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EFFECT OF PHONON HEATING IN NUCLEAR SPIN-LATTICE RELAXATION

L. L. BUISHVILI, N. P. GIORGADZE, and G. R. KHUTSISHVILI

Physics Institute, Georgian Academy of Sciences

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The possibility that a phonon bottleneck (PB) effect may appear in nuclear spin-lattice relaxation is discussed under the assumption that the relaxation is due to paramagnetic impurities. The case of small impurity concentration is considered, when the nuclear spin relaxation proceeds as a result of interaction with the impurity with simultaneous participation of the lattice. The case of a sufficiently large impurity concentration, when nuclear relaxation proceeds via the electron-spin dipole-dipole reservoir, is also considered. It is shown that the condition for the occurrence of a PB effect in the nuclear relaxation is very stringent; this is connected with the small heat capacity of the nuclear Zeeman reservoir. In this case, even when the PB coefficient is great, the appearance of a PB effect depends on the duration of the NMR saturation. Moreover, when the PB effect is absent in the spin-lattice relaxation of the nuclei but occurs in that of the electrons, the nuclear spin-lattice relaxation time is given by a familiar expression in terms of the electron spin-lattice relaxation time T_{sp} in the absence of a PB (and not in terms of the experimentally observed relaxation time of an electron spin in PB conditions).

1. THE phonon heating effect (usually called the phonon bottleneck effect) in electron spin-lattice relaxation is well known; in it, phonons of the Zeeman frequency are heated in a one-phonon process, receiving the energy of the relaxing spins. The experimentally observed rate at which the spin system reaches equilibrium with the heat reservoir is determined by the rate of transfer of energy from the "resonance" phonons to the thermostat.

A phonon bottleneck (PB) occurs at low temperatures, high magnetic fields and high impurity concentrations. Under these conditions, the heat capacity of the phonon system is relatively small, as is also the rate of transfer of energy from the "resonance" phonons to the thermostat. Under PB conditions, the experimentally observed relaxation time becomes dependent on the sample dimensions, and its temperature dependence also changes.

It was recently noted by Day, Otsuka, and Josephson[1] that the relaxation time also depends on the sample dimensions in the case of nuclear spin-lattice relaxation at low temperatures and strong magnetic fields, and on this basis the authors concluded that heating of "resonance" phonons can also play a role in nuclear spin-lattice relaxation. However, the theory on which they relied in interpreting the experimental results did not permit them to carry out a subsequent calculation of the PB effect.

Murtazin[2] treated theoretically the effect of a PB on the nuclear spin-lattice relaxation, but did not take account of the change in the temperature of the electron Zeeman subsystem in the nuclear spin-lattice relaxation process; this change, as will be shown below, plays an essential role.

Finally, we note that Josephson (private communication) has considered the question of the role of the PB in nuclear spin-lattice relaxation within the framework of the shell-of-influence model;[3] it is concluded that, in each case, this role is unimportant under the conditions of the Berkeley group's experiments.

It is important that, in all the papers discussed above, a small impurity concentration was assumed. At large concentrations the dipole-dipole interaction of the electron spins plays an important role: the nuclear spin-lattice relaxation proceeds via the dipole-dipole reservoir, and in this situation, the PB picture differs markedly from the situation found at small concentrations.

In this paper an attempt is made, from a unique standpoint, to take account of the PB effect in nuclear relaxation under conditions when the relaxation is due to paramagnetic impurities; in each case we distinguish an aggregate of weakly interacting subsystems, and describe these by applying the non-equilibrium statistical operator (NSO) method developed by Zubarev.[4]

2. First we shall examine the case of small concentration of paramagnetic impurity, when the interaction between impurity atoms can be neglected. Under these conditions, relaxation of a nuclear spin proceeds by means of interaction with a paramagnetic impurity with simultaneous participation of the lattice; then the whole system can be represented as an aggregate of the following subsystems: nuclear Zeeman, electron Zeeman[1] and resonance-phonon subsystem (with definite widths), and the thermostat, with which only the phonons are directly connected.

