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Phase diagrams of ordered nuclear spins in LiH : a new phase at positive temperature ?

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Résumé. — Un ordre antiferromagnétique des spins nucléaires $^7\text{Li}$ et $^1\text{H}$ est produit par une polarisation dynamique suivie d'une désaimantation adiabatique dans le référentiel tournant. Le champ magnétique est parallèle à la direction [001]. L'ordre a été étudié, pour des températures de spin positive et négative, à la fois par des mesures de R.M.N. et par diffraction de neutrons. La polarisation de sous-réseau en champ effectif nul a été mesurée en fonction de la température. Les diagrammes de phases entropie/champ effectif et température/champ effectif ont été établis. A température positive, les résultats suggèrent l'existence d'une nouvelle phase, non prévue par l'approximation de Weiss.

Abstract. — An antiferromagnetic order of the nuclear spins of $^7\text{Li}$ and $^1\text{H}$ is produced by Dynamic Polarization followed by Adiabatic Demagnetization in the Rotating Frame. The magnetic field is parallel to a [001] direction, and both positive and negative spin temperatures are investigated. The ordering is studied by means of Nuclear Magnetic Resonance and neutron diffraction. The sublattice proton polarization in zero effective field is measured as a function of temperature. The entropy/effective field and temperature/effective field phase diagram are established. At positive temperature, the results suggest the onset of a new phase, not predicted by the Weiss-field approximation.

Introduction.

In the studies of nuclear magnetic ordering, a collection of nuclear magnetic moments in a crystal are put into experimental conditions where they can undergo a transition to a spontaneous magnetic ordering. This ordering is due to internuclear forces, which, so far as we are concerned, are purely dipolar. Owing to the weakness of the nuclear magnetic moments, the critical field is of the order of ten Gauss, and the critical temperature is lower than one microkelvin. This rather extreme experimental condition can be achieved in a two-step process: first the entropy of the system is reduced by means of Dynamic Nuclear Polarization (D.N.P.) in high field. Then the effective field is eliminated by Adiabatic Demagnetization in the Rotating Frame (A.D.R.F.), which consists in performing an adiabatic fast passage on the spins, stopped exactly at the center of the resonance. It can be shown that, although the spin system is still subjected to a strong external magnetic field, the Hamiltonian responsible for the ordering is only the dipolar Hamiltonian, or rather the truncated dipolar Hamiltonian, which is that part of the total dipolar Hamiltonian which commutes with the Zeeman Hamiltonian [1]. One attractive feature of this technique is the ability to study the ordered state by Nuclear Magnetic Resonance (N.M.R.) in high field, and reference [1] reviews a number of results obtained in this line. However, the study of nuclear magnetic ordering has taken up a new dimension with the use of neutron diffraction.

Slow neutron diffraction is widely used in the study of electronic ordered structures. Its use in the study of nuclear ordering is more recent. The interaction between an electronic moment and the neutron is of magnetic origin. Owing to this interaction, the scattering of the neutron depends on the relative orientations of the electron and neutron spins. If the interaction between a nuclear spin and a neutron were purely magnetic, this method would be useless, because of the weakness of the nuclear magnetic moment. Fortunately, apart from the magnetic interaction, there exists another interaction between the spin of the nucleus and that of the neutron, the origin of which is in the nuclear forces.
A detailed study of neutron diffraction by an isolated nucleus and by a target containing polarized nuclei is given in [2].

The scattering amplitude of a neutron by a nucleus of spin $I$ can be written:

$$a = b_0 + bI \cdot S,$$

where $b$ and $b_0$ are two constants determined experimentally.

Equation (1) allows one to define a « pseudomagnetic moment » $\mu^*$, directly related to $b$ by:

$$\mu^* = \frac{I}{|\langle g_n \rangle|} \frac{b}{r_0} \mu_B$$

$r_0$ is the classical radius of the electron, $\mu_B$ is the Bohr magneton, $|\langle g_n \rangle| = 1.91$, and $\mu^*$ is a fictitious magnetic moment which, under certain conditions, would scatter the neutrons in the same way as does the nuclear spin [2].

