathscr{H}_{LF} &= \mathscr{H}'_{ss} + \mathscr{H}_\Delta, \\ \mathscr{H}_\Delta &= -(\omega_a - \bar{\omega}) I_a^z - (\omega_b - \bar{\omega}) I_b^z \\ &= -(\omega_a - \omega_b)(x_b I_a^z - x_a I_b^z). \end{aligned} \tag{2}$$

The results of Provotorov's theory and the work in Refs. 4 and 5 have been repeatedly confirmed by experiment.[6]

However, a recent investigation[7] of cross relaxation at submicrokelvin spin temperatures and weak constant magnetic fields [several times higher than $(\bar{\gamma} T_2)^{-1}$] showed that a cross-relaxation process equalizing the temperatures of the two Zeeman subsystems takes place under these conditions.

In the experiment in Ref. 7 cross relaxation was studied by observing the evolution of two NMR lines corresponding to the two silver isotopes present in metallic silver, $^{107}$Ag and $^{109}$Ag. The experiment was performed in the following manner. The Zeeman subsystems of the $^{107}$Ag and $^{109}$Ag nuclei were first cooled by adiabatic demagnetization in the laboratory coordinate system to a very low temperature (100–200 nK). Then the $^{109}$Ag Zeeman subsystem was heated by applying an almost saturating variable field with its frequency. (The time of this operation will henceforth be called the initial moment in time.) Then the variable field was removed, and the strength of the constant field was lowered to a value several times greater than $(\bar{\gamma} T_2)^{-1}$. After the sample had been in the weak constant field for a time considerably shorter than the spin-lattice relaxation time, the strength of the constant field was increased, and the intensities of the two NMR lines were compared with the pattern observed at the initial moment in time. It was found that the evolution of the spin system in the weak constant field resulted in the establishment of thermal equilibrium corresponding to a single temperature between the two Zeeman subsystems. This temperature was higher than the initial temperature of the $^{107}$Ag spins and lower than the initial temperature of the $^{109}$Ag spins. Since an interaction with the lattice could not yet become apparent and since the sample was in the weak field for a time far greater than the time of ordinary cross relaxation by flip-flops, it should be expected that the spins evolved under the action of the nonsecular part of the *dd* interaction, which produces transitions that are less probable than flip-flops.

Oja, Annila, and Takano[7] were able to attribute the observed behavior of the nuclear spins to cross relaxation caused by a part of the nonsecular *dd* interaction of the form $C_{ij}I^z_{ai}I^{\pm}_{bj}$, which produces single spin flips (flip-stops). Such processes in weak fields have a fairly high probability. The computed dependence[7] of the time of cross relaxation by means of flip-stops $\tau_x$ on the strength of the constant magnetic field in which the cross-relaxation process took place was consistent with the experimental data. However the observed dependence of $\tau_x$ on the initial partial polarizations of the spins was not explained, since the expression for $\tau_x$ used for the machine calculation was suitable only in the high-temperature approximation. Therefore, it would be interesting to investigate the dynamics of the cross-relaxation process just described by performing calculations without restrictions on the Zeeman temperatures. Departure from the high-temperature, i.e., linear, approximation should make it possible to account for the dependence of $\tau_x$ on the initial polarizations of the spins.

Following Ref. 7, we start out with the Hamiltonians

$$\mathscr{H}=\mathscr{H}_0+\mathscr{H}', \quad \mathscr{H}_0=\mathscr{H}_z+\mathscr{H}_{LF},$$

$$\mathscr{H}_{LF}=\mathscr{H}^*_{RK}+\mathscr{H}_\Delta,$$

where $\mathscr{H}_z$ and $\mathscr{H}_\Delta$ are defined by expressions (1) and (2). The role of the secular spin-spin interactions in the case of metallic silver is played by the redefined Ruderman–Kittel interaction $\mathscr{H}^*_{RK}$ (see below). (According to the data in Ref. 7, the secular part of the *dd* interaction is characterized by a far smaller heat capacity than $\mathscr{H}^*_{RK}$ and $\mathscr{H}_\Delta$; therefore, its contribution to $\mathscr{H}_{LF}$ can be neglected). "Slow" cross relaxation by means of flip-stops is governed by the Hamiltonian