The Hamiltonian of the system has the form ($\hbar = 1$)

$$\mathscr{H} = \omega_s \sum_n S_n^z - \omega_I \sum_i I_i^z + \sum_\omega \mathscr{H}_\omega + \mathscr{H}_0 + \mathscr{H}', \tag{1}$$

where the first two terms represent the Zeeman energies of the electrons and nuclei respectively, the third

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[1] In fact, inasmuch as the interaction between electron spins is neglected, it is, strictly speaking, incorrect to introduce an electron Zeeman subsystem. It is more correct to speak of occupation numbers. However, if we confine ourselves to electron spin ½, there will be, in all, one independent parameter; we can take the temperature as this parameter and formally treat the electron Zeeman reservoir as a subsystem.

term represents the phonon energy, and the fourth the energy of the thermostat. Finally, the interaction between the subsystems is

$$\mathscr{H}' = \mathscr{H}_{Is} + \mathscr{H}_{sL} + \sum_{\omega} \mathscr{H}_{0\omega}. \tag{2}$$

The first term here denotes the effective part of the dipole-dipole interaction between the electron and nuclear spins:

$$\mathscr{H}_{Is} = \frac{1}{2}\sum_{in}(v_{in}^{+z}I_i^{-} + v_{in}^{-z}I_i^{+})S_n^{z}, \tag{3a}$$

The second denotes the electron-spin-lattice interaction, chosen for simplicity to be linear in the electron spins:[2)]

$$\mathscr{H}_{sL} = \sum_{n} \mathbf{LS}_n, \tag{3b}$$

and the third is the interaction between the phonons and the thermostat.

We turn now to the derivation of equations describing the evolution of the inverse temperatures β_n (n labels the subsystems) of the separate subsystems.[3)] Setting up operator equations of motion for the Hamiltonians of the subsystems:

$$\begin{gathered}
\omega_s\frac{dS^z}{dt} = \frac{\omega_s}{2i}\sum_{n}(L^{-}S_n^{+} - L^{+}S_n^{-}) \equiv \mathscr{K}_s,\\
-\omega_I\frac{dI^z}{dt} = \frac{\omega_I}{2i}\sum_{in}(v_{in}^{-z}I_i^{+} - v_{in}^{+z}I_i^{-})S_n^{z} \equiv \mathscr{K}_I,\\
\frac{d\mathscr{H}_\omega}{dt} = -\frac{1}{2}\sum_{n}(S_n^{-}L_\omega^{+} + S_n^{+}L_\omega^{-}) + \frac{d\mathscr{H}_{0\omega}}{dt} \equiv \mathscr{K}_\omega,
\end{gathered} \tag{4}$$

where

$$L_\omega^{\pm} = i^{-1}[L_\omega^{\pm}\mathscr{H}_\omega], \quad S^z = \sum_{n} S_n^z, \quad I^z = \sum_{i} I_i^z,$$

and following [4], we easily derive the NSO in the form

$$\rho = Q\exp\Big\{-\beta_0\mathscr{H}_0 - \sum_{\omega}\beta(\omega)\mathscr{H}_\omega - \beta_s\omega_s S^z + \beta_I\omega_I I^z$$
$$+ \int_{-\infty}^{0} dt\, e^{\varepsilon t}\Big[\sum_{\omega}(\beta(\omega) - \beta_0)\mathscr{K}_\omega(t) + (\beta_s - \beta_0)\mathscr{K}_S(t) + (\beta_I - \beta_0)\mathscr{K}_I(t)\Big]\Big\} \tag{5}$$

where

$$A(t) = e^{i\mathscr{H}t}Ae^{-i\mathscr{H}t}, \quad \varepsilon > 0.$$

The expression (5) for the NSO is valid for times greater than the short time necessary for the establishment of internal equilibrium in the subsystems which we have distinguished.

Further, expanding the NSO in small temperature differences and applying the high-temperature approximation ($\beta_S\omega_S \ll 1$, $\beta_I\omega_I \ll 1$) for the electron and nuclear Zeeman energies, after certain calculations we find for the average fluxes

$$\overline{\mathscr{K}_m} = \sum_{n}(\beta_n - \beta_0)\mathscr{L}_{mn}, \tag{6}$$

where

$$\mathscr{L}_{mn} = \int_{-\infty}^{0} dt\, e^{\varepsilon t}\frac{1}{\beta_0}\int_{0}^{\beta_0} d\lambda\, \mathrm{Sp}\,(\rho_L\,\mathscr{K}_m(0)\,e^{-\lambda\mathscr{H}_L}\mathscr{K}_n(t)\,e^{\lambda\mathscr{H}_L}),$$
$$\rho_L = \frac{e^{-\beta_0\mathscr{H}_L}}{\mathrm{Sp}\,e^{-\beta_0\mathscr{H}_L}}, \quad \mathscr{H}_L = \mathscr{H}_0 + \sum_{\omega}\frac{\beta(\omega)}{\beta_0}\mathscr{H}_\omega. \tag{7}$$

We introduce the quantities

$$c_s = {}^1\!/_4\,\omega_s^2N_s, \quad c_I = {}^1\!/_3\,\omega_I^2I(I+1)N_I, \quad c(\omega) = 3\omega^2\Delta(\omega)\,/\,2\pi^2c^3\beta_0^2, \tag{8}$$

where N_S and N_I are the electron and nuclear spin concentrations, c is the velocity of sound, and $\Delta(\omega)$ is the width of the corresponding phonon subsystem. These quantities are proportional to the heat capacities of the corresponding subsystems.

