Spin-wave theory of NMR in solids at low temperatures

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A new approach is suggested for describing NMR at large values of the nuclear polarization $p\,(1-p\ll 1)$ in the spin-wave approximation. The shape of the NMR line is discussed. Saturation equations are derived. The specific heats of the spin system are calculated.

1. INTRODUCTION

The growing research interest on the dynamics of solid-state spin systems at low temperatures[1] stems from the development of methods for dynamic polarization of nuclei[1,2] which make it possible to achieve values of the nuclear-spin polarization close to unity. The spin temperature corresponding to such polarizations is well below the lattice temperature.

We assume that a system of nuclear spins in a strong polarizing field $\mathbf{H}_0$ (directed along the z axis) is also subjected to an rf field $2\mathbf{H}_1\cos\omega t$, directed perpendicular to $\mathbf{H}_0$. This system is described by the Hamiltonian

$$\mathcal{H}=-\omega_0 S_z+\mathcal{H}_{dz}-2\omega_1\cos\omega t S_x, \tag{1}$$

where $\omega_0=\gamma H_0$, $\omega_1=\gamma H_1$ (γ is the gyromagnetic ratio), the operators S_j ($j=x,y,z$) are the projections of the total spin angular momentum onto the j axis, and $\mathcal{H}_{dz}$ is the part of the dipole-dipole interaction (DDI) which is secular with respect to the z axis. In the absence of an rf field, Hamiltonian (1) consists of two commuting parts, and the equilibrium density matrix

$$\rho_0=\exp\{\alpha\omega_0 S_z-\beta_d\mathcal{H}_{dz}\}/\mathrm{Sp}\exp\{\alpha\omega_0 S_z-\beta_d\mathcal{H}_{dz}\} \tag{2}$$

is determined[3] by two independent thermodynamic parameters (reciprocal temperatures), α and β_d.

Under the conditions $\alpha\omega_0\ll 1$ and $\beta_d\omega_{\mathrm{loc}}\ll 1$ (ω_{loc} is value of the DDI in frequency units) the high-temperature approximation is valid. In that approximation it becomes possible to expand (2) in $\alpha\omega_0$ and $\beta_d\omega_{\mathrm{loc}}$ and to retain only the terms which are linear in these parameters.[3,4] At low spin temperatures, with $\alpha\omega_0\gtrsim 1$, and possibly $\beta_d\omega_{\mathrm{loc}}\gtrsim 1$, important deviations from the predictions of the high-temperature theory arise. Those deviations are known as "nonlinear effects."[1] The existing approaches[5–9] for the case of a high nuclear polarization ($\alpha\omega_0\gg 1$) remain of a high-temperature nature in terms of β_d and thus cannot be taken to describe the saturation of the NMR line and other effects which are accompanied by a pronounced cooling of the DDI reservoir. It is furthermore not possible to follow the transition of the system of nuclear spins to a magnetically ordered state.[1]

In the present paper we offer an approach for describing diverse phenomena in a system of nuclear spins with a high polarization for arbitrary values of the dipole temperature, in particular, for the case $\beta_d\omega_{\mathrm{loc}}\gtrsim 1$. This approach starts from an examination of elementary excitations of the spin system from the state of complete order.

Since we have $[\omega_0 S_z,\ \mathcal{H}_{dz}]=0$, these operators have a common basis, consisting of their eigenfunctions. The ground state for the Hamiltonian $\mathcal{H}_0=-\omega_0 S_z+\mathcal{H}_{dz}$ is the state in which all the spins have their maximum z projection. We denote this state by $|0\rangle$. It is not difficult to verify that the state

$$|\mathbf{k}\rangle=\frac{1}{\sqrt{N}}\sum_{\mathbf{l}}\exp(i\mathbf{k}\mathbf{l})S_{\mathbf{l}}^{-}|0\rangle, \tag{3}$$

where $S_{\mathbf{l}}^{-}$ is the lowering operator for the spin at site 1, and N is the total number of spins, is also an eigenstate of $\mathcal{H}_0$, with an eigenvalue greater than $|0\rangle$. The state $|\mathbf{k}\rangle$ is a state with one flipped spin and a polarization $p=1-2/N$ (for spins $S=1/2$). The lowest-lying excitations of the system are thus the spin waves in (3). Correspondingly, states with a high energy are (approximately) states with several excited spin waves.[10] As in a description of magnetic materials,[11] one can thus treat this system of spins as a gas of interacting magnons.

The role played by the magnon-magnon interaction decreases in importance with decreasing magnon density n/N and thus with increasing polarization $p=1-2n/N$. At a low density, the primary processes are the creation of magnons by the rf field and a four-magnon process: the scattering of a pair of spin waves (magnons) by each other. In the absence of an rf field, and at a fixed value of the polarization, scattering processes lead to an equilibrium distribution for the numbers of magnons:

