Dipole magnetic ordering in nuclear spin-spin systems

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Magnetic dipole-dipole interactions in a nuclear-spin system can lead to ordering of the spins only at temperatures $\sim 10^{-6}$°K. For nuclear antiferro- and ferromagnetic states to occur in this case, however, only the nuclear-spin system must be cooled to this temperature. This becomes possible in a number of cases, since the spin-lattice relaxation time becomes large enough already at a crystal-lattice temperature $\sim$0.1–0.3°K, and the spin system is well insulated from the lattice. We discuss dynamic methods of obtaining near-zero positive and negative spin temperatures in a solid by adiabatic demagnetization of the nuclear-spin system. A simple theory is described, which yields the possible ordered configurations of the spins in the crystals. Methods of observing ordered states are described, together with the results of recent experiments that confirm the onset of nuclear antiferro- and ferromagnetic states.

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1. INTRODUCTION

Recently, owing to considerable progress in the development of the thermodynamics of spin systems, cryogenic techniques and the technique of dynamic polarization of nuclei in the theory of NMR in solids, it has become possible to realize and observe ordering of the system of nuclear spins in solid diamagnetic dielectrics. The conditions under which one can expect ordering of nuclear structures to be produced by nuclear magnetic dipole-dipole interaction (i.e., the spontaneous onset of nuclear antiferromagnetism and ferromagnetism) were assumed until recently to be fantastic, primarily because of the small values of the magnetic moments μ of the nuclei. An estimate of the transition temperature T_N, which can be based on the obvious relation $k_B T_N \approx \mu H_L$, $H_L = \mu/a^3$ (here a is the average distance between nuclei in the crystal, H_L is the intensity of the local field, and k_B is Boltzmann's constant) shows that one should expect transition temperatures $T_N \sim 10^{-6}-10^{-7}$ °K. A more reliable estimate of the phase-transition temperature (the Curie temperature) and of the energy of the dipole magnetic interaction can be based on the width of the nuclear magnetic resonance (NMR) line. For the crystals LiF and CaF, which were well investigated by the NMR method, and for which the main interaction between the nuclear spins is magnetic dipole interaction, this width $\delta\nu$ is equal to several kHz. Therefore the relation $h\delta\nu = k_B T_N$ yields $T \sim 10^{-7}$ °K ($k_B/h \approx 2 \times 10^{10}$ Hz).

A surprising exception is crystalline He^3, the spin-spin interactions in which are of exchange origin. The expected transition temperature, as shown by estimates, amounts in this case to several thousandths of a degree.[1] For all other nuclear spins, the interactions are magnetic in nature. These can be either the direct long-range magnetic dipole-dipole interactions or the indirect interactions realized via the electrons. The latter interactions are of tensor character and their magnitude depends significantly on the electronic structure of the crystal, on its symmetry, etc. One can expect in certain cases the energy of the direct interactions to be of the same order as the energy of the exchange interactions in He^3.

The values obtained for T_N are listed in Table I in accord with the character of the interaction. For comparison, the table lists the values of the transition temperatures for the electronic spin systems.

Modern cryogenic techniques make it possible to lower the temperature of the crystal, in volumes sufficient for the performance of the experiment, to 10^{-3} °K. This makes it possible to investigate experimentally the magnetic transition in He^3 also in certain systems with indirect interaction. Attempts to cool the samples to temperatures 10^{-7} °K can raise only a smile. Moreover, in this case one can even doubt that a solid lattice can be described with the aid of the temperature concept. Indeed, long before the sample is cooled to such a temperature, all the physical properties of the crystal, except those connected with the electron and nuclear spins, cease to change noticeably. The entropy of the lattice approaches a constant value and its change can no longer be discerned. This makes it impossible to measure such low temperatures, and consequently to use them. The nuclear spins remain the last refuge of the entropy. When the temperature is lowered, only their energy and their entropy still vary noticeably and by the same token make it possible to measure infralow temperatures.

TABLE I

Particles	Magnetic moment, μ_B	Type of interaction	H, Oe	T_N, °K
Electrons	1	Exchange	$\lesssim 10^7$	10^3
		Dipole	$\lesssim 10^4$	1
Nuclei	10^3	Exchange	$\lesssim 10^4$	10^{-3}
		Indirect	$\lesssim 10^4$	10^{-3}
		Dipole	$\lesssim 10$	$10^{-6}-10^{-7}$

The appreciable increase in the time of nuclear spin-lattice relaxation which occurs when the sample is cooled, offers evidence of increasing insulation of the spin system from the lattice and the validity of treating its thermodynamics independently. This therefore suggests naturally the possibility of obtaining ordered states of nuclei by cooling not the lattice of the entire crystal as a whole, but only of the nuclear spin system. It turns out that for this purpose it is no need to cool the crystal to extremely low temperatures. The time of the spin-lattice relaxation becomes sufficiently large already at a temperature amounting to several tenths of a degree Kelvin.

This simple idea, which was formulated in practice in the first papers, [2,5] has led to the appearance of a new trend in solid state physics, namely the theory of nuclear antiferromagnetism and ferromagnetism. [6,15].

The study of ordered states produced under the influence of only dipole magnetic interactions is of interest primarily because in this case one knows exactly the law of interaction between the particles. [5] This case is in a way unique.[1)] It makes possible, at least in principle, quantitative comparisons of the calculated and experimentally measured physical quantities that characterize these states. No such procedure can be used for other known cases of electron and nuclear magnetic ordering, for which the nature of the ordering is not always sufficiently well known. It thus becomes possible to verify rigorously the approximations usually made in the statistical theory. This in turn should become quite useful both in the development of the research and in the region of electron ordering.

The first successful experiment was carried out by a group of scientists at Saclay headed by Anatole Abragam in 1969. They observed, for the first time, the antiferromagnetic state of fluorine nuclei in CaF_2. By now this state has been sufficiently well investigated by nuclear magnetic resonance methods in CaF_2 and LaF crystals oriented in various directions relative to the external magnetic field, for both positive and negative spin temperatures. A recent communication reports observation of nuclear ferromagnetic structure in CaF_2.

To obtain the ordered state of a system of nuclear spins, it was necessary to use the entire arsenal of modern theory of nuclear magnetic resonance necessary not only to obtain this state, but also to observe the phase transitions that occur in the nuclear-spin system. This also called for great creative efforts and led in turn to the development of new methods of studying magnetic properties of solids.

The present review is aimed at acquainting the reader with the present status of the problem of nuclear ordering due to dipole-dipole interactions, with the principles of the theory of this phenomenon, and with certain methods of its observation.

2. THEORY OF DIPOLE NUCLEAR ORDERING

For a correct understanding of the results of the rather complicated experiments described below, it is first necessary to have a clearer idea of how a spin system can be cooled to the required temperature, and also to be able to calculate the possible spin-ordering structures due to the dipole-dipole interaction. The latter is essential not so much for the determination of the transition temperature as for the prediction of the possible types of ordered structures. It should be noted that in contrast to the case of electron ordering, the resultant ordered nuclear structures depend significantly not only on the magnitude but also on the sign of the spin temperature, as well as on the type of the sample crystal lattice and an orientation of the magnetic field relative to the crystal axes.

a) Spin temperature

The concept of spin temperature is presently used extensively in solid-state physics. It has been the subject of a rather extensive literature. Its physical meaning has been treated in the splendid review by Powles [3a], the thermodynamics of the processes is dealt with in [3b], and a serious foundation and various applications to the electron theory of solids can be found in [3c, 5, 6]. In what follows, we shall need to make extensive use of this concept, and we therefore remind the reader of some of its aspects.

Initially the spin temperature was regarded only as some convenient parameter introduced formally to describe the populations of the spin magnetic sublevels in magnetic fields that are strong in comparison with the local field H_L. Strictly speaking, this connection should be established only for the case of two-level systems ($s = 1/2$) although the possibility of introducing the concept of a negative absolute temperature is much more extensive. It agrees incontrovertibly with the definition of the temperature in thermodynamics and generalizes the latter in natural fashion.

For a system of N spins ($s = 1/2$) that are in thermal equilibrium, the populations N_1 and N_2 of the lower and upper sublevels of a two-level system are connected by the relation

$$N_1 = N_2 e^{\Delta E/k_B T_s}, \tag{1}$$

where $\Delta E/k_B$ is the distance in temperature units, measured from the lower sublevel. If it is assumed that relation (1) is valid not only in the case of thermal equilibrium, then it becomes necessary to postulate that the temperature T of the spin system cannot only differ from the temperature T_L of the remaining degrees of freedom of the crystal (lattice), but also assume negative values in case of population inversion ($N_1 < N_2$.

In thermal equilibrium, the temperature of the spin system, of course, is equal to the temperature T_L of the lattice. This equilibrium can be disturbed in many ways, particularly by applying a radio-frequency (RF) field of resonant frequency, if its amplitude is sufficient to be able to change the initial sublevel population difference within a time shorter than the spin-lattice relaxation time. In particular, to attain a state with $T_S < 0$ we can use the so-called 180° RF pulse, which reverses the direction of the system magnetization.

Such a formal introduction of the concept of negative absolute temperature, while lucid and in many cases convenient, is in fact not more than a symbol

$$\frac{1}{T_s} = \frac{k_B}{\Delta E} \ln \frac{N_1}{N_2}$$

and contains no information whatever concerning the

[1)] There are known crystals containing rare-earth ions with pure dipole-dipole interactions between them, and with negligibly small exchange interactions in comparison. [14] The transition temperatures in these cases turn out to be 0.1–1° K. However, the effects considered below by the spin-lattice interaction, which is very strong in comparison with the nuclear interaction.

state of the spin system, so that in essence one can get along without it.

It is easily seen that the existing general methods of statistical physics afford a possibility of introducing not only positive but also negative temperatures.

The average internal energy of a thermodynamic system

$$\langle U\rangle = N\frac{\sum\limits_{n=1}^{q}\varepsilon_n e^{-\varepsilon_n/k_BT_s}}{\sum\limits_{n=1}^{q}e^{-\varepsilon_n/k_BT_s}} = -N\frac{\partial}{\partial\beta_s}\ln\sum_{n=1}^{q}e^{-\beta_s\varepsilon_n},\quad \beta_s=\frac{1}{k_BT_s} \tag{2}$$

is finite at $T_S > 0$ and diverges at arbitrary $T_S < 0$, if the number of the energy levels q is infinite. However, if the number of levels is finite, then the energy is finite also at $T_S < 0$. The latter takes place for a system of noninteracting spins s having two s + 1 sublevels. Since the spin subsystem is always only part of a system with an infinite spectrum, to separate this system and to make it thermodynamically autonomous it is necessary that its coupling to the remaining degrees of freedom be broken in some manner, or greatly impeded.