Assuming, within the framework of the NSO method, that the process is quasi-static,[4] we obtain the following system of equations for the time evolution of the inverse temperatures of the different subsystems:

$$\begin{aligned}
\frac{d\beta_I}{dt} &= -\frac{1}{T^{+}}\Big[\beta_I - \frac{\omega_s+\omega_I}{\omega_I}\beta(\omega_s+\omega_I) + \frac{\omega_s}{\omega_I}\beta_s\Big]\\
&\quad - \frac{1}{T^{-}}\Big[\beta_I + \frac{\omega_s-\omega_I}{\omega_I}\beta(\omega_s-\omega_I) - \frac{\omega_s}{\omega_I}\beta_s\Big],\\
\frac{d\beta_s}{dt} &= -\frac{\beta_s - \beta(\omega_s)}{T_{sp}} - \frac{4\omega_I I(I+1)N_I}{3\omega_s N_s}\frac{1}{T^{+}}\Big[\beta_I + \frac{\omega_s}{\omega_I}\beta_s\\
&\quad - \frac{\omega_s+\omega_I}{\omega_I}\beta(\omega_s+\omega_I)\Big] + \frac{4\omega_I I(I+1)N_I}{3\omega_s N_s}\frac{1}{T^{-}}\Big[\beta_I\\
&\quad - \frac{\omega_s}{\omega_I}\beta_s + \frac{\omega_s-\omega_I}{\omega_I}\beta(\omega_s-\omega_I)\Big],\\
\frac{d\beta(\omega_s)}{dt} &= -\frac{\beta(\omega_s) - \beta_s}{T_{ps}} - \frac{\beta(\omega_s) - \beta_0}{T_0},\\
\frac{d\beta(\omega_s\pm\omega_I)}{dt} &= \pm\frac{\omega_I(\omega_s\pm\omega_I)I(I+1)N_I}{3c^{\pm}T^{\pm}}\Big[\beta_I \pm \frac{\omega_s}{\omega_I}\beta_s\\
&\quad \mp \frac{\omega_s\pm\omega_I}{\omega_I}\beta(\omega_s\pm\omega_I)\Big] - \frac{\beta(\omega_s\pm\omega_I) - \beta_0}{T_0},
\end{aligned} \tag{9}$$

where

$$\frac{1}{T_{sp}} = \pi L^{+-}(\omega_s), \quad \frac{1}{T_{ps}} = \frac{c_s}{c_p}\frac{1}{T_{sp}},$$
$$\frac{1}{T^{\pm}} = \frac{\pi}{8}\frac{1}{\omega_I^2}\sum_{n}|v_{in}^{+z}|^2L^{+-}(\omega_s\pm\omega_I), \tag{10}$$
$$L^{+-}(\omega) = \mathrm{Sp}\,(\rho_L L_\omega^{+}L_\omega^{-}),$$
$$c_p = c(\omega_s), \quad c^{\pm} = c(\omega_s\pm\omega_I) \approx c_p,$$

and $1/T_0$ is the rate of relaxation of the phonons with the thermostat, which is a phenomenological constant in this treatment. For simplicity, we assume that it does not depend on the frequency.

The system of equations (9) describes the process of establishing thermodynamic equilibrium between the subsystems making up the system under consideration. In the general case, the investigation of these equations is difficult and it is advisable to examine the different special cases of practical interest.

3. First we shall discuss briefly the role of the PB in electron relaxation, i.e., we exclude the nuclear spin system from the treatment.[6-8] The whole system will now consist of three subsystems: the electron Zeeman subsystem (s) and the subsystems of the resonance phonons (p) and of the thermostat (0), which includes the remaining phonons and the helium bath.

The system of equations (9) takes the form

$$\frac{d\beta_s}{dt} = -\frac{\beta_s - \beta_p}{T_{sp}}, \quad \frac{d\beta_p}{dt} = -\frac{\beta_p - \beta_s}{T_{ps}} - \frac{\beta_p - \beta_0}{T_0}. \tag{11}$$

[2)] The lattice operator L can be represented by its spectral decomposition $L = \sum_{\omega} L_\omega$, where L_ω is a linear combination of phonon creation and annihilation operators, since, being interested in PB effects, we shall consider only one-phonon processes below.

[3)] We shall assume that the temperature of the nuclear Zeeman subsystem remains spatially uniform in the relaxation process (for more details on this, see [5]).

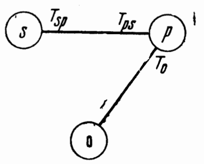

FIG. 1

A scheme of the relaxations is shown in Fig. 1.

