NUCLEAR MAGNETIC ORDERING

M. GOLDMAN

Centre d'Etudes Nucléaires de Saclay, 91-Gif sur Yvette, France

ABSTRACT

Because of the smallness of dipolar interactions between nuclear spins in diamagnetic solids, temperatures of the order of 10^{-6} K or less are required to produce nuclear magnetic ordering. In our study, we cool only the nuclear spins in a two-step process. The spins are first polarized in high field by the 'solid effect' to an equivalent temperature of a few mdeg and then demagnetized in the rotating frame, which lowers their temperature below 10^{-6}K. Experiments have been so far mostly limited to magnetic resonance measurements on the ^{19}F spins in CaF_2. The parallel and perpendicular susceptibilities exhibit a behaviour characteristic of antiferromagnetism. Results on perpendicular susceptibility and critical field are in qualititative agreement with an extension of the Weiss field theory. Neutron diffraction experiments on CaF_2 and magnetic ordering studies on LiF are in progress.

I INTRODUCTION

The study of nuclear magnetic ordering has been pursued for several years at Saclay[1–6]. It now involves A. Abragam, M. Chapellier, J. F. Jacquinot, V. Bouffard and S. Cox, besides the author. Neutron diffraction studies related to nuclear ordering are also being done by C. Long, P. Mériel and G. L. Bachella.

All results obtained so far are of nuclear magnetic measurements performed on the ^{19}F spin system in CaF_2, and limited to situations where theory predicts the occurrence of nuclear antiferromagnetism. A new experimental set up is at present being installed with the hope of studying nuclear magnetic ordering in LiF and LiH. On the other hand, preliminary neutron diffraction measurements have been performed in order to determine the experimental conditions that will allow characterization of nuclear magnetic ordered structures by neutron diffraction.

The survey of this study that is now presented emphasizes the general principles of production of nuclear ordering, the theoretical approach for predicting the properties of the ordered state, and the nature of the information yielded by experiment. The experimental results, still too few to be considered more than preliminary, provide however qualitative or semi-quantitative confirmation of the correctness of the predictions. Little will be said of the experimental and technical difficulties that limit the rate of obtaining results.

II PRINCIPLE OF THE PRODUCTION OF NUCLEAR MAGNETIC ORDERING

We consider nuclear spin systems subjected to pure dipole–dipole interactions. If nuclear magnetic ordering is to take place at low temperature the transition temperature for that ordering must be such that kT_c is comparable with the spin–spin interaction between nuclei nearest neighbours, that is typically a few kHz. Since $k \simeq 20$ kMHz, this corresponds to values of T_c of the order of 10^{-6}K. The problem of producing nuclear magnetic ordering is then that of cooling to such low temperatures nuclear spin systems in low or zero field. The procedure we have chosen is to work with dielectric solids under conditions where the nuclear spins are very loosely coupled to the lattice, and to cool the nuclear spins only, whereas the rest of the lattice remains at relatively high temperature. The choice of the lattice temperature is in part dictated by the conditions of having a sufficiently slow nuclear spin–lattice relaxation.

The cooling of the nuclei is performed in a two-step process. The first step consists in cooling the nuclear spins in a high d.c. magnetic field through the dynamic enhancement of their polarization. For spins $\frac{1}{2}$, for instance, the polarization is related to the temperature by the equation

$$P = \tanh(\hbar\omega_n/2kT_S) \tag{1}$$

where ω_n is the Larmor frequency of the spins and T_S their temperature. It is apparent from this equation that increasing the polarization is equivalent to reducing the temperature. For instance, nuclei of Larmor frequency $\omega_n/2\pi = 100$ MHz polarized to 50 per cent have a spin temperature:

$$T_S = 4.5 \times 10^{-3}\text{K} \tag{2}$$

The dynamic polarization of the nuclei is performed by the 'solid effect'[7], which consists in inducing by an rf field mutual-flip transitions between the nuclear spins and paramagnetic electronic spins present at low concentration in the sample. It is possible by this method to impart to the nuclei a polarization either equal or opposite to the thermal equilibrium polarization of the electronic spins which, under proper conditions is very close to unity. For instance, electronic spins $\frac{1}{2}$ of Larmor frequency $\omega_e/2\pi = 130$ GHz at a temperature $T_L = 0.5$K have an equilibrium polarization