$$n_{\mathbf{k}}=\{\exp[\beta(\varepsilon_{\mathbf{k}}-\mu)]-1\}^{-1}, \tag{4}$$

where $\varepsilon_{\mathbf{k}}$ is the energy of the magnons with wave vector $\mathbf{k}$, and β and μ are the reciprocal temperature and the chemical potential, i.e., two independent thermodynamic parameters which play the same role as α and β_d in (2). When a weak rf field, of a strength such that the magnon creation rate is considerably lower than the rate at which an equilibrium is established by scattering processes, is applied to the system, distribution (4) remains the same, but β and μ vary slowly in time. The saturation of the spin system by a weak rf field can be described in these terms. Under the condition $1-p\ll 1$, with a weak interaction of magnons, the thermodynamic characteristics of the system can easily be expressed in terms of $n_{\mathbf{k}}$. In particular, for the magnetization M and the total energy E we have

$$M=\frac{1}{2}N-\sum_{\mathbf{k}}n_{\mathbf{k}},$$

$$E=\sum_{\mathbf{k}}n_{\mathbf{k}}\varepsilon_{\mathbf{k}}.$$

In a state of total thermal equilibrium (in the absence of

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an rf field) we have $\mu = 0$. A weak rf field drives the system away from equilibrium, and the system then evolves through a sequence of quasiequilibrium states. If, at saturation, the energy of the magnons created by the rf field is lower than the average energy of the magnons which already exist in the system, this system will cool down (below we will discuss only the case $\beta > 0$). Since the number of magnons in the system increases in the process, it follows directly from (4) that the chemical potential μ increases upon saturation in this regime. When μ reaches the lower boundary of the magnon spectrum, $\varepsilon_{\mathbf{k}}$, a Bose condensation begins in the gas of magnons and gives rise to an ordering of the transverse components of the nuclear magnetic moments. As we will see below, this ordering arises at temperatures $\beta\omega_{\text{loc}} \gg 1$ under the condition $1 - p \ll 1$. The reason is that in the case of a high longitudinal polarization the transverse components of the magnetic moments are reduced, so the interaction between them is weakened. Consequently, even if we ignore Bose condensation there exists a wide temperature range in which this new approach is applicable.

Below we construct a Hamiltonian for the spin system of a solid in a strong magnetic field in the spin-wave representation, discuss the shape of the NMR line, derive saturation equations, and calculate the specific heats of the spin subsystems. This new approach can also serve as the starting point for studying spin-lattice relaxation at low temperatures, dynamic nuclear polarization, and the transitions of a spin system to an ordered state.

2. SPIN-WAVE REPRESENTATION OF THE HAMILTONIAN

Let us examine Hamiltonian (1) for a system of N nuclear spins ($S = 1/2$) at the sites of a regular lattice. In a strong field ($\omega_0 \gg \omega_{\text{loc}}$), the DDI Hamiltonian is[3,4]

$$\mathcal{H}_{dz} = \frac{1}{2}\sum_{\mathbf{l},\mathbf{l}'}^{N} b_{\mathbf{l},\mathbf{l}'}\,(3S_{\mathbf{l}}^{z}S_{\mathbf{l}'}^{z} - S_{\mathbf{l}}S_{\mathbf{l}'}), \qquad b_{\mathbf{ll}'} = \gamma^2\hbar^2\frac{1-3\cos^2\theta_{\mathbf{l},\mathbf{l}'}}{2|\mathbf{l}'-\mathbf{l}|^3}, \tag{5}$$

where $\theta_{\mathbf{l},\mathbf{l}'}$ is the angle between the vector $\boldsymbol{\delta} = \mathbf{l}' - \mathbf{l}$, which connects the positions of spins $\mathbf{l}$ and $\mathbf{l}'$ and the z axis, and the operator $S_{\mathbf{l}}^{j}$ projects the spin of the nucleus at site $\mathbf{l}$ onto axis j ($j = x,y,z$).

Our problem here is to analyze the dynamics of the system at temperatures so low that excitations of the system from the $|0\rangle$ ground state can be described in the spin-wave approximation.[11] In this case the spin operators $S_{\mathbf{l}}^{\pm} = S_{\mathbf{l}}^{x} \pm iS_{\mathbf{l}}^{y}$ are replaced by Bose creation and annihilation operators $a_{\mathbf{l}}^{+}$, $a_{\mathbf{l}}$, by means of the following relations:[12]

$$\begin{aligned} S_{\mathbf{l}}^{+} &= a_{\mathbf{l}}, \\ S_{\mathbf{l}}^{-} &= a_{\mathbf{l}}^{+} - a_{\mathbf{l}}^{+}a_{\mathbf{l}}^{+}a_{\mathbf{l}}, \\ S_{\mathbf{l}}^{z} &= {}^{1}/_{2} - a_{\mathbf{l}}^{+}a_{\mathbf{l}}. \end{aligned} \tag{6}$$

Taking Fourier transforms, we go over to magnon creation and annihilation operators:

$$a_{\mathbf{k}}^{+} = \frac{1}{\sqrt{N}}\sum_{\mathbf{l}} a_{\mathbf{l}}^{+}\exp(-i\mathbf{kl}), \quad a_{\mathbf{k}} = \frac{1}{\sqrt{N}}\sum_{\mathbf{l}} a_{\mathbf{l}}\exp(i\mathbf{kl}). \tag{7}$$

