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SPIN-LATTICE RELAXATION OF A NUCLEAR ANTIFERROMAGNET

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Résumé. — Nous considérons l’influence de l’ordre antiferromagnétique nucléaire sur la relaxation spin-réseau de l’énergie dipolaire nucléaire par des impuretés paramagnétiques. Les prédictions diffèrent selon que le temps de corrélation $\tau_4$ du couplage spin-réseau est plus court ou plus long que $T_2$. Lorsque $\tau_4 \ll T_2$, la relaxation est plus lente dans l’état antiféro que dans l’état paramagnétique, lorsque $\tau_4 \gg T_2$, la vitesse de relaxation présente un maximum à la transition. Les résultats obtenus dans des cristaux de fluorure de calcium sont conformes aux prévisions théoriques correspondant à $\tau_4 \ll T_2$.

Abstract. — We consider the influence of antiferromagnetic nuclear ordering on the spin-lattice relaxation of the nuclear dipolar energy by paramagnetic impurities. The predictions are different depending whether the correlation time $\tau_4$ of the spin-lattice coupling is shorter or longer than $T_2$. When $\tau_4 \ll T_2$, relaxation is slower in the antiferromagnetic than in the paramagnetic state. When $\tau_4 \gg T_2$, the relaxation rate is maximum at the transition. The experimental results in calcium fluoride crystals agree with the theoretical predictions for the case $\tau_4 \ll T_2$.

1. Introduction. — The purpose of this article is to study the influence of the magnetic ordering of a nuclear spin system on its spin-lattice relaxation.

In the high-temperature limit (the system is then in a paramagnetic state), it is well known that spin-lattice relaxation is generally exponential. A condition for this is that the state of the system be characterized by a spin temperature. This is the case for instance in diamagnetic solids where relaxation is caused by paramagnetic impurities at low concentration, except for the few nuclei in the immediate vicinity of the impurities. The inverse temperature $\beta$ of the system varies exponentially with a time constant $T_1$, as a consequence of the fact that the density matrix is linear in $\beta$, in this high temperature limit. Since most measurable quantities are proportional to $\beta$, they vary toward their thermal equilibrium value with the same time constant $T_1$. Let us consider for instance a system which has been demagnetized in the rotating frame (see for instance ref. [1]). Examples of quantities which are proportional to the inverse temperature in the rotating frame are: the amplitude of the resonance signal, observed either in the absorption or in the dispersion mode with a small non saturating r.f. field; or the dispersion signal observed with a saturating r.f. field applied at exact resonance; or the amplitude of the free-decay signal following an r.f. pulse [2]. As for the entropy, whose departure from its infinite-temperature value is proportional to $\beta^2$, it varies with a time constant $\frac{1}{2} T_1$.

When on the other hand the nuclear spin system is in an ordered state, there is no reason why its inverse temperature should decay exponentially. Furthermore, the various physical properties of the system are complicated and different functions of $\beta$, so that each of them is expected to vary in a different non-exponential way. It is then necessary to specify which of them is under investigation. In the following, we focus our attention on the time evolution under the effect of spin-lattice relaxation of the dipolar energy of the system, a quantity which can easily be measured [3].

The method of production of nuclear magnetic ordering has been described elsewhere [4]. We recall briefly its principle. Nuclear magnetic ordering is produced by a two-step process. First, the nuclear spins are dynamically polarized in high field by the Solid Effect, which reduces their entropy to a low value; secondly, the polarized nuclear spins are adiabatically demagnetized to zero field. Under the effect of their dipole-dipole coupling, and provided their entropy is sufficiently low they undergo a transition to an ordered state. In all experiments performed so far, we have used adiabatic demagnetization in the rotating frame, that is, with the external d.c. field always present, we have performed adiabatic fast
passages stopped at resonance. The ordered structure produced in that way depends both on the orientation of the d.c. field with respect to the crystalline axes, and on the sign of the spin temperature. In particular, in a simple cubic system of nuclear spins $\frac{1}{2}$, such as $^{19}$F in calcium fluoride, one predicts the occurrence of the antiferromagnetic structure pictured in figure 1, when the adiabatic demagnetization in the rotating frame is performed at negative temperature with the external d.c. field parallel to a four-fold crystalline axis. A number of experimental studies have been devoted to that case [4, 5], and it is to that case that we will eventually specialize the study of spin-lattice relaxation.

![FIG. 1. Antiferromagnetic structure of CaF$_2$ after adiabatic demagnetization in the rotating frame, with $H_0 \parallel [100]$ and $T < 0$.](image)

We will consider the case when the relaxation is caused by paramagnetic impurities. For the comparison between theory and experiment, the time constant $T_1$ of the exponential decay in the low-energy limit (that is at high temperature) will be taken as an adjustable parameter to be fitted to the experimental results.

