QUANTUM-STATISTICAL THEORY OF THE DYNAMICAL POLARIZATION OF NUCLEI IN THE CASE OF NON-UNIFORM ESR LINE BROADENING

L. L. BUISHVILI, M. D. ZVIADADZE, and G. R. KHUTSISHVILI

Institute of Physics, Academy of Sciences, Georgian S.S.R.

We use a quantum-statistical method to derive general equations to describe the behavior of the electron-nuclear spin system of a crystal containing paramagnetic impurities under the action of variable magnetic fields. We assume that the electron spin resonance lines are non-uniformly broadened and the dipole-dipole interaction of the impurity electron spins is considered to be a separate reservoir. We study on the basis of the general equations the relaxation of the spin system and the dynamical nuclear polarization, taking spectral diffusion into account.

1. In solids containing paramagnetic impurities when the forbidden paramagnetic resonance is saturated in a variable magnetic field at right angles to a constant field, the nuclei acquire a large polarization. This phenomenon is called dynamical nuclear polarization (DNP) and is by itself a powerful means to polarize them.

A rigorous theoretical consideration of DNP on the basis of the concept of a spin temperature was given in [1,2] where it was assumed that the electron spin resonance (ESR) line width was caused by dipole-dipole (d-d) interaction and that the different spins possessed the same Larmor frequencies. These assumptions correspond to a uniform ESR line broadening and are not justified in the case of non-uniform line broadening when there is a distribution of spins over Larmor frequencies around some central frequency $\omega_0 = \gamma_S H$ ($\gamma_S > 0$ is the gyromagnetic ratio for the electron spins, H a constant magnetic field parallel to the z-axis).

Let us write out some causes leading to a non-uniform ESR line broadening:[3] a) non-uniformity of the external magnetic field; b) anisotropy of the g-factor in the case of a polycrystalline sample; c) a spread in the values of the internal crystalline field caused by lattice defects; d) hyperfine interaction (HFI) of the electron spin with the nuclei (alkali-halide crystals with F-centers, semiconductors with donor and acceptor impurities, dilute paramagnetic salt).

According to Portis [3] the electronic spin system under conditions of non-uniform broadening can be considered as a sytem of spin packets with different resonance frequencies ω_n (n—number of the packet) each of which contains N_n magnetically equivalent spins so that $N = \Sigma N_n$ is the total number of spins (it is equal to the number of paramagnetic impurity ions). The n-th packet is described by a "uniform" function of the form $\varphi(\omega - \omega_n)$ with a width Δ which for not too small spin concentrations is caused mainly by the secular part of the d-d interaction. The distribution of the spin packets is described by the ratio $g_n = N_n/N$. In the limit of a continuous distribution of resonance frequencies $g_n \to g(\omega - \omega_n)$ where $g(\omega - \omega_0)$ is a "non-uniform" function with a shape with a width $\Delta^* = 1/T_2^*$. Both functions of the form $\varphi(\omega - \omega')$ and

$g(\omega' - \omega_0)$ are usually assumed to be normalized:

$$\int_{-\infty}^{\infty} \varphi(\omega - \omega') d\omega = 1, \quad \int_{-\infty}^{\infty} g(\omega' - \omega_0) d\omega' = 1.$$

The condition $\Delta^* \ll \Delta$ correspond to a uniform ESR line broadening, and the condition $\Delta^* \gg \Delta$ to non-uniform broadening; an intermediate case when $\Delta^* \sim \Delta$ is also possible. When the broadening is non-uniform a large number of spin packets is fitted into an absorption line and it is just this case which will interest us in the following.

There is no consistent DNP theory for the case $\Delta \ll \Delta^*$, and there are only some attempts [2,4,5] at a semiphenomenological explanation of the experimental facts. In the present paper we present a strictly quantum-mechanical theory of DNP for the case of a non-uniform ESR line broadening taking the d-d reservoir and spectral diffusion into account. For the sake of simplicity our considerations are restricted to the uniform case for the nuclear spin system, i.e., we assume that in the DNP process it is in a state of internal equilibrium characterized by a single spin temperature.[1] This corresponds to the case of a fast nuclear spin diffusion. Moreover, the interaction between the nuclear spins which is responsible for establishing the internal equilibrium in the nuclear subsystem is not explicitly distinguished. As usual we assume that the following inequalities are satisfied:

$$\Delta \ll \omega_I \ll \Delta^* \ll \omega_n,$$

where ω_I is the nuclear resonance frequency. We must note that when $\omega_I \gg \Delta^*$ we get a picture of DNP where the ESR line width does not play an important role.

The variable magnetic field acting upon the spin system will be considered as a quantal subsystem consisting of two modes - an electronic and a nuclear one - each of which interacts in resonance fashion with the corresponding spin-system. In final reckoning the classical character of the variable field is taken into account as follows: the inverse of the mode temperature is put equal to zero and the quantal correlation func-

---

[1] The nuclei in the immediate vicinity of a paramagnetic center are excluded from our considerations.

tions are replaced by classical ones. This way to describe a variable field, proposed in[6] leads to a time-independent total Hamiltonian of the spin-system. The inclusion of two modes in our consideration enables us to formulate general equations in a form which is suitable for describing a number of effects connected with electron-nuclear double resonances.

To elucidate the physical importance of the quantum-statistical procedure used in this paper we make some remarks. In the electron-nuclear spin-system of a crystal in contact with a variable field and with a lattice, such as we are considering, we can distinguish two time scales: a small time τ and a large time T. After the elapsing of a time τ a certain kind of smoothing out is approached in the behavior of the spin-system when the details of the initial information are lost, a quasi-equilibrium state is established in which each subsystem in internal equilibrium and the subsequent development in time is determined by the slowly changing macroscopic parameters. The slow process of evolution of the quasi-equilibrium state to a state of complete equilibrium proceeds over a time T and is described by a non-equilibrium density matrix the form of which can be established based on a method worked out by Zubarev.[7] This method makes it possible to describe the equations for statistical averages of those operators which commute with the interaction which is important over the small time scale. In our problem this condition is satisfied by the Zeeman energies of the different spin packets, the Zeeman energy of the nuclear spins, the secular part of the d-d interaction of the electron spins, the Hamiltonians of the lattice and the variable field and therefore the corresponding degrees of freedom will be considered as separate subsystems each of which is in internal equilibrium at its own temperature.