Using the Fourier components of the DDI constants,

$$b_{\mathbf{k}} = \sum_{\boldsymbol{\delta}} b_{\boldsymbol{\delta}}\exp(-i\mathbf{k}\boldsymbol{\delta}), \quad \boldsymbol{\delta} = \mathbf{l} - \mathbf{l}' \tag{8}$$

and the orthogonality relation

$$\frac{1}{N}\sum_{\boldsymbol{\delta}}\exp[i(\mathbf{k}-\mathbf{k}')\boldsymbol{\delta}] = \Delta_{\mathbf{k},\mathbf{k}'}, \tag{9}$$

we find the following representation of $\mathcal{H}_{dz}$:

$$\mathcal{H}_{dz} = -\frac{1}{4}b_0 N + \sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}'a_{\mathbf{k}}^{+}a_{\mathbf{k}} + \frac{1}{4N}\sum_{\mathbf{k},\mathbf{p},\mathbf{q}}\Gamma_{\mathbf{k},\mathbf{p}}^{\mathbf{q}}a_{\mathbf{k}-\mathbf{q}}^{+}a_{\mathbf{p}+\mathbf{q}}^{+}a_{\mathbf{k}}a_{\mathbf{p}}, \tag{10}$$

where

$$\varepsilon_{\mathbf{k}}' = -b_0 - {}^{1}/_{2}b_{\mathbf{k}}, \tag{11}$$

$$\Gamma_{\mathbf{k},\mathbf{p}}^{\mathbf{q}} = b_{\mathbf{p}+\mathbf{q}} + b_{\mathbf{q}-\mathbf{k}} + 2b_{\mathbf{q}} + 2b_{\mathbf{p}+\mathbf{q}-\mathbf{k}}. \tag{12}$$

The Hamiltonian of the interaction with the field $\mathbf{H}_0$,

$$\mathcal{H}_z = -\frac{N}{2}\omega_0 + \omega_0\sum_{\mathbf{k}} a_{\mathbf{k}}^{+}a_{\mathbf{k}} \tag{13}$$

shifts the energy $\varepsilon_{\mathbf{k}}'$ by ω_0, so the energies of the system become

$$\varepsilon_{\mathbf{k}} = \varepsilon_{\mathbf{k}}' + \omega_0. \tag{14}$$

The Hamiltonian $\mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_{dz}$ describes a gas of magnons with a conserved number of particles. Here $\varepsilon_{\mathbf{k}}$ are the energies of the magnons, $\Gamma_{\mathbf{k},\mathbf{p}}^{\mathbf{q}}/4N$ is the scattering amplitude for magnons with wave vectors $\mathbf{k}$ and $\mathbf{p}$, and $\mathbf{q}$ is the momentum transferred in the course of the scattering.

Assuming the amplitude of the rf field to be small, and restricting the discussion to one-magnon terms, we can write the Hamiltonian of the interaction with the rf field as

$$\mathcal{H}_{\text{rf}} = -N^{1/2}\omega_1(a_0 + a_0^{+})\cos\omega t. \tag{15}$$

This interaction alters the total number of magnons and thus the z projection of the total magnetization. The total Hamiltonian can thus be written in the following form (we are omitting an inconsequential constant):

$$\mathcal{H} = \sum_{\mathbf{k}}\varepsilon_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}} + \frac{1}{4N}\sum_{\mathbf{k},\mathbf{p},\mathbf{q}}\Gamma_{\mathbf{k},\mathbf{p}}^{\mathbf{q}}a_{\mathbf{k}-\mathbf{q}}^{+}a_{\mathbf{p}+\mathbf{q}}^{+}a_{\mathbf{k}}a_{\mathbf{p}} - \omega_1 N^{1/2}(a_0 + a_0^{+})\cos\omega t. \tag{16}$$

As in research on spin dynamics, it is convenient to transform to a rotating coordinate system[3,4] in which the system of spins can be described by a time-independent Hamiltonian. To make this transformation, we need to make a transformation in the equation for the density matrix,

$$i\dot{\rho} = [\mathcal{H}, \rho]. \tag{17}$$

This transformation is

$$\rho(t) = \exp\left(-i\omega t\sum_{\mathbf{k}} a_{\mathbf{k}}^{+}a_{\mathbf{k}}\right)\rho^{*}(t)\exp\left(i\omega t\sum_{\mathbf{k}} a_{\mathbf{k}}^{+}a_{\mathbf{k}}\right). \tag{18}$$

Now ignoring the terms which oscillate at a frequency of 2ω, we find that in the evolution equation

$$i\dot{\rho}^{*} = [\mathcal{H}^{*}, \rho^{*}] \tag{19}$$

the Hamiltonian $\mathcal{H}^{*}$ does not depend on the time and is given by

$$\mathcal{H}^{\cdot} = \sum_{\mathbf{k}} \tilde{\varepsilon}_{\mathbf{k}} a_{\mathbf{k}}^{+} a_{\mathbf{k}} + \frac{1}{4N} \sum_{\mathbf{k},\mathbf{p},\mathbf{q}} \Gamma_{\mathbf{k},\mathbf{p}}^{\mathbf{q}} a_{\mathbf{k}-\mathbf{q}}^{+} a_{\mathbf{p}+\mathbf{q}}^{+} a_{\mathbf{k}} a_{\mathbf{p}} - {}^{1}/_{2} N^{1/2} \omega_1 (a_0 + a_0^{+}), \quad (20)$$

where

$$\tilde{\varepsilon}_{\mathbf{k}} = \varepsilon_{\mathbf{k}}' + \Delta \quad (\Delta = \omega_0 - \omega). \quad (21)$$

To transform from spin operators, which act in a finite-dimensional space, to Bose operators, which act in an infinite-dimensional space, we need a special study.[11] The results of a corresponding analysis show[11] that this approach is legitimate as long as the magnon density n/N is small. Hamiltonian (16) is thus a good approximation of Hamiltonian (1) at high values of the polarization $p = 1 - 2n/N$.