2. Theory. — We consider a nuclear spin system whose Hamiltonian is of the form:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(t)$$

(1)

The main Hamiltonian $\mathcal{H}_0$ is the sum of a Zeeman interaction $\omega_0 I_z$ plus a dipole-dipole interaction term $\mathcal{H}_D$. We are in high field and as usual we truncate $\mathcal{H}_D$, so as to retain only the part $\mathcal{H}_D'$ which commutes with $I_x$. It is of the form:

$$\mathcal{H}_D = \frac{1}{2} \sum_{i,j} A_{ij} [2 I_i^+ I_j^- - \frac{1}{2}(I_i^+ I_j^+ + I_i^- I_j^-)]$$

(2)

with:

$$A_{ij} = \frac{1}{2} \gamma^2 \hbar (1 - 3 \cos^2 \theta_{ij}) r_{ij}^{-3}$$

(3)

where $\theta_{ij}$ is the angle between the applied field $\mathbf{H}_0$ and $r_{ij}$.

$\mathcal{H}_1(t)$ is the spin-lattice coupling responsible for the nuclear spin-lattice relaxation.

The derivation of the equation governing the evolution of the dipolar energy is made in a standard fashion (see for instance ref. [1] ch. III). Its major steps are the following. The nuclear density matrix $\sigma$ varies according to:

$$\frac{d\sigma}{dt} = -i[\mathcal{H}_0 + \mathcal{H}_1(t), \sigma]$$

(4)

We use a canonical transformation through a unitary operator:

$$U(t) = \exp(i\mathcal{H}_0 t)$$

(5)

and we define, for every operator $Q$:

$$\tilde{Q} = U Q U^+$$

(6)

We have, in this representation:

$$\frac{d\tilde{\sigma}}{dt} = -i[\mathcal{H}_1(t), \tilde{\sigma}(t)]$$

We expand this equation to the second order in $\mathcal{H}_1$, then we go back to the Schrödinger representation, and we obtain:

$$\frac{d\sigma}{dt} = -i\langle [\mathcal{H}_1(t), \sigma(0)] \rangle_{av} -$$

$$-\left(\int_{0}^{\infty} [\mathcal{H}_1(0), [V_1(-\tau), \sigma(0)]] d\tau \right)_{av}$$

(7)

where $\langle \rangle_{av}$ means an ensemble (or time) average over the random coupling $\mathcal{H}_1(t)$. We suppose that $\langle \mathcal{H}_1(t) \rangle_{av} = 0$, so that the first term on the right-hand side of eq. (7) vanishes. A condition for the validity of eq. (7) is that

$$U(t) \sigma(0) U(t) = \sigma(0)$$

(8)

which can be assumed to be valid even when the system is in an antiferromagnetic state which breaks the symmetry of the Hamiltonian. A short discussion of this point can be found in reference [3].

During the evolution we are interested in, the inverse spin-temperature is so much higher than the lattice inverse temperature that we can take the latter to be zero. In any case, when the inverse spin-temperature is high, it is not permissible to replace in eq. (7), as is usual in the high-temperature approximation, $\sigma(0)$ by $(\sigma(0) - \sigma_0)$, where $\sigma_0$ is the density matrix at thermal equilibrium at the lattice temperature.

By multiplying both sides of eq. (7) by $\mathcal{H}_D$ and taking the traces we obtain:

$$\frac{d}{dt} \langle \mathcal{H}_D \rangle = -\int_{0}^{\infty} \langle [\mathcal{H}_D, \mathcal{H}_1(t)] \rangle_{av} d\tau$$

(9)

where we use the notation:

$$\langle Q \rangle = \langle \text{Tr} \{\sigma(0) Q\} \rangle_{av}$$

(10)
Let us now turn to the form of $\mathcal{K}_1(t)$. We suppose that the relaxation is caused by the dipolar coupling of the nuclear spins $I$ with the spins $S$ of paramagnetic impurities at low concentration randomly distributed in the sample. The spin orientation of each impurity varies randomly around an average value under the effect either of its own spin-lattice relaxation, or of flip-flop transitions with nearby impurities (we suppose in that case that the electronic spin-spin reservoir is much more strongly coupled to the lattice than to the nuclear spin-spin reservoir, so that its temperature is always equal to that of the lattice). We call $\tau_c$ the correlation time of this fluctuation and we suppose that $\omega_0 \tau_c \gg 1$. In that case the coupling terms which are effective for the spin-lattice relaxation are of the form:

$$\mathcal{K}_1(t) = \sum_{i,n} C_{in} \hat{I}_i^z \left[ S_n^x(t) - (S_n^z)_{av} \right]$$  \hspace{1cm} (11)

where the sum is restricted to the nuclear spins outside the diffusion barrier of the impurities. In this treatment we will neglect the possibility of a diffusion-limited relaxation.