The pseudomagnetic moments of various species have been measured systematically [3]; the proton spin turned out to carry the highest nuclear $\mu^*: 5.4 \mu_B$. Henceforth, the first observation of a nuclear antiferromagnetic structure was performed in LiH [4, 5].

Neutron diffraction has demonstrated clearly the occurrence of the antiferromagnetic structure in LiH at $T < 0$ for $H//\langle 001 \rangle$, but the signal-to-noise ratio in the EL3 reactor [6] was too weak for: 1) conveniently observing the structure at $T > 0$, and 2) studying the phase diagrams, even at $T < 0$. The new reactor ORPHEE of Saclay, thanks to a neutron flux about ten times higher did allow these two observations, which are reported in this article.

1. Ordered structures in LiH in non-zero effective field: phase diagrams.

The crystalline structure of LiH is that of two interpenetrating fcc sublattices of $^7$Li and of $^1$H. The $\mu^*$ of $^7$Li is $-0.67 \mu_B$. The nuclear spins of the two species are $I = 1/2$ for protons (gyromagnetic ratio $\gamma_1$) and $S = 3/2$ for $^7$Li (gyromagnetic ratio $\gamma_5$). The truncated dipolar of Hamiltonian of this system is:

$$\mathcal{H}_d = \frac{1}{2} \sum_{i,j} A_{ij} (2 I_{ix} I_{jx} - I_{ix} I_{jx} - I_{iy} I_{jy}) +$$
$$+ \frac{1}{2} \sum_{\mu, \nu} B_{\mu \nu} (2 S_{\mu x} S_{\nu x} - S_{\mu x} S_{\nu x} - S_{\mu y} S_{\nu y})$$
$$+ \sum_{\mu, \nu} C_{i,\mu} (2 I_{ix} S_{\mu x}),$$

with

$$A_{ij} = \gamma_1^2 h (1 - 3 \cos^2 \theta_{ij})/2 r_{ij}^3 \quad (A_{ii} = 0)$$

$$B_{\mu \nu} = \gamma_5^2 h (1 - 3 \cos^2 \theta_{\mu \nu})/2 r_{\mu \nu}^3 \quad (B_{\mu \mu} = 0)$$

and

$$C_{i,\mu} = \gamma_1 \gamma_5 h (1 - 3 \cos^2 \theta_{i,\mu})/2 r_{i,\mu}^3.$$
compute the free energy of the various possible phases.

The energy of the mixed phase is written:

\[ E = N x [\Delta (3 p_C + \alpha p_C) / 2 + (3 p_C \omega_C + p_C \omega_e) / 4] + \\
+ N (1 - x) [\Delta p_A \alpha + 3 (p_A \omega_A + p_B \omega_B) / 4 + (p_a \omega_a + p_b \omega_b) / 4] / 2 \]  

(5)

with

\[ p_{AF} = \frac{3}{\alpha} \cdot \frac{p_A + p_B}{2} + \frac{p_a + p_b}{2} = - \gamma_s \hbar \]

and

\[ \alpha = \frac{\gamma_I}{\gamma_S} = 2.421 \, . \]

The \( \omega_a \)'s are the Larmor frequencies in the various Weiss fields, and are written:

\[ \omega_A = - \left( 1 - \frac{1}{2} \alpha \psi q_2 p_{AF} + 3 q_1 \frac{p_A - p_B}{2} + \\
+ q_3 \frac{p_a - p_b}{2} + \frac{r}{\alpha} \hbar \right) \]

\[ \omega_B = - \left( 1 - \frac{1}{2} \alpha \psi q_2 p_{AF} - 3 q_1 \frac{p_A - p_B}{2} - \\
- q_3 \frac{p_a - p_b}{2} + \frac{r}{\alpha} \hbar \right) \]

\[ \omega_a = - \left( \frac{1}{2} \alpha^2 \psi q_2 p_{AF} + 3 q_3 \frac{p_A - p_B}{2} + \\
+ q_1 \alpha^2 \frac{p_a - p_b}{2} + r x p \right) \]