2. The Hamiltonian of the spin-system of the crystal will be written in the form[2]

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1, \qquad \mathcal{H}_0 = \mathcal{H}_S + \mathcal{H}_d + \mathcal{H}_I + \mathcal{H}_L + \mathcal{H}_h,$$

$$\mathcal{H}_1 = \mathcal{H}_{SL} + \mathcal{H}_{CR} + \mathcal{H}_{SI} + \mathcal{H}_{Sh} + \mathcal{H}_{Ih},$$

$$\mathcal{H}_S = \sum_n{}' \mathcal{H}_n = \sum_{in} \omega_n S_{ni}^z, \qquad \mathcal{H}_I = -\omega_I \sum_m I_m^z,$$

$$\mathcal{H}_d = \frac{1}{2} \sum_{nn'ij} A_{ij} S_{ni}^z S_{n'j}^z + \sum_{nij} B_{ij} S_{ni}^+ S_{ni}^-,$$

$$\mathcal{H}_{SL} = \frac{1}{2} \sum_{ni} \{L^+ S_{ni}^- + L^- S_{ni}^+\}, \qquad \mathcal{H}_{CR} = \sum_{n \neq n'ij} B_{ij} S_{ni}^+ S_{n'j}^-,$$

$$\mathcal{H}_{Sh} = \frac{1}{2} \sum_{ni} \{h_S^+ S_{ni}^- + h_S^- S_{ni}^+\}, \qquad \mathcal{H}_{Ih} = \frac{1}{2} \sum_m \{h_I^+ I_m^- + h_I^- I_m^+\},$$

$$\mathcal{H}_{SI} = \frac{1}{2} \sum_{inm} \{v^{+z}(im) I_m^- + v^{-z}(im) I_m^+\} S_{ni}^z.$$

Here $\mathcal{H}_S$ and $\mathcal{H}_I$ are the Zeeman energies of the electronic and nuclear spins; $\mathcal{H}_L$ the lattice Hamiltonian; $\mathcal{H}_d$ that part of the d-d interaction which commutes with the Zeeman energy $\mathcal{H}_n$ of a separate spin packet; $\mathcal{H}_h = \mathcal{H}_h^S + \mathcal{H}_h^I$ where $\mathcal{H}_h^S$ and $\mathcal{H}_h^I$ are the Hamiltonians of the transverse variable magnetic fields with frequencies Ω_S and Ω_I which are at resonance, respectively, with

the electronic and nuclear spin systems; $h_S^\pm$, $h_I^\pm$ operators describing these fields; $\mathcal{H}_{SL}$ the spin-orbit interaction; $\mathcal{H}_{SI}$ the anisotropic part of the HFI responsible for the DNP, $\mathcal{H}_{CR}$ the interaction between different spin packets causing spectral diffusion[8] i.e., the process of cross-relaxation in the limits of a non-uniformly broadened line, $\mathcal{H}_{Sh}$ and $\mathcal{H}_{Ih}$ the interactions of electronic and nuclear spins with their resonance fields (the action of the variable fields on "foreign" spins will in the following be neglected); S_{ni}^α ($\alpha = x, y, z$) the electronic spin operator at the i-th lattice site and belonging to the n-th packet; I_m^α the nuclear spin operator at the m-th site. The operators $S_{ni}^\pm = S_{ni}^x \pm iS_{ni}^y$, $I_m^\pm = I_m^x \pm iI_m^y$ satisfy the usual commutation relations for angular momenta:

$$[S_{ni}^z, S_{n'j}^\pm] = \pm \delta_{nn'}\delta_{ij}S_{ni}^\pm, \quad [S_{ni}^\pm, S_{n'j}^\mp] = \pm 2\delta_{nn'}\delta_{ij}S_{ni}^z,$$

$$[I_m^z, I_{m'}^\pm] = \pm \delta_{mm'}I_m^\pm, \quad [I_m^\pm, I_{m'}^\mp] = \pm 2\delta_{mm'}I_m^z;$$

$L^\pm$ are lattice operators, $\omega_I = \gamma_I H$, γ_I the nuclear gyromagnetic ratio, and we assume that $\hbar = 1$.

We consider $\mathcal{H}_n$, $\mathcal{H}_d$, $\mathcal{H}_I$, $\mathcal{H}_L$, $\mathcal{H}_h$ as subsystems and denote by β_n, β_d, β_I, β_L, and $\beta_h = 0$ the corresponding inverse temperatures.[3] The spin-system as a whole will thus in the process of absorbing the energy of the variable field be in a quasi-equilibrium state. Under those conditions we can apply the method of constructing the non-equilibrium density matrix worked out by Zubarev.[7] The equations of motion for the Heisenberg operators of the subsystems have the form

$$\frac{d\tilde{\mathcal{H}}_n}{dt} = \frac{1}{i}[\tilde{\mathcal{H}}_n, \tilde{\mathcal{H}}] = \tilde{K}_n(t), \qquad \frac{d\tilde{\mathcal{H}}_I}{dt} = \frac{1}{i}[\tilde{\mathcal{H}}_I, \tilde{\mathcal{H}}] = \tilde{K}_I(t),$$

$$\frac{d\tilde{\mathcal{H}}_d}{dt} = \frac{1}{i}[\tilde{\mathcal{H}}_d, \tilde{\mathcal{H}}] = \tilde{K}_d(t), \qquad \frac{d\tilde{\mathcal{H}}_h}{dt} = \frac{1}{i}[\tilde{\mathcal{H}}_h, \tilde{\mathcal{H}}] = \tilde{K}_h(t),$$

$$\frac{d\tilde{\mathcal{H}}_L}{dt} = \frac{1}{i}[\tilde{\mathcal{H}}_L, \tilde{\mathcal{H}}] = \tilde{K}_L(t) = -\left\{ \sum_n \tilde{K}_n(t) + \tilde{K}_d(t) + \tilde{K}_I(t) + \tilde{K}_h(t) \right\},$$

(1)

where $\tilde{K}_n(t)$, $\tilde{K}_I(t)$, ... are current operators, $\tilde{Q}(t) = e^{i\mathcal{H}t}Qe^{-i\mathcal{H}t}$ (Q an arbitrary operator in the Schrödinger representation). The last equations are a consequence of the energy conservation law in operator form.[9] Following Zubarev[7], we can use Eqs. (1) to construct generalized integrals of motion and using then the non-equilibrium density matrix ρ for the stationary case. In the high-temperature approximation for the magnetic subsystems we get

---

[3]The possibility to characterize the d-d reservoir by a single temperature is connected with the fact that $\mathcal{H}_d$ contains terms such as

$$\mathcal{H}_d^{nn'} = -\frac{1}{2} \sum_{ij} A_{ij} S_{ni}^z S_{n'j}^z \quad (n \neq n'),$$

which commute with the Zeeman energy of the packets but do not commute with the energies of the d-d interaction of separate packets. $\mathcal{H}_d^{nn}$ causes a fast exchange of energy between different d-d reservoirs without changing the Zeeman energy and leads to an equalization of the temperatures of these reservoirs over a time which is of the order of the small time τ which we mentioned earlier.

$$\rho = \frac{\exp(-\beta_L \mathscr{H}_L)}{\mathrm{Sp}\exp(-\beta_L \mathscr{H}_L)}\left\{1 - \sum_n \beta_n \mathscr{H}_n - \beta_I \mathscr{H}_I - \beta_d \mathscr{H}_d\right.$$

$$+ \frac{1}{\beta_L}\int_0^{\beta_L} d\lambda \int_{-\infty}^0 e^{\varepsilon t} e^{\lambda \mathscr{H}_L}\left[\sum_n (\beta_n - \beta_L)\tilde{K}_n(t) + (\beta_d - \beta_L)\tilde{K}_d(t)\right.$$

$$\left.\left. + (\beta_I - \beta_L)\tilde{K}_I(t) - \beta_L\tilde{K}_h(t)\right]e^{-\lambda \mathscr{H}_L}\,dt\right\}. \qquad (2)$$

