SOVIET PHYSICS JETP VOLUME 29, NUMBER 1 JULY, 1969

POLARIZATION OF NUCLEI BY DYNAMIC COOLING

M. A. KOZHUSHNER

Institute of Chemical Physics, USSR Academy of Sciences

Zh. Eksp. Teor. Fiz. 56, 246–255 (January, 1969)

The dynamic cooling technique for enhancing nuclear polarization is investigated theoretically. The electron spin system temperature decreases when the EPR is saturated by an alternating field whose frequency is shifted relative to the center of the EPR line. The nuclear spin system temperatures also decrease strongly in the presence of strong coupling between the electron and nuclear spin systems; this leads to an increase of the nuclear polarization. Cases of high and low temperature are considered. A criterion of the efficiency of the method is obtained (inequality (12)) and an equation is derived for the effective spin temperature of the system (Eq. (25)). Since large paramagnetic-center concentrations are required, the leakage factor is usually small and does not restrict the nuclear polarization, whose magnitude may be larger than that theoretically attainable in other DNP methods. Another advantage of the method is the high rate of variation of the polarization sign; a shortcoming is the necessity of using higher microwave power than in the usual DNP method.

THE method of dynamic polarization of nuclear spins (DNP), proposed in 1958[1,2], was used many times to obtain in practice high polarization of nuclear spins, and was analyzed theoretically[3]. In[4-6] there were obtained rigorous quantum-mechanical equations describing DNP in the case of a homogeneously broadened EPR line, with account taken of the change of the temperature of the dipole-dipole electron spin reservoir (DDS)[7] during the process of obtaining DNP. Buishvili[5] investigated DNP in the case of an alternating field parallel to a constant external field. Abragam and Borghini[6] took into account the coupling between DDS and the nuclear Zeeman system (NZS), which occurs only in saturation of forbidden transitions. It was shown in[4], however, that the coupling between the NZS and the DDS is realized not only via the alternating field that saturates the forbidden transitions, but also directly, as a result of the presence of the interaction between the electron and nuclear spins. If the temperature of the DDS is lowered for some reason, this can lead to a lowering of the NZS temperature, and consequently to an increase of the nuclear polarization. DNP following a decrease of the DDS temperature in the case of two sorts of nuclear spins was observed by Goldman and Landesman[8]. Recently, DNP due to the presence of such a direct coupling between the NZS and DDS was observed in an electron-nuclear spin system[9].

In the present paper we present a theoretical analysis of the method of DNP via cooling the DDS (we call this the dynamic cooling (DC) method), and we investigate both the case of high temperatures and the case of low temperatures (which is of interest in applications). Quantitative criteria are obtained for the efficiency of the DC method, and these relate the EPR line width to the values of the constant and alternating magnetic fields.

Physically, the gist of the DC method is as follows. As is well known[7], when EPR is saturated by an alternating field whose frequency ω is shifted relative to the Zeeman frequency of the electron ω_e ($\omega - \omega_e = \Delta$), each flipping of the electron spin is accompanied by a change of the DDS energy by an amount $\hbar\Delta$. This means that if the projection of the total electron spin of the system changes by δS^z, then the energy of the DDS changes by $\hbar\Delta S^z$. If $\Delta < 0$, then such a decrease of the DDS energy leads to a lowering of the DDS temperature. When $\Delta > 0$, the DDS temperature can become negative and small in absolute magnitude (since DDS is a system with a limited energy spectrum, the pumping of a sufficiently high energy in it can lead to inversion of the level population). But if the NZS is strongly coupled to the DDS, then the NZS temperature also decreases, i.e., the nuclear polarization increases, and its sign depends on the sign of Δ. In the DC method we are essentially using the presence of such a coupling (as will be shown below, this can be attained either by increasing the electron-spin concentration, or by decreasing the constant magnetic field). The alternating field saturates the EPR in such a way as to lower the DDS temperature, and with it also the NZS temperature. Therefore the frequency of the alternating field is chosen not such as to saturate the forbidden transitions, but such as to decrease as much as possible to DDS temperature.