The spectrum $\varepsilon_{\mathbf{k}}$ ($\tilde{\varepsilon}_{\mathbf{k}}$) is anisotropic and depends on the orientation of the crystal with respect to the field $\mathbf{H}_0$. The state with the lowest energy is always realized at the boundary of the Brillouin zone at $\mathbf{k} \neq 0$. As a simple illustration we consider a crystal with a cubic lattice in the [001] orientation, and we retain only the interactions with nearest neighbors. We then find from (5), (11), and (14)

$$\varepsilon_{\mathbf{k}} = \omega_0 + \frac{\gamma^2 \hbar^2}{2a^3} (2 \cos k_z a - \cos k_x a - \cos k_y a), \quad (22)$$

where a is the lattice constant. The energy $\varepsilon_{\mathbf{k}}$ reaches its minimum value in the case

$$k_x = k_y = 0, \quad k_z = \pi/a. \quad (23)$$

If we wish to discuss the case of low dipole temperatures, $\beta\omega_{\text{loc}} \gg 1$, in which only states near the bottom of the band are excited, we can use the long-wavelength approximation; i.e., we can restrict the discussion to small values of

$$\delta\mathbf{k} = \mathbf{k} - \mathbf{I}\pi/a, \quad (24)$$

where $\mathbf{I}$ is a unit vector along the z axis. Dispersion relation (22) can then be put in the form

$$\varepsilon_{\mathbf{k}} \approx \omega_0 + c(\delta\mathbf{k})^2 a^2 (1 + \cos^2\varphi) - 8c, \quad (25)$$

where φ is the angle between $\delta\mathbf{k}$ and $\mathbf{I}$, and $c = \gamma^2\hbar^2/4a^3$.

3. SHAPE OF THE NMR LINE

The spatially uniform rf field in (15) leads to the creation and annihilation of magnons with a wave vector $\mathbf{k} = 0$. We first consider the limiting case $p \to 1$. In this case the magnon scattering processes become inconsequential, and the spectrum of the Hamiltonian $\mathcal{H}_0 = \mathcal{H}_z + \mathcal{H}_{dz}$ becomes a spectrum of one-magnon excitations $\varepsilon_{\mathbf{k}}$. Selection rules imposed by energy conservation have the consequence that transitions in the spin system (the creation of magnons) are caused only by an rf field with the frequency [see (11) and (14)]

$$\omega = \varepsilon_0 = \omega_0 - {}^{3}/_{2} b_0. \quad (26)$$

The shape of the NMR absorption line in the limit $p \to 1$ is thus a δ-function at the frequency ε_0. For spherical crystal samples with a cubic structure we would have $b_0 = 0$ (Ref. 1). The shift of the NMR line given by (26) is thus not of fundamental importance, and we will assume below that the sample is spherical and that the crystal lattice has a symmetry high enough that we can assume $b_0 = 0$.

The broadening of the level ε_0, and of the NMR line along with it, occurs because scattering processes keep the lifetime τ_0 of a magnon with $\mathbf{k} = 0$ finite. The average lifetime of magnons with $\mathbf{k} = 0$ is given by[13]

$$\tau_0^{-1} = \frac{\pi}{N^2} \sum_{\mathbf{p},\mathbf{q}} |\Gamma_{0,\mathbf{p}}^{\mathbf{q}}|^2 \{n_{\mathbf{p}}(n_{-\mathbf{q}}+1)(n_{\mathbf{p}+\mathbf{q}}+1) - (n_{\mathbf{p}}+1) n_{-\mathbf{q}} n_{\mathbf{p}+\mathbf{q}}\} \times \Delta(\varepsilon_0 + \varepsilon_{\mathbf{p}} - \varepsilon_{-\mathbf{q}} - \varepsilon_{\mathbf{p}+\mathbf{q}}), \quad (27)$$

where the occupation numbers $n_{\mathbf{p}}$ are described by distribution (4). Expression (27) also determines the width of the NMR line.