$$P_{e(\text{eq})} = \tanh(\hbar\omega_e/2kT_L) \simeq 0.999992 \tag{3}$$

The second step of the nuclear cooling consists in an adiabatic demagnetization of the nuclei from the high initial field H_0 to zero. In zero applied field, the nuclei still feel the local dipolar field H_L of their neighbours. As an order of magnitude the ratio of final to initial temperatures is comparable with

$$T_f/T_i \sim H_L/H_0 \tag{4}$$

Using as typical values $H \sim 20$ kG and $H_L \sim 2$ G, this ratio is of the order of 10^{-4}. This estimate, together with equation 2 shows that, starting from a temperature $T_L \sim 1$K in a field $H \sim 20$ kG, it is possible by this two-step

cooling method to reach the desired final temperature range of 10^{-6}K in zero field.

As is well known in nuclear magnetic resonance, the nuclear adiabatic demagnetization does not need to be done by actually decreasing the applied field to zero but can equally well be performed in the rotating frame. When a nuclear spin system of Larmor frequency ω_n in high field is irradiated with an rf field H_1 rotating at a frequency ω, the evolution of its density matrix, in a frame rotating at that frequency ω around the direction of the d.c. field, is governed by the time-independent effective Hamiltonian (in frequency units)

$$\mathscr{H}_{\text{eff}} = \Delta I_z + \omega_1 I_x + \mathscr{H}'_{\text{D}} \tag{5}$$

where

$$\Delta = \omega_n - \omega, \ \omega_1 = -\gamma H_1,$$

and $\mathscr{H}'_{\text{D}}$ is the secular part of the dipole–dipole interactions. It is assumed, and well verified by experiment that, provided Δ is not too large, the system reaches quickly a state of quasi-equilibrium characterized by a density matrix in the rotating frame of the form:

$$\sigma = \exp(-\hbar\mathscr{H}_{\text{eff}}/kT_{\text{S}})/Tr\{\exp(-\hbar\mathscr{H}_{\text{eff}}/kT_{\text{S}})\} \tag{6}$$

The adiabatic demagnetization in the rotating frame consists in a decrease of Δ from a relatively large value to zero. This decrease has to be slow enough for the system to be at all times in a state close to equilibrium, in which case the entropy of the system is conserved during the demagnetization.

When $\Delta = 0$, and provided ω_1 is small enough, the effective Hamiltonian reduces to the truncated dipole–dipole interactions $\mathscr{H}'_{\text{D}}$. It is the low-temperature properties of a system subjected to this Hamiltonian that we seek to investigate. When the system consists of one spin species, this Hamiltonian is of the form:

$$\mathscr{H}'_{\text{D}} = \tfrac{1}{2}\sum_{i,j} A_{ij}[2I^i_z I^j_z - \tfrac{1}{2}(I^i_+ I^j_- + I^i_- I^j_+)] \tag{7}$$

with

$$A_{ij} = (\gamma^2\hbar/2r^3_{ij})(1 - 3\cos^2\theta_{ij}) \tag{8}$$

where r_{ij} is the distance between spins I_i and I_j and θ_{ij} the angle the vector joining them makes with the direction of the applied d.c. field.

Since the form of the secular Hamiltonian $\mathscr{H}'_{\text{D}}$ depends on the orientation of the d.c. magnetic field with respect to the crystalline axes, it is possible to change $\mathscr{H}'_{\text{D}}$ within limits simply by rotating the crystal in the field. One can thus, with one crystal, study the map of ordered states of the nuclear spin system as a function of orientation of the d.c. magnetic field. Another possibility offered by nuclear spin systems isolated from the lattice is the choice of the sign of the temperature. When starting the demagnetization in the rotating frame, if the effective field $h = -\Delta/\gamma$ is chosen parallel to the magnetization, the temperature of the system is positive and remains so during the adiabatic demagnetization. The properties of the system at low positive temperatures are those of the lower part of its energy spectrum. If on the contrary h is chosen antiparallel to the magnetization the spin tempera-

ture is negative. The properties of the system at negative temperatures of low absolute value are those of the upper part of its spectrum.