The Hamiltonian of the investigated spin system is

$$\hat{\mathscr{H}} = \hbar\omega_e \sum_i \hat{S}_i^z + \hat{\mathscr{H}}_{ss} - \hbar\omega_n \sum_k \hat{I}_k^z + 2H_1\hbar\gamma_e \sum_i \hat{S}_i^x \cos\omega t + \hat{\mathscr{H}}_{sI}. \quad (1)$$

Here $\hat{S}_i^{z,x}$ and $\hat{I}_k^z$ are the operators of the projections of the i-th electron spin and the k-th nuclear spin on the axis designated by the superior indices, $\omega_e = \gamma_e H_0$, $\omega_n = \gamma_n H_0$, H_0 is the constant magnetic field, directed along the z axis, γ_e and γ_n are the gyromagnetic ratios for the electrons and the nuclei, $2H_1$ is the amplitude of the alternating field with frequency ω;

$$\hat{\mathscr{H}}_{ss} = \sum_{i \neq j} (A_{ij} \hat{S}_i^z \hat{S}_j^z + B_{ij} \hat{S}_i^+ \hat{S}_j^-) \quad (2)$$

is the secular part of the dipole-dipole interaction of the electron spins and commutes with $\Sigma_i \hat{S}_i^z$;

$$\hat{\mathscr{H}}_{sI} = \sum_{i,k} (\alpha_{ik} \hat{S}_i^z \hat{I}_k^+ + \alpha_{ik}^* \hat{S}_i^z \hat{I}_k^-)$$

is the operator of the dipole-dipole interaction of the electron and nuclear spins (we have retained only that part of the interaction which couples most strongly the electron and nuclear spin systems). Furthermore, we have not written out the spin-lattice interaction, which will be taken into account in the equations by introducing the corresponding relaxation times.

The first term on the right side of (1) is the operator of the Zeeman energy of the electrons and determines the electron Zeeman energy system (EZS), the second is the DDS energy operator, and the third the NZS energy operator. As shown in[4-7], different temperatures are established in each of these three energy reservoirs in a time on the order of the correlation time in the electron and nuclear spin systems. These temperatures change slowly (within a time on the order of the relaxation time), owing to the presence of interactions that couple these energy systems. Therefore the density matrix can be represented in the form

$$\rho = \text{const}\cdot\exp\left\{-\frac{\hbar\omega_e}{kT_s}\hat{S}^z - \frac{\hat{\mathscr{H}}_{ss}}{kT_{ss}} + \frac{\hbar\omega_n}{kT_n}\hat{I}^z\right\}, \tag{3}$$

where T_s, T_{ss}, and T_n are respectively the EZS, DDS, and NZS temperatures. For the reciprocal temperatures ($\beta \equiv 1/kT$) we obtain the following equation[4] (in the case when $\hbar\omega_e/kT_0 \ll 1$):

$$\frac{\partial\beta_s}{\partial t} = -(\gamma_e H_1)^2\pi g(\Delta)\left(\beta_s + \beta_{ss}\frac{\Delta}{\omega_e}\right) - \frac{1}{\tau_s}\left(\beta_s - \frac{1}{kT_0}\right); \tag{4a}$$

$$\begin{aligned}\frac{\partial\beta_{ss}}{\partial t} = &-(\gamma_e H_1)^2\pi g(\Delta)\frac{\Delta\cdot\omega_e}{\omega_0^2}\left(\beta_s + \beta_{ss}\frac{\Delta}{\omega_e}\right) - \frac{1}{\tau_{ss}}\left(\beta_{ss} - \frac{1}{kT_0}\right)\\ &- \pi g_1(\omega_n)\frac{1}{N_s}\frac{1}{\hbar^2}\sum_{i,k}|\alpha_{ik}|^2\left(\frac{\omega_n}{\omega_0}\right)^2(\beta_{ss} - \beta_n);\end{aligned} \tag{4b}$$

$$\begin{aligned}\frac{\partial\beta_n}{\partial t} = &-(\gamma_e H_1)^2\pi g'(\omega, \omega_e, \omega_n)\left(\beta_n + \beta_s\frac{\omega_e}{\omega_n} + \frac{\Delta - \omega_n}{\omega_n}\beta_{ss}\right)\\ &-(\gamma_e H_1)^2\pi g''(\omega, \omega_e, \omega_n)\left(\beta_n - \beta_s\frac{\omega_e}{\omega_n} - \frac{\Delta + \omega_n}{\omega_n}\beta_{ss}\right)\\ &-\pi\frac{1}{N_I}\frac{1}{\hbar^2}\sum_{i,k}|\alpha_{ik}|^2 g_1(\omega_n)(\beta_n - \beta_{ss}) - \frac{1}{\tau_n}\left(\beta_n - \frac{1}{kT_0}\right).\end{aligned} \tag{4c}$$