\[ \omega_b = - \left( \frac{1}{2} \alpha^2 \psi q_2 p_{AF} - 3 q_3 \frac{p_A - p_B}{2} - \\
- q_1 \alpha^2 \frac{p_a - p_b}{2} + r x p \right) \]

\[ \omega_C = - \left( \frac{1}{2} \psi + 1 \right) \alpha q_2 p_{AF} + \\
+ \alpha q_2 \left( \frac{3}{\alpha} p_C + p_c \right) + \frac{r}{\alpha} \hbar \]

\[ \omega_c = - \left( \frac{1}{2} \psi + 1 \right) \alpha^2 q_2 p_{AF} + \\
+ \alpha^2 q_2 \left( \frac{3}{\alpha} p_C + p_c \right) + r x p \]  

(6)

\[ q_1 = B(k_0), \quad q_2 = B(0) = A(0) / \alpha^2, \quad q_3 = C(k_0), \]

\[ r = - \alpha^2 (\psi / 2 + 1) q_2. \] \( \psi \) is a constant depending upon the shape of the sample (for a spherical shape, \( \psi = 0 \)), and

\[ P = 3 p_C / \alpha + p_c - p_{AF} \, . \]

The entropy of the structure is equal to:

\[ S_i = N x (s^{3/2} + s^{1/2}) + N (1 - x) \times \\
\times (s^{3/2} + s^{3/2} + s^{1/2} + s^{1/2}) / 2 \]  

(7)

\[ s^{3/2} \] and \( s^{1/2} \) are the entropies for respectively a spin \( S = 3/2 \) and a spin \( I = 1/2 \).

The principle of the calculation consists in determining \( p_A, p_B, p_C, p_a, p_b, x \) and the inverse temperature \( \beta \) in such a way as to maximize (at negative temperature), or minimize (at positive temperature) the free energy \( F = E - S_i / k_B \beta \).

We have then a system of 8 equations:

\[ S_i = \text{Const.}, \quad \frac{\partial F}{\partial p_a} = 0, \quad \text{with } \alpha = A, B, C, a, b, c, \]

and

\[ \frac{\partial F}{\partial x} = 0 \, . \]  

(8)

The free energy determined for the mixed phase is then compared to those of purely paramagnetic or purely antiferromagnetic phases. The field-entropy phase diagrams obtained by this methods are shown in figures 2 and 3.

Fig. 2. — Predicted effective field/entropy phase diagram with \( H / (001) \) at negative temperature in the Weiss-field approximation.

Fig. 3. — Predicted effective field/entropy phase diagram with \( H / (001) \) at positive temperature in the Weiss-field approximation.
One can also plot the field-temperature phase diagrams. The only change consists in fixing \( j_8 \) instead of \( S_1 \).

In CaF\(_2\), a more refined phase diagram could be computed, using the restricted-trace approximation [8]. In LiH, this method yields a system of non-linear equations that is absolutely intractable.

2. Experimental methods

The D.N.P. is performed using F-centres, created by electronic irradiation [9]. The magnetic field is oriented along a [001] direction of the crystal. The maximum polarization obtained on these samples is of order 85% for \(^7\)Li, which corresponds to 97% for \(^1\)H, after 3 days of microwave irradiation. The A.D.R.F. must be performed simultaneously on both \(^1\)H and \(^7\)Li nuclei. The ordered structures have been produced and studied in a field of 5.5 tesla. The electronics of the N.M.R. has been renewed since the EL3 experiments. It is now driven by a Commodore P.E.T./C.B.M. microcomputer, equipped with a home-made MC-12 « multichannel » card in which the N.M.R. spectra are recorded. This allowed versatile operation, and easy processing of the recorded data.

The P.E.T./C.B.M. was also used to drive a series of coaxial relays in order to automate the switching between the high-level R.F. conditions for the A.D.R.F. to the low-level conditions for the N.M.R. recording. The advantage of this automation is twofold: 1) It is possible to set elaborate sequences like the one described in section 3.2. 2) It eliminates the presence of any human operator near the magnet, which is highly desirable because of the high neutron leak on the 3T1 channel of ORPHEE.