$$\mathscr{H}'=\mathscr{H}_{CR}=\frac{1}{2}\sum_{i,j}\{C_{ij}(I^+_{ai}I^z_{bj}+I^+_{bi}I^z_{aj})$$
$$+\text{binding energy}\}.$$

The initial conditions for "slow" cross relaxation are set by the two unequal temperatures $\beta_z^{-1}$ and $\beta_{LF}^{-1}$ (the averaged Zeeman subsystem is heated, and the reservoir $\mathscr{H}_{LF}$ is "cooled" by saturating one of the NMR lines, i.e., by saturating the averaged Zeeman subsystem with detuning relative to the center of gravity of the NMR spectrum[8,9]). Then $\beta_a^{-1}$ and $\beta_b^{-1}$, which correspond to the partial Zeeman subsystems with $\mathscr{H}_a$ and $\mathscr{H}_b$, are also not equal to one another.

Let us examine the processes occurring in weak fields. The two NMR lines completely or partially overlap in such fields, and the decisive role in $\mathscr{H}_{LF}$ is played by the Ruderman-Kittel interaction

$$\mathscr{H}_{RK}=\sum_{i<j}J_{ij}\mathbf{I}_i\mathbf{I}_j,$$

therefore, we assume that $\mathscr{H}_{LF}\approx\mathscr{H}_{RK}$. Since we are dealing with ultralow spin temperatures that are smaller than the nuclear Zeeman frequencies, we redefine $\mathscr{H}_z$ and $\mathscr{H}_{RK}$ by analogy to Ref. 10 by eliminating the part corresponding to the low-temperature shift of the resonant frequencies of the spins from $\mathscr{H}_{RK}$ and adding it to $\mathscr{H}_z$. The purpose of this operation is to separate the part corresponding to uniform precession from $\mathscr{H}_{RK}$ and to leave only the dynamic part responsible for the short scale of $T_2$. (We note that $\mathscr{H}_{RK}$ includes the interactions of both identical and non-identical spins and that the interaction of the latter causes spin-spin relaxation.) The redefined Hamiltonian $\mathscr{H}_{RK}$ takes the form

$$\mathscr{H}^*_{RK}=\frac{1}{2}\sum_{\substack{i,j\\(i\neq j)}}\left(J_{ij}-N_I^{-1}\sum_{j'}J_{ij'}\right)\mathbf{I}_i\mathbf{I}_j, \tag{3}$$

where $N_I$ is the total number of nuclear spins. Addition of the term related to the frequency shift to $\mathscr{H}_z$ does not perceptibly alter the mean Zeeman frequency; therefore, we neglect it.

Since the nuclear spins were in an unordered state in the situation described in Ref. 7, the mean energy $\mathscr{H}^*_{RK}$ can be calculated in the high-temperature approximation with respect to $\beta_{LF}^{-1}$. Then we have

$$\overline{\mathscr{H}^*_{RK}}=-\frac{N_I}{4}\,\omega^{*2}_{RK}\beta_{LF},$$

where

$$\omega^{*2}_{RK}=\frac{(1-p^2)(3-p^2)}{2}\,zJ^2, \quad p=\tanh\frac{\bar{\omega}\beta_z}{2},$$

and $z$ is the number of nearest-neighbor nuclear spins. It is assumed here that $I_a=I_b=1/2$, which corresponds to the case of the $^{107}$Ag and $^{109}$Ag nuclei, and it has been taken into account that only nearest-neighbor nuclear spins characterized by identical interaction constants $J_{ij}=J$ contribute to the sums.