Eq. (11) can be written in the form:

$$\mathcal{K}_1(t) = VF(t)$$  \hspace{1cm} (12)

where:

$$V = \sum_i \frac{\hat{h}_i I_i^z}{\tau_c}$$  \hspace{1cm} (13)

and $F(t)$ is a random function of time such that:

$$(F(t))_{av} = 0 ,$$

and

$$(F(0)(F(t))_{av} = \exp(-|t|/\tau_c).$$  \hspace{1cm} (14)

Since $V$ commutes with $I_\sigma$, we have:

$$P(t) = \exp(i\mathcal{K}_0^z t) V \exp(-i\mathcal{K}_0^z t).$$  \hspace{1cm} (15)

Since furthermore $\mathcal{K}_0$ commute with $\mathcal{K}_0$, and according to the condition (8), eq. (9) becomes:

$$\frac{d}{dt} \langle \mathcal{K}_0^z \rangle = - \int_0^\infty \exp(-\tau/\tau_c) \times$$

$$\times \left\langle [\mathcal{K}_0^z, P(t)], V \right\rangle \right) \right) \right) dt.$$  \hspace{1cm} (16)

We assume that the decay time of the trace under the integral is roughly of the order of $T_2$, the free-induction decay time at high temperature. We will consider two limiting cases, corresponding to $\tau_c \ll T_2$ and $\tau_c \gg T_2$, respectively.

i) $\tau_c \ll T_2$. — Under the integral of eq. (16), the exponential factor decays much more rapidly than the trace. We can then neglect the decay of the latter, and we obtain:

$$\frac{d}{dt} \langle \mathcal{K}_0^z \rangle = - \tau_c \left\langle [\mathcal{K}_0^z, V], V \right\rangle$$  \hspace{1cm} (17)

or else, according to eqs. (2) and (13):

$$\frac{d}{dt} \langle \mathcal{K}_0^z \rangle = \frac{1}{4} \tau_c \sum_{i,j} A_{ij} \left( \frac{\hat{h}_i - \hat{h}_j}{\tau} \right)_{av} \times$$

$$\times \left\langle I_i^+ I_j^- + I_i^- I_j^+ \right\rangle.$$  \hspace{1cm} (18)

ii) $\tau_c \gg T_2$. — According to eq. (15), the trace on the right-hand side of eq. (16) is equal to:

$$\left\langle [\mathcal{K}_0^z, P(t)], V \right\rangle = - i \frac{d}{dt} \left\langle [P(t), V] \right\rangle .$$

Eq. (16) can then be integrated by parts:

$$\frac{d}{dt} \langle \mathcal{K}_0^z \rangle = i \int_0^\infty \exp(-\tau/\tau_c) \frac{d}{dt} \left\langle [P(t), V] \right\rangle \right) \right) dt .$$  \hspace{1cm} (19)

In the limit when $\tau_c$ is very long, this can be written:

$$\frac{d}{dt} \langle \mathcal{K}_0^z \rangle = \frac{1}{\tau_c} \lim_{\tau \to -\infty} \int_0^{\infty} \exp(\tau/\tau_c) \times$$

$$\times \right\langle [\mathcal{K}_0^z, P(t)], V \right\rangle \right) \right) \right) \right) dt .$$  \hspace{1cm} (20)

Under this form, the limit is seen to be proportional to the linear response of the quantity $V$ to the adiabatic introduction of the perturbation $V$, according to linear-response theory [6]; it is also equal to the expectation value $\langle V \rangle$ when the system is at thermal equilibrium with respect to the Hamiltonian $\mathcal{K}_0^z + V$. We can then write:

$$\frac{d}{dt} \langle \mathcal{K}_0^z \rangle = - \frac{1}{\tau_c} \chi_{V \to V} .$$  \hspace{1cm} (21)

This result can be given a simple physical interpretation, already discussed in reference [7]. If the coupling $\mathcal{K}_1(t) = VF(t)$ were time-independent (i.e. $F(t) = F(0) = 1$), then the terms $\mathcal{K}_0^z$ and $V$ would reach thermal equilibrium in a time of the order of $T_2$. If $F(t)$ varies slowly (i.e. $\tau_c \gg T_2$), both terms still constitute at all times a single thermal reservoir in a state characterized by a single inverse temperature $\beta$. More explicitly, let $\beta$ and $\beta'$ be the inverse temperatures corresponding to $\mathcal{K}_0^z$ and $V$, respectively. We can write the following evolution equations:

$$\frac{d}{dt} \langle \mathcal{K}_0^z(\beta) \rangle = \frac{d}{dt} \langle \mathcal{K}_0^z(\beta) \rangle_{SL} + g(\beta, \beta')$$  \hspace{1cm} (22)

$$\frac{d}{dt} \langle V(\beta') \rangle = \frac{d}{dt} \langle V(\beta') \rangle_{SL} - g(\beta, \beta')$$  \hspace{1cm} (22')

where $d/dt \langle \cdots \rangle_{SL}$ stands for the evolution due to the spin-lattice coupling. Since only the term $V$ is coupled to the lattice, we have:

$$\frac{d}{dt} \langle \mathcal{K}_0^z(\beta) \rangle_{SL} = 0 ,$$
and 
\[ \frac{d}{dt} \langle V(\beta') \rangle_{SL} = - \frac{1}{\tau_0} \langle V(\beta') \rangle. \]

The term \( g \) causes an evolution of \( \beta \) and \( \beta' \) toward a common value at a rate of the order of \( T_2^{-1} \gg \tau_0^{-1} \). We have then at all times \( \beta' \approx \beta \). We get rid of the unknown function \( g \) by summing eqs. (22) and (22'), which yields:
\[ \frac{d}{dt} \langle \mathcal{H}_D'(\beta) + V(\beta) \rangle = - \frac{1}{\tau_0} \langle V(\beta) \rangle. \]

If now we suppose that \( \langle V(\beta) \rangle \approx \langle \mathcal{H}_D'(\beta) \rangle \), we recover eq. (21).

