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Nuclear magnetic ordering in Ca(OH)$_2$. II. Restricted trace approximation

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Résumé. — Les phases magnétiques du système quasi bi-dimensionnel des spins des protons dans (OH)$_2$Ca sont étudiées en utilisant la méthode de la trace restreinte. Les résultats sont utilisés pour la description de l'évolution du système des spins nucléaires pendant une désaimantation adiabatique dans le référentiel tournant (DART) utilisée pour refroidir ce système de spins. Le cas où la température des spins nucléaires est négative et le champ magnétique extérieur est orienté parallèlement à l'axe c du cristal est étudié en détail. Pour des champs effectifs nuls on prévoit un état antiferromagnétique. Néanmoins, on trouve qu'il est possible qu'on passe par un état ferromagnétique pendant la DART, ce résultat expliquant les observations expérimentales antérieures.

Abstract. — The magnetic phases of the quasi two-dimensional proton spin system in Ca(OH)$_2$ are studied using the restricted trace approximation. The results are used to describe the evolution of the nuclear spin system during the adiabatic demagnetization in the rotating frame (ADRF), which is used to cool this spin system. The case that the nuclear spin temperature is negative and the external magnetic field is oriented parallel to the crystalline c-axis is studied in detail. If the effective field is equal to zero, the ground state is found to be antiferromagnetic. However, during the ADRF one may pass through a ferromagnetic phase, explaining earlier experimental results.

1. Introduction.

This paper concerns the ferromagnetic ordering of the quasi two-dimensional proton spin system in a Ca(OH)$_2$ (Fig. 1), observed by J. Marks [1] and J. C. M. Sprenkels [2]. Their studies were performed using a three step cooling procedure, introduced by Abragam and coworkers [3]. First, the sample is cooled to 0.5 K using a $^3$He evaporation cryostat and a magnetic field $B_0$ of about 3 T is applied. Then, the polarization $p_0 = \langle I_z \rangle / I$ of the proton spins $I = \frac{1}{2}$, is increased to typically $p^0 = 0.7$, using dynamic nuclear polarization (DNP) [4], corresponding to a reduction of the entropy of nuclear spin system to

$$s^0 = s^0/k = N \left[ \ln 2 - \frac{1}{2} \ln \left( 1 + p^0 \right) \ln \left( 1 + p^0 \right) + \ln \left( 1 - p^0 \right) \right], \quad (1.1)$$

where $N$ is the total number of spins. We have rendered the entropy dimensionless by dividing it by Boltzman's constant $k$. 

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In the final step of the cooling process, the Zeeman order which has been produced by the DNP, is transformed into dipolar order. This is achieved by an adiabatic demagnetization in the rotating frame (ADRF) [4]. In this step the externally applied magnetic field $B_0$ is kept constant contrary to the practice in a real adiabatic demagnetization. Instead an rf field $2B_1 \cos \omega t$ is applied in a direction perpendicular to the applied static magnetic field $B_0$. Its frequency $\omega$ is chosen in the neighbourhood of the nuclear Larmor frequency $\omega_0 = \gamma |B_0|$, where $\gamma = 2 \pi \times 42.5759 \times 10^6 \text{s}^{-1} \text{T}^{-1}$ is the gyromagnetic ratio of the proton spins. During the ADRF, one first varies this frequency until it is equal to $\omega_0$. Subsequently, the amplitude $2 |B_1|$ of the rf-field is reduced to zero.

In order to describe the nuclear spin system during an ADRF, one uses a frame of reference $(x, y, z)$ rotating at the rf frequency $\omega$ around its z-axis, which is chosen parallel to the externally applied magnetic field $B_0$. Furthermore, the x-axis of this rotating frame is chosen parallel to the component of the rf field, which rotates in the same direction as the rotating frame. In this rotating frame of reference, the Hamiltonian is given in frequency units by:

$$\mathcal{H} = \Delta \sum_i I_z^i + \omega_1 \sum_i I_x^i + \mathcal{H}_D \tag{1.2}$$