Here $\Delta = \omega - \omega_e$; T_0 is the equilibrium lattice temperature;

$$g(\Delta) = {}^1\!/_2\,\text{Sp}\,\{\hat{S}^+(\Delta)\hat{S}^-\}/\,\text{Sp}\,\{(\hat{S}^z)^2\} \tag{5}$$

are functions of the EPR line shape;

$$g_1(\omega_n) = N_s\,\text{Sp}\,\{\hat{S}_i^z(\omega_n)\hat{S}_i^z\}/\,\text{Sp}\,\{(\hat{S}^z)^2\}; \tag{6}$$

$g'(\omega, \omega_e, \omega_n)$ and $g''(\omega, \omega_e, \omega_n)$ are line-shape functions for the two types of forbidden transitions ($\omega \approx \omega_e + \omega_n$ and $\omega \approx \omega_e - \omega_n$); $\hat{S}(\omega)$ is the Fourier component of the operator

$$\hat{S}(t) \equiv \exp\left(\frac{i}{\hbar}\hat{\mathscr{H}}_{ss}t\right)\hat{S}\exp\left(-\frac{i}{\hbar}\hat{\mathscr{H}}_{ss}t\right);$$

$$\omega_0^2 = \frac{1}{\hbar^2}\,\text{Sp}\,\{\hat{\mathscr{H}}_{ss}^2\}/\,\text{Sp}\,\{(\hat{S}^z)^2\} \tag{7}$$

is the characteristic precession frequency of the electron spin in the local fields produced by other electron spins, N_s and N_I are the numbers of electron and nuclear spins in the sample; τ_s and τ_{ss} are the spin-lattice relaxation times for the EZS and DDS, respectively, τ_n is the time of the nuclear spin-lattice relaxation due to the coupling of the NZS with the lattice.

Let us examine the physical meaning of the different terms in (4). The first two terms in the right sides of (4a) and (4b) represent the influence of the allowed transitions and the spin-lattice relaxation on the EZS and DDS[7]. We usually did not take into account the very weak influence of the forbidden transitions on the state of the electron spin system. The third terms in (4b) and (4c) describe the coupling between the NZS and DDS. This coupling is determined principally by the value of $g_1(\omega_n)$—the Fourier component of the correlation function $N_s\,\text{Tr}\,\{\hat{S}_i^z(t)\hat{S}_i^z\}/\text{Tr}\,\{(\hat{S}^z)^2\}$. The quantity $g_1(\omega_n)$ determines the intensity of absorption or emission of quanta of energy $\hbar\omega_n$ by the dipole-dipole system with the aid of $\mathscr{H}_{sl}$. The widths of the functions $g_1(\omega)$ and $g(\omega)$, determined, for example, from the second moment, are interrelated (see (17) below). We can therefore say that the efficiency of this coupling depends on the EPR line width and on the value of H_0. The first two terms in (4c) represent the coupling between the EZS, NZS, and DDS, which is established as a result of the excitation of the forbidden transitions. We shall henceforth consider only the saturation of the allowed transitions in EPR by the alternating field, and the associated changes of β_s, β_{ss}, and β_n. Since the frequencies of the forbidden and allowed transitions are shifted relative to each other by approximately ω_n, which is larger than the EPR line width, we shall disregard the forbidden transition.

Let us study the stationary case, i.e., equate to zero the right sides of (4). We then get from (4c)

$$\beta_n = \frac{a}{1+a}\beta_{ss} + \frac{1}{1+a}\frac{1}{kT_0}, \tag{8}$$

where

$$a = \pi\frac{1}{N_I}\frac{1}{\hbar^2}\sum_{i,k}|\alpha_{ik}|^2 g_1(\omega_n)\tau_n. \tag{9}$$

The quantity τ_n^{-1} in (4c) and (9) is the rate of the nuclear spin-lattice relaxation due to all other mechanisms except the coupling between NZS and DDS (third term in (4c)). At large concentrations of the paramagnetic centers, the main contribution to τ_n^{-1} is made by the mechanism of relaxation of nuclear spins with paramagnetic centers (by nuclei we mean here throughout protons, $I_n = 1/2$, and therefore we disregard quadrupole relaxation)[3]:

$$\tau_n^{-1} = \frac{1}{N_I}\frac{1}{\hbar^2}\sum_{i,k}|\alpha_{ik}|^2\frac{1}{\omega_n^2}\frac{1}{\tau_s}. \tag{10}$$