2.1 USE OF NEUTRON DIFFRACTION. — All the experiments described here have been performed with the magnetic field parallel to the [001] direction. The principle of the measurements is wellknown: it is based on the appearance, in the antiferromagnetic state, of a so-called « superstructure line », corresponding to the 110 reflection. The latter is absent in the paramagnetic state. The neutron wavelength is \( \lambda = 1.134 \) Å.

The intensity of the diffraction line is obtained by means of a « rocking-curve »: a neutron counter with an aperture wider than the outgoing diffracted beam is placed in the approximate position of the reflection. The neutron counts at fixed time intervals are plotted as a function of the angular position of the crystal, which is rotated along a vertical axis [11]. The intensity of the line is proportional to the area of the curve obtained in this way.

The 110 line contains a small contribution (about 1%) of the 220 reflection at \( \lambda / 2 \) wavelength. This contribution has been measured and is systematically subtracted from the intensity measurements on the 110 reflection.

The broadening of the lines has been studied in [12]. It was shown that the broadening of the superstructure lines is due to the presence of small antiferromagnetic domains of thickness about 180 Å. Furthermore, the Lorentzian shape of the superstructure lines revealed a Poisson distribution of the domain size in the direction of the diffracted beam.

Sublattice polarization as a function of the intensity. — The intensity of a diffraction line is related to the scattering factor \( F \) through:

\[
I = kAByF^2/\sin(2\theta)
\]

where

\[ k = \text{an instrumental factor}, \quad A = \text{the absorption of LiH in the given angular position}, \quad B = \text{the absorption of } ^3\text{He contained in the dilute phase}, \quad y = \text{the extinction coefficient and } \theta = \text{the Bragg angle of the reflection}. \]

The numerical values of these factors for the two lines studied are:

- \( A_{110} = 0.726 \), \( A_{220} = 0.667 \), \( B_{110} = 0.522 \), \( B_{220} = 0.440 \), \( 2\theta_{110} = 22.94 \) deg.,
- \( 2\theta_{220} = 46.86 \) deg. and \( y(220) = 0.694 \) at zero nuclear polarization.

The value of \( k \) is deduced from the intensity of the 220 reflection. The extinction for the 220 line, as well as the absorption have been deduced from the variation of intensity of this line as a function both of the wavelength at zero polarization and of the proton polarization for a given wavelength (Fig. 4) [13]. For the 110 line the extinction is negli-

Fig. 4. — Intensity of the 220 reflection as a function of the proton polarization. a) Without absorption nor extinction. b) Without extinction but with absorption. c) With extinction but without absorption. d) With both absorption and extinction. The best fit with the experimental data (full circles) corresponds to a mosaic distribution of FWHM \( 3 \times 10^{-4} \) radian.
gible, because each domain, owing to its small thickness \( d \approx 180 \text{ Å} \), produces an angular dispersion of the diffracted waves of order \( \lambda / d \approx 0.3 \text{ deg} \). Very few neutrons can be scattered more than once.

The factor \( F_{220} \) at zero polarization is related to the scattering amplitudes by:

\[
|F_{220}| = |b_0 + b_{0\text{Li}}|
\]  
(10)
with

\[
b_{0\text{H}} = -0.374 \quad \text{and} \quad b_{0\text{Li}} = -0.207 .
\]

In zero effective field, let us name

\[
P_H = |P_a| = |P_b| \quad \text{and} \quad P_{\text{Li}} = |P_A| = |P_B|.
\]

One has:

\[
\begin{align*}
F_{110} &= b_H IP_H + b_{\text{Li}} SP_{\text{Li}} \quad \text{for} \quad T > 0 \\
F_{110} &= b_H IP_H - b_{\text{Li}} SP_{\text{Li}} \quad \text{for} \quad T < 0
\end{align*}
\]  
(11)
with

\[
b_H I = 1.46 \quad \text{and} \quad b_{\text{Li}} S = -0.17
\]

\( P_{\text{Li}} \) is deduced from \( P_H \) by assuming that the ratio \( P_{\text{Li}}/P_H \) is as deduced from the Weiss-field approximation. This last hypothesis is not completely correct, but the error it induces can be neglected, since the contribution of \( P_{\text{Li}} \) to the diffracted beam intensity is only about 20% of that of \( P_H \).

