Pulsed variation of temperature of dipole-dipole interaction reservoir in nuclear-nuclear double resonance

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The effect of pulsed transfer of order from a Zeeman spin system to a dipole-dipole reservoir is investigated for a multispin system. The local field is calculated in a rotating coordinate system for the case of pure dipole-dipole interaction in a LiF single crystal, which makes it possible to compare—in the Gaussian approximation—the theory with experiment when the dipole-dipole interaction reservoir is cooled by a $90°$–$\theta_{90°}$ pulse series. It is pointed out that the nonresonant saturation of an NMR line can be used in detection of nuclear magnetic resonances in multispin systems.

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1. Lowering of the spin temperature in nuclei in a solid by the application of strong static magnetic fields is used widely in various NMR experiments. Nuclear–nuclear double resonance (NNDR) plays a major role in these experiments[1,2] and it can be used to study the dynamics of spin–spin processes, record high-resolution spectra of solids, and detect very weak NMR signals. The NNDR method utilizing cooling of the reservoir of dipole–dipole interactions[3,4] has certain advantages. The influence of this reservoir in NMR during continuous application of an hf magnetic field is discussed by Provotorov[5] and investigations of the same reservoir under pulse resonance illumination conditions are reported in[6,7]. Experiments involving pulsed cooling in NNDR have been carried out in solids with two or more types of spin. In such cases it is frequently necessary to allow for the contribution of nonresonant spins to the total dipole–dipole reservoir. Therefore, it would be desirable to investigate in greater detail this specific case in order to determine the temperature and optimal conditions for cooling of the reservoir. Moreover, it would be interesting to test the possibility of using pulsed nonresonant saturation of the NMR line to lower the temperature of the reservoir.

2. The application to nuclei in a solid of a series of $90° - \tau_{12} - \theta_{90°}$ hf pulses at the resonance frequency lowers the temperature of the dipole–dipole interaction reservoir. The cooling effect can be described quantitatively by a method presented in[7] and also bearing in mind that the secular part of the dipole–dipole interaction is now of the form

$$\mathcal{H}'_D = d + u,$$
$$d = a_{ij}(3I_z^i I_z^j - \mathbf{I}^i\mathbf{I}^j), \quad u = b_{ik} I_z^i S_z^k,$$

where I and S are the resonant and nonresonant spins. Calculations show that

$$\frac{\beta}{\beta_L} = \frac{(A\cos\theta + B)H_0 \sin\theta}{\gamma_I {}^1H_L^2} = K\frac{H_0}{{}^1H_L}. \tag{1}$$

Here, β is the reciprocal temperature of the reservoir; β_L is the initial reciprocal temperature of the reservoir equal to the lattice temperature; H_0 is the resonance value of the magnetic field and γ_I is the gyromagnetic ratio of nuclei of type I; θ is the angle of rotation of the magnetization by the second hf pulse; K is the reservoir cooling coefficient ($K = 1$ corresponds to the adiabatic cooling of the reservoir). The quantity ${}^1H_L$, which occurs in Eq. (1), is defined by

$${}^1H_L^2 = \frac{1}{3}{}^1M_{2II} + {}^1M_{2IS} + \frac{1}{3}\frac{\gamma_S^2 N_S S(S+1)}{\gamma_I^2 N_I I(I+1)}{}^sM_{2SS}, \tag{2}$$

where ${}^1M_{2II}$, ${}^1M_{2IS}$, and ${}^sM_{2SS}$ are the second moments of the NMR line at the frequencies of the nuclei I and S (units: G^2); N_I and N_S are the concentrations of the nuclei.

Equation (2) is the energy definition of the local field in a rotating coordinate system. It is based on the invariance of the dipole–dipole energy relative to the selection of this coordinate system.[7] Therefore, it does not represent the local field deduced from the line profile. The local field defined by Eq. (2) can be used to find the energy characteristics of the investigated switch system and in our case to find the temperature of the dipole–dipole reservoir.

