Nuclear cross-relaxation induced by a paramagnetic impurity

L. L. Buishvili, M. D. Zviadadze, and B. D. Mikaberidze

Physics Institute, Academy of Sciences, Georgian SSR
(Submitted April 15, 1975)
Zh. Eksp. Teor. Fiz. **69**, 2118-2123 (December 1975)

A mechanism induced by the electron dipole-dipole reservoir is proposed for the cross-relaxation between nuclei close to an impurity ion. It is shown that the induced-diffusion coefficient is always smaller than the coefficient of free nuclear diffusion.

1. It is well known[1,2] that in the relaxation of the nuclei of the matrix of a nonmetallic diamagnetic crystal diluted by a paramagnetic impurity, two mechanisms play the principal role: direct relaxation due to fluctuations of the local magnetic field produced at the nucleus by the impurity, and nuclear spin diffusion due to the dipole-dipole flip-flop transitions (ff-transitions, below) of neighboring nuclei, conserving the total Zeeman energy of the nuclear spins. At sufficiently low temperatures the static local-field component, proportional to the equilibrium value $\langle S_{nz}\rangle_0$ of the z-component of the spin of the n-th ion, induces a strong shift in the resonance frequencies of the nuclei in its immediate environment, which makes ff-processes between the nearby nuclei difficult. Thus, about each magnetic ion there is a diffusion barrier with a certain radius δ[3], inside which the spin-diffusion (SD) coefficient $D \approx 0$.

Recently, an effective decrease of δ has been observed in a number of experiments[4,5]. To explain this phenomenon the mechanism proposed earlier by Horvitz[6] for energy exchange between the nearby nuclei has been invoked[4]; in this mechanism the energy difference $\hbar(\omega_1 - \omega_2)$ of the nuclei with Zeeman frequencies ω_1 and ω_2 participating in the ff-process is transferred to the lattice. The latter was treated classically, i.e., as a subsystem with infinite temperature[7]. In such conditions the exchange reduces to an ordinary diffusion process with an effective diffusion coefficient D_p.

The Horvitz mechanism becomes important and leads to decrease of δ in the case when direct coupling between the nuclei and direct relaxation of the nuclei to the lattice are ineffective, i.e., when the conditions $|\omega_1 - \omega_2| > \Delta_I$ and $\omega_{1,2}\tau_1 \gg 1$ are fulfilled, where Δ_I is the nuclear cross-relaxation width and τ_1 is the electronic spin-lattice relaxation time. However, at low temperatures and sufficiently high impurity concentrations it is necessary to replace τ_1 by τ_s (τ_s is the longitudinal spin-spin correlation time for the electron spin) and introduce the dipole-dipole reservoir (DDR) of electron spins into the analysis[8]. In this case, unlike in the Horvitz mechanism, the energy $\hbar(\omega_1 - \omega_2)$ will be transferred directly to the DDR. Inasmuch as the specific heat of the DDR is small, its temperature can change greatly in the process of energy exchange between nearby nuclei with participation of the DDR, as a result of which the actual exchange process will be suppressed. This paper is devoted to a study of this mechanism.

2. Omitting terms that are unimportant for the analysis, we write the Hamiltonian of the system in the form

$$\mathcal{H}=\mathcal{H}_0+\mathcal{H}_{11}', \quad \mathcal{H}_0=\sum_{\alpha=1}^{2}\mathcal{H}_{\alpha z}+\mathcal{H}_d, \quad \mathcal{H}_{\alpha z}=-\hbar\omega_\alpha\sum_k I_{\alpha k}{}^z,$$

$$\mathcal{H}_d=\mathcal{H}_{ss}+\mathcal{H}_{11}+\mathcal{H}_{1s}, \quad \mathcal{H}_{1s}=\sum_{\alpha=1}^{2}\sum_{kn}V_{kn}I_{\alpha k}{}^z\delta S_{nz},$$