By means of formulae (9), (10) and (11), and reporting the numerical values, one gets:

\[
\frac{I_{110}}{I_{220}} = 10.304 F_{110}^2 .
\]  
(12)

Formula (12) is used for measuring the sublattice polarization. Furthermore, the disappearance of the superstructure line indicates unambiguously the disappearance of the ordered state, or rather the disappearance of the predicted antiferromagnetic structures. This property has been used to plot the experimental phase diagrams (section 3.2).

2.2 N.M.R. MEASUREMENTS. — Our crystal contains three spin species: \( ^7\text{Li}, ^1\text{H} \) and \( ^6\text{Li} \). Their Larmor frequencies in a field of 5.5 tesla are respectively 90 600 MHz, 233 125 MHz and 34.3 MHz. The two former frequencies have been carefully adjusted in order that their resonance fields coincide within a few tenths of Gauss, by a method which is explained below.

2.2.1 Measurements on \( ^7\text{Li} \) and \( ^1\text{H} \). — The entropy in the demagnetized state is deduced from the polarizations prior to the A.D.R.F. When the latter is not stopped exactly at resonance, the effective field (relative to the resonance field) is equal to the field at which the absorption signal vanishes. This can be proved quite generally and provides an easy way of determining the effective field. In particular, one can check that the two species are in the same effective field, and this method was used to adjust the two N.M.R. frequencies.

2.2.2 Measurements on \( ^6\text{Li} \). — Two types of information are obtained from the N.M.R. of this stable isotope of \( ^6\text{Li} \) (of concentration 3% and spin \( I = 1 \)): 1) In the antiferromagnetic state, the signal is split into two (or more!) lines, because \( ^6\text{Li} \) spins belonging to different sublattices experience different average dipolar fields from the ordered spins. 2) The temperature \( T = 1/k_B \beta \) of the spin system can be deduced from the absorption signal, as shown in [14].

3. Experimental results.

3.1 ENTROPY FIELD PHASE DIAGRAM. — In this type of experiment, the two spin species \( ^1\text{H} \) and \( ^7\text{Li} \) are subjected to an adiabatic fast passage, until complete reversal of the polarizations. This is done slowly enough to allow continuous neutrons counting. The appearance and the disappearance of the superstructure signal take place at the transition field \( H_{c2} \) (Fig. 5). The entropy is deduced to within a

5% uncertainty from the entropy before and after the demagnetization, which are not too different, since the yield of the A.D.R.F. is of order 90% (to improve somewhat the accuracy, the entropy is assumed to vary linearly as a function of the effective field between \( + \) and \( -35 \text{ G from resonance} \), an admittedly crude approximation). The results of this method are given in figure 6 for \( T < 0 \).

The critical effective field \( H_{c2} \) is theoretically equal to 11.8 G at zero entropy. The measured value is significantly higher. A similar, although smaller effect was seen in \( \text{CaF}_2 \) [8], where the restricted
trace approximation gave much better predictions than the Weiss-field approximation. However, in LiH, there is another explanation to this discrepancy, as will be pointed out later.

The transition field $H_{c1}$ between the antiferromagnetic state and the mixed phase could not be measured by neutrons with enough confidence, in spite of several attempts. One of these attempts was based upon the appearance of a cusp in the curve of the neutron counts as a function of the effective-field: it is shown in [10] that at constant temperature, the various polarizations $P_A, \ldots, P_{c}$ remain constant in the whole field interval of the mixed phase, so that the parameter $x$ must vary linearly with $\Delta$. Theoretical calculations not reproduced here and the measurements of section 3.2 (Fig. 8) indicate that the temperature is indeed almost constant in the mixed phase (as well as in the pure antiferromagnetic phase below $H_{c1}$). In this case, the intensity of the neutron signal should vary linearly between $H_{c2}$ and $H_{c3}$. Below $H_{c1}$, the neutron signal is proportional to $(P_A - P_B)^2$, which theory does not predict to vary significantly as a function of $\Delta$; this signal should therefore remain constant, whence the expected cusp at $H_{c1}$. No such cusp was found (Fig. 5).