According to the fluctuation dissipation theorem,[14] an absorption line (the imaginary part of the susceptibility) is related by a Fourier transformation to the response function describing the response of the system to an infinitely weak perturbation. In the case at hand, this perturbation is an rf field pulse which rotates the spins through an infinitely small angle around an axis perpendicular to the field $\mathbf{H}_0$. This response function is proportional to the correlation function[1]

$$R_0(t) = \langle [S^-, S^+(t)] \rangle = \text{Sp}\,[S^-, S^+(t)]\rho_0, \quad (28)$$

where the density matrix ρ_0 is given by (2), $S^{\pm} = \Sigma_1 S_1^{\pm}$, and the time dependence of the correlation function is determined by the DDI in the transformation to the rotating coordinate system. Using (6) and (7) to transform this correlation function, we find a response function expressed in terms of magnon creation and annihilation operators:

$$R_0(t) = \langle [a_0, a_0^{+}(t)] \rangle. \quad (29)$$

The pulse which we are discussing here creates a nonequilibrium number of coherent magnons with $\mathbf{k} = 0$. Since there are few such magnons (the pulse is infinitely weak), the time evolution of their number is determined by the scattering of these magnons by equilibrium (thermal) magnons. Their number (and thus the transverse magnetization) therefore decreases exponentially with the time:

$$R_0(t) = \langle [a_0, a_0^{+}] \rangle \exp(-|t|/\tau_0) = \exp(-|t|/\tau_0). \quad (30)$$

The response function of the NMR line is thus a Lorentzian curve which is truncated at the frequency $\Delta \sim \omega_{\text{loc}}$ and which has a half-width τ_0^{-1}:

$$g(\Delta) = \frac{1}{\pi} \frac{\tau_0}{1 + \Delta^2 \tau_0^2}. \quad (31)$$

The function $g(\Delta)$, which is related by a Fourier transformation to the response function $R_0(t)$, vanishes at one of the Δ values.[1] In the discussion which follows, we show that the corresponding values satisfies $|\Delta| \gtrsim \omega_{\text{loc}}$ under the conditions for which the approach of this paper is applicable.

At high dipole temperatures, $\beta\omega_{\text{loc}} \ll 1$, at which we have $n/N \ll 1$ (this case is possible with $\mu \neq 0$), we can ignore the terms quadratic in $n_{\mathbf{k}}$ in (27) by virtue of the condition $n_{\mathbf{k}}/N \ll 1$, and we can take $n_{\mathbf{p}}$ through the summation sign. Using (12), we then find

$$\tau_0^{-1} = \frac{n}{N} \frac{36\pi}{N} \sum_{\mathbf{p},\mathbf{q}} |b_{\mathbf{q}}|^2 \Delta\left(\frac{1}{2} b_{\mathbf{p}+\mathbf{q}} + \frac{1}{2} b_{-\mathbf{q}} - \frac{1}{2} b_{\mathbf{p}}\right). \quad (32)$$

Using

$$\frac{n}{N}=\frac{1-p}{2}, \quad \frac{1}{N}\sum_{\mathbf{q}}|b_{\mathbf{q}}|^2=\frac{4}{3}\omega_{\text{loc}}^2,$$

and using the estimate ω_{loc}^{-1} for the local density of states, we find

$$\tau_0^{-1}\approx\omega_{\text{loc}}(1-p). \tag{33}$$

This estimate of the linewidth agrees with that derived in Ref. 1 by a moment method under the assumption of a Lorentzian lineshape.

Up to this point, the four-magnon term in (16) has been considered only in connection with magnon scattering processes. However, we need to allow for the circumstance that the four-magnon term causes not only a damping of spin waves but also a shift of their frequencies. This shift is determined by the diagonal part of $\Gamma^{\mathbf{q}}_{\mathbf{k},\mathbf{p}}$ ($\mathbf{q}=0$ and $\mathbf{k}=\mathbf{p}-\mathbf{q}$). This diagonal part can be written in the form

$$\mathcal{H}_{sec}=\frac{1}{2}\sum_{\mathbf{k}}\Delta\varepsilon_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}}, \tag{34}$$

where

$$\Delta\varepsilon_{\mathbf{k}}=\frac{1}{2N}\left(\sum_{\mathbf{p}\neq\mathbf{k}}\Gamma^{0}_{\mathbf{k},\mathbf{p}}a_{\mathbf{p}}^{+}a_{\mathbf{p}}+\sum_{\mathbf{q}\neq 0}\Gamma^{\mathbf{q}}_{\mathbf{k}-\mathbf{q},\mathbf{k}}a^{+}_{\mathbf{k}-\mathbf{q}}a_{\mathbf{k}-\mathbf{q}}\right). \tag{35}$$

To find an approximate expression for the shifts $\Delta\varepsilon_{\mathbf{k}}$, we take an average of (35) over the quasiequilibrium distribution of magnons [the density matrix corresponding to this quasiequilibrium is given by (39)]:

$$\overline{\Delta\varepsilon_{\mathbf{k}}}=\frac{1}{2N}\left(\sum_{\mathbf{p}\neq\mathbf{k}}\Gamma^{0}_{\mathbf{k},\mathbf{p}}n_{\mathbf{p}}+\sum_{\mathbf{q}\neq 0}\Gamma^{\mathbf{q}}_{\mathbf{k}-\mathbf{q},\mathbf{k}}n_{\mathbf{k}-\mathbf{q}}\right). \tag{36}$$

In particular, for the shift of the level with $\mathbf{k}=0$ we find

$$\overline{\Delta\varepsilon_0}=\frac{1}{2N}\sum_{\mathbf{p}}(\Gamma^{0}_{0,\mathbf{p}}+\Gamma^{-\mathbf{p}}_{\mathbf{p},0})n_{\mathbf{p}}, \tag{37}$$

where we have used $\Gamma^{0}_{0,0}=0$ [see (12)]. At high temperatures, at which $n_{\mathbf{p}}$ can be taken through the summation sign in (37), it is a simple matter to show, with the help of (12), that we have $\overline{\Delta\varepsilon_0}=0$.