$$\mathcal{H}_{11}'=\sum_{i\neq j}B_{ij}(I_{1i}{}^{+}I_{2j}{}^{-}+I_{1i}{}^{-}I_{2j}{}^{+}),$$

where $\mathcal{H}_{ss}$ ($\mathcal{H}_{II}$) is the secular part of the dipole-dipole interaction of the electronic (nuclear) spins, $\mathcal{H}_{\alpha z}$ is the Zeeman energy of nuclei of the type α ($\alpha = 1, 2$), $\mathcal{H}_{II}'$ is that part of the nuclear dipole-dipole interaction that gives rise to the ff-processes for the different types of nuclei and is regarded as a perturbation, and $\mathcal{H}_{1s}$ is the longitudinal component of the interaction of the nuclei with the ions and is responsible for the local-field fluctuations at the nuclei; $\delta S_{nz} = S_{nz} - \langle S_{nz}\rangle_0$.

Distinguishing $\mathcal{H}_{1z}$, $\mathcal{H}_{2z}$ and $\mathcal{H}_d$ as subsystems and denoting the corresponding inverse temperatures by β_1, β_2 and β_d, we can construct the nonequilibrium statistical operator[9] and derive equations describing the evolution of the parameters β_1, β_2 and β_d in time. Omitting the calculations, which are completely analogous to the derivation of the usual-cross-relaxation equations[10], we arrive at the following system:

$$\frac{d\beta_1}{dt} = -\frac{\omega_2}{\omega_1}\frac{d\beta_2}{dt} = -W_{cr}(\Delta)\left\{\beta_1 - \frac{\omega_2}{\omega_1}\beta_2 - \frac{\Delta}{\omega_1}\beta_d\right\},$$

$$\frac{d\beta_d}{dt} = \frac{\omega_1(\omega_1 N_1 - \omega_2 N_2)}{N_s\omega_d^2}W_{cr}(\Delta)\left\{\beta_1 - \frac{\omega_2}{\omega_1}\beta_2 - \frac{\Delta}{\omega_1}\beta_d\right\} - \frac{\beta_d - \beta_L}{T_1'}, \quad (1)$$

where T_1' is the spin-lattice relaxation time of the DDR, $\Delta \equiv \omega_1 - \omega_2$, N_1 and N_2 are the numbers of nuclei with ω_1 and ω_2 respectively, N_s is the number of impurity ions, $\omega_d^2 = (\text{Tr}\,\mathcal{H}_d^2)/(\hbar^2 \text{Tr} S_z^2)$, and β_L is the inverse temperature of the lattice. The probability $W_{cr}(\Delta)$ of cross-relaxation of nearby nuclei with participation of the DDR is determined by the formula

$$W_{cr}(\Delta) = \frac{1}{\langle\mathcal{H}_{11}'^2\rangle}\int_{-\infty}^{0} e^{\varepsilon t}\langle K_1 K_1(t)\rangle dt, \quad (2)$$

where it is assumed that $\varepsilon \to +0$, $\langle\ldots\rangle \equiv \text{Tr}(\ldots)/\text{Tr}\,1$ and

$$K_1 = \frac{1}{i\hbar}[\mathcal{H}_{1s}, \mathcal{H}_{11}'], \quad K_1(t) = \exp\left(\frac{i}{\hbar}\mathcal{H}_0 t\right)K_1\exp\left(-\frac{i}{\hbar}\mathcal{H}_0 t\right).$$