Another attempt to measure $H_{c2}$ was based upon the observation of the width of the 220 diffracted beam. An extra width was expected between $H_{c2}$ and $H_{c1}$, due to the presence of thin domains with different magnetizations (the longitudinal susceptibility in the antiferromagnetic state is lower than in the paramagnetic state). Accordingly, a cadmium mask was made, with two horizontal slots in such a way as to mask completely the 220 line (this could be checked before A.D.R.F. by performing a rocking curve in the 220 position, and observing no diffraction line). During the A.D.R.F., only that component of the neutron diffracted beam which corresponds to a broadening of the 220 line, i.e. the part which goes through the two slots, is detected. Indeed, we observed a signal below $H_{c2}$, but it did not vanish completely as expected in low effective field. Furthermore, the broadening was not the same at $\Delta > 0$ and $\Delta < 0$ (Fig. 7).

If the mixed-antiferro transition is masked, this is likely to be due to the inhomogeneity of the internal field in the magnetized state, which, with our sample shape ($5 \times 5 \times 0.5$ mm$^3$), is of several Gauss i.e. of the same order as the critical field itself. Other attempts were performed on samples with an ellipsoidal shape, where a smaller internal field inhomogeneity is expected. Unfortunately, the pure LiH crystals from which we start the irradiations had been kept at room temperature since their growing (10 years ago) and contained a strong proportion of metallic lithium, which prevented us from obtaining high enough nuclear polarizations to observe the ordered states correctly. This did not happen to the rectangular samples, which had been prepared shortly after growing and kept in liquid nitrogen to maintain their content in F-centres.

3.2 TEMPERATURE EFFECTIVE FIELD PHASE DIAGRAM. — To establish the phase diagram, we have used two different methods:

— The disappearance of the neutron superstructure signal indicates the transition; the temperature and the effective field are then deduced from the resonance signals of the different spin species. The measurement simply consists in stopping the A.D.R.F. in non-zero effective field, then letting the spin system relax until complete disappearance of the neutron signal.

— A second method, which owes very little to neutrons, consists in measuring by N.M.R. the
temperature and the effective field in the course of the demagnetization, and trying to detect the transitions by the presence of an anomaly in the slopes of the curves. One can predict from a simple thermodynamical argument that, at constant entropy, the slope of the curve should be positive above \( H_{c2} \), and negative below \( H_{c1} \): this is due to the fact that:

\[
\left( \frac{\partial T}{\partial H} \right)_S = -\left( \frac{\partial M}{\partial S} \right)_H = -\left( \frac{\partial T}{\partial S} \right)_H \left( \frac{\partial M}{\partial T} \right)_H \cdot (14)
\]

Since the entropy \( S \) is an increasing function of temperature \( T \), \( \frac{\partial M}{\partial T} \) should have opposite signs.

It is well known that \( \frac{\partial M}{\partial H} \) is negative in the paramagnetic state and positive in the antiferromagnetic state, whence the predicted property. In the mixed phase, things are not so clear cut, but a Weiss-field calculation indicates that \( \frac{\partial T}{\partial H} \) is negative, and even more than in the antiferromagnetic state. Besides the observations by N.M.R., it is still possible to count neutrons in the 110 position, and this can give a rough verification of the transition field \( H_{c2} \).

A N.M.R. method is rather difficult to operate, because it involves a number of manipulations in the magnetic field, which should be done rapidly with respect to the dipolar relaxation time (of order 20 min). Figure 8 shows the type of curve obtained. \( H_{c2} \) is identified as the field where \( T \) is minimum (point A). \( H_{c1} \) could correspond to the second change in the slope (point B). If this were the case, this method would constitute the only experimental determination of \( H_{c1} \) available in LiH. The fact that the remagnetization curve is above the demagnetization one above a certain field could be explained by a large lack a reversibility induced by an hysteresis in the formation of domains.