**Calculation of the Relaxation Rates within Approximate Theories of Nuclear Ordering.** — Eq. (18) and (21) are exact expressions for the relaxation rate of the dipolar energy in the two limiting cases that we considered. We will now solve them with the help of specific approximations to nuclear magnetic ordering. We analyze in turn the limiting cases when \( \tau_c \ll T_2 \) and \( \tau_c \gg T_2 \), and we specialize from now on the study to the antiferromagnetic structure of figure 1.

1st case \( \tau_c \ll T_2 \). — According to eq. (18), the relaxation rate of the energy is proportional to the correlation of the transverse spin components. At high temperature, that is at low energy in the paramagnetic state, the dipolar energy and the correlation functions are all proportional to the inverse temperature \( \beta \). We have then:
\[ \frac{d}{dt} \langle \mathcal{H}_D' \rangle = - \eta \langle \mathcal{H}_D' \rangle \]
and the relaxation of the energy is exponential, as is well known. When the temperature decreases below the transition temperature, the energy increases very steeply, because of the energy associated with long-range order, whereas the correlation between transverse spin components varies but slowly. As a consequence, \(- \frac{d}{dt} (\ln \langle \mathcal{H}_D' \rangle)\) must decrease. We expect then on physical grounds a slowing down of the relaxation in the ordered state, as compared to the paramagnetic state, which is confirmed by the following approximate calculation.

We calculate the expectation values on the right-hand side of eq. (18) by the restricted-trace approximation [8], whose principle is the following. In the antiferromagnetic state, the system splits into two sublattices \( \mathcal{A} \) and \( \mathcal{B} \) in which the spins carry different longitudinal polarizations \( p_A \) and \( p_B \). The latter are determined by the condition that they maximize the restricted partition function:
\[ \text{Tr} \exp(-\beta \mathcal{C}) \]
where the trace is restricted to the Hilbert subspace corresponding to well-defined values of \( p_A \) and \( p_B \). The lowest non-trivial order of approximation consists in expanding this restricted trace up to \( \beta^2 \). Within the same order of approximation, the expectation value of an operator \( Q \), which is taken equal to:
\[ \langle Q \rangle = \text{Tr} \left\{ Q \exp(-\beta \mathcal{C}) \right\} / \text{Tr} \left\{ \exp(-\beta \mathcal{C}) \right\} \]

is expanded to the first order in \( \beta \):
\[ \langle Q \rangle \approx \frac{\text{Tr} \left\{ Q \right\}}{\text{Tr} \left\{ 1 \right\}} + \beta \left[ \frac{\text{Tr} \left\{ Q \right\}}{\text{Tr} \left\{ 1 \right\}} \times \frac{\text{Tr} \left\{ \mathcal{C} \right\}}{\text{Tr} \left\{ 1 \right\}} - \frac{\text{Tr} \left\{ Q \mathcal{C} \right\}}{\text{Tr} \left\{ 1 \right\}} \right]. \] (23)

When the effective field is zero, \( \mathcal{C} = \mathcal{H}_D' \) and 
\[ p_A = -p_B = p. \]

We call \( K_0 = (0, 0, \pi/a) \) the vector corresponding to the antiferromagnetic structure; that is, when the origin is taken at a lattice site of sublattice \( \mathcal{A} \), the polarization of the spin located at \( r_i \) is:
\[ p_i = p \exp(iK_0 \cdot r_i). \]

To the first-order restricted-trace approximation, the dipolar energy has the following value [8]:
\[ \langle \mathcal{H}_D' \rangle = N \left\{ \frac{1}{4} A(K_0) p^2 - \frac{1}{16} \beta [D(3 - 4 p^2 + 2 p^4) - \varepsilon p^2] \right\} \] (24)

where \( N \) is the number of nuclear spins in the sample, and:
\[ A(K_0) = \sum_j A_{ij} \exp[iK_0 \cdot (r_i - r_j)] \]
\[ = 9.687 \left( \frac{\gamma^2 \hbar}{2 a^3} \right) \]
where \( a \) is the lattice parameter,
\[ D = \sum_j A_{ij} = 13.357 \left( \frac{\gamma^2 \hbar}{2 a^3} \right)^2, \]
\[ \varepsilon = \sum_j A_{ij} \exp[iK_0 \cdot (r_i - r_j)] = -3.396 \left( \frac{\gamma^2 \hbar}{2 a^3} \right)^2. \]

This approximation yields, for eq. (18):
\[ \frac{d}{dt} \langle \mathcal{H}_D' \rangle = \frac{1}{64} \beta \tau_c \sum_{i,j} A_{ij}^2 (|h_i - h_j|^2)_{av} \times \{ 1 - p^2 \exp[iK_0 \cdot (r_i - r_j)] \}. \] (25)
In order to estimate the importance of the term in $p^2$, let us make the rough assumption that on the average the random fields are uncorrelated:

$$\langle [h_i - h_j]^2 \rangle_{av} = 2 \tilde{h}^2 = \text{Const.},$$

independently of the subscripts $i$ and $j$.