If this is accomplished, then the spin system can be characterized by an internal energy, entropy, and other thermodynamic functions. Assuming that the entropy of the spin system is specified as a function of the internal energy, we can define the spin temperature T_S in a general manner, using the well known thermodynamic relation

$$\left(\frac{\partial\langle S\rangle}{\partial\langle U\rangle}\right)_\alpha=\frac{1}{T_s}, \tag{3}$$

where the derivative is taken at constant values of all the external parameters α. The equilibrium entropy S of the spin system is also the subject of the well known definition

$$\langle S\rangle = -k_B\,\mathrm{Sp}\,(\rho\ln\rho)$$

in terms of the spin-density operator

$$\rho=\frac{\exp(-\hat{\mathscr{H}}/k_BT_s)}{\mathrm{Sp}\exp(-\hat{\mathscr{H}}/k_BT_s)},$$

where $\hat{\mathscr{H}}$ is the Hamiltonian of the spin system. This definition of the spin temperature is valid when the off-diagonal elements of the density matrix (in the energy representation) vanish, i.e., after the lapse of the time τ_2 following the termination of the RF pulse.[6] A time larger than or of the order of τ_2 is sufficient to establish in a spin system a state of internal equilibrium, and the system can be described with the aid of the spin temperature. The latter can then differ significantly from the lattice temperature T_L, if the spin-lattice relaxation time $\tau_2 \gg \tau_1$. This condition is practically always satisfied in solids, where the spin-spin interactions are much stronger than the spin-lattice interactions.[5]

The entropy of a system of $N = N_1 + N_2$ spins ($s = 1/2$) distributed over two levels can be easily calculated from Boltzmann's formula

$$S=k_B\ln\frac{N!}{(N-N_2)!\,N_2!},$$

which, as can be readily verified, can be transformed by means of Stirling's formula into

$$S=-k_BN\left[\left(1-\frac{N_2}{N}\right)\ln\left(1-\frac{N_2}{N}\right)+\frac{N_2}{N}\ln\frac{N_2}{N}\right]. \tag{4}$$

The internal energy U of the spin system, assuming $\epsilon_1 = 0$ and $\epsilon_2 = \Delta E$, is equal to

$$U=N_2\Delta E=\frac{N_2}{N}N\Delta E. \tag{5}$$

The function S(U) has a maximum at $N_2/N = N_1/N = 1/2$ and vanishes at $N_2 = 0$ and $N_2 = N$, i.e., when all the spins are concentrated either at the lower or the upper sublevel (Fig. 1). In accordance with the definition of T_S (formula (3) or (5)), the maximum of the entropy corresponds (depending on the direction from which it is approached) to a temperature $T_S = \pm\infty$, and at the points $N_2 = 0$ and $N_2 = N$ the temperature is +0 and −0, respectively.

In thermal equilibrium, according to (3), (4), and (5) ($T_S = T_L = T$) we have

$$\ln\frac{1-(N_2/N)}{N_2/N}=\frac{\Delta E}{k_BT},$$

from which we obtain for the populations N_1 and N_2 for the lower and upper sublevels

$$N_1=\frac{N}{1+e^{-\Delta E/k_BT}},\qquad N_2=\frac{N}{1+e^{\Delta E/k_BT}}$$

and, as expected, $N_1 = N_2\exp[\Delta E/k_BT]$ and $N_1(T) = N_2(-T)$. The internal energy is equal to

$$\langle U\rangle=\frac{N\Delta E}{1+e^{\Delta E/k_BT}}. \tag{6}$$

It is now easy to find the dependence of the specific heat c_S of the spin system on the temperature

$$c_s=\frac{d\langle U\rangle}{dT}=Nk_B\left(\frac{\Delta E}{k_BT}\right)^2\frac{e^{\Delta E/k_BT}}{(1+e^{\Delta E/k_BT})^2}.$$

For low temperatures $T < \Delta E/k_B$ we have

$$c_s=Nk_B\left(\frac{\Delta E}{k_BT}\right)^2e^{-\Delta E/k_BT}.$$

The specific heat of a spin system has a broad maximum at $T_m \approx \Delta E/2k_B$, the position of which depends on the distance between the sublevels, and thus on the field intensity (Fig. 2). For nuclear sublevels in a field $H_0 \sim 10^4$ Oe, $\Delta E/k_B \sim 10^{-2}$ °K, the maximum is located at a temperature 5×10^{-3} °K.

For low temperatures, the Debye specific heat of the crystal lattice is[4]

$$c_L=234k_BN\left(\frac{T}{\Theta}\right)^3,$$

and therefore (at $T = T_S$)

$$\frac{c_s}{c_L}=\frac{5}{234}\frac{\Theta^3(\Delta E)^2}{k_B^3}\frac{e^{-\Delta E/k_BT}}{T^5},$$

where Θ is the Debye temperature.

The ratio of the specific heats has a maximum at a temperature $\Delta E/5k_B$. At this maximum and in its vicinity, the specific heat of the spin system is larger by many orders of magnitude than the specific heat of the lattice. Therefore, at sufficiently low temperatures, the thermal properties of the crystals can be substantially affected not only by the electronic moments of the possible paramagnetic impurities, but also by the magnetic moments of the nuclei. At infralow temperatures they are also decisive in diamagnetic substances.

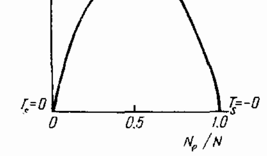

FIG. 1. Entropy S of a system of N spins (s = 1/2) vs. their internal energy U in relative units ($U/N\Delta E = N_2/N$).

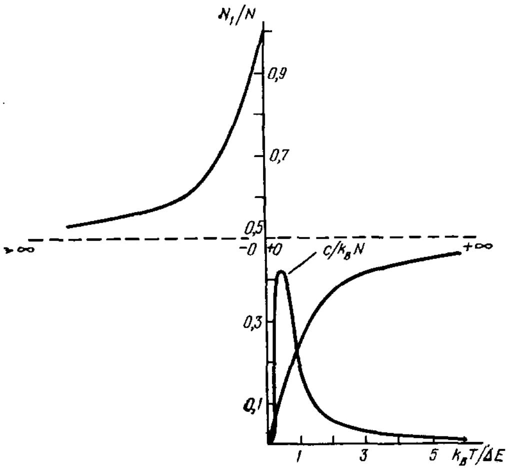

FIG. 2. Dependence of the relative opulation of the lower level N_1 of a two-level spin system and of its specific heat c on the temperature T in a constant magnetic field ($H_0 = \Delta E/2\mu$). The states with $N_1/N = 0$ and 1 must be characterized by temperatures +0 and −0 respectively. The states with $N_1/N = 0.5$ correspond to temperatures $\pm\infty$, depending on the direction from which they are approached. The specific heat has a maximum at $T_m \sim \Delta E/2k_B$.

The description of the state of the system with the aid of this already generally introduced concept of (positive and negative) spin temperature is quite consistent, noncontradictory[3], and as we shall see, necessary. Yet so far it contains nothing essentially new in comparison with the description in the language of populations.

The spin temperature concept acquires a new physical aspect primarily when it is extended to include the case of magnetic fields so weak that the interaction of the spin with the magnetic field is comparable with or smaller than the spin-spin interaction. This was stimulated by the first experiments with the system of the spins of Li^7 in LiF crystals[5], which are characterized by a large spin-lattice relaxation time ($\tau_1 \sim 5$ min). It was experimentally observed that if such a crystal is magnetized in a strong magnetic field H_0, and then this field is reduced within a time much shorter than τ_1 to a value lower than the local field intensity H_L and then the field is returned to its previous value after a few seconds ($t > \tau_2$), then the magnetization of the Li^7 nuclei will hardly differ in its magnitude and direction from the initial one. This seemed impossible to understand inasmuch as in a zero field, from the point of view of the theory, spin-spin interactions with characteristic time $\tau_2 \ll \tau_1$ should destroy completely the nuclear polarization, which can be restored in a strong field only after the lapse of a time τ_1. A similar experiment was carried out with a system in which the initial magnetization was opposite to the field, corresponding to a negative spin temperature. After the crystal was returned to the strong field, the magnitude and antiparallel orientation of the magnetization were restored.

These experiments were explained by Abragam and Proctor[2], who have assumed that during the spin-spin relaxation time τ_2 the system reaches an internal-equilibrium state characterized by a Boltzmann distribution of the populations. This is valid in the case of weak magnetic fields, when the energy of the spin system is determined mainly by the spin-spin interaction. Then, if the magnetic field is reduced to zero rapidly in comparison with τ_1 but slowly in comparison with τ_2, in such a way that internal equilibrium can be established in the spin system at each instant of time, adiabatic demagnetization takes place, accompanied by conservation of its total entropy. It follows therefore that the ordering of the spins in a field H_0 is conserved as $H_0 \rightarrow 0$, but now already in the local fields produced by the spins themselves. The spin-system temperature T_S (in a zero field) then turns out to be lower than the lattice temperature. As we shall show below, we have here already a hint that a spin system can go over into an ordered state in the absence of an external magnetic field, inasmuch as the concept of spin temperature leads directly to the possibility of lowering the energy of the spin system.

If the spin system had a negative temperature prior to the demagnetization, then we can arrive, using similar arguments, at the conclusion that the spin temperature increases following adiabatic demagnetization (it decreases in absolute value, i.e., it approaches zero from the negative side). This means that spin ordering in local fields is possible at both positive and negative temperatures, a fact of extreme interest and importance, for at the same nuclear-spin-system entropy the properties of the ordered state turn out to be strongly dependent on the sign of the temperature. As a result, we can investigate the lower branch of the energy spectrum of the system for positive temperatures and its upper branch for negative ones. The latter would be impossible if the nuclear spin system were to remain at all times in equilibrium with the cooled lattice, since the latter can only have a positive temperature. This is one of the main distinguishing features of nuclear spin ordering.

A decrease of a spin-entropy system with either a positive or negative temperature in local fields corresponds to a decrease in the absolute value of T_S. This process will be called cooling. Bearing in mind this "symmetry" in the behavior of the system with positive and negative temperatures, the sign of the temperature will henceforth be indicated only when necessary.

The next important generalization of the concept of spin temperature, which we shall use, is its definition and introduction in a rotating system of coordinates[3,5,6]. A spin system situated in an external homogeneous magnetic field and in an RF field H_1 rotating about the field H_0 with frequency ω, can be conveniently considered in a coordinate system that rotates with frequency $\omega \sim \gamma H_0$ around the direction of the field H_0. In this coordinate system, in accordance with the Larmor theorem, the field H_0 vanishes (or nearly vanishes), and the RF field is perceived as static. The spin precession in this coordinate system occurs around the direction of the field H_1. On changing over to a rotating coordinate system, the Hamiltonian of the system changes, and consequently also the spin temperature.

An important extension of the concept of spin temperature is the subdivision, considered in detail below, of the nuclear spin system (in a rotating coordinate system) into two independent subsystems, Zeeman and dipole, each of which can be characterized by its own temperature. These two subsystems correspond to a spin energy in an external constant magnetic field and to an energy of the dipole-dipole magnetic interaction between the nuclear spins, which lifts the degeneracy and spreads each Zeeman level into a band.