Nuclear spin systems subjected to truncated dipole–dipole interactions offer a 'clean' problem for the study of magnetic ordering. The Hamiltonian of these systems is known accurately and one is left with a well-defined problem of statistical mechanics, that of relating known microscopic interactions to the macrascopic properties of the systems. The approximate statistical methods of magnetism have to be tested on systems with interactions markedly different from the usual Heisenberg interactions. Furthermore the quantity most directly accessible to measurement is the entropy of the system, which is simply related to the initial polarization and which does not vary during the demagnetization. The various quantities measured in the demagnetized state are then known as functions of entropy.

The entropy being very sensitive to short-range order, the correct account of its value is a very severe test for the validity of any approximate theory. It will be shown later how one can measure the energy and the temperature of the system, and then study the variation of other quantities as a function of these.

The 'cleanliness' of the problem can in fact be claimed only for pure samples, whereas the samples studied contain, by necessity, paramagnetic impurities in order to polarize the nuclei by the solid effect. The concentration of these impurities needs to be kept very low in order not to disturb the nuclear ordering phenomenon, while still allowing large nuclear dynamic polarization. Satisfaction of these contradicting requirements is but one of the difficulties of this kind of experiments.

The study of nuclear magnetic ordering has been started with the simplest possible system, a simple cubic array of nuclear spins $\frac{1}{2}$. all of the same nuclear species, namely ^{19}F spins in CaF_2. The theoretical analysis will be mostly limited to this simple system, which will make it easier to exhibit the main features expected from theory. We will also, as a rule, consider only samples of spherical shape.

III THEORETICAL ANALYSIS OF NUCLEAR MAGNETIC ORDERING

The kind of theoretical developments required depends largely on the nature of the physical measurements that can be performed.

The first prediction to be made is that of the structures of the nuclear ordered states. Unambiguous confirmations of these structures cannot be obtained from nuclear magnetic measurements but only from neutron diffraction studies. The difficulties and problems raised by neutron diffraction will be discussed later. In the absence of direct structural determination, the purpose of nuclear magnetic experiments must be to measure as many physical quantities as possible, compare them to predictions from as good theories as possible and to hope for overall agreement. The situation has been quite analogous in the study of magnetic ordering of electronic spins, where the advent of neutron diffraction ascertained the existence of long-conjectured antiferromagnetism.

We will first discuss the nature of the ordered structure, then the various

nmr measurements that can be done and the kind of information they yield, and finally the type of approximate theories used for predicting the properties of the ordered states.

(A) Nuclear magnetic ordered structures

The method we use is based on the local Weiss-field approximation[8]. A particular spin $\boldsymbol{I}_i$ experiencing a local field $\boldsymbol{H}_i$ from its neighbours, we write that

$$\langle \boldsymbol{I}_i \rangle = \tfrac{1}{2}(\boldsymbol{H}_i/|\boldsymbol{H}_i|)\tanh(\tfrac{1}{2}\beta\gamma\boldsymbol{H}_i) \tag{9}$$

where β is the inverse temperature. The magnetizations becoming infinitely small at the critical temperature, we have

$$\langle \boldsymbol{I}_i \rangle = \tfrac{1}{2}(\boldsymbol{H}_i/|\boldsymbol{H}_i|)\tfrac{1}{2}\beta_c\gamma\boldsymbol{H}_i = \tfrac{1}{4}\beta_c\gamma\boldsymbol{H}_i \tag{9'}$$