It is seen from (8) that in order to obtain large β_n, i.e., $\beta_n \approx \beta_{ss}$, it is necessary to satisfy the condition

$$a \gg 1. \tag{11}$$

Substituting (10) in (9), we get in lieu of (11)

$$a = \pi g_1(\omega_n)\omega_n^2\tau_s \gg 1. \tag{12}$$

If condition (12) is satisfied, then in the case of strong EPR saturation, when the saturation parameter is

$$s = (\gamma_e H_1)^2\pi g(\Delta)\tau_s \gg 1, \tag{13}$$

we get from (4) (see[6])

$$\beta_n = -\frac{\omega_e\Delta}{(\tau_s/\tau_{ss})\,\omega_0^2 + \Delta^2 + f\omega_n^2}\,\frac{1}{kT_0}, \tag{14}$$

where f is the leakage factor

$$f = \frac{N_I}{N_s}\frac{\tau_s}{\tau_n}. \tag{15}$$

It should be recalled that the time τ_n, which must be substituted in (15), is larger than the true nuclear spin-lattice relaxation time τ_n', which is determined not only by the spin-lattice relaxation via the electron spins (10), but also by the coupling between the NZS and DDS. If

τ_n' is measured under conditions when the electron spin system is in equilibrium and $a \gg 1$, then

$$\tau_n' \approx \tau_n / a. \tag{16}$$

Thus, the leakage factor f, determined by formula (15), differs from the usually determined leakage factor, which contains τ_n' in lieu of τ_n[3].

In order to determine the conditions under which (12) is satisfied, we calculate the second moment of $g_1(\omega)$:

$$M_2' = \int \omega^2 g_1(\omega)\, d\omega.$$

In the case of an isotropic electronic g-factor (as is usually the case in paramagnetic organic radicals)

$$M_2' = {}^2/_9 M_2, \tag{17}$$

where $M_2 = \int \omega^2 g(\omega) d\omega$ is the second moment of the EPR line-shape function. If we assume that $g(\omega)$ is a Gaussian function, then the half-width at half-height is $\delta \approx \sqrt{M_2}$, and (12) goes over into

$$a \approx \tau_s \frac{\sqrt{2\pi}}{\delta} \omega_n{}^2 \exp\left(-9\omega_n{}^2/4\delta^2\right) \gg 1. \tag{12a}$$

In a field $H_0 = 10^4$ Oe, at $\tau_S \approx 10^{-1}$ sec (typical time for organic free radicals at helium temperatures), we find that (12a) is satisfied when $\delta \geq \omega_n/3$, or expressing δ in Oersteds, we get $\delta > 5-6$ Oe. Naturally, the estimate of the EPR line width, and consequently of the paramagnetic-center concentration necessary to obtain an appreciable polarization depends on the behavior of $g_1(\omega)$ at large ω, however, one can hardly expect an appreciable deviation from the estimate just presented for δ. The maximum value of β_n, according to (14), is obtained when $|\Delta| = \sqrt{\tau_2/\tau_{SS}}\omega_0$, and turns out to be

$$(\beta_n)_{max} = \frac{\omega_e}{2\sqrt{\tau_s/\tau_{ss}}\,\omega_0} \frac{1}{kT_0} \operatorname{sign} \Delta. \tag{18}$$

(We assume that $f \ll 1$). Calculating ω_0 with the aid of (7), we get[6] $\omega_0 = \sqrt{M_2/3}$. In the case $H_0 = 10^4$ Oe considered by us, assuming $\tau_S/\tau_{SS} = 2$, we get $(\beta_n)_{max} \approx 1000(kT_0)^{-1}$, i.e., the nuclear polarization in the DC method can be larger than in the ordinary DNP method.

We now proceed to consider the case of greatest practical interest, that of low temperatures, $\hbar\omega_e/kT_0 \gtrsim 1$. At low temperatures, and consequently at appreciable polarization of the electron spins, we can no longer regard the EZS and the DDS as statistically independent systems. In order for two energy systems to be regarded as statistically independent, it is necessary to satisfy the following conditions: a) the set of eigenstates of the Hamiltonians defining each system must not change when the populations of these states change in the other system; b) the populations of the states in each system can be specified independently (i.e., the temperatures in each system are independent).