The concept of a spin temperature in strong and weak magnetic fields and in rotating coordinate systems is not only useful and convenient for the description of spin systems. It makes it possible in a number of cases to draw such new important conclusions which could hardly be guessed without introducing this concept.

b) Cooling of spin system by adiabatic demagnetization

The process of adiabatic demagnetization can be used to cool a spin system if it is reliably insulated from the lattice. Experience has shown, however, that this does not lead to the required sufficiently low temperature. Indeed, from the condition of equality of the magnetization of the spins in the field H_0 and in the local field H_L, we get the equality

$$T_i = T_L \frac{H_L}{H_0}, \tag{7}$$

where T_i is the final spin temperature. If we assume $H_0 = 25$ kOe, and that the lattice temperature has the easily attainable value $T_L = 1$°K as well as $H_L \sim 10$ Oe, we get for T_i the value 4×10^{-4} °K, which is at least two or three orders of magnitude higher than the value required for a transition to the ordered state. One might try a way out by increasing the initial magnetic polarization, i.e., the ratio H_0/T_L, by two or three orders of magnitude, using superconducting magnets and more modern methods of cooling. However, when these conditions are satisfied, the spin-lattice relaxation time may turn out to be exceedingly large. The system of nuclear spins will reach extremely slowly and "with difficulty" the thermal-equilibrium state corresponding to the required initial temperature $\sim 10^{-2}$ °K.

Since the problem lies in the value of the initial polarization, we can dispense with the "brute force" approach to its solution and use technically more realizable methods, for example the method of dynamic polarization of nuclei, which at present makes it possible to obtain a nuclear polarization exceeding 80% and even approaching 100%.[7,17] Then, for example, protons with an initial polarization of only 50% in a field of 25 kOe, at a lattice temperature T = 1°K, correspond to nuclear spin temperature 5×10^{-3} °K. This value is already acceptable for the subsequent adiabatic demagnetization for the purpose of reaching the expected transition temperature.

A transition to a zero magnetic field has two serious shortcomings. First, in a zero magnetic field we lose the possibility of using the very sensitive resonance methods for the observation of the ordered states. Second, in weak fields the spin-lattice relaxation time is as a rule very short, thus upsetting the dependable insulation that is essential in these experiments between the nuclear spins and the lattice. These difficulties can be circumvented if the demagnetization is carried out in a system that interacts with the RF field and is under conditions close to resonance. It is to the analysis of this situation, which is the basis of an exceedingly clever procedure for experimentally observing magnetic structures of nuclear spins, that we now proceed.

c) Adiabatic cooling in a rotating coordinate system

If an RF field H_1 rotating with frequency ω in the (x, y) plane is applied to a crystal spin system placed in a constant field H_0 parallel to the Oz axis, then the Hamiltonian of the system takes the form

$$\mathscr{H} = \hbar\omega_0 I_z + \frac{\hbar\omega_1}{2}\left(I_+ e^{-i\omega t} + I_- e^{i\omega t}\right) + \mathscr{H}_d,$$

where $\omega_0 = \gamma H_0$, $\omega_1 = \gamma H_1$, and $\mathscr{H}_d$ is the energy of the magnetic dipole-dipole interaction between the nuclear spins, which will be assumed to be the principal interaction

$$\mathscr{H}_d = \sum_{i<k} B_{ik}\left[\mathbf{I}_i\mathbf{I}_k - 3r_{ik}^{-2}(\mathbf{I}_i r_{ik})(\mathbf{I}_k r_{ik})\right], \quad B_{ik} = \hbar^2\gamma^2 r_{ik}^{-3}. \tag{8}$$

In the preceding section we introduced the concept of spin temperature to describe a spin state that differs from equilibrium and results from adiabatic demagnetization. In the case considered here, the Zeeman energy of the spins contains the time explicitly, and therefore it is not clear beforehand how one can introduce the spin temperature for such a system. It is easy to note, however, that it can be introduced by changing over to a coordinate system rotating with the frequency ω of the RF field about the $\mathbf{H}_0$ direction. This can be done with the aid of a unitary transformation $\tilde{\mathscr{H}} = U\mathscr{H}U^{-1}$, where $U = \exp(i\omega I_z t)$,

$$\tilde{\mathscr{H}} = \hbar(\omega_0 - \omega) I_z + \hbar\omega_1 I_x + \mathscr{H}_d^{(0)} + \mathscr{H}_d(t). \tag{9}$$

The interaction of the spins with the external fields is described at present, as we see, by the time-independent Hamiltonian $\mathscr{H}_M$, which includes the first two terms in (9):

$$\mathscr{H}_M = \hbar\left[(\omega_0 - \omega) I_z + \omega_1 I_x\right],$$

this being equivalent to their interaction with an effective magnetic field $\mathbf{H}_{\text{eff}} = \mathbf{i}H_1 + \mathbf{k}(H_0 - \omega/\gamma)$ ($\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are the unit vectors of the axes x, y, and z). The dipole interaction breaks up in the rotating coordinate system into two parts: secular

$$\mathscr{H}_d^{(0)} = \sum_{i<k} A_{ik}\left(3I_{iz}I_{kz} - \mathbf{I}_i\mathbf{I}_k\right), \quad A_{ik} = \frac{\hbar^2\gamma^2}{2r_{ik}^3}\left(1 - 3\cos^2\theta_{ik}\right), \tag{10}$$

(θ_{ik} is the angle between the vector $\mathbf{r}_{ik}$ and the field $\mathbf{H}_0$), independent of the time and commuting with the z-component of the total angular momentum, and nonsecular $\mathscr{H}_d(t)$, which oscillates with time at frequencies ω and 2ω. If the frequency ω is close to the resonant frequency ω_0, then the influence of $\mathscr{H}_d(t)$ can be neglected, for in this case the terms containing the time are incapable of causing resonant transitions between the Zeeman sublevels, which are determined by an effective magnetic field proportional to H_1. As a result ($\omega_0 \gg \omega_1$) we obtain the abbreviated Hamiltonian

$$\mathscr{H} = \hbar(\omega_0 - \omega) I_z + \hbar\omega_1 I_x + \mathscr{H}_d^{(0)}, \tag{11}$$

which describes the state of the spin system in a rotating coordinate system. In this coordinate system the spin system can already be described with the aid of some temperature.

To explain the many experimentally observed singularities in the behavior of the RF susceptibility, the reversible fast passage in solids[5], and others, it is not only convenient but essential to use the concept of a spin temperature in a rotating coordinate system. This was first demonstrated by Redfield[8] for the case of strong RF fields $H_1 > H_2$, when the strong-saturation condition is satisfied, i.e., when the interaction of the spins with the RF field is stronger than with the lattice. The concept of the spin temperature was introduced in practically the same manner as before, except that the role of the constant field is now played not by the external field H_0 but by H_{eff}.[3b]

If $H_1 \ll H_2$, then a situation arises that cannot be described with the aid of a single spin temperature. As shown first by Provotorov[9], in this case it is necessary[6] to introduce the concept of two generally speaking unequal spin temperatures T_{zl} and T_d, which describe the quasi-equilibrium in subsystems with energies represented by the Hamiltonian $\mathscr{H}_z = \hbar(\omega_0 - \omega)I_z$ (the Zeeman pool) and $H_d^{(0)}$ (the dipole pool).

The Hamiltonian $\mathscr{H}_z$ ($\mathscr{H}_d \gg \hbar\omega$, $\hbar I_x$) describes the interaction of the spins with the RF field in a rotating coordinate system. Then $\hbar\omega$ and I_x should be regarded as small perturbations of the principal Hamiltonian $\mathscr{H}_0 = \mathscr{H}_z + \mathscr{H}_d^{(0)}$, which is the sum of two commuting operators—integrals of the motion. This means that, neglecting the interaction with the RF field, the system can be broken into two independent subsystems, Zeeman and dipole, with energies represented by the Hamiltonians $\mathscr{H}_z$ and $\mathscr{H}_d^{(0)}$ respectively.[6] Then the relaxation of the system will proceed in two stages. First, an internal equilibrium characterized by a definite temperature is established in each of the subsystems under the influence of the spin-spin interactions. In general, the temperatures T_{zl} and T_d of the Zeeman and dipole subsystems are not equal. The next step is to equalize the temperatures of the subsystems by contact via the RF field.[3b]

The form of the operator ρ that describes the system in the quasi-equilibrium state can be determined, as is usually done in statistical physics, from the conditions that the entropy $S = k_B \mathrm{Tr}(\rho \ln \rho)$ be extremal. The extremum of the latter, in turn, is obtained from the extremum of the functional[10]

$$\mathscr{L}(\rho) = -\mathrm{Sp}(\rho \ln \rho) - \beta_{zl}\,\mathrm{Sp}(\rho\mathscr{H}_z) - \beta_d\,\mathrm{Sp}(\rho\mathscr{H}_d^{(0)}) - \lambda\,\mathrm{Sp}\,\rho,$$

where β_{zl}, β_d, and λ are Lagrangian multipliers determined from the conditions $\mathrm{Tr}\,\rho = 1$ and $\mathrm{Tr}(\rho\mathscr{H}_0) = \mathrm{const}$. The vanishing of the first variation of $\mathscr{L}(r)$ leads to the sought expression for ρ:

$$\rho \sim \exp(-\beta_{zl}\mathscr{H}_z - \beta_d\mathscr{H}_d^{(0)}),$$

where β_{zl} and β_d, as can be easily verified, have the meaning of reciprocal temperature, $\beta_{zl} = (k_B T_{zl})^{-1}$ and $\beta_d(k_B T_d)^{-1}$, and characterize not only the average energy of the Zeeman and dipole subsystems, but also the degree of the ordering. An increase of β_z corresponds to the ordering of the spins in a constant magnetic field $H_0 - (\omega/\gamma)$ (in a rotating coordinate system), while an increase of β_d leads to ordering in local fields.

Of course, the spin system Zeeman temperature T_{zl} in a rotating coordinate system is not equal to the temperature T_z in the laboratory frame. They are connected by the obvious relation

$$T_z = \frac{\omega_0}{\Delta} T_{zl}, \text{ where } \Delta = \omega_0 - \omega. \tag{12}$$

To find the equation for the time variation of β_z and β_d, which describe the approach of the system to equilibrium under the influence of the RF field, it is necessary to specify the form of the nonequilibrium statistical operator (NSO). To solve this problem we shall follow Zubarev's method[10] and express the NSO in the form

$$\rho = \mathrm{const}\cdot\exp\left\{-\beta_z\mathscr{H}_z - \beta_d\mathscr{H}_d^{(0)} + \int_{-\infty}^{0} e^{\varepsilon t}[k_z(t)\beta_z + k_d\langle t\rangle\beta_d]\,dt\right\}$$

or in the high-temperature approximation

$$\rho = \mathrm{const}\cdot\left\{1 - \beta_z\mathscr{H}_z - \beta_d\mathscr{H}_d^{(0)} + \int_{\infty}^{0} e^{\varepsilon t}(k_z(t)\beta_z + k_d(t)\beta_d)\,dt\right\}, \tag{13}$$

where the operators $k_z(t)$ and $k_d(t)$ in the Heisenberg representation are determined by the equations known from quantum mechanics

$$k_z = \dot{\mathscr{H}}_z = (i\hbar)^{-1}[\mathscr{H}_z, \mathbf{H}], \tag{13a}$$

$$k_d = \mathscr{H}_d^{(0)} = (i\hbar)^{-1}[\mathscr{H}_d^{(0)}, \mathbf{H}] \tag{13b}$$

under the condition $k_d + k_z = 0$, which expresses the law of energy conservation of the combined system. Averaging the left-hand and right-hand parts of (13a) with the aid of expression (13) for the NSO

$$\left\langle \frac{d}{dt}\mathscr{H}_z \right\rangle = \frac{d}{dt}E_z = \langle k_z\rangle, \tag{14}$$

where $E_z = \mathrm{Tr}[\rho(t)\mathscr{H}_z]$ and $\langle k_z\rangle = \mathrm{Tr}[\rho(t)k_z]$, we are able to obtain the connection between the reciprocal temperatures β_z and β_d. Calculating separately E_z and $\langle k_z\rangle$, we obtain

$$E_z = -\frac{NI(I+1)}{3}\Delta^2\beta_z(t), \tag{15}$$

$$\langle k_z\rangle = \frac{1}{6}\sqrt{\frac{2\pi}{\omega_L^2}}\,\omega_1^2\Delta^2 I(I+1)\,Ne^{-\Delta^2/2\omega_L^2}(\beta_z - \beta_d), \tag{16}$$

$$\omega_L^2 = \frac{\mathrm{Sp}\,(\mathscr{H}_d^{(0)^2})}{\mathrm{Sp}\,(\hbar\gamma I_z)^2},$$

where we have used the known approximation

$$\mathrm{Sp}\,(I_i^y I_k^y(t)) = \mathrm{Sp}\,(I_i^y I_k^y)\,e^{-(t^2\omega_L^2/2)+it\Delta}.$$