One shows easily that

$$\overline{\mathscr{H}}_n = -\beta_n\langle \mathscr{H}_n^2\rangle, \qquad \overline{\mathscr{H}}_I = -\beta_I\langle \mathscr{H}_I^2\rangle, \qquad \overline{\mathscr{H}}_d = -\beta_d\langle \mathscr{H}_d^2\rangle, \qquad (3)$$

where $\langle \ldots \rangle = \mathrm{Tr}(\ldots)/\mathrm{Tr}\,1$, $\overline{Q} \equiv \mathrm{Tr}\,\rho Q$. Similarly

$$\overline{K}_I = L_{II}(\beta_I - \beta_L) + \sum_n L_{In}(\beta_n - \beta_L) + L_{Id}(\beta_d - \beta_L) - L_{Ih}\beta_L,$$

$$\overline{K}_n = \sum_{n'} L_{nn'}(\beta_{n'} - \beta_L) + L_{nI}(\beta_n - \beta_L) + L_{nd}(\beta_d - \beta_L) - L_{nh}\beta_L,$$

$$\overline{K}_d = L_{dd}(\beta_d - \beta_L) + \sum_n L_{dn}(\beta_n - \beta_L) + L_{dI}(\beta_I - \beta_L) - L_{dh}\beta_L. \qquad (4)$$

The kinetic coefficients L_{ik} are determined from the formulae

$$L_{ik} = L_{ki} = \frac{1}{\beta_L}\int_0^{\beta_L} d\lambda \int_{-\infty}^0 e^{\varepsilon t}\frac{1}{\langle \exp(-\beta_L \mathscr{H}_L)\rangle}$$

$$\times \langle e^{-\beta_L \mathscr{H}_L}K_i e^{-\lambda \mathscr{H}_L}\tilde{K}_k(t)e^{\lambda \mathscr{H}_L}\rangle\,dt. \qquad (5)$$

The symmetry properties of the kinetic coefficients used in (5) are the usual Onsager relations. The transition to the limit $\varepsilon \to +0$ in (5) must be made after the integrals have been evaluated.

In the stationary case neither ρ in (2) nor as a result the quantities occurring in (3) and (4) are time-dependent. In the following we assume that Eqs. (3) and (4) remain valid also when β_I, β_n, and β_d depend on the time. This assumption physically corresponds to considering a quasi-static process when the dispersion of the kinetic coefficients can be neglected. Averaging Eqs. (1) using the density matrix $\rho(t)$ evaluated by means of (2) with the change $\beta_{I,n,d} \to \beta_{I,n,d}(t)$, and bearing in mind what we have said, we get the following equations for the inverse temperatures:

$$\frac{d\beta_I}{dt} = -\frac{\overline{K}_I}{\langle \mathscr{H}_I^2\rangle}, \qquad \frac{d\beta_n}{dt} = -\frac{\overline{K}_n}{\langle \mathscr{H}_n^2\rangle}, \qquad \frac{d\beta_d}{dt} = -\frac{\overline{K}_d}{\langle \mathscr{H}_d^2\rangle}. \qquad (6)$$

To evaluate the kinetic coefficients we must consider the interaction $\mathscr{H}_1$ between the subsystems to be a small perturbation. In second-order perturbation theory the correlators $\langle K\tilde{K}(t)\rangle$ which occur in (5) have the form

$$\tilde{K}(t) = K^0(t) - \int_0^t dt_1 \int_0^{t_1} dt_2 [[K^0(t), \mathscr{H}_1^0(t_1)], \mathscr{H}_1^0(t_2)], \qquad (7)$$

where the index 0 indicates operators taken in the interaction representation according to the usual rule $Q^0(t) = \exp(i\mathscr{H}_0 t)Q\exp(-i\mathscr{H}_0 t)$ and where we have borne in mind that terms linear in $\mathscr{H}_1$ do not contribute to the quantities which are of interest to us. Straightforward though cumbersome calculations of the kinetic coefficients, using Eqs. (7) and (5) lead after neglecting unimportant terms to the following set to determine the inverse temperatures:

$$\frac{d\beta_I}{dt} = -\frac{\beta_I - \beta_L}{T_{IL}} - \sum_n g_n\frac{\beta_n - \beta_L}{T_{IS}(\omega_n)} - \frac{\beta_d - \beta_L}{T_{Id}}$$

$$- \sum_{n\neq n'} g_n g_{n'} W_1^{CR}(\omega_n - \omega_{n'} - \omega_I)\left\{\beta_I + \frac{\omega_n - \omega_{n'} - \omega_I}{\omega_I}\beta_d\right.$$

$$\left.+ \frac{\omega_{n'}\beta_{n'} - \omega_n\beta_n}{\omega_I}\right\} - 2\sum_n g_n W(\Omega_S - \omega_n - \omega_I)\left\{\beta_I + \frac{\omega_n}{\omega_I}\beta_n\right.$$

$$\left.+ \frac{\Omega_S - \omega_n - \omega_I}{\omega_I}\beta_d\right\} - 2\sum_n g_n W(\Omega_S - \omega_n + \omega_I)\left\{\beta_I - \frac{\omega_n}{\omega_I}\beta_n\right.$$

$$\left.- \frac{\Omega_S - \omega_n + \omega_I}{\omega_I}\beta_d\right\} - 2W_I(\Omega_I - \omega_I)\beta_I; \qquad (8a)$$

$$\frac{d\beta_n}{dt} = -\frac{\beta_n - \beta_L}{T_{SL}(\omega_n)} - \frac{\beta_I - \beta_L}{T_{SI}(\omega_n)} - \frac{\beta_d - \beta_L}{T_{Sd}(\omega_n)} + \sum_{n'} g_{n'} W_2^{CR}(\omega_n - \omega_{n'})$$

$$\times\left\{\frac{\omega_n - \omega_{n'}}{\omega_n}\beta_d + \frac{\omega_{n'}\beta_{n'} - \omega_n\beta_n}{\omega_n}\right\} - \frac{N_I}{N}\sum_{n'} g_{n'}\left\{W_1^{CR}(\omega_n - \omega_{n'} + \omega_I)\right.$$

$$\times\left[\beta_I - \frac{\omega_n - \omega_{n'} + \omega_I}{\omega_I}\beta_d - \frac{\omega_{n'}\beta_{n'} - \omega_n\beta_n}{\omega_I}\right] - W_1^{CR}(\omega_n - \omega_{n'} - \omega_I)$$

$$\times\left[\beta_I + \frac{\omega_n - \omega_{n'} - \omega_I}{\omega_I}\beta_d + \frac{\omega_{n'}\beta_{n'} - \omega_n\beta_n}{\omega_I}\right] + 2W_1^{CR}(\omega_n - \omega_{n'})$$

$$\times\left[\frac{\omega_n - \omega_{n'}}{\omega_I}\beta_d + \frac{\omega_{n'}\beta_{n'} - \omega_n\beta_n}{\omega_I}\right]\right\}$$

$$- 2\frac{N_I\omega_I}{N\omega_n}\left\{W(\Omega_S - \omega_n - \omega_I)\left[\beta_I + \frac{\Omega_S - \omega_n - \omega_I}{\omega_I}\beta_d + \frac{\omega_n}{\omega_I}\beta_n\right]\right.$$

$$- W(\Omega_S - \omega_n + \omega_I)\left[\beta_I - \frac{\Omega_S - \omega_n + \omega_I}{\omega_I}\beta_d - \frac{\omega_n}{\omega_I}\beta_n\right]$$