The case of low dipole temperatures, $\beta\omega_{\text{loc}}\gg 1$, is one of practical interest. We denote by ε^* the energy of the lowest-lying state in the magnon spectrum $\varepsilon_{\mathbf{k}}$. Since only the states near ε^* are occupied in this case, it is a simple matter to find, with the help of (11), (12), and (14), that the level shift $\overline{\Delta\varepsilon^*}$ near ε^* is

$$\overline{\Delta\varepsilon^*}=4(\omega_0-\varepsilon^*)n/N=2(\omega_0-\varepsilon^*)(1-p). \tag{38}$$

In this case there is also a shift of the center of the absorption line, by an amount

$$\overline{\Delta\varepsilon_0}=3(\omega_0-\varepsilon^*)(1-p). \tag{38'}$$

This shift of the center of the line is accompanied by a change in the wings of the line, in such a way that the first moment, M_1, remains zero at $b_0=0$. The shift of the center of the line is of a fluctuational nature here and is analogous to the shift calculated in Ref. 15.

4. SATURATION OF THE NMR LINE

The saturation process can be described as follows. The application of rf field (15), whose frequency ω may differ by the Larmor frequency ω_0 by an amount $\Delta=\omega_0-\omega$, changes the z component of the magnetization and thus the total number of magnons. If the rate of change of the number of magnons is low in comparison with the rate at which an equilibrium is established as a result of scattering [the latter rate is on the order of $\omega_{\text{loc}}(1-p)$ according to (33)], the system remains in a quasiequilibrium state in the rotating coordinate system, and the density matrix becomes

$$\rho(t)=\frac{1}{Z}\exp\left\{-\beta(t)\left[\mathcal{H}_0-\mu(t)\sum_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}}\right]\right\}, \tag{39}$$

where the partition function Z is found from

$$Z=\operatorname{Sp}\exp\left\{-\beta(t)\left[\mathcal{H}_0-\mu(t)\sum_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}}\right]\right\}, \tag{40}$$

and the parameters $\beta(t)$ and $\mu(t)$ vary slowly in time.

Using the standard method[1,3] for seeking a solution of Eq. (19) with the structure in (39), we find the saturation equations

$$\begin{aligned} dn/dt&=NW(\Delta),\\ dE/dt&=0, \end{aligned} \tag{41}$$

where

$$n=\operatorname{Sp}\sum_{\mathbf{k}}a_{\mathbf{k}}^{+}a_{\mathbf{k}}\rho=\sum_{\mathbf{k}}n_{\mathbf{k}}, \quad E=\operatorname{Sp}\mathcal{H}_0\rho\approx\sum_{\mathbf{k}}n_{\mathbf{k}}\varepsilon_{\mathbf{k}} \tag{42}$$

are the total number of magnons and the energy of the system,

$$W(\Delta)={}^1/_2\pi\omega_1^2 g(\Delta) \tag{43}$$

is the probability for transitions stimulated by the rf field, and the lineshape function is

$$g(\Delta)=\frac{1}{2\pi}\int_{-\infty}^{\infty}e^{i\Delta t}\langle[a_0,a_0^{+}(t)]\rangle dt. \tag{44}$$

Here

$$\begin{aligned} a_0^{+}(t)=&\exp\left\{\frac{it}{4N}\sum_{\mathbf{k},\mathbf{p},\mathbf{q}}\Gamma_{\mathbf{k},\mathbf{p}}a^{\pm}_{\mathbf{k}-\mathbf{q}}a^{+}_{\mathbf{p}+\mathbf{q}}a_{\mathbf{k}}a_{\mathbf{p}}\right\}a_0^{+}\\ &\times\exp\left\{-\frac{it}{4N}\sum_{\mathbf{k},\mathbf{p},\mathbf{q}}\Gamma^{\mathbf{q}}_{\mathbf{k},\mathbf{p}}a_{\mathbf{k}-\mathbf{q}}a^{+}_{\mathbf{p}+\mathbf{q}}a_{\mathbf{k}}a_{\mathbf{p}}\right\}. \end{aligned} \tag{45}$$

The shape function $g(\Delta)$ is identical to that introduced in the preceding section of this paper. The function $g(\Delta)$ is sometimes expressed in terms of the symmetrized correlation function $\langle[a_0,a_0^{+}(t)]_{+}\rangle$, where $[a_0,a_0^{+}(t)]_{+}=a_0a_0(t)a_0^{+}(t)a_0$. In the case at hand, it is a simple matter to show that

$$\begin{aligned} g(\Delta)&=-\frac{1}{2\pi}\operatorname{th}\frac{\beta\mu}{2}\int_{-\infty}^{\infty}e^{i\Delta t}\langle[a_0,a_0^{+}(t)]_{+}\rangle dt\\ &=-\frac{1}{2\pi}\operatorname{th}\frac{\beta\mu}{2}\operatorname{cth}\frac{\beta(\Delta-\mu)}{2}\int_{-\infty}^{\infty}e^{i\Delta t}\frac{\langle[a_0,a_0^{+}(t)]_{+}\rangle}{\langle[a_0,a_0^{+}]_{+}\rangle}dt. \end{aligned} \tag{46}$$

It follows, in particular, from (46) that under the condition $\mu=0$ we have $g(\Delta)=0$. With $\mu=\varepsilon^*-\omega<0$, however, Bose condensation[1)] begins in the system, and the dynamics of the system cannot be described by Eqs. (41). The Lorentzian approximation, (31), of the function $g(\Delta)$ thus does

not contradict the rigorous results of Ref. 1 under the condition $|\Delta| \lesssim \omega_{loc}$.