There are N such equations for the N spins of the sample. Among all structures satisfying equation 9′ the stable one, that is the one of lowest free energy, is that corresponding to the lowest value of $|\beta_c|$. It can also be shown that this structure remains the stable one down to zero temperature. The local field $\boldsymbol{H}_i$ is related to the dipole–dipole energy by the equation

$$\langle \mathscr{H}'_{\mathrm{D}} \rangle = -\tfrac{1}{2}\gamma \sum_i \boldsymbol{H}_i \cdot \boldsymbol{I}_i \tag{10}$$

This method predicts in CaF_2 the occurrence of three different antiferromagnetic structures corresponding to

$$I_z^i = I_0 \exp(i\boldsymbol{k} \cdot \boldsymbol{r}_i) \tag{11a}$$

$$\beta_c = -2[A(\boldsymbol{k})]^{-1} \tag{11b}$$

where $A(\boldsymbol{k})$ is the Fourier transform of A_{ij}

$$A(\boldsymbol{k}) = \sum_j A_{ij} \exp[i\boldsymbol{k} \cdot (\boldsymbol{r}_i - \boldsymbol{r}_j)] \tag{12}$$

These structures are:

Structure I: Magnetic field $H_0 \| [001]$

Negative temperature. The vector $\boldsymbol{k}$ of equation (11a) is the vector $\boldsymbol{k}_1(k_{1x} = 0;\ k_{1y} = 0;\ k_{1z} = \pi/a)$ where a is the crystalline parameter.

In alternate planes (001) the nuclear spins are successively parallel and antiparallel to H_0.

The Néel temperature is:

$$T_{\mathrm{N}} = -6.2 \times 10^{-7}\mathrm{K}$$

Structure II: Magnetic field $H_0 \| [001]$

Positive temperature. The vector $\boldsymbol{k}$ is

$$\boldsymbol{k}_2\left(k_{2x} = \frac{\pi}{a};\ k_{2y} = \frac{\pi}{a};\ k_{2z} = 0\right)$$

Alternate planes (110) carry opposite magnetizations parallel to H_0. The Neél temperature is

$$T_{\mathrm{N}} = 3.4 \times 10^{-7}\mathrm{K}$$

Structure III: Magnetic field $H_0 \| [110]$
Positive temperature. The vector $\boldsymbol{k}$ is

$$\boldsymbol{k}_3 \left(k_{3x} = 0;\ k_{3y} = 0;\ k_{3z} = \frac{\pi}{a} \right)$$

Alternate planes (001) carry opposite magnetizations parallel to H_0.
The Néel temperature is

$$T_N = 3.1 \times 10^{-7} \text{K}$$

There are cases, for instance when $H_0 \| [111]$, when equations 9′ have no simple solution, which makes us suspect that the stable structure may be rather complicated. We have not pushed further the investigation of these cases.

Calculation predicts the same antiferromagnetic structures for LiF and LiH, each sublattice containing spins of both nuclear species.

(B) Nuclear magnetic measurements

All measurements will be analyzed with reference to antiferromagnetic structures.

1. *Dispersion signal during a fast passage*

The adiabatic demagnetization in the rotating frame is performed under rf irradiation by sweeping the field from a value far from resonance down to resonance. If the sweep proceeds further it corresponds to adiabatic remagnetization. The whole process is the well-known fast passage during which it is possible to observe the dispersion signal, that is the magnetization in phase with the rf field. Viewed from the rotating frame this magnetization is static and proportional to the transverse susceptibility $\chi_\perp$ of the system. Particularly interesting is the value of $\chi_\perp$ at the centre of the passage, that is in zero effective field. Furthermore, the variation of the signal through the passage can yield the value of the critical field for the transition from the high-effective-field paramagnetic structure to the low-effective-field antiferromagnetic structure.

2. *Longitudinal magnetization*

The magnetization along the d.c. field direction in the presence of a small effective field is proportional to the parallel susceptibility $\chi_\parallel$ of the system. This magnetization being static in the rotating as well as in the laboratory frame is much more difficult to measure than the transverse magnetization. The most direct method to determine it is to measure the field created by the magnetized sample in its neighbourhood. This is done practically by recording the shift of the nuclear resonance frequency of liquid helium-3 bathing the sample.