$$\left.- 2W_S(\Omega_S - \omega_n)\left[\beta_n + \frac{\Omega_S - \omega_n}{\omega_n}\beta_d\right]\right\}; \qquad (8b)$$

$$\frac{d\beta_d}{dt} = -\frac{\beta_d - \beta_L}{T_{dL}} - \sum_n g_n\frac{\beta_n - \beta_L}{T_{dS}(\omega_n)} - \frac{\beta_I - \beta_L}{T_{dI}}$$

$$- \frac{1}{\omega_d^2}\sum_{n\neq n'} g_n g_{n'} W_2^{CR}(\omega_n - \omega_{n'})\omega_n(\omega_n - \omega_{n'})(\beta_d - \beta_n)$$

$$- \frac{N_I\omega_I^2}{N\omega_d^2}\sum_{n\neq n'} g_n g_{n'}\left\{W_1^{CR}(\omega_n - \omega_{n'} - \omega_I)\frac{\omega_n - \omega_{n'} - \omega_I}{\omega_I}\right.$$

$$\times\frac{\omega_I\beta_I + (\omega_n - \omega_{n'} - \omega_I)\beta_d - \omega_n\beta_n + \omega_{n'}\beta_{n'}}{\omega_I}$$

$$\left.- 2W_1^{CR}(\omega_n - \omega_{n'})\frac{\omega_n - \omega_{n'}}{\omega_I}\frac{(\omega_n - \omega_{n'})\beta_d - \omega_n\beta_n}{\omega_I}\right\}$$

$$- 2\frac{N_I\omega_I^2}{N\omega_d^2}\sum_n g_n\left\{W(\Omega_S - \omega - \omega_I)\frac{\Omega_S - \omega_n - \omega_I}{\omega_I}\right.$$

$$\times\frac{\omega_I\beta_I + (\Omega_S - \omega_n - \omega_I)\beta_d + \omega_n\beta_n}{\omega_I} - W(\Omega_S - \omega_n + \omega_I)$$

$$\times\frac{\Omega_S - \omega_n + \omega_I}{\omega_I}\frac{\omega_I\beta_I - (\Omega_S - \omega_n + \omega_I)\beta_d - \omega_n\beta_n}{\omega_I}$$

$$\left.- 2\sum_n g_n\frac{\omega_S - \omega_n}{\omega_d^2}[(\Omega_S - \omega_n)\beta_d + \omega_n\beta_n]W_S(\Omega_S - \omega_n)\right. \qquad (8c)$$

The relaxation times and transition probabilities are determined by the formulae

$$\frac{1}{T_{IL}} = \frac{\pi v^2}{8\omega_I^2}\sum_n g_n\int_{-\infty}^{\infty}\varphi(\omega)\{L(\omega + \omega_n + \omega_I) + L(\omega + \omega_n - \omega_I)\}d\omega,$$

$$\frac{1}{T_{IS}(\omega_n)} = \frac{\pi v^2}{8\omega_I^2}\frac{\omega_n}{\omega_I}\int_{-\infty}^{\infty}\varphi(\omega)\{L(\omega + \omega_n + \omega_I) - L(\omega + \omega_n - \omega_I)\}d\omega,$$

$$\frac{1}{T_{Id}} = \frac{\pi v^2}{8\omega_I^2}\sum_n g_n\frac{1}{\omega_I}\int_{-\infty}^{\infty}\omega\varphi(\omega)\{L(\omega + \omega_n + \omega_I) - L(\omega + \omega_n - \omega_I)\}d\omega,$$

$$\frac{1}{T_{SL}(\omega_n)} = \pi\int_{-\infty}^{\infty}\varphi(\omega)L(\omega + \omega_n)d\omega, \qquad (9a)$$

$$\frac{1}{T_{Sd}(\omega_n)} = \frac{\pi}{\omega_n}\int_{-\infty}^{\infty}\omega\varphi(\omega)L(\omega + \omega_n)d\omega,$$

$$\frac{1}{T_{SI}(\omega_n)} = \frac{N_I}{N}\frac{\omega_I^2}{\omega_n^2}\frac{1}{T_{IS}(\omega_n)}, \qquad \frac{1}{T_{dI}} = \frac{N_I}{N}\frac{\omega_I^2}{\omega_d^2}\frac{1}{T_{Id}};$$

$$W_1^{CR}(\omega_n - \omega_{n'} \pm \omega_I) = f \frac{\pi N}{4N_I \omega_I^2} \Big[\sum_j{}' B_{ij}{}^2 |v^{+z}(m)$$

$$- v^{+z}(m + i - j)|^2 \Big] \varphi(\omega_n - \omega_{n'} \pm \omega_I),$$

$$W_2^{CR}(\omega_n - \omega_{n'}) = 2\pi f \Big(\sum_j{}' B_{ij}{}^2 \Big)^2 \varphi_1(\omega_n - \omega_{n'}),$$

$$W(\Omega_S - \omega_n \pm \omega_I) = \frac{\pi v^2 \omega_{1S}^2}{16\omega_I^2} \varphi(\Omega_S - \omega_n \pm \omega_I),$$

$$W_S(\Omega_S - \omega_n) = \frac{\pi \omega_{1S}^2}{2} \varphi(\Omega_S - \omega_n),$$

$$W_I(\Omega_I - \omega_I) = \frac{\pi \omega_{1I}^2}{2} \delta(\Omega_I - \omega_I). \quad (9b)$$

Here N_I is the number of nuclear spins $f = N/N_0$ the concentration of paramagnetic impurities, N_0 the number of sites in the crystal lattice of the sample; the dashed sum Σ' indicates a summation over all sites;

$$v^2 = \frac{1}{N_I} \sum_{inm} |v^{+z}(im)|^2, \quad \omega_d^2 = \frac{\langle \mathcal{H}_d^2 \rangle}{\Big\langle \Big(\sum_{in} S_{in}{}^z \Big)^2 \Big\rangle}.$$

The correlation functions $h_{S,I}(t)$ describing the variable field are taken in the form

$$h_S(t) = \langle h_S^{-0}(t) h_S^+ \rangle = 2\omega_{1S}^2 \cos \Omega_S t,$$

$$h_I(t) = \langle h_I^{-0}(t) h_I^+ \rangle = 2\omega_{1I}^2 \cos \Omega_I t;$$

$\omega_{1S} = \gamma_S H_{1S}$, $\omega_{1I} = \gamma_I H_{1I}$, where H_{1S}, H_{1I} are the semi-amplitudes of the variable fields. We assume $S = I = \frac{1}{2}$ so that $\langle S_{ni}^+ S_{ni}^- \rangle = \langle I_m^+ I_m^- \rangle = \frac{1}{2}$ and

$$\langle \mathcal{H}_I^2 \rangle = \frac{1}{4}N_I \omega_I^2, \quad \langle \mathcal{H}_n^2 \rangle = \frac{1}{4}N_n \omega_n^2, \quad \langle \mathcal{H}_d^2 \rangle = \frac{1}{4}N\omega_d^2; \quad (10)$$

$L(\omega)$, $\varphi(\omega)$, $\varphi_1(\omega)$ are Fourier transforms of correlation functions:[4]

$$L(t) = \frac{\langle \exp(-\beta_L \mathcal{H}_L) L^{-0}(t) L^+ \rangle}{\langle \exp(-\beta_L \mathcal{H}_L) \rangle},$$

$$\varphi(t) = \frac{\langle S_{ni}^+(t) S_{ni}^- \rangle}{\langle S_{ni}^+ S_{ni}^- \rangle} = \varphi(-t), \quad \varphi_1(t) = [\varphi(t)]^2; \quad (11)$$

here $S_{ni}^+(t) = \exp(i\mathcal{H}_d t) S_{ni}^+ \exp(-i\mathcal{H}_d t)$.