We then obtain:

$$\frac{d}{dt} \langle \mathcal{K}_D' \rangle \simeq \frac{1}{32} \beta \tau_\xi \bar{N} \tilde{h}^2 (3 - 8p^2)$$

where $\xi$ is positive constant.

In the high temperature limit, $p = 0$ and we have:

$$\beta = -16 \langle \mathcal{K}_D' \rangle / (3 \bar{N} D),$$

whence:

$$\frac{d}{dt} \langle \mathcal{K}_D' \rangle = -\frac{16 \xi}{3D} \langle \mathcal{K}_D' \rangle.$$  \hspace{1cm} (26)

If we call $T_1$ the characteristic time-constant of the exponential decay in this limit, we finally obtain:

$$\frac{d}{dt} \langle \mathcal{K}_D' \rangle = \frac{3}{16} \frac{N D}{T_1} \beta.$$  \hspace{1cm} (27)

We have plotted the variations with $\langle \mathcal{K}_D' \rangle$ of the quantities $-T_1 \frac{d}{dt} \langle \mathcal{K}_D' \rangle$ and $-T_1 \frac{d}{dt} \langle \ln \langle \mathcal{K}_D' \rangle \rangle$ in figures 2 and 3 respectively. As anticipated, the relaxation rate remains constant at low energy and decreases in the ordered state. The corresponding variation of $\langle \mathcal{K}_D' \rangle$ as a function of $(t/T_1)$ is plotted on figure 4. The figures correspond to the case of calcium fluoride. The origin of time, in figure 4, is of course arbitrary. It has to be adjusted to the initial value of the energy.

2nd case $\tau_c \gg T_2$. — We use for calculating the susceptibility $\chi$ of eq. (21) a makeshift combination of local Weiss-field and restricted-trace approximations. The paramagnetic impurities create at the sites of the nuclear spins an inhomogeneous dipolar field superimposed on the Weiss-field experienced by these nuclear spins in the ordered state. This causes an inhomogeneous departure of the individual spin polarizations with respect to the perfect ordered state. This departure in turn changes the Weiss-field seen by the nuclear spins, which contributes self-consistently to their inhomogeneous change of polarization. The susceptibility $\chi_{V-V}$ is equal to the Zeeman energy of the nuclear spins in the field of the impurities. As shown below, this susceptibility goes through a maximum at the transition temperature. What is predicted is then that, starting from the paramagnetic state, the slope $-\frac{d}{dt} (\ln \langle \mathcal{K}_D' \rangle) / dt$ increases with energy up to the transition energy, and then decreases.

According to the local Weiss-field approximation, the polarization of a spin 1/2 $I_i$ is related to the total field it experiences through:

$$p_i = \tanh (\frac{1}{2} \beta \omega_i)$$  \hspace{1cm} (29)

where $\omega_i$ is the Larmor frequency corresponding to that total field. The frequency $\omega_i$ is a sum of contributions from the Weiss-field in the perfect antiferromagnetic state, the impurity field, and the Weiss-field arising from the departure from perfect ordering. Since the impurity concentration is low, we can consider separately the effect of each impurity and

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**FIG. 2.** — Variation as a function of dipolar energy of the reduced time-derivative of this same energy under the effect of spin-lattice relaxation in CaF$_2$. The curves correspond to theory in the limiting cases $\tau_c < T_2$ and $\tau_c > T_2$. The experimental points are deduced from those of figure 4.

**FIG. 3.** — Variation as a function of dipolar energy of its reduced spin-lattice relaxation rate in CaF$_2$. Theoretical curves for $\tau_c < T_2$ and $\tau_c > T_2$, and experimental points.
then sum up their effects. We write, in the vicinity of a particular impurity:

\[ \omega_i = \omega_i^0 + h_i + \delta_i \]  

(30)

where the terms on the right-hand site correspond to the normal Weiss-field, the impurity field and the modified Weiss-field, respectively. As a rough approximation, we expand for simplicity the right-hand side of eq. (29) to the first order in \( h_i \) and \( \delta_i \):

\[ p_i \approx \tanh \left( -\frac{1}{2} \beta \omega_i^0 \right) - \frac{1}{2} \beta (h_i + \delta_i) \left[ 1 - \tanh^2 \left( -\frac{1}{2} \beta \omega_i^0 \right) \right]. \]