Substituting (15) and (16) in (14) we obtain

$$\frac{d\beta_z}{dt} = -2W\langle\beta_z - \beta_d) \tag{17}$$

and

$$\frac{d\beta_d}{dt} = 2qW(\beta_z - \beta_d), \tag{18}$$

where

$$W = \frac{\omega_1^2}{4}\sqrt{\frac{2\pi}{\omega_L^2}}\,e^{-\pi^2/2\omega_L^2},\ q = \frac{\Delta^2}{\omega_L}.$$

The last equation of (18) is obtained from the condition $\langle\dot{\mathscr{H}}\rangle = -\langle\dot{\mathscr{H}}_d^0\rangle$.

Equations (17) and (18) describe the variation of the Zeeman and dipole temperatures which occur under the influence of the RF field in a rotating coordinate system. They are valid for times $t \ll \tau_1$ but longer than the spin-spin relaxation time τ_2.

Assume that at the initial instant of time the dipole system is characterized by a temperature $1/\beta_0$ and the Zeeman system by the temperature $1/\alpha_0$ which is not equal to the lattice temperature. The latter is determined by the degree of polarization of the nuclei prior to the start of the RF saturation. If the polarization P_0 differs from the equilibrium value, then we can set $\alpha_0 = (P_0/P_L)\alpha_L$ (where P_L is the equilibrium polarization of the nuclei at the temperature) equal to $k_B T_L = \alpha_L^{-1}$. Under the specified initial conditions, the solution of the equations for the spin temperatures in the case of strong saturation takes the form

$$\beta_z = \beta_d = \frac{\beta_0}{1 + (\Delta^2/\omega_L^2)}\left(1 + \frac{\Delta\omega_0}{\omega_L^2}\frac{\alpha_0}{\beta_0}\right) \approx \frac{\Delta\omega_0}{\omega_L^2 + \Delta^2}\alpha_0. \tag{19}$$

The fact that the subsystem temperatures are equal indicates that a single temperature has been established in the rotating coordinate system. It is easily seen that these temperatures have a resonant dependence and assume minimum values

$$T_d = T_{zl} = 2\frac{\omega_L}{\omega_0}\eta T_L, \quad \eta = \frac{P_L}{P_0} \tag{20}$$

at $|\Delta| = \omega_L$.

The results can be given a simple qualitative interpretation that explains the reason for the decreased temperature (decreased energy) of the dipole pool. Each act of absorption of an RF quantum by the spin system leads to a reorientation of the nuclear spin. A nuclear-spin consisting of two subsystems (Zeeman and dipole) is insulated from the lattice, therefore the energy of the absorbed RF quantum is distributed among these subsystems. Since, however, the frequency of the quantum is nearly but not exactly resonant, the character of the energy distribution depends on the sign of Δ (Fig. 3).

If $\Delta > 0$, then the energy needed for spin flip in an external field is drawn from the dipole pool, and the latter is cooled (the Zeeman subsystem is heated). This leads to a predominant population of the lower energy sublevels in the dipole system. Then $T_d > 0$ (Fig. 3b). When $\Delta < 0$, the excess energy released in the course of the RF transitions of the spins is transferred from the spin system to the dipole system. It is easily seen that in this case the spin temperature is negative and corresponds to a predominant population of the states of the dipole system with the highest energies (Fig. 3c).

With such a demagnetizing process, the total entropy of the system is conserved. The order that exists in the Zeeman system is transferred to the dipole system.

The value of T_d can be decreased by another factor of two in comparison with the value given by (20) if, after starting the strong RF saturation on the wing of the resonance curve, Δ is reduced to zero within a time less than τ_1, i.e., adiabatically. In this case, the spin ordering in the magnetic field goes over completely into ordering in the local fields.

By adiabatic demagnetization of nuclei[2)] that have been previously polarized with the aid of the solid effect we can, as follows from (20), obtain a dipole temperature that ensures the transition of the spins to an ordered state. For protons with a polarization $P_0 = 50\%$ obtained in a field $H_0 = 25$ kOe at 0.7°K, we get $T_d = 1 \times 10^{-7}$ °K. For fluorine nuclei under the same conditions we have $T_d = 2 \times 10^{-6}$ °K at $H_0 \parallel [001]$ at $T_d = 1.3 \times 10^{-6}$ °K at $H_0 \parallel [011]$.

The magnetic fields used in the experiments aimed at cooling a spin system and obtaining a dipole temperature low enough for the appearance of nuclear ordering are rather strong (27 kOe for CaF_2 and 55 kOe for LiF[15]). The reason, as already indicated, is that as the field is increased the spin-lattice relaxation time increases, all the interfering couplings of the nuclear spins are broken, and the dipole part of the Hamiltonian, which is responsible for the ordering, assumes the simple form employed above.

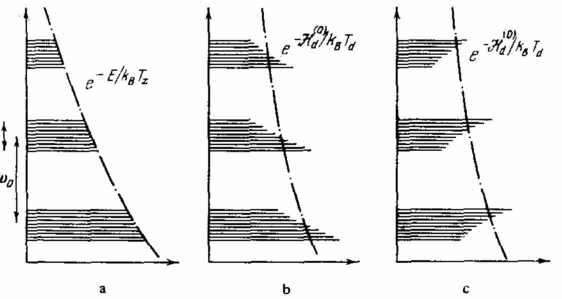

FIG. 3. Possible distributions of the populations over the Zeeman sublevels of a system of nuclear spins in a magnetic field, corresponding to thermal equilibrium ($T_d = T_z$) and to the cases when the dipole and Zeeman temperatures are not equal: $T_d > 0$ (b) and $T_d < 0$ (c).

3. THEORY OF ORDERED SPIN CONFIGURATIONS DUE TO MAGNETIC DIPOLE-DIPOLE INTERACTION

One of the main problems arising in the theory of the ordering of the nuclear spins is to determine nuclear-spin-system states such that the spins have the lowest or the highest energy at a definite magnetic field orientation H_0 relative to the crystal axes. These states correspond to the positive and negative values of the spin temperature.

Our next task is the interpretation of a fully determined aggregate of experiments, in which antiferromagnetic and ferromagnetic ordering of the nuclear spins was observed. We therefore confine ourselves to consideration of only simplest magnetic structures of this type. As will be seen below, this limitation is fully permissible for the explanation of the first successful experiments carried out on CaF_2 crystals, in which the magnetically-active F^{19} nuclei (nuclear spin $I = 1/2$) form a primitive cubic lattice. The theoretical methods used to explain the properties of magnetically-ordered states in a system of nuclear spins between which dipole-dipole interaction takes place can be borrowed from the field of electron ferromagnetism. These are approximate methods, but they permit to describe the considered phenomena at least qualitatively, and in some cases also quantitatively. We can name four such methods.

a) The classical method of Luttinger and Tisza [11]

In this method one determines at $T = 0$, the classical expression for the energy of the system of spins between which a dipole interaction (in this case secular) takes place. The next step is to find ordered spin configurations such that this energy is extremal (i.e., minimal or maximal). We shall discuss this method in detail later on.

b) The spin-wave approximation [14]

This approximation is considered in the quantum-mechanical analysis of the antiferromagnetic state. It does not make it possible to obtain structures that are stable at $T = 0$, and is customarily used to ascertain whether a given structure, obtained by the classical approach, is applicable from the point of view of quantum mechanics.

The Hamiltonian of the system is given by (10), and the equations of motion of the operator $I_+ = I_x + iI_y$ in Heisenberg representation are written in the form

$$i\frac{dI_{i+}}{dt} = -[\mathcal{H}, I_{i+}] = \sum_j A_{ij}(2I_{i+}I_{jz} + I_{iz}I_{j+}).$$

The spin-wave approximation consists essentially of replacing I_{jz} by $+1/2$ or $-1/2$, depending on the localization of the spin in any one of the sublattices of the antiferromagnetic structure obtained beforehand by classical calculation. The resultant linearized equation of motion of the operators I_{i+} make it possible to determine elementary excitations of the boson type (spin waves or magnons), and then calculate the sublattice magnetizations.

It turns out that even at $T = 0$ these magnetizations differ from those corresponding to complete alignment in

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[2)] The process of adiabatic magnetization is customarily called in this case adiabatic demagnetization in a rotating coordinate system.

each sublattice. This is due to the so-called spin deviations.

In order for the antiferromagnetic structures obtained from the classical calculation to be acceptable in the spin-wave approximation, it is necessary that the energies of all the elementary excitations have the corresponding sign, namely positive for a structure stable at $T > 0$ and negative at $T < 0$. In addition, the spin deviations should be small at zero temperatures.

c) The Weiss field approximation

The idea underlying this well-known method is that only the average field produced at the location of a given spin by all the remaining spins is taken into account when the interaction between the spins is considered. This average field, called the Weiss field, is then the same at all points of the given sublattice, and the contribution of each sublattice is proportional to its magnetization. In the Weiss-field approximation one calculates the entropy of a system of nuclear spins and other thermodynamic functions, after which the usual thermodynamic rules are employed to find stable spin configurations. This method has been applied most consistently to the group of phenomena in question in a recent paper by Goldman et al.[19].

d) The random-phase approximation [14]

This method is used to refine the spin-wave approximation when the temperature is not too low. It consists of replacing the quantities I_{iz} and I_{jz} in the evolution equation written out above by their average statistical values at the system temperature. The elementary perturbations have the same form as in the spin-wave approximation, but their energies are multiplied by a coefficient determined by the sublattice polarizations, which in turn depend on the temperature. A numerical calculation makes it possible to find the polarizations of the sublattices as functions of the effective field and of the temperature, and also the energy and the entropy of the system.