The coefficients A and B in Eq. (1) are defined by

$$A = -\mathrm{Tr}\{i[d, I_y]\exp(-i\mathcal{H}_D'\tau) I_y \exp(i\mathcal{H}_D'\tau)\}/\mathrm{Tr}\, I_y^2, \tag{3}$$
$$B = -\mathrm{Tr}\{i[u, I_y]\exp(-i\mathcal{H}_D'\tau) I_y \exp(i\mathcal{H}_D'\tau)\}/\mathrm{Tr}\, I_y^2. \tag{4}$$

In the case of a single-spin system we have $B = 0$ and it then follows from Eq. (1) that the maximum cooling occurs for $\theta = 45°$ when the pulse separation τ_{12} corresponds to the moment and the derivative of the Zeeman free induction signal $G(t)$ has its maximum. Then, the ratio β/β_L is proportional to the derivative of $G(t)$ at this moment.[6,7]

We shall now consider the case of a two-spin system. (The case of a multispin system is easily reduced to the two-spin case.) If the NMR line profile is Gaussian, the free-induction signal is

$${}^1G(t) = \exp[-{}^1M_2 t^2/2] = \exp[({}^1M_{2II} + {}^1M_{2IS})t^2/2]. \tag{5}$$

In the Gaussian approximation the coefficients A and B in Eq. (1) become

$$A = -{}^1M_{2II} t \exp[-M_2 t^2/2], \tag{6}$$
$$B = -{}^1M_{2IS} t \exp[-M_2 t^2/2]. \tag{7}$$

A direct esimate of Eqs. (3) and (4) up to the second-order approximation[1] confirms this correspondence. Following[7] and using Eqs. (6) and (7), we obtain the following approximate expression for the signal $\langle I_y\rangle_D$

TABLE 1. Calculated and measured parameters of LiF single crystal in reservoir cooling experiments.

LiF	[100]	[110]	[111]	LiF	[100]	[110]	[111]
${}^{F}M_{2(F-F)}$, G^2	6.473	9.236	10.16	θ^{meas}	75°±2.4°	57°±1.5°	46.7°±1°
${}^{F}M_{2(F-Li)}$, G^2	25.90	7.434	1.278	K^{calc}	0.524	0.441	0.413
${}^{F}H_L^{calc}$, G	5.422	3.525	2.604	K^{meas}	0.58±0.02	0.5±0.02	0.51±0.02
				H_{1Li}, G	1.52±0.08	1.07±0.08	0.88±0.08
${}^{Li}H_L^{calc}$, G	6.101	3.967	2.929	K_1^{calc}	0.49	0.49	0.48
${}^{Li}H_L^{meas}$, G	7.58±0.3	4.67±0.2	3.00±0.2	K_1^{meas}	0.49±0.02	0.48±0.02	0.3±0.02
τ_{12}^{calc}, sec	7	9.7	12	${}^{F}T_{1z}$, msec	23±1	19.5±1	11.3±0.6
τ_{12}^{meas}, sec	6.6±0.2	9.2±0.3	12.6±0.5				
θ^{calc}	77°	57.7°	47.4°				

proportional to the dipole–dipole reservoir temperature in the case of two types of spin[11]:

$$\langle I_y\rangle_D = \beta \operatorname{Sp} I_y^2 \frac{\partial G}{\partial t}\left[\frac{{}^{I}M_{2II}\cos\theta + {}^{I}M_{2IS}}{{}^{I}M_{2II}+{}^{I}M_{2IS}}\right]\sin\theta. \qquad (8)$$

Thus, not only in the case of small angles θ[7] but also within the limits of validity of the Gaussian approximation is the $\langle I_y\rangle_D$ signal proportional to $\partial G/\partial t$.

The use of Eqs. (1), (6), and (7) gives the separation β/β_L between the pulses for which the ratio has its maximum value: $\tau_{12} = 1/\sqrt{M_2}$. Comparison with the single-spin case shows that an extremum of the dipole–dipole reservoir cooling again corresponds to the maximum value of the derivative of the free-induction signal. In this case the value of τ_{12} is independent of θ and, consequently, the process of achieving a maximum cooling of the reservoir should start with selection of τ_{12}.

3. Our analysis gives numerical estimates of the values of K, θ, and τ_{12} corresponding to the β/β_L maximum in the case of a LiF single crystal (Table 1).