3. *Absorption signal in the demagnetized state*

If the fast passage is stopped at exact resonance and the driving rf field turned off, it is possible to observe the magnetic absorption signal with a

small, non-saturating rf field, from which it is possible to draw several pieces of information.

Let ω_n be the nuclear Larmor frequency. The absorption at the frequency $\omega_n + \Delta$ corresponds, in the rotating frame, to the absorption from a *rotating* rf field of frequency $+\Delta$. We observe in effect the antiferromagnetic resonance with a rotating field of low frequency (a few kHz) while benefiting from the sensitivity of magnetic resonance at the high frequency $\omega_n (\sim 100$ MHz). This measurement yields the antiferromagnetic resonance frequency, which is simply related to the sublattice magnetizations, as well as the width of the resonance lines, which depends on spin–spin relaxation in the antiferromagnetic state.

The first moment of the absorption signal (or more exactly $\int \Delta v(\Delta)\, d\Delta$) is proportional to the spin–spin energy $\langle \mathscr{H}'_D \rangle$. Knowledge of this energy as a function of entropy yields the temperature of the system, through the relation

$$dS/d\langle \mathscr{H}'_D \rangle = T_S \tag{13}$$

Furthermore, the variation of $\langle \mathscr{H}'_D \rangle$ as a function of time is a measure of spin–lattice relaxation in the antiferromagnetic state.

4. Miscellaneous measurements

Suppose that besides the nuclear spins whose ordering is being studied the sample contains a small amount of nuclear spins of different species, whose perturbing effect on the system will be negligible. These nuclei can be for instance ^{87}Sr in SrF_2 or ^6Li in LiF or LiH. When irradiated at a distance Δ from their resonance, their effective Zeeman coupling ΔS_z gets thermally coupled to the dipole–dipole reservoir of the main spins. The measurement of $\langle S_z \rangle$ after equilibrium has been reached yields directly the value of the temperature T_S. For the case of ^6Li in LiF, since there are lithium nuclei in each sublattice of the predicted antiferromagnetic structures the ^6Li resonance must split into two lines whose distance is proportional to the sublattice magnetizations: we observe nuclear magnetic resonance in an antiferromagnet.

(C) Approximate theoretical approaches

The main theoretical effort has been concentrated first on the Weiss field approximation, because of its simplicity, and on an extension of the Weiss field approximation, the reduced trace method. Spin wave and random phase approximations, which yield rather poor results at the price of heavy computation, will not be considered here.

1. Weiss-field approximation[9]

This approximation, already used for finding the stable structures, approximates the coupling of a spin $\boldsymbol{I}_i$ with the others by a Zeeman coupling with the average field created by these other spins. The nuclear magnetization is obtained self-consistently from equation 9. This approximation retains only the long-range order of the system and neglects its short-range order. It predicts that however small the initial polarization the system becomes anti-

ferromagnetic after adiabatic demagnetization. This obviously wrong result is due to the poor value of the entropy in this approximation.

An approximate value of transition entropy can be obtained by combining Weiss-field approximation and high temperature approximation for spin temperature theory, as follows. Within the Weiss-field approximation, the transverse susceptibility $\chi_\perp$ in the antiferromagnetic state is found to be independent of temperature (that is also of entropy) and equal to

$$\chi_\perp = \xi/A(\boldsymbol{k}) = -\xi\beta_c \tag{14}$$

where ξ is a numerical constant.

The constancy of $\chi_\perp$ is a well-known characteristic property of antiferromagnets containing one spin species.

On the other hand, at high temperature, i.e. low initial polarization P_i, $\chi_\perp$ in the demagnetized state is proportional to P_i and equal to

$$\chi_\perp = \xi P_i/(\gamma H'_L) \tag{15}$$

where H'_L is the local field in the rotating frame.