The DDS energy depends on different spin configurations, i.e., on the mutual orientations of the electron spins. Let the electron polarization p_S have a fully defined value, i.e., T_S is specified, then the set of the microstates—configurations whose populations determine the macrostate of the independent DDS—is limited by the requirement that each microstate corresponds to this polarization. The statistical weight of the configurations corresponding to large p_S (close to unity) is much smaller than the statistical weight of the configurations, corresponding to $p_S \approx 0$. Therefore, in the high temperature case ($\hbar\omega_e/kT_0 \ll 1$), when p_S is close to zero, the permissible configurations—states—include a large fraction of the eigenstates of $\hat{\mathscr{H}}_{SS}$, as a result of which we can assume that $\hat{\mathscr{H}}_{SS}$ defines the DDS well. We can change arbitrarily the population of the majority of the states of $\hat{\mathscr{H}}_{SS}$ without changing p_S in practice (if the latter is small) or, conversely, we can change the polarization without hardly changing either the set of states $\hat{\mathscr{H}}_{SS}$ or their populations. This means that we can specify two statistically independent systems, EZS and DDS[10].

The situation changes radically in the low-temperature case ($\hbar\omega_e/kT_0 \gtrsim 1$). Now p_S is close to unity, and the set of admissible states of $\hat{\mathscr{H}}_{SS}$ is greatly reduced, i.e., most degrees of freedom of the Hamiltonian $\hat{\mathscr{H}}_{SS}$ are "frozen." In the limiting case $p_S = 1$, only one configuration is possible. To define the DDS it is necessary to separate from $\hat{\mathscr{H}}_{SS}$ that part which corresponds to the "unfrozen" degrees of freedom. Change of the polarization, i.e., a change of T_S, changes strongly the number and the energy spectrum of the admissible configurations, i.e., it is necessary to redefine the DDS. This means that at low temperatures the separation of the electron spin system into two statistically independent subsystems EZS and DDS is impossible.

We shall consider the case of strong EPR saturation. Then, as shown by Redfield[11], the electron spin system (ESS) in the stationary state can be described by a single spin temperature T* (see also[6]). Redfield's approximation is valid in the case $\tau_C \ll \tau_S$, where τ_C is the correlation time in the ESS. If the EPR line is broadened by dipole-dipole interaction, then $\tau_C \approx \omega_0^{-1}$, where ω_0 is approximately equal to the EPR line width, and the inequality $\tau_C \ll \tau_S$ is violated only for electronic polarizations $p_S \approx 1$, such that $\omega_0 \sim \tau_S^{-1}$. The density matrix of the ESS and NZS, in the case of strong EPR saturation, takes in this case the form

$$\rho = \frac{\exp\left[(\hbar\Delta\hat{S}^z - \hat{\mathscr{H}}_{ss})/kT^* + \hbar\omega_n\hat{I}^z/kT_n\right]}{\operatorname{Sp}\left\{\exp\left[(\hbar\Delta\hat{S}^z - \hat{\mathscr{H}}_{ss})/kT^* + \hbar\omega_n\hat{I}^z/kT_n\right]\right\}} \tag{19}$$

(We assume that $\gamma_e H_1 \ll \omega_0$, which is true even in strong saturation if $\omega_0 \gg \tau_S^{-1}$). If we disregard the spin-lattice relaxation, T* can be determined from the energy conservation law[7]:

$$-\hbar\Delta\cdot\bar{S}^z + \bar{\mathscr{H}}_{ss} = \text{const}, \tag{20}$$

where the bar denotes statistical averaging. The interaction $\hat{\mathscr{H}}_{Sl}$ equalizes T_n and T*, but only if (11) is satisfied, just as in the high-temperature case $T_n \approx T^*$, except that now $g_1(\omega)$ is defined by

$$g_1(\omega_n) = \operatorname{Sp}\{\hat{S}_i{}^z(\omega_n) S_i{}^z \rho\}. \tag{21}$$

We call immediate attention to the fact that the larger the electron polarization p_S, the smaller the frequency region at which $g_1(\omega)$ differs noticeably from zero. Indeed, for the second moment M_2' if the ESS is in equilibrium at the temperature T_S, we can readily obtain

$$M_2' = M_2'(\infty)\operatorname{ch}^{-2}(\hbar\omega_e/2kT_s), \tag{22}$$

where $M_2'(\infty)$ is the second moment of $g_1(\omega)$ calculated for an infinitely large temperature T_S. Recognizing that $p_S = \tanh(\hbar\omega_e/2kT_S)$, we obtain

$$M_2' = M_2'(\infty)(1 - p_s^2). \tag{22a}$$

Thus, the condition (11) that the temperature of the NZS be equalized with T* is satisfied the worse, the larger the stationary electron polarization. This factor must be taken into account when choosing the optimal conditions for obtaining large nuclear polarization by the dynamic cooling method.