1) **The Luttinger and Tisza method. Formulation of the problem.** Consider a crystal with a primitive cubic lattice, at the points of which are located atoms having nuclear spin moments I. There is a dipole-dipole interaction between the spins, and its energy (9) is conveniently rewritten in the form

$$E = -\frac{1}{2}\sum_{n\nu}\sum_{m\mu\alpha\beta} d^{\alpha\beta}_{n\nu,\,m\mu} I^{\alpha}_{n\nu} I^{\beta}_{m\mu}; \tag{21}$$

where the numbers $\mathbf{n} = (n_1, n_2, n_3)$ and $\mathbf{m} = (m_1, m_2, m_3)$ number the unit cell of the lattice (n_i and m_i are integers, both positive and negative), $\boldsymbol{\nu} = (\nu_1, \nu_2, \nu_3)$ and $\boldsymbol{\mu} = (\mu_1, \mu_2, \mu_3)$ ($\nu_i, \mu_i = 0, 1$) number the points of the unit cell, with $(\mathbf{n}\cdot\boldsymbol{\nu}) \neq (\mathbf{m}\cdot\boldsymbol{\mu})$; $\alpha, \beta = (x, y, z)$. The coordinate axes are directed along the principal axes of the crystal lattice.

The quantity $d^{\alpha\beta}_{n\nu,m\mu}$ determines the coordinate dependence of the energy of the dipole interaction of two spins and is given by

$$d^{\alpha\beta}_{n\nu,\,m\mu} = d^{\alpha\beta}(\mathbf{r}) = \frac{\hbar^2\gamma^2}{r^5}(3x^{\alpha}x^{\beta} - \delta_{\alpha\beta}r^2), \tag{22}$$

where $\mathbf{r} = \mathbf{R}_{n\nu} - \mathbf{R}_{m\mu}$.

The problem is to find a spin-moment vector distribution that corresponds to a minimum or to a maximum of the energy (21) subject to the additional conditions

$$(\mathbf{I}_{n\nu}\cdot\mathbf{I}_{n\nu}) = I^2, \tag{23}$$

which mean the value of the spin at each site remains constant (only its orientation can change).

Following the original method of Luttinger and Tisza[1], we assume that the variables I in (21) are purely classical vector quantities. In this approach, the formulated problem reduces to determining the conditional extremum of a quadratic form. Its solution by the direct method, however, encounters considerable mathematical difficulties, since a large number of additional conditions makes it necessary to solve a system consisting of a large number of equations.

We therefore consider first the possible ordered configurations of nuclear spins forming a primitive cubic lattice with constant a. Such configurations, of course, can be defined only with account taken of the symmetry of the ordering. Let Γ be the group of three dimensional translations $(al_1)\mathbf{i} + (al_2)\mathbf{j} + (al_3)\mathbf{k}$ (l_i are integers, and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors collinear with the crystal axes). The most ordered configuration is one in which the spin arrangement is invariant to the group Γ, i.e., the case when all the spins are equal and parallel to one another.

A more general class of ordered configurations, the class Γ^2, is obtained if we stipulate only their invariance to translations of the type $(2al_1)\mathbf{i} + (2al_2)\mathbf{j} + (2al_3)\mathbf{k}$, which form the subgroup Γ^2 of group Γ. We assume henceforth that the sought configurations with extremal values of the energy belong to the class Γ^2. To construct such a configuration we can single out eight spins $\mathbf{I}_{n\nu}$ at a fixed $\mathbf{n}$, and the total configuration over the crystal is obtained by all possible translations of Γ^2. Of course, this does not account for all the possible ordered configurations, but configurations of class Γ^2 are the simplest that admit of antiferromagnetic and ferromagnetic ordering of the spins.

In this case we can transform somewhat expression (21), recognizing that $\mathbf{I}_{n\nu}$ does not depend on $\mathbf{n}$, and expressing the radius vector of the spin $(\mathbf{n}\cdot\nu)$ in the form $\mathbf{R}_{n\nu} = a(\nu + 2\mathbf{n})$. Then the quantity $\mathbf{r}$ in (22) is equal to

$$\mathbf{r} = a(\boldsymbol{\nu} - \boldsymbol{\mu} + 2\mathbf{l}), \tag{24}$$

where $\mathbf{l} = \mathbf{n} - \mathbf{m}$.

Substituting these expressions in (21) and summing over n, we obtain

$$E = -\frac{N}{16}\sum_{\nu\mu}\sum_{\alpha\beta} I^{\alpha}_{\nu} F^{\alpha\beta}_{\nu\mu} I^{\beta}_{\mu}, \tag{25}$$

where

$$F^{\alpha\beta}_{\nu\mu} = \sum_{l_1, l_2, l_3=-\infty}^{+\infty} d^{\alpha\beta}_{\nu\mu}(\mathbf{l}) \tag{26}$$

and N is the number of spins in a sample.

It is easy to show that the matrix $F^{\alpha\beta}_{\nu\mu}$ has the following property[11]:

$$F^{\alpha\beta}_{\nu\mu} = \delta_{\alpha\beta}F^{\alpha\alpha}_{\nu\mu}, \quad F^{xx}_{\nu\mu} = F^{yy}_{\nu\mu} = F^{zz}_{\nu\mu}, \quad F^{\alpha\alpha}_{\nu\mu} = F^{\alpha\alpha}_{\mu\nu}.$$

As a result, the energy (25) takes the form

$$E = -\frac{N}{16}\sum_{\nu\mu\alpha} I^{\alpha}_{\nu} F^{\alpha\alpha}_{\nu\mu} I^{\alpha}_{\mu}.$$

The final problem of finding ordered spin configurations corresponding to extremal values of the dipole energy becomes greatly simplified if we reduce first the quadratic form (25) to a sum of squares, which is equivalent to diagonalization of the matrix $F^{\alpha\beta}_{\mu\nu}$. As a result, this matrix $F^{\alpha\beta}_{\mu\nu}$ with dimensionality 24 was reduced to three 8×8 matrices $F^{\alpha\alpha}_{\nu\mu}$ (α = x, y, z), and the diagonalization of this matrix was therefore somewhat simplified.

2) **Basis configurations.** Each spin configuration of class Γ^2 can be described by an aggregate of 24 quantities, i.e., by triplets of Cartesian components of the eight spins $\mathbf{I}_\nu$ of one unit cell. We shall treat this aggregate as a vector in a certain 24-dimensional space $\mathscr{L}$.

In this space, the operations of addition, of multiplication by scalar, and of the scalar product are defined by the expressions

$$\mathbf{P}+\mathbf{Q}=\{\mathbf{P}_\nu+\mathbf{q}_\nu\},\quad c\cdot\mathbf{P}=\{c\cdot\mathbf{P}_\nu\},$$
$$\mathbf{P}\cdot\mathbf{Q}=\sum_{\nu_1,\nu_2,\nu_3=0,1}\mathbf{P}_\nu\cdot\mathbf{q}_\nu,$$

Therefore when the condition (23) is satisfied the vector of the configuration **P** has a norm squared equal to

$$\mathbf{PP}=8I^2. \tag{27}$$

The matrix $F^{\alpha\beta}_{\mu\nu}$ can be treated as a certain representation of a linear operator acting in the space $\mathscr{L}$. Then the diagonalization of this matrix is effected by an orthogonal transformation in the space $\mathscr{L}$, which leaves (27) invariant (rotation). The new coordinate system is given by the orthogonal set of vectors $\mathbf{A}_i$ (i = 1, 2, ..., 24), which we shall call basis configurations. They are analogous to the normal coordinates introduced to describe vibrational systems.

In accordance with the fact that the matrix $F^{\alpha\beta}_{\nu\mu}$ reduces to three identical 8×8 matrices $F^{\alpha\beta}_{\nu\mu}$, the 24 basis configurations break up into three groups $\mathbf{x}^i$, $\mathbf{y}^i$, $\mathbf{z}^i$ (i = 1, ..., 8), in which the configurations are made up of spins directed along the axes x, y, and z respectively.

The eight nonvanishing components of the basis configuration $\mathbf{z}^i$ are given by the expressions

$$z^i_\mu=I\cdot(-1)^{\alpha_i\mu_1+\beta_i\mu_2+\gamma_i\mu_3}\qquad (i=1,2,\ldots,8), \tag{28}$$

where α_i, β_i, γ_i = 0 or 1, and the set (α_i, β_i, γ_i) number the basis configurations. The possible cases and the corresponding designations of the basis configurations $\mathbf{z}^i$ are listed in Table II. The configurations themselves are shown in Fig. 4.

The basis configurations $\mathbf{x}^i$ and $\mathbf{y}^i$ are obtained from $\mathbf{z}^i$ by corresponding rotations. The $\mathbf{z}^i$ are orthogonal, i.e., as can be readily verified, they satisfy the relations

$$\mathbf{z}^i\cdot\mathbf{z}^j=8I^2\delta_{ij}. \tag{29}$$

3) **Calculation of the characteristic values.** The task of this section is to prove that the basis configurations $\mathbf{x}^i$, $\mathbf{y}^i$, and $\mathbf{z}^i$ are the eigenconfigurations for the corresponding matrices $F^{xx}_{\nu\mu}$, $F^{yy}_{\nu\mu}$, and $F^{zz}_{\nu\mu}$. Since the matrices are identical, it suffices to verify this for the basis configurations $\mathbf{z}^i$. We calculate in passing the characteristic or eigenvalues of these matrices.

TABLE II. Basis configurations.

	z^1	z^2	z^3	z^4	z^5	z^6	z^7	z^8
α	0	0	1	0	1	0	1	1
β	0	0	0	1	1	1	0	1
γ	0	1	0	0	0	1	1	1

It is necessary to prove that the z^i satisfy the equations and to find f_i.

$$\sum_\mu F^{zz}_{\nu\mu}z^i_\mu=f_iz^i_\nu,$$

If we use the definitions (22), (24), and (26) and the relation (28), then these equations can be reduced to the form

$$\frac{\hbar^2\gamma^2}{8a^3}\sum_{\mu_1,\mu_2,\mu_3=0,1}(-1)^{\alpha_i\mu_1+\beta_i\mu_2+\gamma_i\mu_3}S_z\left(\frac{\nu-\mu}{2}\right)=f_i(-1)^{\alpha_i\nu_1+\beta_i\nu_2+\gamma_i\nu_3}, \tag{30}$$

where ν_1, ν_2, ν_3 = 0 or 1, and

$$S_z(\eta)=\sum_{l_1,l_2,l_3=-\infty}^{\infty}\frac{2(l_3+\eta_3)^2-(l_1+\eta_1)^2-(l_2+\eta_2)^2}{[(l_1+\eta_1)^2+(l_2+\eta^2)^2+(l_3+\eta_3)^2]^{5/2}}. \tag{31}$$

Thus, the problem has been reduced to calculating the quantity $S_z(\boldsymbol{\eta})$. It can be readily shown that numerous symmetry relations exist in this case, for example

$$S_z(\eta_1,\eta_2,\eta_3)=S_z(\eta_2,\eta_1,\eta_3),$$

and to find f_i it suffices to know only two quantities $S_z(1/2, 0, 0)$ and $S_z(0, 1/2, 1/2)$, whose values, according to[11], are

$$S_z\left(\frac{1}{2},0,0\right)=-15.040,$$
$$S_z\left(0,\frac{1}{2},\frac{1}{2}\right)=4.334.$$

For a spherical sample we obtain the following eigenvalues:

$$\left.\begin{array}{ll} f_1=0, & f_5=5.353\,\dfrac{\gamma^2\hbar^2}{a^3},\\ f_2=9.687. & f_6=f_7=2{,}676\,\dfrac{\gamma^2\hbar^2}{a^3},\\ f_3=f_4=-4.844\,\dfrac{\gamma^2\hbar^2}{a_3}, & f_8=0. \end{array}\right\} \tag{32}$$

In view of the complete identity of the matrices $F^{\alpha\alpha}_{\mu\nu}$, the matrices $F^{xx}_{\nu\mu}$ and $F^{yy}_{\nu\mu}$ will have the same eigenvalues.