It is obvious that β_s and β_p relax as the sum of two exponentials and, since $c_p \ll c_s$, the character of the relaxation is completely determined by the quantity

$$\sigma = \frac{T_0}{T_{ps}} = \frac{c_s/T_{sp}}{c_p/T_0} \tag{12}$$

and is practically independent of whether or not the resonance-phonon system is brought out of equilibrium with the lattice during the saturation of the electron resonance. It is therefore natural to define σ as the PB coefficient in the electron relaxation. We note that c_s/T_{sp} characterizes the rate of energy transfer in the part s → p, and c_p/T_0 in the part p → 0.

If $\sigma \ll 1$, on saturation of the electron resonance ($\beta_s \to 0$), the resonance-phonon subsystem does not come out of equilibrium with the lattice at all. Therefore, in the case under consideration, there will not in practice be a fast stage of relaxation of resonance phonons with the thermostat with rate $1/T_0$. But in the slow stage, β_s relaxes to $\beta_p = \beta_0$ at a rate $1/T_{sp}$. This is the usual relaxation picture. There is no PB effect here.

If $\sigma \gg 1$, on saturation of the EPR, the resonance-phonon subsystem will or will not be brought out of equilibrium with the lattice, depending on the duration of the saturation. However, irrespective of this, the relaxation will contain both stages. In the fast stage, equilibrium is established between the subsystems s and p with a relaxation rate $1/T_{ps} + 1/T_{sp} \approx 1/T_{ps}$. In this stage, β_s is practically unchanged and the subsystem s, as it were, draws the subsystem p toward itself. Then β_s and β_p, while remaining equal to each other, relax to β_0 with a rate

$$\frac{c_p}{c_s + c_p}\frac{1}{T_0} \approx \frac{c_p}{c_s}\frac{1}{T_0}.$$

Thus, if $\sigma \gg 1$, the observed relaxation time of subsystem s will be equal to $(c_s/c_p)T_0$.

We remark that, taking into account that $c_p \ll c_s$ it is easy to show[6,7] that for an arbitrary value of σ the quantities β_s and β_p relax to β_0 like the sum of two exponentials with relaxation times $T_0/(1+\sigma)$ and $T_{sp}(1+\sigma)$. The dependence of T_0 on the sample dimensions, impurity concentration, temperature and external field is determined by the phonon relaxation mechanism.[7]

4. We now take the nuclear spin system into account, assuming, however, that spectral diffusion in the interval $2\omega_I$ about the frequency ω_s in the phonon spectrum ensures that the phonons with frequencies ω_s and $\omega_s \pm \omega_I$ have a single temperature. Then the resonance phonons can be treated as a single subsystem with temperature β_r. The whole system will now consist of four subsystems: the nuclear Zeeman (I), the electron Zeeman (s), and the subsystems of the resonance phonons (r) and the thermostat (0).

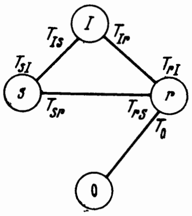

FIG. 2

In this case the system of equations (9) takes the form

$$\frac{d\beta_I}{dt} = \frac{\beta_I - \beta_s}{T_{Is}} - \frac{\beta_I - \beta_r}{T_{Ir}} \quad \frac{d\beta_s}{dt} = \frac{\beta_s - \beta_I}{T_{sI}} - \frac{\beta_s - \beta_r}{T_{sr}}, \tag{13}$$

$$\frac{d\beta_r}{dt} = -\frac{\beta_r - \beta_I}{T_{rI}} - \frac{\beta_r - \beta_s}{T_{rs}} - \frac{\beta_r - \beta_0}{T_0},$$

where

$$\frac{1}{T_{Is}} = \frac{2}{T_{IL}}, \quad \frac{1}{T_{Ir}} = \frac{3}{T_{IL}}, \quad \frac{1}{T_{sI}} = \frac{c_I}{c_s}\frac{1}{T_{Is}},$$

$$\frac{1}{T_{rI}} = \frac{c_I}{c_r}\frac{1}{T_{Ir}}, \quad \frac{1}{T_{rs}} = \frac{c_s}{c_r}\frac{1}{T_{sr}},$$

$$\frac{1}{T_{sr}} = \left[1 + \frac{I(I+1)N_I}{3N_s}\frac{1}{\omega_I^2}\sum_n |v_{in}^{+z}|^2\right]\frac{1}{T_{sp}} \approx \frac{1}{T_{sp}}, \tag{14}$$

$$\frac{1}{T_{IL}} = \frac{1}{4\omega_I^2}\sum_n |v_{in}^{+z}|^2 \frac{1}{T_{sp}}.$$

The relaxation scheme is shown in Fig. 2.