Since in the perfect ordered state, the polarizations are:

\[ p_i^0 = \tanh \left( -\frac{1}{2} \beta \omega_i^0 \right) = \pm p, \]

their departure from perfect ordering is:

\[ e_i = p_i - p_i^0 = -\frac{1}{2} \beta (1 - p^2) (h_i + \delta_i). \]  

(31)

We now introduce the space Fourier transforms of all localized quantities:

\[ e(k) = \frac{1}{\sqrt{N}} \sum_i e_i \exp(i \mathbf{k} \cdot \mathbf{r}_i), \]

\[ h(k) = \sum_i h_i \exp(i \mathbf{k} \cdot \mathbf{r}_i), \]

\[ \delta(k) = \sum_i \delta_i \exp(i \mathbf{k} \cdot \mathbf{r}_i), \]

where \( N \) is the number of nuclear spins and \( \mathbf{k} \) is a vector of the reciprocal lattice belonging to the first Brillouin zone. The origin is taken at the site of the impurity. As this origin is a centre of symmetry and \( h_i \) is a dipolar field, we have \( h(k) = h(-k) \). On the other hand we have, according to the local Weiss-field approximation:

\[ \delta_i = \sum_j A_{ij} e_j, \]

whence:

\[ \delta(k) = \sqrt{N} A(k) e(k) \]  

(32)

with:

\[ A(k) = \sum_i A_{ij} \exp[i \mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)]. \]

We also have \( A(k) = A(-k) \).

By taking the Fourier transforms of both sides of eq. (31), we obtain:

\[ e(k) = -\frac{1}{2} \beta (1 - p^2) \left[ h(k) + \delta(k) \right]. \]

Or else, according to eq. (32):

\[ e(k) = -\frac{1}{2} \beta (1 - p^2) \left[ \frac{h(k)}{\sqrt{N}} + A(k) e(k) \right] \]

which yields:

\[ e(k) = -\frac{1}{2} \frac{1}{\sqrt{N}} \beta (1 - p^2) \times \left[ 1 + \frac{1}{2} \beta (1 - p^2) A(k) \right]. \]

(33)

This describes the departure from perfect order created by one impurity. Its contribution to the susceptibility \( \chi_{v-v} \) is:

\[ \frac{1}{2} \sum h_i e_i = \frac{1}{2} \sum_k h(k) e(k). \]

The \( n \) impurities of the sample yield equal contributions to \( \chi \), and we obtain, according to eqs. (21) and (33):

\[ \frac{d}{dt} \langle \mathcal{X}_D \rangle = \frac{n}{4 N \tau_e} \beta (1 - p^2) \times \frac{h(k)^2}{\sum_k \left[ 1 + \frac{1}{2} \beta (1 - p^2) A(k) \right]^2}. \]  

(34)

It can be shown that \( \frac{1}{2} \beta (1 - p^2) \) is minimum for \( \beta = \beta_c \) (we recall that \( \beta < 0 \)). This is due to the fast increase of the polarization \( p \) below the transition. It is easily proved by an expansion of the Weiss-field equation:

\[ p = \tanh \left[ -\frac{1}{2} \beta A(K_0) p \right] \]  

around the transition inverse temperature:

\[ \beta_c = -\frac{2}{\beta A(K_0)}. \]  

(36)

For those modes \( k \) for which \( A(k) \) is close to \( A(K_0) \), the polarization departure \( e(k) \) is sharply peaked at the transition. As a consequence, the sum on the right-hand side of eq. (34) is maximum at \( \beta = \beta_c \). Since on the other hand \( \langle \mathcal{X}_D \rangle \) is a monotonic function of \( \beta \), we find that both

\[ -\frac{d}{dt} \langle \mathcal{X}_D \rangle \quad \text{and} \quad -\frac{d}{dt} (\ln \langle \mathcal{X}_D \rangle) \]

are maximum at \( \beta = \beta_c \), as anticipated.

The Weiss-field approximation is not suitable for describing the variation of \( d \langle \mathcal{X}_D \rangle /dt \) as a function of energy, because it predicts that the latter vanishes in the paramagnetic phase. It is not possible either to use eq. (34) while calculating the energy as a function of \( \beta \) through the restricted-trace formula (24). The reason is that the value of \( | \beta_c | \) in the restricted-trace approximation is higher than that predicted by eq. (36), which would cause a spurious divergence of the right-hand side of eq. (34) around the transition. To avoid this we express eq. (34) as a function of
reduced temperature, that is we write according to eq. (36):

\[
\frac{1}{2} \beta = - \left( \frac{\beta_0}{\beta_c} \right) A(K_0).
\] (37)

We insert this value into eq. (34) and we compute both \( \langle K'_D \rangle \) and \( \beta_e \) through the restricted-trace approximation. We use as before the relaxation time \( T_1 \) in the high-temperature limit, so as to eliminate the unknown quantities, and we obtain finally:

\[
\frac{d}{dt} \langle K'_D \rangle = \beta (1 - p^2) \frac{3 N_D}{16 T_1} \times \\
\times \sum_k \frac{h(k)^2}{1 - \left( \frac{\beta_e}{\beta_c} \right) (1 - p^2) \left( A(k)/A(K_0) \right)} \sum_k h(k)^2.
\] (38)

It is in fact possible to avoid the approximation (37) and to calculate \( K_{1,2} \) within the restricted-trace approximation too. This however does not modify the qualitative features of eq. (38), and the effort is not warranted by the approximate character of the theory.