Saturation equations (41) reflect energy conservation in the rotating coordinate system and the change in the number of magnons in the system as a result of transitions induced by the rf field. From (41) we directly find the following equations for the rates of change of the reciprocal temperature and the chemical potential:

$$\frac{d\beta}{dt}=\frac{E_\mu}{E_\beta n_\mu - E_\mu n_\beta}W(\Delta),$$
$$\frac{d\mu}{dt}=-\frac{E_\beta}{E_\beta n_\mu - E_\mu n_\beta}W(\Delta). \quad (47)$$

The specific heats E_μ, E_β, n_μ, and n_β here are determined by

$$E_\mu=-\frac{1}{N}\frac{\partial E}{\partial \mu}\Big|_\beta, \quad E_\beta=-\frac{1}{N}\frac{\partial E}{\partial \beta}\Big|_\mu, \quad n_\mu=-\frac{1}{N}\frac{\partial n}{\partial \mu}\Big|_\beta$$
$$n_\beta=-\frac{1}{N}\frac{\partial n}{\partial \beta}\Big|_\mu. \quad (48)$$

An advantage of this approach is that the specific heats E_μ, E_β, n_μ, and n_β of the spin systems which appear in (47) can be calculated from the ε_k spectrum and relations (4) and (42). Since the quantities which are actually measured experimentally are[1] the polarization $p(t)$ and the dipole energy of this system, $E_d(t)=E-n(t)\Delta$, we will use (41) to derive equations which determine the time evolution of these quantities. The corresponding equations are

$$dp/dt=-2W(\Delta),$$
$$dE_d/dt=-N\Delta W(\Delta). \quad (49)$$

At saturation [under the condition $W(\Delta)>0$], the polarization decreases monotonically, and at $\Delta=\omega_0-\omega>0$ the dipole energy of the system also decreases. In this sense we can assume that at $\Delta>0$ the dipole system cools down. This effect is completely analogous to the cooling of the DDI reservoir in the theory of saturation at high temperatures.[3] Since the dipole energy is proportional to the reciprocal (β) of the temperature of the dipole subsystem in the high-temperature case, under the condition $\beta>0$ the decrease in E_d is accompanied by a decrease in β^{-1}. At low temperatures, the relationship between E_d and β is more complex.

Another interesting question is the change in the chemical potential $\mu(t)$ in the saturation process according to Eqs. (47). If the system is in thermal equilibrium before saturation begins, we have $\mu(0)=0$ in the laboratory coordinate system. When the rf field is turned on, a zero value of the chemical potential in the laboratory coordinate system no longer corresponds to the equilibrium value. After the rf field is applied, the system tends toward a state of thermodynamic equilibrium in the rotating coordinate system, in which the Hamiltonian does not depend on the time. In this rotating coordinate system, the chemical potential is $\tilde{\mu}=\mu-\omega=\mu-\omega_0+\Delta$, while β and n_k are the same as in the laboratory system. A value $\tilde{\mu}=0$ would correspond to $\mu=\omega_0-\Delta$, but Bose condensation begins as early as $\mu=\varepsilon^*<\omega_0-\Delta$, and the approach developed here can no longer be taken to analyze the behavior of the spin system.

We turn now to the question of the steady state reached in the course of the saturation of the system. For this purpose we consider the case in which the saturation occurs at the wing of the NMR line. If the temperature in the steady state is such that the condition $\beta_{st}\omega_{loc}\gg 1$ holds, the magnons are primarily in a narrow energy band near the lowest-lying state in the magnon spectrum, ε^*. In the course of the saturation process, a level shift occurs [see (38)] as a result of the interaction of magnons. When this shift, $\overline{\Delta\varepsilon^*}$, becomes equal to $\omega-\varepsilon^*$, the frequency of the rf field is at the edge of the line, and no further saturation of this system can occur. We thus find an expression for the steady-state polarization:

$$p_{st}=1-(\omega-\varepsilon^*)/2(\omega_0-\varepsilon^*). \quad (50)$$

Since the saturation occurs at the edge of the line, i.e., since we have $\omega-\varepsilon^*\ll\omega_0-\varepsilon^*\approx\omega_{loc}$, then we have $1-p_{st}\ll 1$.

5. CALCULATION OF SPECIFIC HEATS

In this section we will calculate the specific heats E_μ, E_β, n_μ, and n_β in the two limiting cases $\beta\omega_{loc}\ll 1$ and $\beta\omega_{loc}\gg 1$. As in the discussion of the saturation equations, we carry out all the calculations in the rotating coordinate system.