In this case $c_I \ll c_r \ll c_s$. In addition, it is easy to show that $T_{sI} \gg T_{sr}$ and $T_{rI} \gg T_{rs}$, whence it follows that the connection between the subsystems s and r is stronger than their connection with the subsystem I. Therefore, in the relaxation process, these subsystems come to internal equilibrium in every case before the exchange of energy between them and the nuclear Zeeman subsystem begins.

Furthermore, it must be stressed that in the relaxation process the subsystem I, because of its small heat capacity, will be drawn toward the internally equilibrated subsystem sr. Hence it is perfectly clear that for a PB effect to be observed in nuclear relaxation it is necessary that the subsystems s and r (in any case, s, since $c_s \gg c_r$) be drawn out of equilibrium with the thermostat at the initial moment.

We shall now consider the different cases. First let $\sigma \ll 1$, i.e., there is no PB in the electron relaxation. Then, as follows from (13), first r relaxes to 0 at a rate $1/T_0$,[4] then s relaxes to r0 at a rate $1/T_{sr}$, and finally, I relaxes to sr0 at a rate $1/T_{IL}$.[5] The nuclear spin-lattice relaxation time is given by the familiar expression (14) in terms of T_{sp}, which practically coincides with the relaxation time T_{sr} of the electron spins under these conditions. The quantity T_{IL} can be brought to the form[6]

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[4] For $\sigma \ll 1$, neither NMR saturation ($\beta_I \to 0$) nor EPR saturation ($\beta_r \to 0$) can draw the resonance-phonon subsystem out of a state of equilibrium with the thermostat. Therefore, this stage of relaxation is absent in reality.

[5] Here we have taken into account that $T_{sr} \ll T_{IL}, T_{Is}, T_{Ir}$.

[6] In the absence of a PB effect, our restriction to the case S = ½ (cf. footnote 1) is unimportant. In fact, if in the nuclear relaxation the electron spins remain in equilibrium with the lattice, the electron Zeeman degrees of freedom can be attributed to the thermostat, and the possibility or impossibility of introducing an electron Zeeman subsystem into the treatment becomes immaterial.

$$T_{IL}=\frac{15}{8\pi}\frac{\delta^3H^2}{\gamma_s^2N_sS(S+1)}T_{sp}, \tag{15}$$

where γ_S is the gyromagnetic ratio of an electron spin and δ is the radius of the diffusion barrier.[5]

Now let $\sigma \gg 1$. Now in the first relaxation stage r comes into internal equilibrium with s with a relaxation rate $1/T_{rs} + 1/T_{sr} \approx 1/T_{rs}$. Therefore, for $t \gg T_{rs}$, the system of equations describing the evolution of β_I and $\beta_S = \beta_r = \beta$ takes the form

$$\begin{gathered}\frac{d\beta_I}{dt}=-\frac{\beta_I-\beta}{T_{IL}},\\ \frac{d\beta}{dt}=-\frac{c_I}{c_s+c_r}\frac{\beta-\beta_I}{T_{IL}}-\frac{c_r}{c_s+c_r}\frac{\beta-\beta_0}{T_0}.\end{gathered} \tag{16}$$

The subsequent behavior of the subsystems depends on the parameter

$$\rho_r=c_sT_0\,/\,c_rT_{IL}. \tag{17}$$

If $\rho_r \ll 1$, the subsystem sr first comes into equilibrium with the thermostat in a time $(c_s/c_r)T_0$ and then the system I will relax to sr0 at a rate $1/T_{IL}$. The nuclear spin relaxation time is again given by (15); however, T_{sp} is not the same as the observed electron spin-lattice relaxation time (which is equal to $(c_s/c_r)T_0$).

If $\rho_r \gg 1$ ($\sigma \gg 1$ automatically), β_I will first relax to β at a rate $1/T_{IL}$ and then the system I_{sr} will relax to the thermostat with a rate c_r/c_sT_0. In other words, the PB effect arises in the nuclear relaxation.