They become equal for an initial polarization P_0 such that

$$P_0 = \gamma H'_L/A(\boldsymbol{k}) \tag{16}$$

The corresponding entropy S_0 is close to the transition entropy S_c. Using the numerical values

for $H_0 \| [001]$ $\quad \gamma H'_L = 3.16\,(\gamma^2\hbar/2a^3)$

$A(\boldsymbol{k}_1) = 9.687\,(\gamma^2\hbar/2a^3)$

$A(\boldsymbol{k}_2) = -5.352\,(\gamma^2\hbar/2a^3)$

for $H_0 \| [110]$ $\quad \gamma H'_L = 1.96\,(\gamma^2\hbar/2a^3)$

$A(\boldsymbol{k}_3) = -4.843\,(\gamma^2\hbar/2a^3)$

we find the following values for P_0:

for $H_0 \| [001]$, $T_S < 0$ $\quad P_0 = 0.326$ (17a)

$T_S > 0$ $\quad P_0 = 0.59$ (17b)

for $H_0 \| [110]$, $T_S > 0$ $\quad P_0 = 0.405$ (17c)

As for the parallel susceptibility $\chi_\parallel$ it is equal to $\chi_\perp$, to first order, in the paramagnetic state, and given by equation 15; in the antiferromagnetic state it decreases when the entropy is decreased and vanishes at zero entropy, that is at initial polarization $P_i = 1$. This behaviour is also characteristic of antiferromagnetism.

Another prediction of the Weiss-field approximation is that $\chi_\perp$ increases when one approaches resonance down to the critical field H_c and then decreases slightly from H_c to 0. The transition is of second order for initial polarizations $P_i \leqslant 65$ per cent and first order above this value.

In the case of LiF, one should be able to measure separately the susceptibilities of the ^{19}F spins and the ^{7}Li spins. It is found from theory that their transverse susceptibilities in zero field are not constant in the antiferro-

magnetic state, due to the fact that the ratio of fluorine-to-lithium polarization in each sublattice depends on temperature. The transverse susceptibility of ^{19}F is expected to decrease, and that of ^{7}Li to increase as the entropy is lowered.

2. Reduced trace method[10–11]

All thermodynamic properties of the system depend on its partition function

$$Z = Tr\{\exp(-\beta\mathscr{H})\} \tag{18}$$

Let us call I and S the nuclear spins in each sublattice $\mathscr{A}$ and $\mathscr{B}$, respectively, of the antiferromagnetic structure. Each sublattice contains $N/2$ spins. If we decompose the Hilbert space of the system into subspaces corresponding each to well defined values of sublattice polarizations

$$\langle \Sigma I_z^i \rangle = \tfrac{1}{4} N p_A$$
$$\langle \Sigma S_z^j \rangle = \tfrac{1}{4} N p_B$$

the trace in equation 18 can be written as a sum of partial traces taken over the various subspaces:

$$Z = \Sigma Tr'\{\exp(-\beta\mathscr{H})\} \tag{19}$$

It is assumed that $Tr'\{\exp(-\beta\mathscr{H})\}$ is sharply peaked at a particular set of values of p_A and p_B, equal to the sublattice polarizations at the temperature β^{-1}. We may in equation 19 replace the sum by the Tr' of maximum value:

$$Z \simeq Tr'\{\exp(-\beta\mathscr{H})\} = Tr'(1) \times \frac{Tr'\{\exp(-\beta\mathscr{H})\}}{Tr'(1)} \tag{20}$$

(where 1 is the unit operator) whence the free energy is given by:

$$\begin{aligned} F &= -\beta^{-1} \ln(Z) \\ &= -\beta^{-1} \ln[Tr'(1)] - \beta^{-1} \ln[Tr'\{\exp(-\beta\mathscr{H})\}/Tr'(1)] \end{aligned} \tag{21}$$

An approximate value of F is obtained by using an expansion of the last bracket in powers of β. The values of p_A and p_B are obtained from:

$$\frac{\partial F}{\partial p_A} = \frac{\partial F}{\partial p_B} = 0 \tag{22}$$

We have used an expansion of βF to β^2. The term in β gives the Weiss-field value for energy and entropy; the term in β^2 introduces a first-order correction for short-range order.