Straightforward calculations give

$$W_{cr}(\Delta) = \frac{8I(I+1)}{3N_1\hbar^2}\sum_{i\neq j}B_{ij}{}^2\pi f(\Delta), \quad (3)$$

where I is the spin of the nucleus and $f(\Delta)$ is the Fourier transform of the correlator

$$f(t) = \left\langle A_{ij}\exp\left(\frac{i}{\hbar}\mathcal{H}_d t\right)A_{ij}{}^{+}\exp\left(-\frac{i}{\hbar}\mathcal{H}_d t\right)\right\rangle \bigg/ \langle A_{ij}A_{ij}{}^{+}\rangle, \quad (4)$$

$$A_{ij} \equiv I_{1i}{}^{+}I_{2j}{}^{-}.$$

We shall compare (3) with the usual probability W of ff-transitions of distant nuclei, which is obtained from (3) if we put $\mathscr{H}_{SS} = \mathscr{H}_{IS} = 0$, $\Delta = 0$ and denote the corresponding correlator (4) by $f_0(t)$:

$$W = \frac{8I(I+1)}{3N_I\hbar^2}\sum_{i\neq j}B_{ij}^2\pi f_0(0). \qquad (5)$$

Since, with allowance for the contribution of the interaction $\mathscr{H}_{SS} + \mathscr{H}_{IS}$ to the correlator (4), its width is

$$\tilde{\Delta}_I \sim 1/\pi f(0) \geq \Delta_I \sim 1/\pi f_0(0),$$

in the general case,

$$W_{cr}(\Delta) = Wf(\Delta)/f_0(0) \leqslant Wf(0)/f_0(0) \sim W\frac{\Delta_I}{\tilde{\Delta}_I} \leqslant W, \qquad (6)$$

so that the probability of induced cross-relaxation of nearby nuclei cannot exceed the probability of ff-transitions of distant nuclei and, as a result, the effective diffusion coefficient D_p of nuclei situated inside the diffusion barrier is always smaller than the coefficient D of free nuclear diffusion. (Here, as in[6], the indirect exchange between nearby nuclei that can, in principle, be induced by the paramagnetic impurity is not taken into account.)

3. We now carry out an approximate calculation of $f(\Delta)$. For the sake of simplicity we shall omit the "nuclear" source of broadening $\mathscr{H}_{II}$ (we assume that $\mathscr{H}_{II} \ll \mathscr{H}_{SS} + \mathscr{H}_{IS}$), but take the interaction $\mathscr{H}_{IS}$ into account exactly in the framework of the stochastic model of magnetic resonance[11]. Setting up the equation of motion

$$\frac{dA_{ij}(t)}{dt} = \frac{i}{\hbar}\sum_n (V_{in}-V_{jn})\delta S_{nz}(t)A_{ij}(t)$$

and considering the quantity

$$\omega_{ij} = \frac{1}{\hbar}\sum_n (V_{in}-V_{jn})\delta S_{nz}(t)$$

as a stochastic variable, it is easy to obtain the following expression in the standard way[11]:

$$f(\Delta) = \begin{cases} (2\pi M_2)^{-1/2}\exp(-\Delta^2/2M_2), & M_2^{1/2}\tau_s\gg 1, & (7.1) \\ \tau_s M_2/\pi[\Delta^2+(\tau_s M_2)^2], & M_2^{1/2}\tau_s\ll 1, & (7.2) \end{cases}$$

where

$$M_2 \equiv \langle\omega_{ij}^2\rangle = \frac{f\langle(\delta S_{nz})^2\rangle}{\hbar^2}\sum_n (V_{in}-V_{jn})^2,$$
$$\qquad (8)$$
$$\tau_s = \int_0^\infty \frac{\langle\omega_{ij}(t)\omega_{ij}(t+\tau)\rangle}{\langle\omega_{ij}^2\rangle}d\tau = \pi\varphi(0)$$

and a random distribution of impurity, with concentration f, has been assumed: $\varphi(0)$ is the zero-frequency Fourier transform of the electronic correlator

$$\varphi(t) = \frac{1}{\langle(\delta S_{nz})^2\rangle}\left\langle \delta S_{nz}\exp\left(\frac{i}{\hbar}\mathscr{H}_{ss}t\right)\delta S_{nz}\exp\left(-\frac{i}{\hbar}\mathscr{H}_{ss}t\right)\right\rangle \qquad (9)$$

with correlation time τ_s, and M_2 and $\tau_s M_2$ play the role of the effective cross-relaxation widths in the corresponding limiting situations.