The picture we have described of the relaxation corresponds, as was noted above, to conditions in which both the nuclear and electron Zeeman subsystems are drawn out of equilibrium with the thermostat. This can be attained, e.g., by simultaneous saturation of both the electron and nuclear resonances. In experiments of this type, ρ_r will play the role of the PB coefficient in the nuclear relaxation. But in typical experiments to observe the PB in nuclear relaxation, the disturbance of the thermodynamic equilibrium is brought about by NMR saturation, and this imposes more stringent conditions on the appearance of the effect. In fact, it is easy to show that if the NMR saturation is of sufficiently long duration in a sufficiently strong variable field ($2WT_{IL} \gg 1$, W is the probability of reorientation of a nuclear spin by the variable field in unit time), the subsystems s and r will be drawn out of equilibrium with the thermostat only under the condition $\rho_S > 1$, where

$$\rho_s=c_IT_0\,/\,c_rT_{IL}. \tag{18}$$

This is much stronger than the condition $\rho_r > 1$. In this case the condition $\rho_S > 1$ is necessary but insufficient for the observation of a PB in nuclear relaxation. For fulfillment of this condition, the character of the relaxation depends also on the duration τ of the saturation of the NMR signal. If $\tau \ll (c_S/c_I)T_{IL}$, the subsystems s and r will remain in equilibrium with the thermostat and β_I will relax like one exponential with relaxation time T_{IL}. But if $\tau > (c_S/c_I)T_{IL}$, the subsystems s and r will be drawn out of equilibrium with the thermostat and β_I will contain two exponentials with relaxation times T_{IL} and $(c_S/c_r)T_0$. In view of this, we shall call ρ_S the PB coefficient in the nuclear relaxation.

We note also that, if $\rho_S \gg 1$, then, automatically, $\rho_r \gg 1$ and $\sigma \gg 1$, since

$$\rho_s=\frac{c_I}{c_s}\rho_r=\frac{c_I}{c_s}\frac{T_{sr}}{T_{IL}}\sigma. \tag{19}$$

Now let there be practically no spectral diffusion in the phonon spectrum. Then in the relaxation process we should, strictly speaking, consider three resonance-phonon subsystems. However, since in Eq. (9) the coefficients of the terms $\beta_S - \beta(\omega_S)$ and $\beta_S - \beta(\omega_S \pm \omega_I)$ are a factor ω_S/ω_I times greater than the coefficients of $\beta_I - \beta_S$ and $\beta_I - \beta(\omega_S \pm \omega_I)$, we can assume that equilibrium is first established between the electron-Zeeman and phonon subsystems, and that these subsystems then come to equilibrium with the nuclear subsystem and the thermostat. Taking this into account, we again arrive at Eqs. (16), the only difference being that by c_r we mean $3c_p$, a quantity which, in principle, is less than c_r.[7] In consequence of this, the conditions for a PB effect to occur in nuclear relaxation in this case are more favorable.

5. We shall now consider the case of sufficiently large impurity concentration, when the nuclear relaxation proceeds via the dipole-dipole reservoir of the electron spin system (subsystem d).[9] Including the subsystem d in the Hamiltonian (1) and confining ourselves to the first order of perturbation theory, in an analogous way we obtain for the inverse temperatures

$$\begin{gathered}\frac{d\beta_I}{dt}=-\frac{\beta_I-\beta_d}{T_{Id}},\\ \frac{d\beta_d}{dt}=-\frac{\beta_d-\beta_I}{T_{dI}}-\frac{\beta_d-\beta_p}{T_{dp}}+\frac{\beta_d-\beta_s}{T_{ds}}.\\ \frac{d\beta_s}{dt}=-\frac{\beta_s-\beta_p}{T_{sp}^*}+\frac{\beta_s-\beta_d}{T_{sd}},\\ \frac{d\beta_p}{dt}=-\frac{\beta_p-\beta_s}{T_{ps}^*}-\frac{\beta_p-\beta_d}{T_{pd}}-\frac{\beta_p-\beta_0}{T_0}\end{gathered} \tag{20}$$

where

$$\frac{1}{T_{Id}}=\frac{\pi}{4}\sum_n|v_{in}{}^{+z}|^2S_{zz}(\omega_I),$$

$$\begin{gathered}S_{zz}(\omega)=\frac{1}{2\pi}\int dt\,e^{i\omega t}\frac{\langle S_n{}^zS_n{}^z(t)\rangle}{\langle(S_n{}^z)^2\rangle},\quad \frac{1}{T_{sp}{}^*}=\left(1+6\frac{c}{c_s}\right)\frac{1}{T_{sp}}\approx\frac{1}{T_{sp}}.\\ \frac{1}{T_{dp}}=\frac{6}{T_{sp}},\quad \frac{1}{T_{ds}}=\frac{4}{T_{sp}},\quad c_d=\frac{\omega_d{}^2N_s}{4},\\ \frac{T_{dI}}{T_{Id}}=\frac{c_d}{c_I},\quad \frac{T_{ds}}{T_{sd}}=\frac{c_d}{c_s},\quad \frac{T_{ps}{}^*}{T_{sp}{}^*}=\frac{c_p}{c_s},\quad \frac{T_{pd}}{T_{dp}}=\frac{c_p}{c_d}.\end{gathered} \tag{21}$$

(Here ω_d is a quantum of the dipole-dipole interaction (cf. [5])).