This approximation has been used for the antiferromagnetic structure I ($H_0 \| [001]$ and $T_S < 0$) to derive as a function of temperature the sublattice magnetizations, energy, entropy, transverse and longitudinal susceptibilities and transition field.

It predicts an entropy transition corresponding to an initial polarization $P_i = 0.38$, a value of $\chi_\perp$ in zero field within 10 per cent of the value of equation

14, and second-order transitions for $P_i \leqslant 0.80$ and first-order transitions above.

This approximation has also been used as part of approximate theories of spin–lattice and spin–spin relaxation in the antiferromagnetic states.

It is intended to push the expansion of equation 21 to β^4.

IV MAGNETIC RESONANCE EXPERIMENTAL RESULTS ON ^{19}F IN CaF_2

Evidence for nuclear antiferromagnetism has been obtained with two different types of crystals of CaF_2.

The first type consists of CaF_2 doped with U^{3+} ions at a nominal concentration of 2×10^{-4} at./Ca^{2+}, the actual concentration, unknown, being probably less than that. The solid effect is performed at 0.5 to 0.6K in a bath of pumped helium-3, in a field $H_0 \simeq 27$ kG with a microwave frequency of 70 GHz, using an esr g-factor equal to 1.86. The maximum nuclear polarization is of the order of 70 per cent calibrated against the thermal-equilibrium signal at 4.2K.

The second crystal is doped with Tm^{2+} ions at a concentration of 2×10^{-4} at./Ca^{2+}. The solid effect, performed at the same temperature and field, uses a microwave frequency of 130 GHz, appropriate to the g-factor of 3.45 of Tm^{2+}. The routine polarization obtained after 2 to 3 hours is about 90 per cent. It is calibrated through the value of the second moment of the absorption line, whose theoretical variation with polarization is given by:

$$M_2 = M_2^0(1 - p^2) \tag{23}$$

The experimental value of the second moment extrapolated to zero polarization is larger than the theoretical value. The difference is attributed to the random fields created by the Tm^{2+} ions. It corresponds to a concentration of 1.5 to 2×10^{-4} at./Ca^{2+}.

The samples have a diameter between 1 and 1.3 mm. After the dynamic polarization, the helium-3 bath is cooled down to 0.28K. At this temperature, the spin–lattice relaxation time of the dipole–dipole interactions is in both crystals about 4 minutes. The Zeeman spin–lattice relaxation time is too long to be measured.

The fast-passage dispersion signals have been observed in the U^{3+}-doped samples with initial polarization up to 55 per cent. With $H_0 \| [001]$ and at negative temperatures, the transverse susceptibility first increases with initial polarization and then becomes constant, as expected. The experimental value of P_0 is about 30 per cent, actually very close to the theoretical value of 32.6 per cent. In the domain of initial polarizations where $\chi_\perp$ is constant, the fast-passage signal exhibits a plateau, in qualitative accordance with theoretical expectation. The values of critical field H_c deduced from these signals, although known with poor accuracy, are in qualitative agreement with theory.

The same measurements performed on the Tm^{2+}-doped sample exhibit the same qualitative features. The value of P_0 they yield is however substantially higher, of the order of 40 to 45 per cent. Investigations are under

way to find out whether this discrepancy is due to the perturbing effect of the Tm^{2+} ions.

Longitudinal susceptibility measurements in zero field have been performed on that same crystal, starting from initial polarizations between 60 and 70 per cent. The experiment consisted in observing as a function of time the effect on the resonance line of nearby ^3He of the modulated field caused by a slow adiabatic modulation of the effective field h experienced by the ^{19}F nuclei around the value 0. This modulated field at the site of ^3He, proportional to the magnetization of the CaF_2 sample, was observed first to increase by about 20 per cent before decreasing, during the heating of the system by spin–lattice relaxation. This observation yields the qualitative result that $\chi_{\|}$ decreases as the temperature is lowered below a threshold value, which is characteristic of antiferromagnets.