If in (7.2) we make the replacement

$$\tau_s \to \frac{\pi\sqrt{3}}{6\omega_{ss}}, \quad \omega_{ss}^2 = \frac{Sp\,\mathscr{H}_{ss}^2}{\hbar^2\,Sp\,S_z^2} = \frac{48f\langle S_{nz}^2\rangle}{\hbar^2}\sum_n' B_{nn'}^2,$$

we obtain an expression coinciding with the result which can be derived by applying the method of moments[7] to $f(\Delta)$ and assuming that $\mathscr{H}_{SS} \gg \mathscr{H}_{IS}$ (in this case ω_{SS} plays the role of a frequency cutoff).

It is of interest to estimate $f(\Delta)$ by regarding H_{IS} as a perturbation, just as was done by Horvitz[6]. Put-

ting $\mathscr{H}_{II} = 0$ in (4) and expanding the quantity

$$\exp\left[\frac{i}{\hbar}(\mathscr{H}_{ss}+\mathscr{H}_{is})t\right]A_{ij}\exp\left[-\frac{i}{\hbar}(\mathscr{H}_{ss}+\mathscr{H}_{is})t\right]$$

in powers of $\mathscr{H}_{IS}$ to terms of second order inclusive, we obtain

$$f(\Delta) = M_2\varphi(\Delta)/\Delta^2, \qquad (10)$$

where M_2 is given by formula (8) and $\varphi(\Delta)$ is the Fourier transform of the correlator (9) at frequency Δ.

We shall discuss the conditions of applicability of the result (10). Since

$$\Delta = \frac{f\langle S_{nz}\rangle_0}{\hbar}\sum_n' (V_{in}-V_{jn}),$$

the estimate

$$|\Delta| < \sqrt{M_2}. \qquad (11)$$

is valid. We assume at the outset that $\sqrt{M_2}\tau_s \ll 1$. By virtue of (11) the inequality $|\Delta|\tau_s \ll 1$ is automatically fulfilled, and, taking (8) into account, we obtain

$$f(\Delta) = M_2\tau_s/\pi\Delta^2. \qquad (12)$$

As we should expect, (12) coincides with (7b) for $|\Delta| \gg M_2\tau_s$, i.e., for detunings greater than the effective cross-relaxation width.

We note that in the case $|\Delta|\tau_s \gg 1$, i.e., for $\sqrt{M_2}\tau_s \gg 1$, the result (10) is incorrect. The point is that, in these conditions, according to the stochastic model, formula (7a) is valid and $f(\Delta)$ is a nonanalytic function of $\mathscr{H}_{IS}$ ($M_2 \sim \mathscr{H}_{IS}^2$) and cannot be expanded in a series in powers of $\mathscr{H}_{IS}$. Consequently, the result (10), obtained by perturbation theory, is correct only when the conditions

$$|\Delta| \gg M_2\tau_s, \quad |\Delta|\tau_s \gg 1 \qquad (13)$$

are fulfilled, and leads, when (6) is taken into account, to the expression

$$W_{cr}(\Delta) = WM_2\tau_s/\pi f_0(0)\Delta^2. \qquad (14)$$

Finally, we note that all our discussions are meaningful only when

$$\frac{1}{\pi f_0(0)} < \begin{cases} M_2\tau_s, & \sqrt{M_2}\,\tau_s \ll 1 \\ \sqrt{M_2}, & \sqrt{M_2}\,\tau_s \gg 1 \end{cases} . \qquad (15)$$

In the opposite case the width of the correlator $f(\Delta)$ is determined by the interaction $\mathscr{H}_{II}$, i.e., coincides in order of magnitude with Δ_I, and we need not take into account the "electronic" source of broadening associated with $\mathscr{H}_{SS}$ and $\mathscr{H}_{IS}$.