It is natural to expect that the contribution from the B-term in $\mathcal{H}_d$ will be small in the correlator $\varphi(t)$ compared with the contribution from the A-term since the first is determined only by the spins of a given packet while the second is determined by the spins of all packets. Because of this we shall not take the B-term into account in actual calculations of correlators. Thanks to that $\varphi(t)$ is independent of n and the consideration can be appreciably simplified. We must note that in deriving Eqs. (8) we used the approximation

$$\langle S_{nj}^+(t) S_{n'j'}^- \rangle \approx \delta_{nn'} \delta_{jj'} \langle S_{ni}^+(t) S_{ni}^- \rangle,$$

i.e., we neglected the correlations in positions of different spins.

---

4)The expression $\varphi_1(t) = [\varphi(t)]^2$ occurs as a consequence of the approximation

$$\langle S_{ni}^+(t) S_{n_1 j}^-(t) S_{n'i'}^+ S_{n_1'j'}^- \rangle \approx \langle S_{ni}^+(t) S_{n'i'}^- \rangle \langle S_{n_1 j}^-(t) S_{n_1'i'}^+ \rangle (n \neq n_1, n' \neq n_1'),$$

which is valid at not too low concentrations of electronic spins. A more exact expression for the cross-relaxation function of the form $\varphi_1(\omega_n - \omega_{n'})$ was calculated in the paper by Kiel.[10]

The probability $W_I^{CR}(\omega_n - \omega_{n'} - \omega_I)$ describes the electron-nuclear cross-relaxation, a process in which an inversion of the spins of two interacting packets with frequencies satisfying the condition $\omega_n - \omega_{n'} \approx \omega_I$ is accompanied by the inversion of the nuclear spin. The term W_I^{CR} neglecting the d-d reservoir was introduced phenomenologically in the papers by Kessenikh et al.[5] The term containing $W_2^{CR}(\omega_n - \omega_{n'})$ leads to spectral diffusion considered in the papers by Portis and Kiel.[8] $W(\Omega_S - \omega_n \pm \omega_I)$ is the probability for forbidden transitions, $W_S(\Omega_S - \omega_n)$ and $W_I(\Omega_I - \omega_I)$ the probabilities for the usual ESR and NMR; T_{IL}, $T_{SL}(\omega_n)$, T_{dL} the spin-lattice relaxation times for $\mathcal{H}_I$, $\mathcal{H}_n$, and $\mathcal{H}_d$.

If we neglect the d-d reservoir, the spectral diffusion, and the electron-nuclear cross-relaxation, we obtain the equations which were applied in the paper by Lambe et al.[11] to explain the so-called "distant ENDOR." Since it is impossible to solve Eqs. (8) in the general form we shall consider some particular cases. In the following we assume $\omega_d^2 \ll \omega_I^2$ and neglect thus the d-d reservoir.

3. We consider first the relaxation process in the case of fast spectral diffusion. We denote by T_{12} the time during which in the electron Zeeman subsystem (EZS) internal equilibrium is established with an inverse temperature β_S common to all spin packets. Let the relaxation time for the nuclear Zeeman subsystem (NZS) be larger than the time T_{12}. Under those conditions the relaxation is described by the equations

$$\frac{d\beta_I}{dt} = -\frac{\beta_I - \beta_L}{\tau_I} + \frac{\beta_S - \beta_L}{\tau_{IS}}, \quad \frac{d\beta_S}{dt} = -\frac{\beta_S - \beta_L}{\tau_S} + \frac{\beta_I - \beta_L}{\tau_{SI}}, \quad (12)$$

where

$$\frac{1}{\tau_I} = \frac{1}{T_{IL}} + \frac{1}{T_{IS}^{CR}}, \quad \frac{1}{\tau_S} = \frac{1}{T_{SL}} + \frac{1}{T_{SI}^{CR}},$$

$$\frac{1}{\tau_{IS}} = \frac{1}{T_{IS}^{CR}} - \frac{1}{T_{IS}}, \quad \frac{1}{\tau_{SI}} = \frac{1}{T_{SI}^{CR}} - \frac{1}{T_{SI}},$$

$$\frac{1}{T_{IS}^{CR}} = W_{CR} \int_{-\infty}^{\infty} d\omega g(\omega - \omega_0) g(\omega - \omega_0 - \omega_I),$$

$$\frac{T_{SI}}{T_{IS}} = \frac{T_{SI}^{CR}}{T_{IS}^{CR}} = \frac{\tau_{SI}}{\tau_{IS}} = \frac{c_S}{c_I},$$

$$W_{CR} = f \frac{\pi N}{4N_I \omega_I^2} \Big(\sum_{im}{}' B_{ij}{}^2 |v^{+z}(m) - v^{+z}(m + i - j)|^2 \Big),$$

c_S and c_I are the specific heats of the electronic and nuclear subsystems and

$$c_S / c_I = N\omega_0^2 / N_I \omega_I^2.$$

One can show[12] that $L(\omega) = L_2 = $ const for a two-phonon electron spin-lattice relaxation process and $L(\omega) = L_1 \omega^2$ for a one-phonon process. Hence, in the first case $T_{IS} = 0$ and the relaxation times are determined by the formulae

$$\frac{1}{\tau_I} = \frac{v^2}{4\omega_I^2} \pi L_2 + \frac{1}{T_{IS}^{CR}}, \quad \frac{1}{\tau_S} = \pi L_2 + \frac{1}{T_{SI}^{CR}}, \quad \frac{1}{\tau_{IS}} = \frac{1}{T_{IS}^{CR}},$$

while in the second case $1/T_{IS} = \pi v^2 \omega_0^2 L_1 / 2\omega_I^2$, and

$$\frac{1}{\tau_I} = \frac{v^2}{4\omega_I^2} \pi \omega_0^2 L_1 + \frac{1}{T_{IS}^{CR}}, \quad \frac{1}{\tau_S} = \pi \omega_0^2 L_1 + \frac{1}{T_{SI}^{CR}},$$

$$\frac{1}{\tau_{IS}} = \frac{1}{T_{IS}^{CR}} - \frac{v^2}{2\omega_I^2} \pi \omega_0^2 L_1.$$

We consider the case $T_{IS}^{CR} \ll T_{IL}$, $T_{SI}^{CR} \ll T_{SL}$, when the EZS and NZS are more strongly coupled with one another than with the lattice. Then $\tau_S \approx T_{SI}^{CR}$, $\tau_I \approx T_{IS}^{CR}$ and the relaxation for two- and one-phonon processes proceeds as follows: equilibrium between the EZS and NZS is fast established, during a time

$$\lambda_+^{-1} = 1/T_{IS}^{CR} + 1/T_{SI}^{CR},$$

after which equilibrium with the lattice is slowly established with a relaxation time

$$\lambda_-^{-1} = \frac{c_S}{c_S + c_I} \frac{1}{T_{SL}} + \frac{c_I}{c_S + c_I} \frac{1}{T_{IL}},$$

In the other limiting case when $T_{SL} \ll T_{SI}^{CR}$, τ_I the EZS comes into equilibrium with the lattice faster than with the NZS and there are independent relaxations of β_S and β_I: the EZS comes fast into equilibrium with the lattice with a relaxation time $\tau_S \approx T_{SL}$; after that the NZS tends to equilibrium more slowly with a relaxation time τ_I.