A scheme of the relaxations is shown in Fig. 3. Usually, $c_d \ll c_I \ll c_p \ll c_s$, and also $T_{dI} \ll T_{ds}$ and $T_{dp} < T_{sp}^*$. Moreover, as can easily be seen, $T_{sp}^* \ll T_{sd}$ and $T_{ps}^* \ll T_{pd}$. In view of the latter condition, the PB coefficient in the electron relaxation will be given by the relation (12) as before. The case under consideration is completely analogous to the preceding case. Therefore, the character of the relaxation de-

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[7] By definition, c_r is the heat capacity of the phonons in the frequency range of the spectral diffusion length; this range is greater than or of the order of ω_I, whereas c_p is the heat capacity of the phonons in a frequency range of the order of the width Δ_p, which, generally speaking, is much less than ω_I.

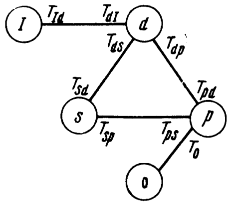

FIG. 3

pends in an essential way on whether the subsystem s has been drawn out of equilibrium with the thermostat at the initial moment.

We shall now consider the different cases. If $\sigma \ll 1$, in the first stage of the relaxation $\beta_p \to \beta_0$ in a time T_0, after which equilibrium is established between the subsystems I and d($\beta_I = \beta_d = \beta$) in a time T_{dI}. Then, under the condition $c_d/c_I \ll 1$, the subsystem s relaxes to the thermostat in a time T_{sp} and, finally, the system Id relaxes to the thermostat in a time $(c_I/2c_d)T_{sp}$.[8] Since $c_d \ll c_I$, the quantity β will change only in the last stage; the nuclear relaxation time T_{IL} will be given by the formula

$$T_{IL} = (c_I/2c_d)T_{sp}. \tag{22}$$

Now let $\sigma \gg 1$. If, in addition, $T_0 \gg T_{dI}$, in a time $t \sim \max(T_{dI}, T_{ps})$ the subsystems I and d, and also the subsystems s and p, come into equilibrium with each other. The system of equations describing the evolution of the subsystems Id and sp takes the form

$$\frac{d\beta}{dt} = -\frac{2c_d}{c_I + c_d}\frac{\beta - \beta'}{T_{sp}}, \tag{23}$$

$$\frac{d\beta'}{dt} = -\frac{2c_d}{c_s + c_p}\frac{\beta' - \beta}{T_{sp}} - \frac{c_p}{c_s + c_p}\frac{\beta' - \beta_0}{T_0}$$

where $\beta = \beta_I = \beta_d$, and $\beta' = \beta_s = \beta_p$. The subsequent character of the relaxation depends on the parameter

$$\rho_r = \frac{c_s/c_p}{c_I/c_d}\frac{T_0}{T_{sp}/2} = 2\frac{c_d}{c_I}\sigma. \tag{24}$$

If $\rho_r \ll 1$, equilibrium is first established between the subsystem sp and the thermostat in a time $(c_s/c_p)T_0$, after which the subsystem Id comes to equilibrium with the thermostat in a time $(c_I/2c_d)T_{sp}$. Change of β_I occurs in practice in the last stage. The relaxation time of β_I is again expressed by formula (22), but T_{sp} does not coincide with the experimentally observed electron spin-lattice relaxation time. This situation corresponds to the presence of a PB in the electron relaxation and its absence in the nuclear relaxation.

But if $\rho_r \gg 1$, internal equilibrium is first established between the subsystems Id and sp in a time $(c_I/2c_d)T_{sp}$. In this stage, β' is practically unchanged and subsystem sp pulls the subsystem Id toward itself. Then relaxation of the system Idsp to the thermostat proceeds in a time $(c_s/c_p)T_0$. The temperature of the nuclei changes in both stages. This situation corresponds to the presence of a PB effect in the nuclear (and also the electron) relaxation.

The relaxation picture we have described is valid if at the initial moment the subsystem s has been brought out of equilibrium with the thermostat. It can be shown that, for NMR saturation of sufficient duration in a strong alternating magnetic field, this will occur under the condition $\rho_s > 1$, where

$$\rho_s = 2\frac{c_d}{c_p}\frac{T_0}{T_{sp}} = 2\frac{c_d}{c_s}\sigma. \tag{25}$$

This is stronger than the condition $\rho_r > 1$. By analogy with the preceding case, we call ρ_s the PB coefficient in the nuclear relaxation.

Finally, we must bear in mind that the condition $\rho_s > 1$ is necessary but not sufficient. For short duration of the NMR saturation, the subsystem s does not come out of equilibrium with the thermostat and there will be no PB effect in the nuclear relaxation.