The results obtained by the two methods are summarized in figure 9. They are in reasonable agreement with each other, but the experimental diagram is flatter and broader than the theoretical one (solid line). One reason is certainly the crudeness of the theoretical model (the Weiss-field approximation), but another can be the shape of the sample, which broadens and shifts the transitions towards high fields.

Only a few points have been obtained at positive temperature, essentially by the first method.

Fig. 8. — Spin temperature as a function of effective field, in the course of the A.D.R.F. with \( H// (001) \) for both signs of temperature. The arrows indicate the sense of variation of the effective field.

Fig. 9. — Temperatureeffective field phase diagram for \( H// (001) \) at positive and negative temperature. The full circles have been obtained by neutron diffraction (first method), the open circles have been obtained by N.M.R., and the dashed lines are deduced from all the experimental points. Solid lines are theoretical (Weiss-field).
3.3 POLARIZATION TEMPERATURE PHASE DIAGRAM. — This diagram had already been established for negative temperature [2], but the results presented here are more accurate; in addition, we present also the results for positive temperature. The method consists in measuring the sublattice polarization via the intensity of the neutron signal, and the temperature via the $^6$Li signal. The result is shown on figure 10. At negative temperature, the experimental curve has a « rounding-off » which could be explained by a temperature inhomogeneity of about 5%, quite likely since the initial polarization may have a spatial inhomogeneity of this order of magnitude.

![Fig. 10. — Proton sublattice polarization as a function of temperature (positive and negative) in zero effective-field. The external field is parallel to (001).](image)

3.4 $^6$Li SIGNAL. — As stated previously, the $^6$Li signal should exhibit two well defined peaks in the antiferromagnetic state. The ratio of these two peaks depends upon the total polarization of $^6$Li. A thermal mixing with the dipolar reservoir in the rotating frame permits an enhancement of the $^6$Li polarization, and an easier observation of these peaks [15].

At negative temperature, this was indeed the case. But at positive temperature, three peaks of unequal intensities had previously been observed [16]. These measurements have been repeated more carefully here, and the splitting in three components turned out to be systematic. A typical $^6$Li spectrum is shown figure 11. The two extreme peaks are those expected for an antiferromagnetic structure, and the central peak is centred at the Larmor frequency.

The evolution of this spectrum in the course of the dipolar relaxation was also studied, and it was discovered that, while the two extreme peaks decreased, the central peak remained unchanged. One likely explanation to this behaviour is that some parts of the sample remain paramagnetic and are responsible for the central peak. However, an unexplained phenomenon was observed: to wit, the long delay between the disappearance of the superstructure neutron signal and that of the structure of the $^6$Li N.M.R. line, the latter being considered as the signature of an ordered phase. In one experiment where the spin system relaxed at positive temperature in zero effective field, the neutron signal disappeared one hour after the end of A.D.R.F., whereas the three peaks in the N.M.R. lines were still visible after two hours. This makes one suspect the existence of an order different from the one theoretically predicted. A superstructure line at another Bragg angle would allow characterization of this new ordered structure, but it is very difficult to search a superstructure line whose angle is unknown, if the lifetime of the ordered state is only a few tens of minutes.

![Fig. 11. — $^6$Li N.M.R. absorption signals at negative and positive temperature after A.D.R.F. to zero effective-field and thermal mixing with the dipolar reservoir. $H$ is parallel to (001).](image)

4. Conclusion.

Combining neutron diffraction and N.M.R., we have plotted the entropy effective field and the temperature effective field phase diagrams in LiH. The inhomogeneity of the internal field due to the rectangular shape of the samples turns out to smoothen the expected « sharp » transitions, and to hamper comparison of the experimental results with the theoretical predictions of the Weiss-field approximation. However, at negative temperature, the general behaviour of the diagrams is, at least schematically, consistent with the predictions.

On the contrary, at positive temperature, the results suggest the onset of ordered structures not predicted by the Weiss-field approximation. This
conclusion stems from a comparison of both N.M.R. and neutron results, and would have been impossible to derive by using either of these technique alone. There is so far no clue, either theoretical or experimental, as to the nature of this new hypothetical ordered structure.

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