We shall now attempt to calculate the stationary ESS temperature T*, equating in accordance with (20) the values of $-\hbar\Delta S^z + \overline{\mathscr{H}}_{ss}$ in the stationary state under the influence of the alternating field and in the initial equilibrium state:

$$\frac{\operatorname{Sp}\{(-\hbar\Delta\hat{S}^z + \hat{\mathscr{H}}_{ss})\exp[(\hbar\Delta\hat{S}^z - \hat{\mathscr{H}}_{ss})\beta^*]\}}{\operatorname{Sp}\{\exp[(\hbar\Delta\hat{S}^z - \hat{\mathscr{H}}_{ss})\beta^*]\}} = \frac{\operatorname{Sp}\{(-\hbar\Delta\hat{S}^z + \hat{\mathscr{H}}_{ss})\exp[-\hbar\omega_e\hat{S}^z\beta_0]\}}{\operatorname{Sp}\{\exp[-\hbar\omega_e\hat{S}^z\beta_0]\}}. \tag{23}$$

Here $\beta^* = 1/kT^*$ and $\beta_0 = 1/kT_0$. In (23) we used, for the ESS density matrix in the equilibrium state the expression

$$\rho_0 = \exp[-\hbar\omega_e\hat{S}^z\beta_0] / \operatorname{Sp}\{\exp[-\hbar\omega_e\hat{S}^z\beta_0]\}.$$

In the equilibrium density matrix ρ_0 we have retained in place of the Hamiltonian $\hbar\omega_e S'^z + \hat{\mathscr{H}}_{ss}$ only the first term, since $\hbar\omega_e S^z \gg \mathscr{H}_{ss}$.

An exact calculation of the expression in the left side of (23) is impossible at present. To calculate approximately the corresponding traces of the matrices, we expand $\exp[(\hbar\Delta\hat{S}^z - \hat{\mathscr{H}}_{ss})\beta^*]$ in a series in $\hat{\mathscr{H}}_{ss}\beta^*$:

$$\exp[(\hbar\Delta\hat{S}^z - \hat{\mathscr{H}}_{ss})\beta^*] = \exp(\hbar\Delta\hat{S}^z\beta^*)\left(1 - \hat{\mathscr{H}}_{ss}\beta^* + \frac{1}{2}\hat{\mathscr{H}}_{ss}^2\beta^{*2} - \ldots\right). \tag{24}$$

In the expressions for the corresponding traces, we can confine ourselves to only a few terms of the resultant series, namely, we retain only the dipole-dipole interaction averaged over the different pairs of the interacting spins, and disregard the dipole-dipole interaction of three, four, and more closely-lying spins. Thus, for example, let us consider the term of the series in the left side of (23)

$$\frac{\operatorname{Sp}\{\exp(\hbar\Delta\cdot\beta^*\hat{S}^z)\cdot(1/3!)\hat{\mathscr{H}}_{ss}^4\beta^{*3}\}}{\operatorname{Sp}\{\exp(\hbar\Delta\cdot\beta^*\hat{S}^z)\}}.$$

It contains both terms of the type a):

$$(\operatorname{Sp}\{\exp(\hbar\Delta\cdot\beta^*\hat{S}^z)\})^{-1}\operatorname{Sp}\{\exp(\hbar\Delta\cdot\beta^*\hat{S}^z)\cdot \cdot\frac{1}{3!}\beta^{*3}\sum_{i\neq k}B_{ik}^4(\hat{S}_i^+\hat{S}_i^-)^2(\hat{S}_k^-\hat{S}_k^+)^2\} = \frac{1}{3!}\beta^{*3}\sum_{i\neq k}B_{ik}^4\frac{1}{4\operatorname{ch}^2(\hbar\Delta\beta^*/2)},$$

and terms of the type b):

$$(\operatorname{Sp}\{\exp(\hbar\Delta\cdot\beta^*\hat{S}^z)\})^{-1}\operatorname{Sp}\left\{\exp(\hbar\Delta\cdot\beta^*\hat{S}^z)\frac{1}{3!}\beta^{*3}\sum_{i\neq k\neq m}B_{ik}^2B_{km}^2\right.$$
$$\left.\times(\hat{S}_i^+\hat{S}_i^-)(\hat{S}_k^-\hat{S}_k^+)(\hat{S}_m^+\hat{S}_m^-)\right\} = \frac{1}{3!}\beta^{*3}\sum_{i\neq k\neq m}B_{ik}^2B_{km}^2\frac{1}{8\operatorname{ch}^3(\hbar\Delta\cdot\beta^*/2)}.$$