The equations describing the evolution of $\beta_z$ and $\beta_{LF}$ under the action of the perturbation $\mathscr{H}_{CR}$, which were derived with the aid of the Zubarev nonequilibrium statistical operator,[11] have the form

$$\frac{d\beta_z}{dt}=-\frac{W_{CR}(\bar{\omega})}{\bar{\omega}(1-p^2)}\tanh\frac{\bar{\omega}(\beta_z-\beta_{LF})}{2},$$

$$\frac{d\beta_{LF}}{dt}=\frac{\bar{\omega}W_{CR}(\bar{\omega})}{\omega^{*2}_{RK}}\tanh\frac{\bar{\omega}(\beta_z-\beta_{LF})}{2}, \tag{4}$$

where

$$W_{CR}(\bar{\omega})=\frac{\pi}{N_I}\sum_{i,j}|C_{ij}|^2\varphi_i(\bar{\omega}),$$

and $\varphi_i(\bar{\omega})$ is the Fourier transform of the correlation function

$$\varphi_i(t)=\frac{\langle I_i^+(t)I_i^-\rangle+\langle I_i^-I_i^+(t)\rangle}{\langle I_i^+I_i^-\rangle+\langle I_i^-I_i^+\rangle}\,. \tag{5}$$

The time dependence in (5) is caused by $\mathscr{H}_{RK}^*$. We note that the first moment of $\varphi_i(\bar{\omega})$ is equal to zero, whence it can be seen that $\mathscr{H}_{RK}^*$ does not contain a term corresponding to the uniform precession.

To monitor the results of "slow" cross relaxation, the spin system was periodically returned adiabatically to a fairly strong constant field, in which the individual NMR lines were resolved, and the equalization of the polarizations of the individual kinds of spins could be conveniently traced.[1)]

Since a dependence of the "slow" cross-relaxation time on the initial conditions in the "strong" field was discovered experimentally, we assume that the partial polarizations of the isotopes $p_a$ and $p_b$ deviate slightly from their initial values $p_{a0}$ and $p_{b0}$, and take into account that the values of the polarizations do not vary during adiabatic variation of the field. Therefore, in Eqs. (4) we replace $p$ by $p_0$, where $p_0=x_ap_{a0}+x_bp_{b0}$. Writing the result in the form of a single equation, we obtain

$$\frac{d}{dt}\left\{\frac{\bar{\omega}(\beta_z-\beta_{LF})}{2}\right\}=-\frac{1}{2(1-p_0^2)}\left\{1+\frac{2\bar{\omega}^2}{zJ^2(3-p_0^2)}\right\}$$

$$\times\tanh\frac{\bar{\omega}(\beta_z-\beta_{LF})}{2}\,W_{CR}(\bar{\omega}),$$

which gives the evolution of $\beta_z$ and $\beta_{LF}$ during "slow" cross relaxation in the form

$$\sinh\left|\frac{\bar{\omega}(\beta_z-\beta_{LF})}{2}\right|=\text{const}\,\exp\left(-\frac{t}{\tau_x}\right). \tag{6}$$

Thus, cross relaxation in a weak field is confined to thermal mixing of the averaged Zeeman subsystem with the reservoir of spin-spin interactions in a characteristic time $\tau_x$. In writing the expression for $\tau_x$ we assume that $\varphi_i(\bar{\omega})$ has a Gaussian form (which is in good agreement with the experiment in Ref. 7) and plug the second moment of this function

$$M_{2i}=\frac{2-p^2}{4}\,zJ^2,$$

which was calculated with the aid of (3), into $\varphi_i(\bar{\omega})$. Then for $\tau_x^{-1}$ we obtain

$$\tau_x^{-1}=\sqrt{\frac{\pi}{2}}\,\frac{1}{(1-p_0^2)\sqrt{(2-p_0^2)zJ^2}}\left\{1+\frac{2\bar{\omega}^2}{zJ^2(3-p_0^2)}\right\}$$

$$\times\frac{1}{N_I}\sum_{i,j}|C_{ij}|^2\exp\left\{-\frac{2\bar{\omega}^2}{zJ^2(2-p_0^2)}\right\}. \tag{7}$$