Experimental work on CaF_2 is now aimed at using samples of lower impurity concentration, in order to investigate and minimize the perturbation caused by the electron paramagnetic ions, and at having lower lattice temperatures, in order to increase the dipole–dipole spin–lattice relaxation time.

V NEUTRON DIFFRACTION EXPERIMENTS

We give only a brief and preliminary report of the neutron diffraction measurements performed so far.

It is common practice to study ordered magnetic structures of electronic spin systems. The neutron coherent scattering amplitude by a paramagnetic ion depending on the relative orientation of their spins because of their magnetic interaction, a periodic magnetic structure gives rise to superlattice neutron diffraction lines allowing determination of that structure.

The nuclear magnetic moments being approximately 1000 times less than those of paramagnetic ions, the magnetic interaction between a neutron and a nucleus is too small to give a significant spin-dependent contribution to scattering amplitude. There is however another source for a spin-dependent contribution to the scattering amplitude, which is the strong interaction between the neutron and the nucleus. This contribution is known and is very large for protons. For ^{19}F nuclei, this contribution was not known but was expected on theoretical grounds to be large enough to allow observation of the superlattice lines of antiferromagnetic CaF_2.

The preliminary experiment that has been done consists in observing the diffraction of polarized neutrons on polarized ^{19}F nuclei and comparing the intensities of diffraction lines when the neutron and nuclear polarizations are parallel and antiparallel. The result is that the spin-dependent contribution is about ten times smaller than expected and in any case much too small to allow determination of ordered structures of ^{19}F spins.

The most promising system on which neutron diffraction study of nuclear magnetic ordering can be attempted is now LiH, on which dynamic polarization studies are just being started.

VI CONCLUSION

The study of nuclear magnetic ordering by the methods described above opens a new field for the investigation of phase transitions.

The existence of spin–spin interactions markedly different and more accurately known than is usually the case in statistical systems widens the possibility of confronting statistical theories with physical reality. Also important in this respect are the possibilities of changing continuously the microscopic interactions in the rotating frame by rotating the sample in the magnetic field and, in systems with several spin species, of having different effective fields for the different spin species.

Furthermore, with the methods of investigation of nuclear magnetic ordering belonging to the field of magnetic resonance, which depart notably from the standard magnetic measurements, the phenomena associated with magnetic ordering are visualized from a different angle. Because of the smallness of the interactions, the properties of these systems give a physical meaning to the temperature scale around 10^{-6}K which, for any other physical system, is hardly distinguishable from absolute zero.

The observation of antiferromagnetism under such unusual conditions as effective interactions in a rotating frame and negative temperature illustrates the usefulness of nuclear spin systems as 'model' systems in thermodynamics.

REFERENCES

[1] A. Abragam, *Compt. Rend.* **251**, 225 (1960).
[2] A. Abragam, *Compt. Rend.* **254**, 1267 (1962).
[3] M. Goldman, in *Magnetic Resonance and Radiofrequency Spectroscopy* (Edited by P. Averbuch) p. 157. North–Holland, Amsterdam (1969).
[4] M. Chapellier, M. Goldman, Vu Hoang Chau and A. Abragam, *Compt. Rend.* **268**, 1530 (1969).
[5] M. Chapellier, M. Goldman, Vu Hoang Chau and A. Abragam, *J. Appl. Phys.* **41**, 849 (1970).
[6] M. Chapellier, *Proc. Low Temp. Conf. LT 12*, Kyoto (1970) (To be published).
[7] A. Abragam and W. G. Proctor, *Compt. Rend.* **246**, 2253 (1958).
[8] J. Villain, *J. Phys. Chem. Solids*, **11**, 303 (1959).
[9] See for instance J. S. Smart, *Effective Field Theories of Magnetism*, W. B. Saunders Co., Philadelphia (1966).
[10] J. G. Kirkwood, *J. Chem. Phys.* **6**, 70 (1938).
[11] R. Brout, *Phase Transitions*, p. 12. Benjamin, New York (1965).