There remains to estimate the sums in eq. (38). The fields \( h_i \) are dipolar fields created by the paramagnetic impurities, whose Fourier transforms have been computed \[9\]. We make a further approximation, as follows. The nuclei which are close to the impurities experience a large electronic field and are not in thermal contact with the average nuclear spins. The latter, which are located outside the diffusion barrier, experience electronic fields which vary slowly over an internuclear distance. It is then reasonable to assume that only small \( k \) values (i.e. \( ka \ll 1 \)) contribute to the sums on the right-hand side of eq. (38). In this limit, the Fourier transforms have the following very simple values \[9\] :

\[
A(k) = \frac{4 \pi}{3} (3 \cos^2 \theta_k - 1) \frac{\gamma^2 h}{2 a^3}
\] (39)

were \( \theta_k \) is the angle between \( k \) and the external d.c. field, and

\[
h(k) \propto A(k).
\]

A straightforward but tedious calculation yields finally:

\[
\frac{d}{dt} \langle K'_D \rangle = \frac{\xi}{\alpha T_1} \left\{ \frac{1}{\sqrt{3 \alpha}} \tanh^{-1} \left( \frac{\sqrt{3 \alpha}}{\sqrt{1 + \alpha}} \right) - 1 \right\}
\] (40)

with:

\[
\alpha = \frac{\beta_0}{\beta_c} (1 - p^2) \frac{4 \pi}{3 A(K_0)} \frac{\gamma^2 h}{2 a^3},
\]

and:

\[
\xi = \frac{15}{64} N_D \beta_0 \cdot \frac{3 A(K_0)}{4 \pi} \cdot \frac{2 a^3}{\gamma^2 h}.
\]

Eq. (40) is valid only when \( \alpha > 0 \), that is at negative temperature \( A(K_0) > 0 \). The expression is slightly different for an ordered structure at positive temperature:

\[
\frac{d}{dt} \langle K'_D \rangle = \frac{\xi}{\alpha T_1} \left\{ \frac{1}{\sqrt{3 \alpha}} \tanh^{-1} \left( \frac{\sqrt{3 \alpha}}{\sqrt{1 + \alpha}} \right) - 1 \right\}
\] (40')

In the present case the predicted variations, as a function of \( \langle K'_D \rangle \), of

\[- T_1 \frac{d}{dt} \langle K'_D \rangle \quad \text{and} \quad T_1 \frac{d}{dt} (\ln \langle K'_D \rangle)
\]

are plotted in figures 2 and 3, respectively. The corresponding variation of \( \langle K'_D \rangle \) with \( (t/T_1) \) is plotted in figure 4.

![Fig. 4. Reduced time-variation of dipolar energy under the effect of spin-lattice relaxation. Theoretical curves for \( \tau_e \ll T_2 \), and \( \tau_e \geq T_2 \), and experimental results. The value of \( T_1 \) is adjusted to the low-energy portion of the decay.](image)

The peak of relaxation rate at the transition is probably over-emphasized by the present approximation. We believe however that it should exist, in the light of a related study: the susceptibility of the dipolar coupling between \( ^{19}F \) and \( ^{43}Ca \) spins to the dipolar field of the calcium nuclei \[10\]. As predicted by a theory analogous to the present one, this susceptibility is observed to go through a maximum at the transition. This study is outside the scope of the present article.

To summarize, the qualitative features of the spin-lattice relaxation, as predicted by the present theory, are the following.

For \( \tau_e \ll T_2 \), \(- d \langle K'_D \rangle/dt \) is approximately proportional to the energy in the paramagnetic state,
and it increases much more slowly with energy in the antiferromagnetic state.

Accordingly, the relaxation rate $-d(<\mathcal{H}_{D}^{2}>)/dt$ is approximately constant in the paramagnetic state, and then decreases.

For $\tau_{c} \gg T_{2}$, $-d(<\mathcal{H}_{D}^{2}>)/dt$ increases faster than $<\mathcal{H}_{D}^{2}>$ in the paramagnetic state, it reaches a maximum at the transition and then decreases.

Accordingly, $-d(<\mathcal{H}_{D}^{2}>)/dt$ increases with energy up to the transition and then decreases.

3. Experimental methods and results. — The experiments have been performed on spherical samples of calcium fluoride, of 1.3 mm diameter, doped with Tm$^{2+}$ ions at a concentration Tm$^{2+}$/F$^{-}$ of $1.2 \times 10^{-5}$. The fluorine spins are dynamically polarized through the Solid Effect with the Tm$^{2+}$ in a field of 27 kG, with a microwave irradiation frequency of 130 GHz. The fluorine polarization obtained after 3 to 4 hours is of the order of 90%. The microwave power is then cut off, the sample is cooled down to below 0.3 K by pumping over the liquid $^3$He bath in which it is immersed, and the adiabatic demagnetization in the rotating frame is performed by applying a r.f. field $H_{1} \approx 30$ mG and sweeping the external field at a rate of 1 G/s down to resonance.