It follows from (13)–(15) that $W_{cr}(\Delta) < W$, as it should be.

4. Entirely analogously, we can consider the situation when the local field created by the impurity at the nucleus fluctuates owing to the electron spin-lattice interaction[6]. All the above formulas and arguments concerning $W_{cr}(\Delta)$ remain valid if τ_s is replaced by the electronic relaxation time τ_l. In particular, in place of (14) we obtain the formula

$$W_{cr}(\Delta) = WM_2\tau_l/\pi f_0(0)\Delta^2, \qquad (16)$$

which is valid in the region

$$|\Delta| \gg M_2\tau_l, \quad |\Delta|\tau_l \ll 1. \qquad (17)$$

If we write the expression (16) for one ion and a pair of nuclei i and j and average it over the distribu-

tion of the frequencies ω_i and ω_j, taking into account that $\Delta = \omega_i - \omega_j$ (we denote the probability in this case by $\overline{W}_{cr}$), it coincides with formula (6) from[6] for W_{cr}. It follows from what has been said above that the result (16) is only applicable in the region (17), and when these conditions are violated it is necessary to use the formulas (7). At the same time, the numerical estimates of Horvitz correspond to the region $|\Delta| \tau_l > 1$, i.e., go outside the limits of applicability of (16), and, naturally, the values of D_p that he obtained are incorrect (in particular, as shown above from general considerations, $\overline{W}_{cr} < W$ always, i.e., $D_p = \overline{W}_{cr} a^2 < D = Wa^2$, where a is the lattice constant).

As an example we shall consider diffusion of protons in $(Ce, La)_2 Mg_3 (NO_3)_{12} \cdot 24H_2O$[12] at temperature $T = 2$ K. In this case, $\tau_1 = 10^{-4}$ sec and $\delta \sim 12$ Å and corresponds to the nuclei of the fourth coordination sphere[6]; $\sqrt{\overline{M}_2}\tau_1 \sim 10$. Making use of formula (7a) and denoting the coefficient of induced diffusion for transitions between nuclei of the fourth and third coordination spheres by $(D_p)_{43}$, we obtain the estimate $(D_p)_{43}/D \sim 0.4$, which differs substantially from the value $D_p/D \sim 2.1$ given in the paper[6] for this case. Unfortunately, it is impossible to estimate the quantity D_p/D from the data of[12]. However, the paper[5], in which the assumption of a gradual decrease of the diffusion coefficient with decreasing distance of the nuclei from the paramagnetic center is used to explain the experimental data, can serve as an indirect confirmation of the validity of the relation $D_p \ll D$.

5. We turn to the analysis of the system (1). We emphasize two important differences between this system and the usual cross-relaxation equations[10]. First, the DDR of the "extraneous" spins, and not that of the spins that are cross-relaxing, participates in (1). Secondly the probability (2) of the corresponding process in the situation of (7b) falls off in a power-law manner as the frequency-detuning Δ increases, whereas ordinarily the probability of cross-relaxation has a Gaussian form, i.e., falls off significantly faster.

We shall assume that the nuclei with frequency ω_2 are fully saturated, i.e., $\beta_2(t) = 0$. Then (1) reduces to the equations

$$\frac{d\beta_1}{dt} = -W_{cr}(\Delta)\left\{\beta_1 - \frac{\Delta}{\omega_1}\beta_d\right\},$$

$$\frac{d\beta_d}{dt} = -\frac{\omega_1(\omega_1 N_1 - \omega_2 N_2)}{N_s \omega_d^2}\frac{d\beta_1}{dt} - \frac{\beta_d - \beta_L}{T_1'}$$

(18)