The value of $\tau_x^{-1}$ characterizes the rate of establishment of complete equilibrium within the spin system in a weak field. This equilibrium signifies, in particular, equalization of the partial Zeeman temperatures $\beta_a^{-1}$ and $\beta_b^{-1}$. Thus, cross relaxation by means of flip-stops results in the establishment of thermal equilibrium between two Zeeman subsystems, i.e., the result of its action is as if the early theories of cross relaxation were correct (of course, it should not be forgotten that the cross relaxation described above is effective only in weak fields). Complete equilibrium is maintained in the spin system as the field increases adiabatically, since the increasing difference terms rapidly bring about equilibrium with $\mathscr{H}_{RK}^*$ with the aid of ordinary cross relaxation by means of flip-flops. The partial polarizations of two kinds of spins with similar frequencies will also be equal in a spin system at equilibrium in a "strong" field. Therefore, $\tau_x^{-1}$ also characterizes the rate of equalization of the partial polarizations. It is seen from (7) that in a sufficiently weak field $\tau_x^{-1}$ increases with increasing $p_0$, and the ratio $\tau_x$(low $p_0$)/$\tau_x$(high $p_0$) increases with increasing strength of the weak field, as was observed experimentally.

Thus, consideration of the nonlinearity associated with rejection of the high-temperature approximation when the polarizations deviate slightly from their initial values makes it possible to explain the dependence of $\tau_x$ on the initial conditions.

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[1)] We note that equal intensities of the NMR lines do not correspond to equal polarizations and equal relative concentrations of the isotopes in the present case (such behavior was explained in Refs. 12 and 13). Therefore, the criterion for equalization of the polarizations in Ref. 7 is the degree of similarity between the relative intensities of the absorption lines and the pattern observed when all the spins are in equilibrium with one another.

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[1] A. Abragam and W. G. Proctor, Phys. Rev. **109**, 1441 (1958).

[2] N. Bloembergen, S. Shapiro, P. S. Perschan, and J. O. Artman, Phys. Rev. **114**, 445 (1959).

[3] B. N. Provotorov, Zh. Eksp. Teor. Fiz. **42**, 882 (1962) [Sov. Phys. JETP **15**, 611 (1962)].

[4] S. Clough and C. A. Scott, J. Phys. C **1**, 919 (1968).

[5] M. I. Rodak, Zh. Eksp. Teor. Fiz. **61**, 832 (1971) [Sov. Phys. JETP **34**, 443 (1972)].

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

[7] A. S. Oja, A. J. Annila and Y. Takano, Phys. Rev. Lett. **65**, 1921 (1990).

[8] B. N. Provotorov, Zh. Eksp. Teor. Fiz., **41**, 1582 (1961) [Sov. Phys. JETP **14**, 1126 (1962)].

[9] V. A. Atsarkin and M. I. Rodak, Usp. Fiz. Nauk **107**, 3 (1972) [Sov. Phys. Usp. **15**, 251 (1972)].

[10] L. L. Buishvili and N. P. Fokina, Fiz. Tverd. Tela (Leningrad) **33**, 1865 (1991) [Sov. Phys. Solid State **33**, 1048 (1991)].

[11] D. N. Zubarev, *Nonequilibrium Statistical Thermodynamics*, Consultants Bureau, New York (1974), Chap. 4.

[12] J. P. Ekström, J. F. Jacquinot, M. T. Loponen, *et al.*, Physica B (Utrecht) **98**, 45 (1979).

[13] P. J. Hakonen, K. K. Nummila, and R. T. Vuorinen, Phys. Rev. B **45**, 2196 (1992).

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