The nuclear signal at the output of a Q-meter is recorded on a multichannel analyzer during linear sweeps of the magnetic field at a rate of 700 G/s. The field sweeps are grouped in sequences of ten passages made at 1 s interval, and the cumulative signal corresponding to each sequence is stored in a calculator. The sequences are repeated every 20 to 30 s. The dipolar energy for each sequence is deduced from the first moment of the corresponding nuclear absorption signal [3]. As explained in this reference, the gain of the receiver is determined by measuring both the area and the second moment of the fluorine resonance signal prior to the demagnetization. This allows an absolute calibration of the dipolar energy with an accuracy of about 5%. The relative saturation of dipolar energy caused by each passage is 1.5 $\times 10^{-4}$.

The dipolar relaxation time in the low-energy limit varies from 160 to 180 s depending on the sample and on the temperature achieved in each run. This relaxation is not due to the Tm$^{2+}$ ions, as proved by its temperature dependence. The relaxation rate caused by these ions is indeed proportional to $(1 - P^{2})/P$, where $P$ is the electronic thermal equilibrium polarization. In high field and at low temperature, this corresponds to:

$$ T_{1} \propto \exp(h\omega/kT). \quad (41) $$

Experimentally, $T_{1}$ varies according to eq. (41) down to 0.6 K and increases much more slowly than predicted by this equation at lower temperatures, which indicates that the relaxation is then caused by a different impurity. We have so far not determined its nature and we have thus no direct knowledge of whether the correlation time $\tau_{c}$ for the relaxation of the dipolar energy is longer or shorter than the nuclear $T_{2}$.

The experimental variation of $<\mathcal{H}_{D}^{2}>$ with time is shown in figure 4. The points correspond to two different experiments. The only adjustment is that of $T_{1}$ in the low-energy limit. These results have been used to compute the variations with $<\mathcal{H}_{D}^{2}>$ of:

$$ - T_{1} d(<\mathcal{H}_{D}^{2}>)/dt \quad \text{and} \quad - T d(ln(<\mathcal{H}_{D}^{2}>))/dt, $$

which are shown in figures 2 and 3, respectively.

The qualitative features of these results are sufficiently clean to substantiate the conclusion that we are in the case when $\tau_{c} \ll T_{2}$. The striking agreement with the numerical predictions for that case is accidental, as evidenced by the results obtained when studying the variation of the $^{43}$Ca-$^{19}$F energy as a function of the $^{19}$F-$^{19}$F energy [10]. This last study yields for the transition energy the value of $\sim 2.5$ kHz per spin, approximately 50% higher than the value $1.62$ kHz per spin predicted by the 1st order restricted-trace approximation. On physical grounds one predicts the occurrence in the paramagnetic domain of a fast increase of the energy associated with the longitudinal correlations at the approach of the transition. This is closely related to the divergence of the susceptibility to a longitudinal periodic field of wave-vector $K_{0}$ (the so-called staggered susceptibility), as evidenced for instance by an approximation of the Ornstein-Zernike type (see for instance [11]). Since the energy associated with transverse correlations is not expected to experience such a large increase we are led, in view of eq. (18), to the qualitative conclusion that the relaxation rate of the dipolar energy must already decrease in the paramagnetic domain at the approach of the transition, which agrees with the results. This discussion establishes that there is no inconsistency between the present results and those of reference [10]. It also sets a limit to the quantitative validity of the present theory of relaxation.

4. Conclusion. — We have developed the theory of spin-lattice relaxation of the dipolar energy in a nuclear spin system which undergoes a transition to an antiferromagnetic phase. We have assumed that the relaxation was due to the coupling of the nuclei with fixed paramagnetic impurities. On very general grounds one predicts a qualitatively different behaviour when the correlation time $\tau_{c}$ of this coupling is longer or shorter than the nuclear inverse linewidth $T_{2}$. When $\tau_{c} \ll T_{2}$, the relaxation rate is expected to decrease steadily as a function of energy below the transition, whereas when $\tau_{c} \gg T_{2}$ this rate is expected to be peaked at the transition and then to decrease.

As the theory is essentially concerned with the change in relaxation rate when going from the paramagnetic to the ordered phase, it is essential to use approximations which cover both phases with the
same formalism. This is the case for the approximations used here: local Weiss-field for the relaxation rate and restricted-trace approximation for the energy.

The experimental results obtained in calcium fluoride exhibit the features expected for the case when $\tau_0 \ll T_2$. The comparison with a different experiment [10] reveals however that the relaxation rate begins to decrease already in the paramagnetic phase, which can be qualitatively interpreted.

Despite its obvious shortcomings, the combination of local Weiss-field and restricted-trace approximations yields a correct order of magnitude for the variation of the spin-lattice relaxation rate.

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