We shall assume that the spins I are those of the F^{19} nuclei and the spins S are of the Li^7 nuclei.

We calculated ${}^{I}M_{2II}$ and ${}^{S}M_{2SS}$ using the formulas given by Lösche[8] for an fcc lattice. The lattice constant was assumed to be $r = 4.02$ Å. In the calculation of ${}^{I}M_{2IS}$ the necessary lattice sum could be represented as a difference between a sum over a simple cubic lattice with the constant $r/2$ and the sum over an fcc lattice with the constant r. The use of appropriate values of the lattice sums from[8] gave the following formula for the contribution made to the second moment of the I nuclei by the I–S dipole–dipole interaction in a crystal oriented in various ways relative to the magnetic field:

$${}^{I}M_{2IS} = \frac{1120{,}6}{r^6}\gamma_S^2\hbar^2 S(S+1)\left[\lambda_1^4+\lambda_2^4+\lambda_3^4-0{,}2987\right]\ (2c^2). \qquad (9)$$

In Eq. (9) the quantities λ_1, λ_2, and λ_3 are the direction cosines of the magnetic field H_0 relative to the crystallographic axes.

In all the calculations of the second moments we allowed for the natural abundance of Li^7 (92.57%) and ignored the contribution of the Li^6 nuclei.

4. We determined the values of K, θ, and τ_{12} experimentally for a LiF + 0.8% NiF_2 single crystal at 77 °K in a field $H_0 = 5300$ G ween the amplitude of the rotating magnetic field was $H_1 \approx 40$ G (Table 1). The precision of the alignment of a crystal in the magnetic field was 1–2°. It should be pointed out immediately that the quoted concentration of Ni^{2+} was obtained from a spectroscopic analysis of the crystal. A direct observation of the ESR of Ni^{2+} gave qualitative confirmation of the presence of these ions and an estimate based on the spin–lattice relaxation time T_{1z} of the F^{19} nuclei confirmed quantitatively the presence of ≈ 0.08% of NiF_2. Allowance for the contribution of the electron–nuclear interaction to the local fields at the nuclei indicated that it should be ~ 10% larger than the values calculated solely for the nuclear dipole–dipole interaction.

5. Let us now consider the case when the dipole–dipole reservoir is cooled by slightly off-resonance pulse saturation of an NMR line. If the duration of the saturating hf pulse is considerably less than the spin–lattice relaxation times of the Zeeman subsystem (T_{1z}) and of the dipole–dipole reservoir (T_{1d}) but much greater than T_2, the change in the reservoir temperature solely due to the application of an hf pulse H_{1S} subject to a detuning $\pm h$ relative to the resonance of the S nuclei is[7]

$$\frac{\beta}{\beta_L} = \pm\frac{H_0 h}{h^2 + H_{1S}^2 + {}^{S}H_L^2} \qquad (10)$$

so that

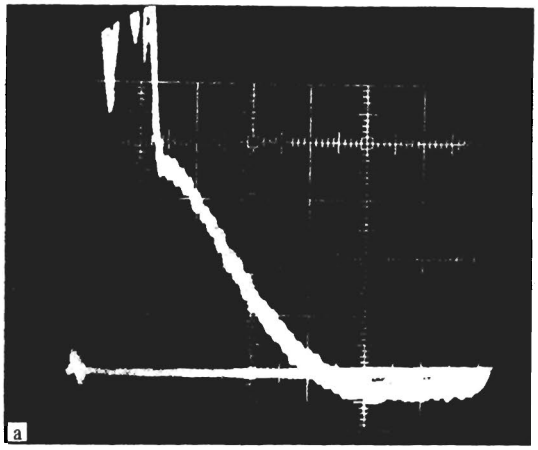
$$\left(\frac{\beta}{\beta_L}\right)_{\max} = \pm\frac{H_0}{2\sqrt{H_{1S}^2+{}^{S}H_L^2}} = K_1\frac{H_0}{{}^{S}H_L}. \qquad (11)$$