Therefore for a non-uniform broadening in the case when cross-relaxation plays a determining role for the NZS, β_I relaxes to β_S. At the same time for a uniform broadening cross-relaxation is in general absent in the relaxation process for the nuclei which is caused by the anisotropic part of the HFI and β_I tends to β_d or β_L depending whether or not the electronic d-d reservoir is taken into account. Because of this the saturation of the usual resonance influences the NZS differently: for a non-uniform broadening when the cross-relaxation mechanism dominates the temperature $1/\beta_I$ and also $1/\beta_S$ increases compared to the lattice temperature $1/\beta_L$ while, generally speaking, for uniform broadening $1/\beta_I \approx 1/\beta_L$, if the d-d reservoir is neglected, and $1/\beta_I \approx 1/|\beta_d| < 1/\beta_L$ (i.e., nuclear polarization is obtained) in the opposite case when saturation does not occur strictly in the resonance point.

In conclusion we must note that when $T_{IL} \ll T_{IS}^{CR}$, $T_{SL} \ll T_{SI}^{CR}$ when cross-relaxation is unimportant the one-phonon process has an interesting singularity: when the ESR is saturated $\beta_S \approx 0$ and in the stationary case $\beta_I \approx 3\beta_L$ i.e., the temperature of the NZS is reduced by a factor three.

This effect is of a general nature. It occurs also for uniform broadening and is a consequence of an additional relaxation term containing T_{IS} in Eq. (8) for β_I which is non-vanishing in the case of a one-phonon process and which is normally neglected.

4. We turn now to a study of the behavior of the spin system under conditions when in the electronic subsystem the spin-lattice relaxation and allowed transitions play the major role while in the nuclear subsystem the electron-nuclear cross-relaxation plays the main role. In that case Eqs. (8) become

$$\int_{-\infty}^{\infty} \int d\omega d\omega' g(\omega - \omega_0) g(\omega' - \omega_0) W_1^{CR}(\omega - \omega' - \omega_I)$$

$$\times \left\{ \beta_I + \frac{\omega'\beta(\omega') - \omega\beta(\omega)}{\omega_I} \right\} = 0,$$

$$[\beta(\omega) - \beta_L]/T_{SL} = -2W_S(\omega - \Omega_S)\beta(\omega). \quad (13)$$

One usually uses for a consideration of non-uniform broadening the following approximations:

$$g(\omega - \omega_0) = \frac{1}{\sqrt{2\pi}\Delta^*} \exp\left\{ -\frac{(\omega - \omega_0)^2}{2\Delta^{*2}} \right\},$$

$$\varphi(\omega - \Omega_S) = \frac{T_2}{\pi} \frac{1}{1 + T_2^2(\omega - \Omega_S)^2}. \quad (14)$$

Using (13) and (14) we easily get

$$\beta_I = \beta_L \left\{ 1 - \frac{4\pi^{3/2}s}{s+1} \frac{\tilde{\Delta}}{\Delta^*} \int_{-\infty}^{\infty} \omega(\omega - \omega_0) g^2(\omega - \omega_0) \tilde{\varphi}(\omega - \Omega_S) d\omega \right\}, \quad (15)$$

where

$$\tilde{\varphi}(\omega - \Omega_S) = \frac{\tilde{\Delta}}{\pi} \frac{1}{\tilde{\Delta}^2 + (\omega - \Omega_S)^2}, \quad \tilde{\Delta} = \frac{\sqrt{s+1}}{T_2}$$

It is clear that $\tilde{\Delta}$ has the meaning of the width of a packet taking saturation into account (s is the saturation parameter). Assuming that $s \gg 1$, but $\alpha \equiv \tilde{\Delta}/\Delta^* \ll 1$ and evaluating the integral occurring in (15) in zeroth approximation in the parameter α, we get finally

$$\beta_I = \beta_L \left\{ 1 - 2\sqrt{\pi}\, \alpha \frac{\Omega_S(\Omega_S - \omega_0)}{\Delta^{*2}} \exp\left[-\frac{(\Omega_S - \omega_0)^2}{\Delta^{*2}} \right] \right\}. \quad (16)$$

Equation (16) shows that saturation of the usual resonance in the center of a non-uniform line does not lead to nuclear polarization. When $\alpha\Omega_S/\Delta^* \gg 1$ and the saturation occurs at frequencies $\Omega_S = \omega_0 \pm \Delta^*/2$ we obtain maximum polarization determined by the formula

$$\beta_I = \pm \sqrt{\frac{2\pi}{e}} \frac{\Omega_S\tilde{\Delta}}{\Delta^{*2}} \beta_L. \quad (17)$$

The result obtained can easily be understood on the basis of a simple model. We separate from the multitude of spin packets three with frequencies ω_2. $\omega_1 = \omega_2 - \omega_I$, and $\omega_3 = \omega_2 + \omega_I$ and consider them as an isolated system described according to (8) by the equations

$$\sum_{n \neq n'=1}^{3} g_n g_{n'} \varphi(\omega_n - \omega_{n'} - \omega_I)(\omega_I\beta_I - \omega_n\beta_n + \omega_{n'}\beta_{n'}) = 0,$$

$$(\beta_n - \beta_L)/T_{SL} = -2W_S(\omega_n - \Omega_S)\beta_n. \quad (18)$$

Saturating the allowed resonance at the frequency $\Omega_S = \omega_2$ and neglecting the width of the packet we get

$$\beta_2 = 0, \quad \beta_1 = \beta_3 = \beta_L, \quad \beta_I \approx -\beta_L \frac{\Omega_S}{\omega_I} \frac{g_3 - g_1}{g_3 + g_1}. \quad (19)$$

We must note that notwithstanding the fact that we have only taken the anisotropic part of the HFI into account, the saturation of the allowed resonance leads to a nuclear polarization effect similar to the Overhauser effect (the usual Overhauser effect is obtained for isotropic HFI[13]). Changing to a continuous representation of the spin packets we get in accordance with (19)

$$\beta_I \approx -\beta_L(\Omega_S - \omega_0)\Omega_S/\Delta^{*2}. \quad (20)$$

The remaining spin packets, apart from those selected for the non-uniform line, are not saturated but they make an additional contribution to the nuclear relaxation and in connection with this there occurs a "loss factor" as in the usual Overhauser effect which leads to a decrease in the polarization effect. The loss factor is equal to the ratio of the total relaxation time to the relaxation time of the process leading to the nuclear polarization and in our case it is of order $\tilde{\Delta}/\Delta^*$ so that if we take all packets into account we must have

$$\beta_I \approx -\beta_L\alpha\Omega_S(\Omega_S - \omega_0)/\Delta^{*2}. \quad (21)$$

The factor $\exp\{-(\Omega_S - \omega_0)^2/\Delta^{*2}\}$ in the frequency range considered is of order unity and its absence in the approximate Eq. (21) is connected with the neglect of the relative weight of the packets.