where $\Delta = \omega_0 - \omega$ is the so-called longitudinal effective field in the rotating frame and $\omega_1$ the transverse effective field. Furthermore, $\mathcal{H}_D'$ is the truncated dipolar Hamiltonian:

$$\mathcal{H}_D' = \sum_{i \neq j} A_{ij} \left[ I_z^i I_z^j - \frac{1}{2} (I_x^i I_x^j + I_y^i I_y^j) \right] \tag{1.3}$$

and

$$A_{ij} = \frac{\mu_0}{2} \frac{\hbar \gamma^2}{2} \frac{1 - 3 \cos^2 \theta_{ij}}{r_{ij}^3}. \tag{1.4}$$
Here \( \hbar \) is Planck's constant, \( r_{ij} \) is the vector connecting the spins \( I' \) and \( I_i \) and \( \theta_{ij} \) is the angle between \( r_{ij} \) and the externally applied magnetic field \( B_0 \). As in our previous paper [5], we assume the shape of the sample such that

\[
A^0 = \sum_i A_{ij} = 0 .
\]  

Using this Hamiltonian in the rotating frame, an ADRF simply consists of reducing the effective fields \( \Delta \) and \( \omega_1 \) adiabatically to 0. Thus, this ADRF leads to a reduction of the temperature in the rotating frame. In order to find the nature of the various magnetic phases during and after such an ADRF, we need to determine the phase diagram of the nuclear spin system at constant entropy as a function of the effective fields \( \Delta \) and \( \omega_1 \). In a previous paper [5], we performed such calculations, using the molecular field approximation, and applying to the circumstances of our experiments, i.e. the case that the longitudinal effective field \( \Delta \) is negative before the ADRF, so the spin temperature is also negative and while the externally applied magnetic field is parallel to the crystalline \( c \)-axis.

In these molecular field calculations we considered the paramagnetic phase shown in figure 2a and two types of ordered phases, a ferromagnet exhibiting a domain structure, where the domains have the shape of pancakes i.e. consist of many planes of proton spins as shown in figure 2b and furthermore an antiferromagnetic state which is shown in figure 2c. In both ordered phases, the nuclear spins within a crystal plane are parallel. The two cases differ however in the direction of the magnetization in successive planes. While in the ferromagnetic state the spins are parallel in many successive crystal planes, the orientation of the spins alternates from plane to plane in the antiferromagnetic state.

The phase diagram resulting from the molecular field approximation is shown in figure 3. It shows that the experimentally observed ferromagnetic phase is expected to occur for all values of the effective fields \( \Delta \) and \( \omega_1 \) such that

\[
\frac{\Delta^2}{A_F^2} + \frac{\omega_1^2}{A_F^2} < (\rho_0)^2 ,
\]  

where \( A_F \) is a dipole sum :

\[
A_F = \sum_j A_{ij}
\]

taken over all spins \( I' \) situated in the same crystal plane as \( I_i \).

However, if \( \Delta = 0 \), the ferromagnetic and antiferromagnetic phases are degenerate, and one cannot decide theoretically, which one will actually occur. This degeneracy arises from the highly two-dimensional nature of the proton spin system in Ca(OH)\(_2\), which is caused by the fact that the proton spins within one crystal plane are much nearer to each other than those in different planes. Then the molecular field that the spins in a given crystal plane experience, is completely due to the dipolar interaction between the spins in that crystal plane, while the contribution of other crystal planes is negligible.

The present paper is devoted to a more elaborate theoretical treatment of the ordered state of the proton spin system in Ca(OH)\(_2\). We will incorporate short range correlations using the restricted trace approximation [6, 7]. We will show that short range order lifts the degeneracy between the two possible ordered states, but that contrary to the experimental results the antiferromagnetic state is favourable. However, an analysis of the development of the nuclear spins system during the cooling procedure, shows that one still passes through the ferromagnetic state. We will show, that in order to understand our experiments, one has to
Fig. 2. — The three magnetic phases of the proton spin system in Ca(OH)\textsubscript{2} that are considered in this paper. The directions \( x \), \( y \) and \( z \) are defined in figure 1. (a) The paramagnetic phase. (b) The ferromagnetic phase. (c) The antiferromagnetic phase.
Fig. 3. — $\omega - \Delta$ phase diagram of the nuclear spin system in Ca(OH)$_2$ for $T < 0$ and $B_0$ parallel to the crystalline $c$-axis and according to the molecular field approximation. The initial polarization is $p^0 = 0.4$.

assume that a ferromagnetic state is created during the ADRF and that a transition to antiferromagnetic order does not take place afterwards because the time constant for such a transition is too long.