We retain only terms of the first type, where only pairs of interacting are taken into account. This is due to the fact that at large electron polarizations ($\hbar\Delta\cdot\beta^*/2 > 1$) these terms are the largest, being proportional to $\cosh^{-2}(\hbar\Delta\cdot\beta^*/2)$, whereas the discarded terms are proportional to $\cosh^{-n}(\hbar\Delta\cdot\beta^*/2)$, where $n > 2$. Physically this is explained by the fact that at large electron polarizations the probability w that several mutually flipped spins turn out to be close to one another (only such configurations contribute to $\overline{\mathscr{H}}_{ss}$) decreases very rapidly with increasing n—the number of the flipped spins, namely, $w \sim \cosh^{-n}(\hbar\Delta\cdot\beta^*/2)$. On the other hand, if we consider the case of small polarizations ($\hbar\Delta\cdot\beta^* \ll 1$), then it is necessary to retain in the series (24) only the first two terms, which give only terms of type a). Thus, if we retain only terms of type a) in the calculation of the traces in (23), then the resultant expression is close to the exact one both in the case of large and in the case of small β^*. It is therefore reasonable to assume that this expression can serve as an interpolation formula for all values of $\hbar\Delta\cdot\beta^*$.

As a matter of fact, in the described procedure the mean value of the energy of the spin system is calculated without allowance for the correlation in the directions of the individual spins. In the Ising model, such a calculation yields for the average energy a result close to the exact value, provided the polarization is not too small[12]. In our case (spin system with anisotropy spin-spin interaction, placed in an external field comparable in order of magnitude with the internal field ($\hbar\Delta \approx A_{ij}$)), is close to the Ising model (the energy spectrum has a gap)[12]. Therefore the interpolation formula for the determination of the stationary β^* can hardly deviate greatly from the exact formula. Taking into account the foregoing considerations, we obtain in lieu of (23)

$$\operatorname{th}r_0 - \operatorname{th}r = \left(\frac{\omega_0}{\Delta}\right)^2 r\cdot\frac{\nu}{6\operatorname{ch}^2 r}\left\{e^{2r}(1-\operatorname{th}r)^4 + \frac{2}{\operatorname{ch}^4 r} + (1+\operatorname{th}r)^4 e^{-2r} + 2\right\}. \tag{25}$$

where $r_0 = \hbar\omega_0/2kT_0$, $r = \hbar\Delta\cdot\beta^*/2$, and the factor ν takes into account the influence of the spin-lattice coupling (ν = 1—3).

For simplicity, we consider a sample in the form of a sphere, so as not to take the demagnetizing field into account. If the sample is not a sphere, then Δ in (25) is the deviation of the frequency of the alternating field from the resonant frequency ω_e, calculated with allowance for the demagnetization field. The problem of finding the stationary spin temperature $T^* = 1/k\beta^*$, and consequently also T_n (if condition (11) is satisfied), reduces to a solution of the transcendental equation (25).

In the study of the optimal conditions under which the maximum nuclear polarization can be obtained in the DC method, it is necessary to take into account the fact that the power P absorbed by the spin system is much larger than in the ordinary DNP method, for in this case the saturated transitions are allowed and not forbidden. Therefore, if the electron-spin density and the field H_0 are very large, difficulties may arise, first with the supply of such a large power, and second with the removal of the heat from the sample to keep the temperature low. The absorbed power is

$$P \approx \frac{\hbar\omega}{\tau_s}(\bar{S}_0^z - \bar{S}^z_{\text{stat}}) = \frac{\hbar\omega n_s V}{2\tau_s}(\operatorname{th}r_0 - \operatorname{th}r), \tag{26}$$

where n_s is the spin density and V is the volume of the sample. An increase of the field H_0 causes also the increase of n_s, because when ω_n is increased it is necessary, in order to satisfy (12) with account taken of (22a), to increase the width $g_1(\omega)$, i.e., to increase the spin density n_s. The value of τ_s also decreases as a rule with increasing H_0. Thus, inasmuch as the experimental technique always calls for the condition $P < P_{max}$, this imposes an upper limit on the possible constant magnetic fields.