5. The stationary equations describing DNP neglecting cross-relaxation spectral diffusion, and the d-d reservoir have in the case of a two-phonon process the form

$$\frac{\beta_I - \beta_L}{T_{IL}} = -2 \int_{-\infty}^{\infty} d\omega g(\omega - \omega_0) W(\Omega_S - \omega - \omega_I)\left[\beta_I + \frac{\omega}{\omega_I}\beta(\omega)\right]$$

$$-2\int_{-\infty}^{\infty} d\omega g(\omega - \omega_0) W(\Omega_S - \omega + \omega_I)\left[\beta_I - \frac{\omega}{\omega_I}\beta(\omega)\right],$$

$$\frac{\beta(\omega) - \beta_L}{T_{SL}} = -2W_S(\Omega_S - \omega)\beta(\omega) - 2\frac{N_I}{N}\Big\{W(\Omega_S - \omega - \omega_I)$$

$$\times\left[\beta(\omega) + \frac{\omega_I}{\omega}\beta_I\right] + W(\Omega_S - \omega + \omega_I)\left[\beta(\omega) - \frac{\omega_I}{\omega}\beta_I\right]\Big\}. \quad (22)$$

We assume that

$$2W(0)T_{IL} \gg 1, \qquad 2\frac{N_I}{N}W(0)T_{SL} \ll 1.$$

(These conditions do not contradict one another as $T_{SL} \ll T_{IL}$.) We can then neglect in the first equation the relaxation term and in the second one the terms connected with forbidden transitions. As a result we get

$$\beta_I = \frac{1}{\omega_I}\int_{-\infty}^{\infty} d\omega \cdot \omega g(\omega - \omega_0)\beta(\omega)[W(\Omega_S - \omega + \omega_I) - W(\Omega_S - \omega - \omega_I)]$$

$$\times\left\{\int_{-\infty}^{\infty} d\omega g(\omega - \omega_0)[W(\Omega_S - \omega + \omega_I) + W(\Omega_S - \omega - \omega_I)]\right\}^{-1},$$

$$\beta(\omega) = \beta_L / [1 + 2T_{SL}W_S(\Omega_S - \omega)]. \quad (23)$$

We introduce the quantities $T_2 = \pi\varphi(0)$, $T_2^* = \pi g(0)$, $s = 2T_{SL}W_S(0) = (\gamma H_1)^2 T_{SL}T_2$. It is clear that $1/T_2 \approx \Delta$, $1/T_2^* \approx \Delta^*$. Bearing in mind that $1/T_2 \ll \omega_I \gg 1/T_2^*$ $\ll \Omega_S$, ω_0 and assuming that $(\omega_I T_2)^2 \gg s$, we get

$$\beta_I = \beta_L\left\{1 + \frac{\Omega_S}{g(\Omega_S - \omega_0)}\cdot\frac{dg(\Omega_S - \omega_0)}{d\Omega_S}\right\}. \quad (24)$$

If Ω_S is sufficiently far from the center of the line

$$\beta_I \approx \beta_L\frac{\Omega_S}{g(\Omega_S - \omega_0)}\frac{dg(\Omega_S - \omega_0)}{d\Omega_S}. \quad (25)$$

The result (25) differs from Eq. (7.29) given by Jeffries[4] in which for the derivation for the enhancement of the polarization absolute rather than relative fractions of the spins taking part in the production of the nuclear polarization were used; in this connection there also occurred an extra factor

$$\Delta\{g(\Omega_S - \omega_0 + \omega_I) + g(\Omega_S - \omega_0 - \omega_I)\} \approx 2\Delta g(\Omega_S - \omega_0).$$

in comparison with (25).

6. We now turn to a study of the influence of the spectral diffusion on DNP. To do this we must first of all solve the equation

$$\frac{\beta(\omega) - \beta_L}{T_{SL}} = \frac{1}{\omega}\int_{-\infty}^{\infty} d\omega' g(\omega' - \omega_0) W_2^{CR}(\omega - \omega')[\omega'\beta(\omega') - \omega\beta(\omega)]$$

$$- 2W_S(\omega - \Omega_S)\beta(\omega). \quad (26)$$

We assume that $g(\omega' - \omega_0)$ is a slowly varying function compared to $W_2^{CR}(\omega - \omega')$ and $\beta(\omega')$, while $\beta(\omega')$ in turn varies more slowly than $W_2^{CR}(\omega - \omega')$. Similar assumptions are made for the derivation of any diffusion equation. Removing $g(\omega' - \omega_0)$ from under

the integral sign and expanding $\beta(\omega')$ in a series near the point $\omega' = \omega$ we get the equation

$$\frac{d^2\beta(\omega)}{d\omega^2} - k^2\beta(\omega) = -k^2\beta_L + k^2\frac{s\pi}{T_2}\varphi(\omega - \Omega_S)\beta(\omega), \quad (27)$$

where

$$k^2 = \frac{1}{DT_{SL}}, \qquad D = \frac{1}{2}g(\omega - \omega_0)W^{CR}\Delta_{CR}^2,$$

$$\Delta_{CR}^2 = \int_{-\infty}^{\infty} (\omega' - \omega)^2\varphi_1(\omega' - \omega)d\omega', \qquad W^{CR} = \frac{W_2^{CR}(0)}{\varphi_1(0)}.$$

In form Eq. (27) is the same as the diffusion equation and was first used in Ref.[8]. D is the diffusion coefficient, $1/k = \sqrt{(DT_{SL})}$ is the frequency distance over which the spin excitation is transferred during a time T_{SL} when spectral diffusion is taken into account.

Assuming that Ω_S lies in the region which is sufficiently close to the center of the non-uniform line we shall look for a solution of Eq. (27) with the boundary conditions[5]

$$\beta(\omega_1) = \beta(\omega_2) = \beta_L, \qquad \omega_{1,2} = \omega_0 \mp \Delta^* / 2. \quad (28)$$

Equation (27) with the boundary conditions (28) is equivalent to the integral equation

$$\beta(\omega) = \beta_L + J(\omega, \omega_1) - J(\omega_2, \omega_1)\frac{\mathrm{sh}[k(\omega - \omega_1)]}{\mathrm{sh}(k\Delta^*)}, \quad (29)$$

where

$$J(\omega, \omega_1) = \frac{s\pi k}{T_2}\int_{\omega_1}^{\omega} \beta(\omega')\varphi(\omega' - \Omega_S)\,\mathrm{sh}[k(\omega - \omega')]d\omega',$$

and in accordance with the slow nature of the change in $g(\omega - \omega_0)$ compared to $\beta(\omega)$ we neglected the frequency dependence of the diffusion coefficient. Since[6]

$$k/T_2 \ll 1, \qquad \Omega_S - \omega_1 \gg 1/T_2, \qquad \omega_2 - \Omega_S \gg 1/T_2,$$

we have

$$J(\omega, \omega_1) \approx \frac{s\pi k}{T_2}\beta(\Omega_S)\,\mathrm{sh}[k(\omega - \Omega_S)]f(\omega - \Omega_S), \quad (30)$$

where

$$f(\omega - \Omega_S) = \int_{\infty}^{\omega - \Omega_S} \varphi(x)dx, \qquad f(0) = \frac{1}{2}, \qquad f(\omega_2 - \Omega_S) \approx 1,$$

$$f(\omega_1 - \Omega_S) \approx 0.$$

According to (30) the approximate solution of Eq. (27) has the form

$$\beta(\omega) = \beta_L + \frac{s\pi k}{T_2}\Big\{\mathrm{sh}[k(\omega - \Omega_S)]f(\omega - \Omega_S)$$

$$- \frac{\mathrm{sh}[k(\omega_2 - \Omega_S)]\,\mathrm{sh}[k(\omega - \omega_1)]}{\mathrm{sh}\,k\Delta^*}\Big\}\beta(\Omega_S),$$

$$\beta(\Omega_S) = \beta_L\Big\{1 + \frac{s\pi k}{T_2}\frac{\mathrm{sh}[k(\omega_2 - \Omega_S)]\,\mathrm{sh}[k(\Omega_S - \omega_1)]}{\mathrm{sh}\,k\Delta^*}\Big\}^{-1} \quad (31)$$