2. Principles of the calculation of the phase diagram.

Basic to the method of the restricted trace approximation is that each of the possible phases of a system of interacting spins can be characterized by the polarization

$$p^i = \langle I^i \rangle / I$$

(2.1)

of the individual spins. E.g., in the paramagnetic phase these polarizations are equal. On the other hand, in a ferromagnetic phase showing domains of type A, B, etc. these polarizations have a constant value $p^i = p^A$, $p^i = p^B$, etc. in each type of domain, while in an antiferromagnetic phase having two sub-lattices A and B of equal size, these polarizations are $p^A$ and $p^B$ respectively.

The determination of the magnetic phase diagram at constant entropy now consists of two steps. For each of the possible phases, we first calculate the values of the polarizations $p^i$ of the individual spins and the value of the temperature $T$, for given values of the entropy $s$ and the externally applied magnetic field $B_0$. For this purpose, we use the thermodynamic principle that in thermodynamic equilibrium the polarizations $p^i$ should be such that

$$- \beta F = \ln \mathcal{Z} = s - \beta E = \text{maximum},$$

(2.2)

where

$$\mathcal{Z} = \text{Tr} \{ e^{-\beta K} \},$$

(2.3)
s is the dimensionless entropy, \( \beta = \frac{\hbar}{kT} \) is the so-called inverse temperature,

\[
E = - \frac{\partial}{\partial \beta} \ln \mathcal{E}
\]  

(2.4)

is the energy of the spin system and \( \mathcal{H} \) is the Hamiltonian of the nuclear spin system as given by equation (1.2).

Subsequently, we determine the phase diagram by investigating for each value of the externally applied magnetic field \( B_0 \), which phase is most favourable at a given value of the entropy. Thus, if the temperature is positive, equation (2.2) implies that we have to choose the phase with the lowest energy \( E \), while at negative temperature, we have to choose the phase with the highest energy \( E \).

Both steps in the determination of the phase diagram require that we obtain expressions of the energy and the entropy as a function of the polarizations \( p^j \) for each of the possible phases.

As a starting point for obtaining these expressions, the restricted trace approximation considers a magnetic phase at a certain strength of the externally applied magnetic field and a given value of the entropy. One then considers all quantum mechanical states \( |\psi\rangle \) for which the polarization of each spin \( I \) has the value \( p^j \) which characterizes this phase. So for each of these quantum mechanical states:

\[
\langle \psi | I^j_l | \psi \rangle = I_{p^j} \mu,
\]

(2.5)

\( \mu = x, y, z \).

Subsequently, one defines the restricted trace \( \text{Tr}' \) as the trace over the subspace of Hilbert space containing all these states \( |\psi\rangle \). The value of such a restricted trace is evidently determined by the polarizations \( p^j \) of the individual spins, so one may consider the set of all possible restricted traces of an operator as a function of these polarizations. Hence, if one succeeds in expressing the entropy and the energy of the spin system in restricted traces, one has succeeded in expressing these thermodynamic quantities in the polarizations \( p^j \).

The restricted trace approximation makes two important assumptions. First, it assumes that one may replace equation (2.2), stating that thermodynamic equilibrium corresponds to a maximum of \( \ln \mathcal{E} \), by the requirement that the values of the polarizations should be such that

\[
\ln \mathcal{E}' = \text{maximum},
\]

(2.6)

where

\[
\mathcal{E}' = \text{Tr}' \{ e^{-\beta \mathcal{H}} \}.
\]

(2.7)

Thus one replaces equation (2.2) by equation (2.6) to calculate the values of the polarizations for each of the possible phases of the spin system.