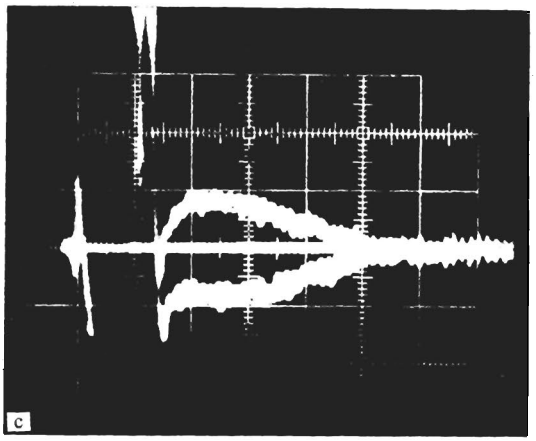
where K_1 is the cooling coefficient of the reservoir in the case of off-resonance saturation of an NMR line.

Our experiments were carried out on the same LiF crystal as before. An hf pulse of H_{1S} amplitude and 2.5 msec duration detuned by h acted upon the S nuclei and this lowered the temperature of the reservoir to a value β. Since the temperature was recorded by a pulse θ at the frequency of the nuclei I, we used

$$K_1 = K_{1\,meas}\frac{{}^{S}H_L}{{}^{I}H_L}, \qquad (12)$$

where $K_{1\,meas}$ is the cooling coefficient measured at the frequency of the I nuclei.





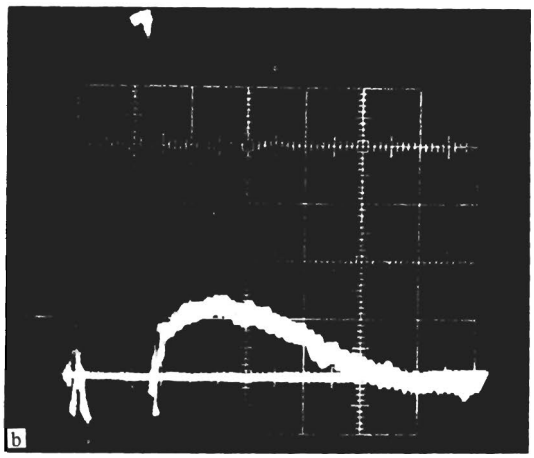


FIG. 1. Oscillograms of free-induction signals of the F^{19} nuclei observed on application of an hf pulse to LiF subjected to a field $H_0 \parallel [110]$: a) Zeeman free induction after a $\theta = 90°$ hf pulse; b) dipole free induction after a $\theta = 57°$ hf pulse, recorded 150 μsec after the end of a $90°-9.2\ \mu\text{sec}-57°_{90°}$ pulse series; c) dipole free induction observed 150 μsec after nonresonant saturation of an NMR line of Li^7 ($h = 4.8$ G). The horizontal scale is 5 μsec/div.

In all three orientations of a crystal the amplitude H_{1S} was detuned to the maximum of the signal proportional to the reservoir temperature. This maximum appeared because of an increase during a pulse, in the time taken to reach an equilibrium between the Zeeman and dipole subsystems when the amplitude H_{1S} was reduced.

These experiments demonstrated that the measured value of ${}^{S}H_{L}^{\text{meas}}$ was greater than the value calculated for the case of the dipole–dipole interaction alone. Estimates indicated that this excess could be due to the presence of Ni^{2+} ions. Therefore, we calculated K_1 using the experimental values of ${}^{S}H_{L}$ (Table 1). The difference between the theoretical and experimental results in the $H_0 \parallel [111]$ orientation could be due to a considerable reduction in the spin–lattice relaxation times T_{1s} and T_{1d} of the Li^7 and F^{19} nuclei in this orientation. Typical oscillograms observed experimentally are shown in Fig. 1.

The cooling coefficients K_1 obtained indicate that nonresonant saturation of NMR line can be used sucessfully to cool the dipole–dipole reservoir in pulse NNDR experiments. Moreover, if the S nuclei have large values of γ_S and N_S or are characterized by a strong quadrupole splitting, we can record NMR lines by controlling the reservoir temperature with the aid of, for example, a pulse θ_I.

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