We shall find the solution of (18) with the initial condition $\beta_1(0) = \beta_d(0) = \beta_L$. We assume first that $W_{cr} \ll 1/T_1'$. For times $t > W_{cr}^{-1}$ the solution has the form $\beta_d = \beta_L$, $\beta_1 = \beta_L \Delta/\omega_1 \ll \beta_L$. Consequently, in a time of the order of W_{cr}^{-1} the saturation is transferred from nuclei of one kind to nuclei of the other kind. This process will be perceived as nuclear spin diffusion induced

by the electronic DDR, with an effective diffusion coefficient $D_p = \overline{W}_{cr} a^2$. This case corresponds to Horvitz's treatment, if we put $\beta_L = 0$ and replace τ_s by τ_1.

If $\overline{W}_{cr} \gg 1/T_1'$, for times $\overline{W}_{cr}^{-1} \ll t \ll T_1'$ we obtain the solution (it is assumed that $\omega_1|\,\omega_1 N_1 - \omega_2 N_2| \gg N_s \omega_d^2$)

$$\beta_1 = \frac{\Delta}{\omega_1}\beta_d, \quad \beta_d = \beta_L \frac{\omega_1(\omega_1 N_1 - \omega_2 N_2)}{N_s \omega_d^2 + \Delta(\omega_1 N_1 - \omega_2 N_2)}.$$

Thus, $|\beta_d| \gg \beta_L$, i.e., there is a strong shift in the DDR temperature (as in ordinary cross-relaxation), as a result of which, transfer of the saturation does not occur (β_1 remains of the order of β_L), i.e., SD is not induced. However, after a time $t > T_1'$ (but $t < T_{1L}$ where T_{1L} is the nuclear spin-lattice relaxation time) has elapsed, again $\beta_d = \beta_L$ and $\beta_1 \approx 0$, i.e., over such times, induced SD with $D_p = a^2/T_1'$ is observed. We note that D_p in the given case does not depend on the distance between the nuclei and, generally speaking, increases monotonically with increasing temperature. Obviously, in this case too, $D_p < D$.

The authors express their sincere gratitude to G. R. Khutsishvili for valuable discussions.

[1] N. Bloembergen, Physica 15, 386 (1949).
[2] G. R. Khutsishvili, Usp. Fiz. Nauk 87, 211 (1965); 96, 441 (1968) [Sov. Phys.-Uspekhi 8, 743 (1966); 11, 802 (1969)].
[3] W. E. Blumberg, Phys. Rev. 119, 79 (1960).
[4] J. P. Wolfe, Phys. Rev. Lett. 31, 907 (1973).
[5] F. L. Aukhadeev, I. I. Valeev, and V. A. Skrebnev, Zh. Eksp. Teor. Fiz. 64, 1699 (1973) [Sov. Phys.-JETP 37, 857 (1973)].
[6] E. P. Horvitz, Phys. Rev. B3, 2868 (1971).
[7] A. Abragam, The Principles of Nuclear Magnetism, Oxford University Press, 1961 (Russ. transl. IIL, M., 1963).
[8] B. N. Provotorov, Zh. Eksp. Teor. Fiz. 41, 1582 (1961) [Sov. Phys.-JETP 14, 1126 (1962)].
[9] D. N. Zubarev, Neravnovesnaya statisticheskaya termodinamika (Non-equilibrium Statistical Thermodynamics), Nauka, M., 1971 (English translation published by Consultants Bureau, N. Y., 1974).
[10] M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Oxford University Press, 1970 (Russ. transl. Mir, M., 1972).
[11] R. Kubo, Lectures in Theoretical Physics 1, 120 (1959) (Boulder Summer Institute for Theoretical Physics, 1958), Interscience, N. Y. (Russ. transl. in: Termodinamika neobratimykh protsessov (Thermodynamics of Irreversible Processes), IIL, M., (1962).
[12] O. S. Leifson and C. D. Jeffries, Phys. Rev. 122, 1781 (1961).

Translated by P. J. Shepherd
227