The second assumption of the restricted trace approximation is that the maximum of \( \ln \mathcal{E}' \) is so sharp that one may approximate

\[
\ln \mathcal{E} \approx \ln \mathcal{E}'.
\]

(2.8)

This second assumption enables one to express the energy and the entropy of the spin system in restricted traces using equations (2.4) and (2.2):

\[
E = - \frac{\partial}{\partial \beta} \ln \mathcal{E} \approx - \frac{\partial}{\partial \beta} \ln \mathcal{E}',
\]

(2.9)

\[
s = \ln \mathcal{E} + \beta E \approx \ln \mathcal{E}' - \beta \frac{\partial}{\partial \beta} \ln \mathcal{E}'.
\]

(2.10)
Using these two assumptions, the phase diagram at constant entropy is now obtained as follows. First, one needs to evaluate the restricted trace given in equation (2.7) for each of the possible phases. For each of these phases one subsequently calculates the polarizations $p'$ of the spins and the inverse temperature $\beta$ by solving equation (2.6) under the condition that the entropy as given by equation (2.10) has a constant value $s^0$. Finally one determines the energy for each phase using equation (2.9) and decides which phase is most favourable.

3. Series expansion in the restricted trace approximation.

The evaluation of the restricted trace in equation (2.7) is still too difficult to be performed exactly. Therefore it is approximated by a series expansion. For this purpose the Hamiltonian is split into two parts $E_0$ and $\mathcal{U}$. We choose the first part, such that it is constant in the subspace of Hilbert space over which the restricted trace is taken. Hence, like a restricted trace, it can be considered as a function of the polarizations $p'$. Then

$$\mathcal{K} = E_0(p') + \mathcal{U}.$$  (3.1)

For this purpose, Goldman [7] simply splits the Hamiltonian in the Zeeman term and the dipolar interaction term. In the case of Ca(OH)$_2$ however, we found such a splitting to lead to divergences. We avoid these divergences by first splitting each spin operator in the Hamiltonian in its expectation value in the restricted part of Hilbert space and a so-called spin deviation operator $\bar{I}_\mu$:

$$I^i_\mu = I p^i_\mu + \bar{I}^i_\mu,$$

$$\mu = x, y, z.$$  (3.2)

Then the Hamiltonian given by equation (1.2) is split in a part which is constant in the part of Hilbert space over which the restricted trace is taken and two terms containing spin deviation operators:

$$\mathcal{K} = E_0(p') + \mathcal{U}_1 + \mathcal{U}_2.$$  (3.3)

The first constant term in $\mathcal{K}$ is given by

$$E_0(p') = \Delta I \sum_i p^i_z + \omega_1 I \sum_i p^i_x + I^2 \sum_{i \neq j} A_{ij} \left[ p^i_x p^j_x - \frac{1}{2} (p^i_x p^j_x + p^i_y p^j_y) \right].$$  (3.4)

Thus, $E_0(p')$ corresponds to the expression for the energy of the nuclear spin system in the molecular field approximation. Using the results of our previous paper [5], we may therefore equate $p^i_y = p^i_z = 0$.

The second term in $\mathcal{K}$ contains the terms linear in the spin deviation operators:

$$\mathcal{U}_1 = \frac{1}{I} \sum_{i, \mu} \left[ \frac{\partial}{\partial p^i_\mu} E_0(p') \right] \bar{I}^i_\mu =$$

$$= \Delta \sum_i \bar{I}^i_z + \omega_1 \sum_i \bar{I}^i_x + 2I \sum_{i \neq j} A_{ij} \left[ p^i_x \bar{I}^j_x - \frac{1}{2} p^i_x p^j_x \bar{I}^j_x \right]$$

$$\mu = x, y, z,$$  (3.5)

while, the third term in $\mathcal{K}$ contains the quadratic terms in the spin deviation operators:
Inserting the Hamiltonian (3.3) in expression (2.7) yields

\[ \ln Z' = -\beta E_0(p') + \ln \left( \text{Tr}' \left\{ \exp \left[ -\beta (\mathcal{U}_1 + \mathcal{U}_2) \right] \right\} \right). \] (3.7)