In conclusion, we call attention to the following fact. In the absence of a PB effect in the electron relaxation, it is possible, by off-center saturation of the EPR line, to lower significantly the temperature of the dipole-dipole reservoir and, consequently, the Zeeman temperature of the nuclei. One of the methods of dynamical polarization of nuclei consists in this.[9, 10] Saturation at the center of the EPR line does not affect the nuclear temperature, since in this case practically no change occurs in the temperature of the dipole-dipole reservoir.

However, if a PB effect occurs in the electron relaxation, on saturation of the EPR line at the center both the Zeeman temperature of the electrons and the temperature of the resonance phonons are increased; this, in turn, will induce an increase in the temperature of the dipole-dipole reservoir and then in the Zeeman temperature of the nuclei. This case can appear experimentally, under conditions such that the line-center EPR saturation is ensured with great precision.

6. We shall now discuss the results obtained. Since $\rho_s/\sigma \ll 1$, in order that $\rho_s \gtrsim 1$ it is necessary that $\sigma \gg 1$. In this situation the appearance of a PB effect in the nuclear relaxation after the removal of the saturating NMR radio-frequency field depends in an essential way on the duration of the NMR saturation. If the duration of the saturation is sufficiently great, a PB will occur and the observed nuclear spin-lattice relaxation time will coincide with the observed relaxation time of an electron spin.

The condition $\rho_s > 1$ for the presence of a PB effect in the nuclear relaxation is very stringent. Despite the smallness of the impurity concentration, in all real cases the heat capacity of the nuclear Zeeman reservoir is significantly less than the heat capacity of the electron Zeeman reservoir. Therefore, the connection between the resonance phonons and the thermostat must be very weak for it to be possible, by saturation of the NMR, to heat markedly the electron Zeeman reservoir and the resonance-phonon subsystem connected with it.

We consider that, in experiments performed up to the present time, there is no PB in the nuclear relaxation. Of a large number of papers, [11] is the only one in which it is stated that the observed nuclear relaxation

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[8] The relaxation picture we have described corresponds to the condition $T_{dI} \gg T_0$. If $T_{dI} \ll T_0$, the first two steps of the relaxation are interchanged.

time depends on the sample dimensions; in it there are no indications about the effect of the duration of the NMR saturation on the character of the nuclear spin-lattice relaxation. Therefore, we are inclined to think that the dependence of the nuclear relaxation time on the sample dimensions obtained in [1] is due to secondary causes.

On the other hand, the situation when there is no PB effect in the nuclear relaxation but a PB is important in the electron relaxation occurs frequently. It occurs with a sufficiently strong field, sufficiently low temperature and sufficiently high impurity concentration (experimental data for lanthanum magnesium nitrate with neodymium, lanthanum and cerium impurities can be found, e.g., in Jeffries' monograph[11]). We consider the important point in our treatment to be the result that, in such a situation ($\sigma \gg 1$, $\rho_S \ll 1$), the nuclear spin-lattice relaxation time T_{IL} is given by the same formulas as in the case when there is no PB effect in the electron relaxation (i.e., by formula (15) or formula (22), depending on the magnitude of the impurity concentration). It is, however, very important that the quantity T_{sp} occurring in this expression is not the same as the observed spin-lattice relaxation time of the electron spins.

In the case $\sigma \ll 1$ the theory of the nuclear relaxation is compared with experiment by checking how well the relation (15), or (22), is fulfilled for measured values of T_{IL} and T_{sp}. In the case $\sigma \gg 1$, it is difficult to measure the quantity T_{sp}. One can, however, compare the formulas (15) and (22) with experiment by making use of the known dependence of T_{sp} on H and T for one-phonon processes ($T_{sp} \propto T^{-1}H^4$ for Kramers ions, and $T_{sp} \propto T^{-1}H^2$ for non-Kramers ions). Conversely, by making use of formula (15) or (22) and the measured dependence of T_{IL} on H and T, one can determine the dependence of T_{sp} on the external field and the temperature.

It should be kept in mind that in this work we are describing the electron spin system by a single Zeeman temperature and a single dipole-dipole temperature. Such a treatment is valid for a homogeneously broadened EPR line, and also for an inhomogeneously broadened line if there is rapid spectral diffusion[9)] (i.e., if in the course of the spin-lattice relaxation time the spin excitation has time to diffuse over the whole inhomogeneously broadened line; such a line behaves on saturation as a homogeneously broadened line).

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[9)] It was shown in [12] that, in the saturation of an inhomogeneously broadened EPR line with limited spectral diffusion, the role of effects due to the dipole-dipole reservoir is small. But in the case of rapid spectral diffusion, the dipole-dipole reservoir plays an important role in the saturation of the line.

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