If we bear in mind that our consideration is valid only provided the conditions $k\Delta^* \gg 1$, $k(\omega_2 - \Omega_S) \gg 1$,

---

$k(\Omega_S - \omega_1) \gg 1$ are satisfied we get finally

$$\beta(\omega) = \frac{\beta_L}{1+s'}\{1 + s'[1 - \exp(-k|\omega - \Omega_s|)]\}. \qquad (32)$$

We assumed that $|\omega - \Omega_S| \gg \Delta$. Here $s' = s\pi k/2T_2$ is the ESR saturation parameter in the case of non-uniform broadening. As $k/T_2 \ll 1$ saturation sets in for non-uniform broadening at a larger amplitude of the variable field than in the case of uniform broadening which is physically completely understandable since the energy of the variable field absorbed at a given frequency Ω_S is redistributed among many spin packets because of spectral diffusion.

For strong ESR saturation $s' \gg 1$ and

$$\beta(\omega) = \beta_L\{1 - \exp(-k|\omega - \Omega_s|)\}. \qquad (33)$$

It is interesting to note that one can easily obtain the solution (33) by taking into account the influence of the saturating variable field using the additional boundary condition $\beta(\Omega_S) = 0$ as was essentially done by Portis.[8]

Substituting $\beta(\omega)$ from (32) into (33) we get after straightforward calculations the following expressions for the inverse temperature of the nuclear subsystem

$$\beta_I = \beta_L \frac{1 + s'(1 - e^{-k\omega_I})}{1+s'}\left\{\frac{\Omega_s}{g(\Omega_s - \omega_0)}\frac{dg(\Omega_s - \omega_0)}{d\Omega_s} + 1\right\}. \qquad (34)$$

For strong saturation and sufficiently far from the center of the non-uniform line

$$\beta_I = \beta_L(1 - e^{-k\omega_I})\frac{\Omega_s}{g(\Omega_s - \omega_0)}\frac{dg(\Omega_s - \omega_0)}{d\Omega_s}. \qquad (35)$$

When $k\omega_I \gg 1$ spectral diffusion is unimportant and the old result (25) is obtained; if, however, $k\omega_I \ll 1$ due to the spectral diffusion the polarization effect is decreased by a factor $1/k\omega_I$. Physically this result is completely understandable. It is clear that $k\omega_I = \sqrt{(T_d/T_{SL})}$ where $T_d = \omega_I^2/D$ is the time for diffusion over a distance ω_I. If $T_d \ll T_{SL}$ the influence of the boundary condition in the point $\omega = \Omega_S$ on the inverse temperature $\beta(\Omega_S \pm \omega_I)$ determining the nuclear polarization dominates under the influence of spin-lattice relaxation, i.e., saturation of the usual resonance at the frequency Ω_S will also cause saturation at the frequencies $\Omega_S \pm \omega_I$ and the effective polarization is approximately reduced by a factor $\sqrt{(T_{SL}/T_d)}$. In the opposite limiting case when $T_d \gg T_{SL}$, $\beta(\Omega_S \pm \omega_I)$ is mainly determined by spin-lattice relaxation and equal to β_L, i.e., spectral diffusion does not affect the DNP.

[1] M. A. Kozhushner and B. N. Provotorov, Fiz. Tverd. Tela 6, 1472 (1964) [Sov. Phys.-Solid State 6, 1152 (1964)]; contribution to the All-Soviet Congress on Solid State Radiospectroscopy, Krasnoyarsk, 1964; J. L. Motchane, Ann. de Physique 7, 139 (1962); L. L. Buishvili, Zh. Eksp. Teor. Fiz. 49, 1868 (1965) [Sov. Phys.-JETP 22, 1277 (1966)]; N. S. Bendiashvili, L. L. Buishvili, and M. D. Zviadadze, Fiz. Tverd. Tela 8, 2919 (1966) [Sov. Phys.-Solid State 8, 2333 (1967)].

[2] A. Abragam and M. Borghini, Progr. Low Temp. Phys. 4, 384 (1964).

[3] A. M. Portis, Phys. Rev. 91, 1070 (1953); Zh. Vanter, Teoriya shiriny linii (Line Width Theory) in the collection of lectures Kvantovaya optika i kvantovaya radiofizika (Quantum Optics and Quantum Electronics) Mir, 1966; S. A. Al'tshuler and B. M. Kozyrev, Elektronnyĭ paramagnitnyĭ rezonans (Electron paramagnetic resonance), Fizmatgiz, 1961 [English translation published by Academic Press, 1964]; J. J. Markham, F-centers in Alkali Halides, Academic Press, New York, 1966.

[4] C. D. Jeffries, Dynamic Nuclear Orientation, Interscience, New York, 1963, Ch. 7.

[5] A. V. Kessenikh, and A. A. Manenkov, Fiz. Tverd. Tela 5, 1143 (1963) [Sov. Phys.-Solid State 5, 935 (1963)]; A. V. Kessenikh, A. A. Manenkov, and G. I. Pyatnitskii, Fiz. Tverd. Tela 6, 827 (1964) [Sov. Phys.-Solid State 6, 641 (1964)].

[6] L. L. Buishvili, Fiz. Tverd. Tela 9, No. 8, (1967) [Sov. Phys.-Solid State, 9, No. 8 (1968)].

[7] D. N. Zubarev, Dokl. Akad. Nauk SSSR 140, 92 (1961) [Sov. Phys.-Doklady 6, 776 (1962)].

[8] A. M. Portis, Phys. Rev. 104, 584 (1956); A. Kiel, Phys. Rev. 125, 1451 (1962).

[9] R. Kubo in Termodinamika neobratimykh protsessov (Thermodynamics of Irreversible Processes), IIL, 1962.

[10] A. Kiel, Phys. Rev. 120, 137 (1960).

[11] J. Lambe, N. Laurance, E. C. McIrvine, and R. W. Terhune, Phys. Rev. 122, 1161 (1961).

[12] I. V. Aleksandrov, Zh. Tekh. Eksp. Khim. 1, 80 (1965).

[13] G. R. Khutsishvili, Usp. Fiz. Nauk 71, 9 (1960) [Sov. Phys.-Usp. 3, 285 (1960)].

Translated by D. ter Haar
103