As a following step in the restricted trace approximation, one expands the second term in this expression. In first order restricted trace approximation, this is done to second order in \(\beta\). However, the occurrence of the term \(\mathcal{U}_1\) in the exponent slows down the convergence of this expansion considerably. This problem is easily solved using the fact that according to equations (2.5) and (3.2) the expectation value of the second term \(\mathcal{V}_1\) of the Hamiltonian,

\[ \langle \psi | \mathcal{V}_1 | \psi \rangle = 0 \] (3.8)

for all states \(|\psi\rangle\), over which the restricted traces are taken. Hence, \(\mathcal{V}_1\) does not contribute to the energy of the nuclear spin system and

\[ \langle \mathcal{V}' \rangle = \frac{\text{Tr}' \left\{ \mathcal{V}_1 \exp \left[ -\beta (E_0(p') + \mathcal{U}_1 + \mathcal{U}_2) \right] \right\} }{\text{Tr}' \left\{ \exp \left[ -\beta (E_0(p') + \mathcal{U}_1 + \mathcal{U}_2) \right] \right\} } = 0. \] (3.9)

Using this fact, we add a term \(\frac{1}{2} \beta \langle \mathcal{V}_1 \rangle\) to the right hand side of equation (3.7) without modifying the result:

\[ \ln Z' = -\beta E_0(p') + \ln \left( \text{Tr}' \left\{ \exp \left[ -\beta (\mathcal{U}_1 + \mathcal{U}_2) \right] \right\} \right) + \frac{1}{2} \beta \langle \mathcal{V}' \rangle. \] (3.10)

Now, we insert equation (3.9) in equation (3.10) and expand up to second order in \(\beta\). We note that using equation (3.8) and Goldman's method for the calculation of restricted traces [7], one finds that several lower order terms in the expansion vanish:

\[ \text{Tr}' \left\{ \mathcal{U}_1 \right\} = \text{Tr}' \left\{ \mathcal{U}_2 \right\} = \text{Tr}' \left\{ \mathcal{U}_1 \mathcal{U}_2 \right\} = 0. \] (3.11)

As a result:

\[ \ln Z' = -\beta E_0(p') + \ln \text{Tr}' \left\{ 1 \right\} + \frac{1}{2} \beta^2 \frac{\text{Tr}' \left\{ \mathcal{V}_2 \right\} }{\text{Tr}' \left\{ 1 \right\} }. \] (3.12)

As remarked above, the restricted traces are taken over the subspace of Hilbert space where the polarizations are given by \(p'\). Hence the term \(\ln \text{Tr}' \left\{ 1 \right\}\) and the quantity

\[ T(p') = \frac{\text{Tr}' \left\{ \mathcal{V}_2 \right\} }{\text{Tr}' \left\{ 1 \right\} } \] (3.13)

are functions of these polarizations. Thus we have expressed \(\ln Z'\) in the polarizations \(p'\).

Using equation (2.9), we can now also express the energy of the spin system in the polarizations:

\[ E(p') = E_0(p') - \beta T(p'). \] (3.14)
Furthermore, using equation (2.10) we find for the entropy

\[ s(p^i) = s_0(p^i) - \frac{1}{2} \beta T(p^i) \]  

(3.15)

where

\[ s_0(p^i) = \ln \text{Tr}' \{1\} \, . \]  

(3.16)

The determination of the phase diagram now consists of the following procedure. We first calculable the polarizations \( p^i \) and the inverse temperature \( \beta \) for each type of magnetic ordering, by maximizing \( \ln \mathcal{Z}' \) or by solving

\[ \frac{\partial}{\partial p^i_a} \left[ -\beta E_0(p^i) + s_0(p^i) + \frac{1}{2} \beta^2 T(p^i) \right] = 0 \]  

(3.17)

at a constant value \( s^0 \) of the entropy. This means we require simultaneously that

\[ s(p^i) = s_0(p^i) - \frac{1}{2} \beta^2 T(p^i) = s^0 \]  

(3.18)

Then we calculate the energy of that particular state, using equation (3.14). Finally, we obtain the phase diagram by choosing the state with the lowest or highest energy, depending on whether the temperature is positive or negative.