4) **Strong and weak conditions.** It follows from the foregoing that $\mathbf{x}^i$, $\mathbf{y}^i$, $\mathbf{z}^i$ (i = 1, ..., 8) form a complete basis of 24 orthogonal vectors in the space $\mathscr{L}$, and solve the problem of the eigenvalues and eigenvectors of the matrix (26). Then any configuration **P** of class Γ^2 can be represented in the form of a linear superposition of the basis configurations $\mathbf{x}^i$, $\mathbf{y}^i$, and $\mathbf{z}^i$:

$$\mathbf{P}=\sum_{i=1}^{8}(a_i\mathbf{x}^i+b_i\mathbf{y}^i+c_i\mathbf{z}^i),$$

where $a_i = (1/8I^2)\mathbf{P}\cdot\mathbf{x}^i$, $b_i = (1/8I^2)\mathbf{P}\cdot\mathbf{y}^i$, $c = (1/8I^2)\mathbf{P}\cdot\mathbf{z}^i$, and its energy, according to (28), takes the form

$$E=-\frac{NI^2}{2}\sum_{i=1}^{8}f_i(a_i^2+b_i^2+c_i^2). \tag{33}$$

The main task is now to find such a configuration of class Γ^2 (i.e., such as a_i, b_i, and c_i) which has the largest and

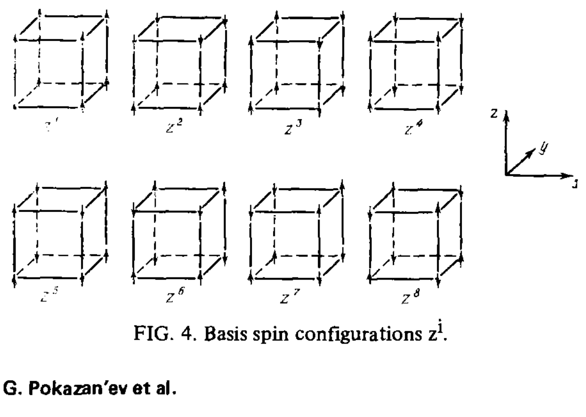

FIG. 4. Basis spin configurations z^i.

smallest energy. The configuration must further more satisfy eight additional conditions that call for the constancy of the spin angular momentum. In terms of the basis configurations, these conditions take the form

$$\left(\sum_{i=1}^{8} a_i x_\nu^i\right)^2 + \left(\sum_{i=1}^{8} b_i y_\nu^i\right)^2 + \left(\sum_{i=1}^{8} c_i z_\nu^i\right)^2 = I^2. \tag{34}$$

This is a so-called strong condition, but it is very difficult to calculate by the method of indeterminant Lagrange multipliers. Therefore the conditions (24) are replaced by single condition, called weak[11]

$$\sum_{i=1}^{8} (a_i^2 + b_i^2 + c_i^2) = 1,$$

which is obtained from the strong condition by summing over ν.

The procedure consists of finding the extremal value of the energy (33) under one weak condition. For example, the smallest value of the energy is proportional to $(-f_m)$, where f_m is the largest of the eigenvalues f_i, and the corresponding configuration is the linear superposition of the basis configurations corresponding to f_m. If some of these configurations satisfy also the strong condition, then the posed problem is solved.

It is seen from (32) that the lowest energy

$$E_{\min} = -\frac{NI^2}{2} f_5 = -5.353 \frac{N\hbar^2\gamma^2 I^2}{2a^3} \tag{35}$$

is possessed by the configuration

$$P_{\min} = a_5 \mathbf{x}^5 + b_5 \mathbf{y}^5 + c_5 \mathbf{z}^5, \quad a_5^2 + b_5^2 + c_5^2 = 1.$$

It is easy to verify that it satisfies the strong condition (34).

The maximum energy

$$E_{\max} = -\frac{NI^2}{2} f_2 = 9.687 \frac{N\hbar^2\gamma^2 I^2}{2a^3} \tag{36}$$

is possessed by the configuration

$$P_{\max} = a_2 \mathbf{x}^2 + b_2 \mathbf{y}^2 + c_2 \mathbf{z}^2, \quad a_2^2 + b_2^2 + c_2^2 = 1,$$

which also satisfies the strong condition.

5) **Ordered spin configurations due to the secular magnetic dipole-dipole interaction.** Inasmuch as in experiments on nuclear ordering one uses the method of adiabatic demagnetization in a rotating coordinate system, the question arises of finding the spin configurations due to the secular dipole-interaction (10) for which, if the spin system is in a rotating RF field, the concept of spin temperature is valid. It is easily seen that the corresponding energy of the interaction of the classical angular momenta in our notation takes the form

$$E = -\frac{N}{16} \sum_{\nu\mu} F_{\nu\mu}^{zz} \left(I_\nu^z I_\mu^z - \frac{1}{2} I_\nu^x I_\mu^x - \frac{1}{2} I_\nu^y I_\mu^y \right). \tag{37}$$

GA characteristic feature of the "secular" dipole interaction is its dependence on the orientation of the external magnetic field relative to the crystal-lattice axes. Therefore the resultant magnetic order also depends on this orientation. Let us consider some particular cases.

5.1) Magnetic field $\mathbf{H}_0$ parallel to the [001] axis. The basis configuration in which the spins are directed along the Oz axis ($\parallel \mathbf{H}_0$) are determined by relation (28) and have the eigenvalues (32).

For negative spin temperatures close to zero, the stable state is an antiferromagnetic state having a maximum energy (36) and corresponding to the basis configuration $\mathbf{z}^2$ (Fig. 5a). The alternating (001) planes have opposite magnetizations parallel to the [001] direction.

At very low positive temperatures, the stable state is the one having the minimum energy (35) corresponding to the basis configuration $\mathbf{z}^5$. In this case the planes (110) have opposite magnetizations parallel to the direction [001] (Fig. 5b).

5.2) Magnetic field $\mathbf{H}_0$ parallel to the [011] axis. The secular part of the total dipole-dipole interaction is separated relative to the projection of the spin angular momentum on the direction of the external field. Therefore in (37) the coordinate system is chosen in such a way that the Oz axis is parallel to $\mathbf{H}_0$. When calculating the eigenvalues of the matrices by means of formula (30), it is necessary to change over in (22) to the coordinate system connected with the crystal-lattice axis. As a result we obtain for S_z, in place of (31), the expression

$$S_z(\eta) = -\frac{1}{2} \sum_{l_1, l_2, l_3 = -\infty}^{\infty} \frac{2(l_1+\eta_1)^2 - (l_2+\eta_2)^2 - (l_3+\eta_3)^2}{[(l_1+\eta_1)^2 + (l_2+\eta_2)^2 + (l_3+\eta_3)^2]^{5/2}}.$$

Calculations show that at very low positive temperature the stable state is antiferromagnetic and corresponds to the basis configuration z^3, when the magnetizations of the alternating (100) planes are opposite and are parallel to the [011] axis (Fig. 5c). The spin-system energy in this state is

$$E_{\min} = -4.844 \frac{N\hbar^2\gamma^2 I^2}{2a^3}. \tag{38}$$

At near-zero negative temperatures there should be realized an antiferromagnetic state corresponding to the basis configuration $\mathbf{z}^6$. The alternating (011) plane have opposite magnetizations parallel to the [011] axis (see Fig. 5c). The energy of this state is

$$E_{\max} = 2.676 \frac{N\hbar^2\gamma^2 I^2}{2a^3}. \tag{39}$$

The predicted ordered spin configurations of class Γ^2 are shown in Fig. 5.

5.3) Magnetic field $\mathbf{H}_0$ parallel to the [111] axis. In the case when the external field is parallel to the [111] axes, the matrix $F_{\nu\mu}^{zz}$ contained in expression (37) for the classical energy of the secular dipole interaction is determined by relations (22) and (26), where the coordinate system is connected with the $\mathbf{H}_0$ direction, i.e., Oz $\parallel$ [111]. It is easy to show that this matrix vanishes in the coordinate system connected with the crystallographic axes. On the basis of the classical approach developed in the present section it is apparently impossible to obtain a correct answer to the question of whether nuclear ordering is realized in this case. This case

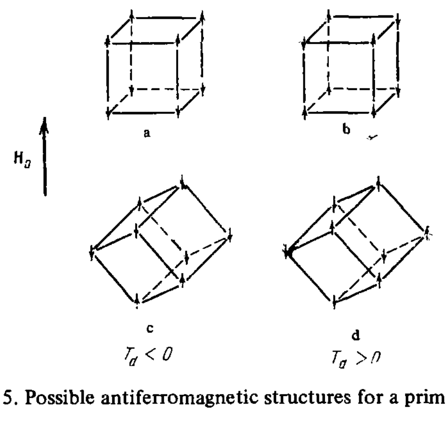

FIG. 5. Possible antiferromagnetic structures for a primitive cubic lattice.

must apparently be calculated on the basis of other more rigorous methods. In view of the negative results obtained by the Luttinger and Tisza method, one cannot deny the possibility of the onset of spin ordering at sufficiently low temperatures. This is indicated, apparently, by a recent report[13,15] of the observation of ferromagnetic domains produced in precisely this field geometry.

6) Possible trends in the generalization of the considered theory. Bearing in mind a description of a definite group of experiments, we have confined ourselves only to the primitive cubic (PC) lattice. However, the procedure described, as shown in[11], can be generalized to body centered (BCC) and face-centered (FCC) cubic lattices. For this purpose, the spin configurations in these lattices must be regarded as consisting respectively of two and four PC configurations, which can be resolved into PC-basis configurations. For example, in the case of a BCC lattice one PC configuration is made up of spins lying in the vertices of the unit cells (l_p), and the other of spins located at the centers of the cells (bc). Then the expression (21) for the energy can be broken up into terms corresponding to the energy of the described PC configurations, which are expressed in terms of the eigenvalues (32) calculated above and also of the interaction energy of these configurations. By a suitable choice of the basis PC configurations, the details of which are described in[11], it is possible to eliminate this energy. By the same token, the quadratic form (21) is reduced to a sum of squares, and the corresponding basis configurations of the BCC lattice will take the form $[\mathbf{P}, \mathbf{Q}]$, where $\mathbf{P}$ are the basis configurations for the spins in l_p and $\mathbf{Q}$ are the basis configurations for the spins in bc.

A similar procedure can be used also for a FCC lattice.

The calculations for the total dipole-dipole configuration show that for spherical samples the spin configurations with minimum energy correspond in all three cubic lattices to the antiferromagnetic state. On the other hand, in the case of a thin long sample, the spins in the BCC and FCC lattices can apparently form a ferromagnetic structure. This was confirmed in later researches based on the spin-wave approximation.[12]

Finally, it can be noted that the method can be used also for lattices other than cubic. A difference arises in the definition of the function $S_z(\boldsymbol{\eta})$ introduced in Chap. 3, and in the detailed structure of the basis configurations. For non-cubic lattices, however, the calculations turned out to be much more complicated.