Thus, if we satisfy the conditions (12) (with allowance for (22a) and (26)), then the solution of (25) yields β^*—the reciprocal temperature of the NZS and the nuclear polarization

$$p_n = \operatorname{th} \frac{\hbar\omega_n\beta^*}{2}. \quad (27)$$

We shall not present a general investigation of the solution of (25) with allowance for conditions (12) and (26). This can be done in each concrete case.

Let us consider two cases showing that at low temperatures the DC method can be quite effective.

1). Sample with organic free radicals and an isotropic g-factor equal to two; the polarized nuclei are protons. $T_0 = 1°K$, $H_0 = 10^4$ Oe. Let $\Delta = \omega_0$ and $\nu = 2$. Solving (25) under these conditions we get $r = 0.225$, i.e., $\beta^* = 2r/\hbar\omega_0 = 0.45\sqrt{3}/\hbar\delta$. At $T_0 = 1°K$ we can assume that $T_1 \simeq 10^{-1}$–10^{-2} sec. From (12a) and (22a) we find that when $\delta = 0.4\,\omega_n$ (or, in Oersteds, $\delta \approx 6$ Oe) $a \approx 10^3 \gg 1$, i.e., condition (4) is satisfied. Then (27) yields

$$p_n = \operatorname{th} \frac{0{,}45\sqrt{3}}{2 \cdot 0{,}4} \approx 0{,}75.$$

The concentration $n_s = 5 \times 10^{19}$ cm^{-3}. The power P absorbed in the sample, according to (24), is $\sim (2-3) \times 10^{-3}$ W/cm^3.

2). In a field $H_0 = 20{,}000$ Oe at $\Delta = \omega_0$ we obtain from (25) $r = 0.35$. Then $p_n = 0.90$. Under these conditions $\delta \approx (12-13)$ Oe, and the absorbed power increases to 10^{-2} W/cm^3. It should be noted that the sign of the polarization p_n can also be easily changed by changing the sign of Δ. The time necessary to change the sign of the polarization is determined by the larger of the two times: the time required to change the sign of Δ, or the electron spin-lattice relaxation time τ_s. The large speed with which the polarization sign is reversed is very important in experiments with polarized targets.

In conclusion, I am grateful to B. N. Provotorov, I. I. Levintov, V. P. Sokolov and the participants of the Seminar of the Theoretical Division of the Institute of Chemical Physics, headed by A. S. Kompaneets, for fruitful discussions.

---

[1] E. Erb, J. L. Motchane, and J. Uebersfeld, Compt. rend. **246**, 2121 (1958).

[2] A. Abragam and W. G. Proctor, ibid. **246**, 2253 (1958).

[3] C. D. Jeffries, Dynamic Nuclear Orientation, Interscience, 1963.

[4] M. A. Kozhushner and B. N. Provotorov, (Paper at the 1964 All-union Conference) in Krasnoyarsk, in: Radiospektroskopiya tverdogo tela (Radiospectroscopy of the Solid State), Atomizdat, 1967. M. A. Kozhushner, Candidate's Dissertation, Inst. of Chem. Phys., Moscow, 1964.

[5] L. L. Buishvili, Zh. Eksp. Teor. Fiz. **49**, 1868 (1965) [Sov. Phys.-JETP **22**, 1277 (1966)].

[6] A. Abragam and M. Borghini, Progress in Low Temperature Physics, vol. IV, Amsterdam, 1964, p. 384.

[7] B. N. Provotorov, Zh. Eksp. Teor. Fiz. **41**, 1582 (1961) [Sov. Phys.-JETP **14**, 1126 (1962)].

[8] M. Goldman and A. Landesman, Phys. Rev. **132**, 610 (1963).

[9] V. A. Atsarkin, A. E. Mefed, and M. I. Rodak, ZhETF Pis. Red. **6**, 942 (1967) [JETP Lett. **6**, 359 (1967)].

[10] I. Phillipot, Phys. Rev. **133A**, 471 (1964).

[11] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).

[12] R. Brout, Phase Transitions, Benjamin, 1965.

Translated by J. G. Adashko
34