The molecular field approximation corresponds to taking the zero order terms in the expansion only. This means that we neglect the terms with \( T(p^i) \). Thus, in the molecular field approximation the polarizations are \( p^i_0 \) and the inverse temperature is \( \beta_0 \) and they are solutions of

\[ \frac{\partial}{\partial p^i_0} \left[ -\beta_0 E_0(p^i_0) + s_0(p^i_0) \right] = 0 \]  

(3.19)

where we require that the entropy has the constant value \( s^0 \), so

\[ s_0(p^i_0) = s^0 \]  

(3.20)

Furthermore, the energy is given by

\[ E(p^i_0) = E_0(p^i_0) \]  

(3.21)

Thus, the zero order terms in the expressions (3.14) and (3.15) for the energy and the entropy, simply correspond to the expressions for these quantities as obtained in the molecular field approximation. However, one should be aware that the actual value of these terms might differ from the value obtained in the molecular field approximation, as the values of the polarizations \( p^i \) might change upon including the higher order terms.

4. Calculation of the restricted traces.

As outlined in the previous section, we can calculate which of the three possible phases will actually occur, by solving the equations (3.17) and (3.18). In order to do this, for each of the phases, first all contributions to these equations must be determined. For the expressions for the energy \( E_0 \) and the entropy \( s_0 \) following from the molecular field approximation, we refer to our previous paper [5]. These expressions will be summarized below. The method for calculating the restricted traces \( T(p^i) \) is described in Goldman's paper on the restricted trace.
approximation [7]. A straightforward application of this method to our Hamiltonian (1.2) yields the following results for each of the three phases.

4.1 THE PARAMAGNETIC PHASE. — As is shown in figure 2a, a paramagnetic phase is characterized by a nuclear polarization which is equal for all proton spins in the sample. Furthermore, in our case the externally applied effective magnetic field $\Delta$ and $\omega_1$ are oriented in the $z$- and $x$-directions respectively so the component of the polarization parallel to the $y$-axis is equal to zero. Then, according to our previous paper [5]:

$$E_0^P(p^i) = \frac{1}{2} N \Delta p_z + \frac{1}{2} N \omega_1 p_x.$$  \hspace{1cm} (4.1)

The contribution of the dipolar interactions vanishes because we have chosen the shape of the sample such that equation (1.5) holds. Furthermore

$$s_0^P(p^i) = N \left[ \ln 2 - \frac{1}{2} \left[ (1 + p) \ln (1 + p) + (1 - p) \ln (1 - p) \right] \right],$$  \hspace{1cm} (4.2)

where $p = \sqrt{p_z^2 + p_x^2}

The restricted trace $T^P(p^i)$ is given by

$$T^P(p^i) = ND^2 \left[ \frac{1}{4} \frac{1}{12} (5 p_z^2 - p_x^2) + \frac{1}{24} (2 p_z^2 - p_x^2)^2 \right]$$  \hspace{1cm} (4.3)

where

$$D^2 = \frac{3}{4N} \sum_{i \neq j} A_{ij}^2$$  \hspace{1cm} (4.4)

is a sum which converges rapidly with the 6th power of the distance between the spins $I^i$ and $I^j$. We determined $D^2$ for the case of Ca(OH)$_2$ in the same way as Sprenkels et al. [2] and found

$$D^2 = (2 \pi)^2 \cdot 50.196 \times 10^6 \text{s}^{-2}.$$  

It should be noted that $T(p^i)$ has been calculated previously by Goldman for the case of a paramagnetic phase in the special situation that $p_x = 0$. For this purpose, he used a high temperature expansion [10], but as is to be expected his and our results are the same.