The considered calculation procedure is applicable in principle also to systems consisting of two sorts of spins. A possible sample of such a system is the LiF crystal, in which there are two sorts of magnetoactive nuclei, Li^7 and F^{19}. However, the calculations become even more complicated, since the nuclei of each element form an FCC lattice and an interaction can occur between the nuclear spins of these elements.

4. EXPERIMENTAL OBSERVATION OF DIPOLE NUCLEAR ORDERING

Let us examine the results of the still scanty experimental papers reporting observation of a transition of a nuclear spin system into an ordered state when the energy of the dipole-dipole pool is lowered by adiabatic demagnetization in a rotating coordinate system. Although the concept of ordering covers both ferromagnetic and antiferromagnetic states, we shall discuss mainly antiferromagnetic nuclear-spin structures, since only the first steps have been made so far in the experimental investigation of the ferromagnetic transition, and the results are not yet sufficiently reliable. In a recent communication[13,15] devoted to the study of magnetic transitions in CaF_2, results are reported of the first experiments which, in the authors' opinion, offer evidence of the onset of ferromagnetic ordering of fewer nuclei in a magnetic field H_0 directed along the [111] axis. According to the magnetic-ordering theory presented in the preceding section, the ferromagnetic states of a CaF_2 crystal having a primitive cubic lattice is unstable. The same conclusion is arrived at also in the theory based on the spin-wave approximation.[14] This indicates that under the assumed limitations, the microscopic theory does not lead to ferromagnetic ordering. This, however, does not contradict an experiment[13] in which ferromagnetic domains were observed, the appearance of which could not be explained within the framework of the microscopic theory with allowance for the dipole interaction alone.[20] We shall dwell briefly on these results, which are in themselves extremely interesting.

a) Methods of observing nuclear ordering

Let the dipole system be cooled to the temperature of the nuclear phase transition and assume that an ordered spin state has been produced in it. In what manner, or more accurately by what sample properties, can one determine experimentally that the spin system is in the antiferromagnetic state?

The most convincing method of observing structures of this kind is the study of scattering of slow neutrons by nuclei, in spite of the smallness of the nuclear magnetic moments. The reason is that the spin part of the electron-nuclear scattering is determined principally by strong nuclear interaction and not by magnetic interaction. It can be shown that the amplitude of the scattering of neutrons by protons can reach a value comparable with the amplitude of the magnetic scattering of neutrons by electrons.[18]

This method, called magnetic neutron diffraction, has been well developed and has given good account of itself in the study of electron magnetism. To apply it to the problem of interest to us it is necessary to resort to a number of concepts of nuclear physics, namely some problems of the theory of nuclear forces, the technique of polarized targets, the peculiarities of the penetration of polarized neutrons through oriented nuclear targets, etc. We hope to discuss these questions, which are of independent interest, in a separate article in this journal. However, the use of this method for the study of nuclear ordering in CaF_2 is impossible, in view of the exceedingly small amplitude of neutron scattering by fluorine nuclei.

The most natural method of observing nuclear ordering in this case is to use the nuclear magnetic resonance methods. In this case, the most sensitive to the character of the ordering is the dependence of the magnetic susceptibility on the temperature. This procedure was used in the successful experiments by French physicists, which will be described below.

We assume that the Weiss molecular field is valid for the description of nuclear antiferromagnetism.[14] Using the two-sublattice model of antiferromagnets, we can calculate, on the basis of general statistical methods, the magnetic susceptibility and determine its temperature dependence[20]. It turns out that the longitudinal susceptibility $\chi_{\parallel}$ relative to the field H_0 has a temperature dependence different from the transverse one $\chi_{\perp}$. Namely, starting with $T = T_N$ (T_N is the phase-transition temperature) $\chi_{\parallel}$ tends to zero with decreasing temperature, while $\chi_{\perp}$ remains constant at

$$\chi_{\perp}^{A} = \alpha A^{-1}, \tag{40}$$

where α is a constant and $A = E/N\hbar^2 I^2$. The temperature dependence of the susceptibility is shown in Fig. 6. At $T > T_N$ we have $\chi_{\perp} = \chi_{\parallel}$ and the dependence on T satisfies the Curie law (the section to the right of the point $T/T_N = 1$ in Fig. 6), and this corresponds to the paramagnetic region. Thus, by plotting the experimental $\chi(T)$ we can determine the magnetic state of the substance. In the case of electronic antiferromagnets, such experiments entail no special difficulties, since their T_N is high enough.

We encounter a different situation in case of nuclear antiferromagnets, for which T_N is of the order of 10^{-6}—10^{-7} °K. As already noted, it is practically impossible to cool a sample to such temperatures, let alone of measuring these temperatures. The only thing that can be done and is being done is to cool the spin degrees of freedom, or more accurately the dipole pool, to the required temperature. This is accomplished, as we have seen, by adiabatic demagnetization in a rotating coordinate system. The spin-system temperature obtained as a result of this process cannot be measured, but can only be calculated from the formula (with allowance for the adiabatic demagnetization)

$$T_d = \frac{\omega_L'}{\omega_0} T_L P_L P_i^{-1}$$

if the quantities in these formulas are known, particularly the initial polarization P_i.

When we identify the spin temperature with the thermodynamic temperature (the spin-temperature hypothesis), we are justified in expecting the magnetic susceptibility of the nuclear spins to have a T_d-dependence analogous to that shown in Fig. 6. It is easily seen that there should exist a certain critical polarization $P_i = P_n$ corresponding to $T_d = T_N$. At this polarization, as a result of adiabatic demagnetization, the system of nuclear spins goes over from the paramagnetic to the antiferromagnetic state.

The critical polarization P_N, and also T_N can be obtained on the basis of the characteristic dependence of $\chi_{\perp}$ on the temperature or on the initial polarization. In the paramagnetic region, during the course of the adiabatic demagnetization, the susceptibility $\chi_{\perp}$ is connected with P_i by the relation

$$\chi_{\perp}^{p} = \frac{\alpha P_i}{\gamma H_L'}, \tag{41}$$

where α is the same coefficient as in (40).

The critical value of P_N is obtained from the equality $\chi_{\perp}^{p} = \chi_{\perp}^{A}$, from which we get on the basis of (40) and (41)

$$P_N = \frac{\omega_L'}{A}, \tag{42}$$

where the value of ω_L' for CaF_2 at different orientations of the field H_0 is given by

$$\omega_L' = \begin{cases} 3{,}16\,\frac{\hbar\gamma^2}{2a^3}, & H_0 \parallel [001], \\ 1{,}96\,\frac{\hbar\gamma^2}{2a^3}, & H_0 \parallel [011]. \end{cases}$$

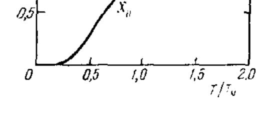

FIG. 6. Proposed temperature dependence (in relative units) of the longitudinal and transverse susceptibilities of a nuclear antiferromagnet in the molecular-field-theory approximation.

With the aid of (35), (36), (38), (39), and (42) we can estimate P_N for different experimentally possible cases:

$$\left.\begin{array}{lll} H_0 \parallel [001], & T_d < 0, & P_N = 0.326, \\ H_0 \parallel [001], & T_d > 0, & P_N = 0.59, \\ H_0 \parallel [011], & T_d > 0, & P_N = 0.405, \\ H_0 \parallel [011], & T_d < 0, & P_N = 0.73. \end{array}\right\} \tag{43}$$

The transition temperature cannot be measured after the demagnetization. In the Weiss-theory approximation, however, it can be calculated from the formula

$$T_N = \frac{\hbar A}{2k}. \tag{44}$$

The characteristic values of T_N for the fluorine nuclei in CaF_2 are

$$\begin{array}{lll} H_0 \parallel [001], & T_d < 0, & T_N = -6.2\cdot 10^{-7}\,°K, \\ H_0 \parallel [001], & T_d > 0, & T_N = 3.4\cdot 10^{-7}\,°K, \\ H_0 \parallel [011], & T_d > 0, & T_N = 3.1\cdot 10^{-7}\,°K, \\ H_0 \parallel [011], & T_d < 0, & T_N = -1.7\cdot 10^{-7}\,°K. \end{array}$$

This raises the question of how to measure the magnetic susceptibility and observe experimentally the transition of the nuclear spins to the ordered state. This can be done with the aid of the adiabatic fast passage technique, developed in the magnetic-resonance practice. By recording the dispersion signal (the so-called resonance signal, which is connected with the motion of the transverse magnetization components), one determines by the same token the transverse susceptibility of the system. But the processes of adiabatic demagnetization in a rotating coordinate system and of the adiabatic fast passage are one and the same thing, and therefore both cycles combine into one. By decreasing the detuning Δ from magnetic-resonance, we simultaneously cool the system, and follow the produced changes in the magnitude and form of the dispersion signal.

If the initial polarization is $P_i < P_N$, then a transition to the ordered state is impossible (insufficient cooling) and we obtain the usual paramagnetic-resonance signal. At $P_i > P_N$, during the adiabatic fast passage, the transition temperature is reached at a definite value of Δ, and the spins are characterized by a constant transverse susceptibility. Therefore, with further decrease of the detuning to zero, the resonance signal should remain unchanged, and consequently a "plateau" should appear on the top of the dispersion curve. By measuring the amplitude of the dispersion signal in the demagnetized state ($\Delta = 0$) at different values of the initial polarization P_i, we can plot $\chi_{\perp}$ as a function of T_d.

b) Description of Experiments

As already indicated, the experiments were performed on CaF_2 and LiF crystals. The samples with ordered structure was prepared in two stages. The first was dynamic polarization of the nuclei with the aid of the solid effect, which corresponds in our notation to cooling of the Zeeman pool to the temperature α_0^{-1}. To this end, a small concentration (one electron per 10^4 nuclear spin) of electron paramagnetic centers (U^{3+} or Tm^{2+}) were produced in the samples. Spherical samples approximately 1 mm in diameter were placed in a helium cryostat. The latter, surrounded by two pairs of crossed Helmholtz coils, was placed in a four-mm waveguide. The solid effect was produced at a temperature 0.7 °K in a field 27 kOe. The first stage lasted about four hours and yielded a polarization ~ 60%. In the succeeding experiments, a polarization close to 100% was reached[15].

To transfer the electron polarization to the nuclei, the spin system was saturated with a microwave field of resonant frequency. When the maximum nuclear polarization was reached, the microwave radiation was turned off.

The second stage of cooling the dipole system consists in adiabatic demagnetization of the nuclear spins in a rotating coordinate system. It was realized by saturating the nuclear system with a stronger RF field, with slow variation of its frequency, which differed little from the resonant frequency. The magnetization occurred at a lattice temperature 0.3–0.4°K, when the spin-lattice relaxation time of the Zeeman subsystem had already become exceedingly large (too large to be measured in practice), and the relaxation time of the dipole subsystem fluctuated, depending on the orientation of the field H_0, between one and five min for CaF_2 at $H_0 = 27$ kOe, $H_0 \parallel [100]$, and ~30 min for LiF at $H_0 = 50$ kOe, $H_0 \parallel [001]$. The demagnetization time amounted to only several minutes (the field was varied at a rate of approximately 1 oersted per second; the RF field amplitude was 50–100 mOe).

c) Experimental results

1) **Antiferromagnetism.** From the calculations presented above it follows that for a CaF_2 crystal in a magnetic field $H_0 \parallel [001]$, at negative spin temperature, one should expect an antiferromagnetic structure to be produced. Figure 7[15] shows a plot of the dispersion signal of the fluorine nuclei in fast passage as a function of the detuning and of the initial polarization P_i. At an initial nuclear polarization $P_i = 28\%$ and a negative temperature, no singularities in the waveform of the dispersion curve were observed. This is understandable, if it is recognized that the smallest dipole temperature reached in the demagnetization is determined by the initial polarization of the nuclei in the magnetic field. Therefore at polarizations smaller than P_N (32.6)%) the spin system remains during the entire time of the demagnetization in a paramagnetic state, and the susceptibility is subject to the Curie law with changing T_d.