High dipole temperatures ($\beta\omega_{loc}\ll 1$)

We carry out an expansion in the small parameter $\beta\varepsilon_k'$ ($\varepsilon_k=\varepsilon_k'+\Delta$) in expression (4) for the magnon numbers. Within terms on the order of $\beta\varepsilon_k'$ we find

$$n_k\approx\frac{1}{\exp[\beta(\Delta-\mu)]-1}-\frac{\beta\varepsilon_k'\exp[\beta(\Delta-\mu)]}{\{\exp[\beta(\Delta-\mu)]-1\}^2}. \quad (51)$$

Using

$$\sum_k\varepsilon_k'=0, \quad \omega_{loc}^2=\frac{\mathrm{Sp}\,\mathcal{H}_{dz}^2}{\mathrm{Sp}\,S_z^2}=\frac{3}{N}\sum_k\varepsilon_k'^2, \quad (52)$$

and also

$$\exp[\beta(\Delta-\mu)]-1\approx 2/(1-p)\approx\exp[\beta(\Delta-\mu)], \quad (53)$$

we find

$$E_\mu={}^1/_2(1-p)[-\beta\Delta+{}^1/_3\beta^2\omega_{loc}^2], \quad (54)$$
$$E_\beta={}^1/_2(1-p)({}^1/_3\omega_{loc}^2+\Delta^2-\Delta\mu), \quad (55)$$
$$n_\mu=-{}^1/_2\beta(1-p), \quad (56)$$
$$n_\beta={}^1/_2(1-p)[\Delta-\mu-{}^1/_3\beta\omega_{loc}]. \quad (57)$$

Low dipole temperatures ($\beta\omega_{loc}\gg 1$)

For this case we restrict the discussion to a system with the simple spectrum in (22). Noting that only the low-lying states are excited, we choose the dispersion relation as in (25). Switching from a summation to an integration in the expression for the total number of magnons, we find

$$n=\frac{V}{8\pi^3}2\pi\int_0^\pi\sin\varphi\,d\varphi\int_0^\infty\frac{(\delta\mathbf{k})^2 d(|\delta\mathbf{k}|)}{\exp\{\beta[c(\delta\mathbf{k})^2a^2(1+\cos^2\varphi)-8c+\Delta-\mu]\}-1} \quad (58)$$

where V is the volume of the sample. Manipulations of the integral in (58) similar to those carried out in Ref. 14 make it possible to rewrite (58) in the simpler form

$$n=\frac{N\sqrt{2}}{16[\pi c\beta(t)]^{3/2}}\sum_{k=1}^{\infty}\frac{\exp[-k\bar{\mu}(t)]}{k^{3/2}}, \tag{59}$$

where

$$\bar{\mu}(t)=\beta(t)[\Delta-\mu(t)-8c] \tag{60}$$

and where we have used $V=Na^3$. Using (59), we find

$$n_\mu=-\frac{\sqrt{2}}{16(c\pi)^{3/2}[\beta(t)]^{1/2}}\sum_{k=1}^{\infty}\frac{\exp[-k\bar{\mu}(t)]}{k^{1/2}}, \tag{61}$$

$$n_\beta=\frac{\sqrt{2}}{16(c\pi)^{3/2}[\beta(t)]^{5/2}}\sum_{k=1}^{\infty}\frac{k\bar{\mu}(t)+1,5}{k^{3/2}}\exp[-k\bar{\mu}(t)]. \tag{62}$$

Correspondingly, from the expression for the energy we find

$$E=\frac{Nc\sqrt{2}}{4\pi^2}\int_0^\infty\frac{x^4\,dx}{\exp\{\beta(t)[c(x^2-8)+\Delta-\bar{\mu}(t)]\}-1}+(\Delta-8c)n. \tag{63}$$

Here we have ignored the energy-level shifts in (38). When they are taken into account, the second term in (63) is replaced by $\Delta+\frac{1}{2}\overline{\Delta\varepsilon^*}-8c$. Expression (63) can be rewritten as

$$E=\frac{3\sqrt{2}Nc}{32\pi^{3/2}[\beta(t)c]^{5/2}}\sum_{k=1}^{\infty}\frac{\exp[-k\bar{\mu}(t)]}{k^{5/2}}+(\Delta-8c)n. \tag{64}$$

Hence

$$E_\mu=-\frac{\sqrt{2}}{16\pi^{3/2}[c\beta(t)]^{3/2}}\times\sum_{k=1}^{\infty}\frac{1,5+(\Delta-8c)\beta(t)k}{k^{3/2}}\exp[-k\bar{\mu}(t)], \tag{65}$$

$$E_\beta=\frac{\sqrt{2}}{64(\pi c)^{3/2}[\beta(t)]^{7/2}}\times\sum_{k=1}^{\infty}\{4\beta(t)(\Delta-8c)[\bar{\mu}(t)k+1,5]k+6\bar{\mu}(t)k+15\}\times\frac{\exp[-k\bar{\mu}(t)]}{k^{5/2}}. \tag{66}$$

We note in conclusion that an analysis under the condition $\omega>\omega_0$ ($\Delta<0$) would be carried out in a completely similar way. The quantities β and μ would change sign, while the role of ε^* would be played by the energy of the state in which ε_k has its maximum possible value.

[1)] The chemical potential μ is being considered in the rotating coordinate system here.

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