At initial polarizations higher than P_N, the shape of the dispersion curve changes. The center of the curve acquires the plateau typical of the transverse susceptibility in the antiferromagnetic state, thus indicating that the susceptibility is independent of the temperature (curve 2 of Fig. 7).

The transition to the ordered state, as predicted by the theoretical analysis, is possible for one and the same crystal at both positive and negative spin temperatures. Therefore the experimental confirmation of these transitions is convincing proof of the validity of introducing the concept of spin temperature also at very low temperatures.

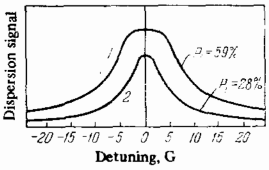

FIG. 7. Dispersion (fast-passage) signal for CaF_2 as a function of the initial polarization P_i.

Figure 8 shows a plot of the dispersion-signal amplitude of the fluorine nuclei in CaF_2 against the initial polarization for two cases corresponding to positive and negative temperatures in a field $H_0 \parallel [001]$.[15,16] Whereas Fig. 7 shows two fast-passage curves, in order to clearly demonstrate the change of the shape of the dispersion signal when the nuclear spin system goes over into the antiferromagnetic state (the appearance of the plateau), to obtain the results shown in Fig. 8, a series of similar curves was plotted for different values of the initial polarization P_i, followed by a determination of the dispersion-signal amplitude at exact resonance. As noted above, the dispersion signal at resonance is proportional to the transverse susceptibility, and the change of the initial polarization leads to a change in the phonon temperature T_d of the system in the demagnetized state. Therefore Fig. 8 describes in fact the change of $\chi_\perp$ as a function of the spin-system temperature. At negative temperature, $\chi_\perp$ ceases to depend on T_d starting with $P_i \sim 35\%$, which is very close to the theoretical value $P_N = 32.6\%$. The theoretically predicted value $P_N = 59\%$ is in qualitative agreement also with the fact that for values of P_i lower than 50%, at positive temperatures, no transition to the ordered state is observed (the curve marked by triangles in Fig. 8). Experiments with larger values of the initial polarization have not been performed.

The longitudinal susceptibility of CaF_2 was measured in[15] with an NMR spectrometer. The experiment was performed at $H_0 \parallel [001]$ and $T_d < 0$. According to the predictions of the theory considered above, under these conditions the critical value of the initial polarization is $P_N = 0.236$ (Eq. (43)). A decrease of the longitudinal susceptibility at $P_i > P_N$ was clearly observed, in full agreement with the expected behavior of $\chi_\parallel$ of a system of nuclear spins in the antiferromagnetic state, since an increase of the polarization corresponds to a decrease in the absolute value of the temperature T_d (see Fig. 6).

The first experiments on the observation of the ordered state of nuclear spins LiF were performed recently. In contrast to CaF_2, it is impossible to order separately each spin system, and both the spins of Li^7 and F^{19} take part in the ordering. Figure 10 shows the results obtained for the transverse susceptibility. These results are not as obvious as in the case of CaF_2. The

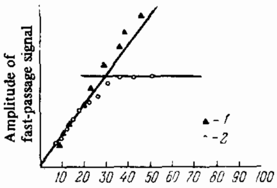

FIG. 8

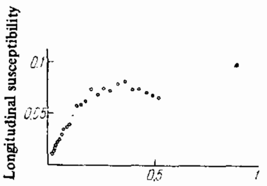

FIG. 9

FIG. 8. Experimentally obtained dependence of the transverse susceptibility of fluorine nuclei in CaF_2 in a rotating coordinate system on the initial polarization at negative (1) and positive (2) temperatures.

FIG. 9. Dependence of the longitudinal susceptibility in a zero field on the initial polarization for a spherical CaF_2 sample at negative temperature.

apparent reason is the low initial polarization of the nuclei, which does not make it possible to reach the plateau. If, however, we compare the dependences of $\chi_\perp$ on the dipole-system energy at $T_d < 0$ and $T_d > 0$, then we must agree with the opinion of the authors of[15] that a transition to the antiferromagnetic state has "almost been obtained."

2) **Ferromagnetism.** It is reported in[13] that nuclear ferromagnetic domains were produced in CaF_2 following adiabatic demagnetization of the fluorine at $T_d < 0$ in a magnetic field $\mathbf{H}_0$ oriented along [111]. In the opinion of the authors, the ferromagnetic-domain structure customarily called "ferrosandwich" is produced under these experimental conditions (Fig. 11). These domains take the form of layers perpendicular to the magnetic field. The domain structure is much larger than the interatomic distance. The magnetization is parallel to the field and reverses sign from layer to layer. Observation of the formation of this ordered state was based on observation of the NMR signal from the Ca^{43} nuclei located at the center of a cube made up of fluorine nuclei. The content of this isotope is low (0.13%) and therefore does not exert a significant influence on the ordering of the fluorine nuclei. The magnetic field produced by the fluorine nuclei, when combined with the external field H_0, causes the precession frequencies of the Ca^{43} spins to be different for the domains with magnetization parallel and antiparallel to the external field. This is revealed experimentally by the splitting of the NMR line when the fluorine spin system goes from the paramagnetic state to the ferromagnetic state.

Figure 12 shows two NMR signals of Ca^{43}. One of them is observed for demagnetization of fluorine nuclei with initial polarization $P_i = 90\%$, and the other after reversal of the magnetization, when the nuclei have again the same polarization as before, and there is no ordering in the spin system. The signal in the demagnetized state consists of two well-separated lines that are symmetrical about the central line. This proves that the fluorine nuclei produce dipole local fields at the locations of the Ca^{43} nuclei and shift the resonance lines in opposite directions. This splitting cannot be the result of an antiferromagnetic structure in the form of two fluorine sublattices, inasmuch as the fields of these sublattices cancel exactly the Ca^{43} NMR line shift connected with each sublattice. The local field at the location of the Ca^{43} nuclei is equal to zero. This point of view is confirmed by observation of an individual Ca^{43} line (Fig. 12b) in the case when the fluorine nuclei are in the antiferromagnetic phase at $H_0 \parallel [100]$. To the contrary, the action of two macroscopic ferromagnetic-structure regions in the form of a sandwich explains the observed effect satisfactorily.

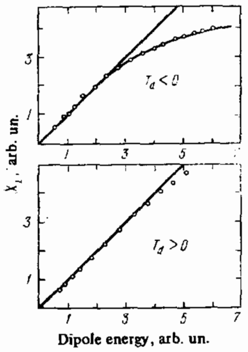

FIG. 10. Dependence of the nuclear susceptibility of LiF on the energy of the dipole-dipole pool ($H_0 \parallel [100]$).

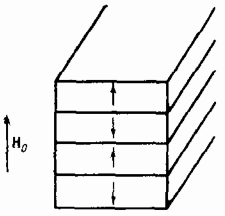

FIG. 11

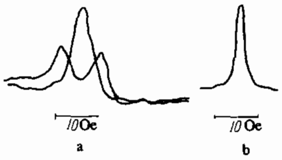

FIG. 12

FIG. 11. Domain structure produced upon demagnetization of CaF_2 in a field $H_0 \parallel [111]$ at a negative dipole temperature. The domain magnetization is indicated by the arrows.

FIG. 12. NMR signals from the nuclei of Ca^{43} (0.13%) in CaF_2 following demagnetization of the nuclear-spin system of the fluorine. The external magnetic field is applied along [111]. One can see clearly two lines that can be due to the action of macroscopic magnetic fields produced by the ferromagnetic domains whose magnetizations are oppositely directed (see Fig. 11). As the nuclear spins of the fluorine relax, the lines come closer together and merge into one when the system goes over into the paramagnetic state.

5. CONCLUSION

We have seen that the conditions for the appearance of ordered states of nuclear spins, which arise spontaneously when magnetic dipole-dipole interactions are produced between them, can be realized at a relatively high crystal-lattice temperature. The nuclear-spin system turns out to be practically insulated from the remaining degrees of freedom of the solid already at a temperature 0.4–0.3°K, and its temperature can be externally controlled and varied in an exceedingly wide range.

With the aid of a strong constant microwave or RF field, using methods of dynamic polarization of nuclei, it is possible to produce in the system a high degree of nuclear-spin orientation both in a physically selected direction, and in a direction opposite to it. The deep cooling of the nuclear system to temperatures 10^{-6}–10^{-7} °K has become possible because of the pioneer work of the Soviet physicists B. N. Provotorov and the French physicist A. Abragam, which served as the basis for the methods of dynamic polarization of nuclei in solids.

The method described above for observing nuclear antiferromagnetism and ferromagnetism is based on measurement of a dispersion signal and of an NMR signal proportional to the transverse nuclear susceptibility of the spin system. It was used by the French physicist and has demonstrated good agreement between the expected and observed dependences of the magnetic susceptibility and of the critical ("spontaneous") magnetization on the temperature, and also the measured values of the phase-transition temperature ("Curie temperature"). This agreement not only confirms the existing theoretical concepts, but also provides additional assurance of the correctness of the interpretation of the experimental results.

At the present time, several groups at Saclay employ not only NMR methods, but also neutron-diffraction methods for the observation and the study of nuclear ordering.

A direct confirmation of the existence of nuclear antiferromagnetism, ferrimagnetism, and ferromagnetism, and also of other possible spin-structure ordering can be obtained from experiments on the scattering of neutrons in targets with oriented nuclear spins. The study of the angular distribution and of the polarization of slow neutrons passing through such a nuclear target makes it possible to determine directly the structure of the nuclear ordering, and to observe the onset and the vanishing of "strong" nuclear magnetism. The most convenient for experiments of this type are primarily LIF crystals, in each sublattice of which there are nuclei of both elements, as is typical of the antiferromagnetic structure. The first successful experiments performed at Saclay confirm this conclusion.

It should be noted that the change of the cross section for the scattering of slow neutrons by the magnetic moments of nuclei, depending on the ordering, does not exceed several microbarns and cannot be observed by means of such an experiment.

Thus, in addition to the well investigated phenomenon of nuclear paramagnetism, there is no other reason of speaking of nuclear antiferromagnetism and probably ferromagnetism.

The progress in the theory and technique of magnetic resonance, and especially the development of methods of dynamic polarization of nuclei, has stimulated the development of new trends in solid-state theory, low-temperature physics, neutron diffraction, neutron magnetism, and the technique of producing targets with oriented nuclei and beams of polarized particles. By the same token, a close connection was observed between a number of trends in solid-state physics and nuclear physics, which previously appeared to be completely unrelated.

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