4.2 THE FERROMAGNETIC PHASE. — As shown in figure 2b, the ferromagnetic phase in Ca(OH)$_2$ is characterized by two types of domains A and B. The polarizations in the $z$ and $x$ directions of all spins in the domains of type A are given by $p_z$ and $p_x$ respectively, while for those in the domains of type B these are $-p_z$ and $p_x$. Because in our case the externally applied effective magnetic fields $\Delta$ and $\omega_1$ are oriented in the $z$- and $x$-directions respectively, the component of the polarization parallel to the $y$-axis is equal to zero in both types of domains. The total number of spins in domains of type A is equal to $xN$ and of those of type B is $(1 - x) N$. Then, according to our previous paper

$$E_0^F(p^i) = \frac{1}{2} N [\Delta(2x - 1)p_z + \omega_1 p_x + 2x(1 - x) A_F p_z^2],$$  \hspace{1cm} (4.5)

where $A_F$ is a dipole sum, which for Ca(OH)$_2$ is equal to [2]

$$A_F = 2 \pi \cdot 35.56 \times 10^3 \text{s}^{-1}.$$  \hspace{1cm} (4.6)
The molecular field value of the entropy, \( s_0 \), is given by

\[
s_0^F(p') = N \left[ \ln 2 - \frac{1}{2} \left[ (1 + p) \ln (1 + p) + (1 - p) \ln (1 - p) \right] \right],
\]

where \( p = \sqrt{p_x^2 + p_z^2} \). For the restricted trace \( T^F(p') \) we find

\[
T^F(p') = ND^2 \left[ \frac{1}{4} - \frac{1}{12} (5p_z^2 - p_x^2) + \frac{1}{24} (2p_z^2 - p_x^2)^2 \right]
\]

where

\[
D^2 = \frac{3}{4N} \sum_{i \neq j} A_{ij}^2 \quad \text{where} \quad i, j \in A,
\]

is a sum which converges rapidly with the 6th power of the distance between the spins \( I^I \) and \( I^J \). Because of this rapid convergence and because in the ferromagnetic phase the domains are large compared to the interatomic distances, the sums \( D^2 \) and \( D^2_F \) can be considered to be equal up to a very high accuracy:

\[
D^2 = D^2 = (2 \pi^2)^2 \times 50.196 \times 10^6 \text{ s}^{-2}.
\]

4.3 The Antiferromagnetic Phase. — As shown in figure 2c, the antiferromagnetic phase in Ca(OH)\(_2\) is characterized by two types of sublattices, A and B, each containing an equal number of spins. All spins in sublattice A have a polarization \( p_A^A \) with components \( p_{zA} \) and \( p_{xA} \), while those in sublattice B have a polarization \( p_B^B \) with components \( p_{zB} \) and \( p_{xB} \).

Then, in the molecular field approximation, the energy is given by

\[
E_0^{AF}(p') = \frac{1}{4} N \left[ (p_{zA}^A p_{zB}^B + p_{zB}^B p_{zA}^A) + \omega_1 (p_{xA}^A p_{xB}^B - p_{xA}^B p_{xB}^A) + A_{AF} \left( (p_{zA}^A - p_{zB}^B)^2 - \frac{1}{2} (p_{xA}^A p_{xB}^B - p_{xA}^B p_{xB}^A)^2 \right) \right].
\]

In this equation, \( A_{AF} \) is a dipole sum, which for Ca(OH)\(_2\) is given by [2]

\[
A_{AF} = A_F = 2 \pi \times 35.56 \times 10^3 \text{ s}^{-1}.
\]

The molecular field value of the entropy of the antiferromagnetic phase is equal to

\[
s_0^{AF}(p') = N \ln 2 - \frac{1}{4} N \left[ (1 + p_A^A) \ln (1 + p_A^A) + (1 - p_A^A) \ln (1 - p_A^A) \right] -
\]

\[
- \frac{1}{4} N \left[ (1 + p_B^B) \ln (1 + p_B^B) + (1 - p_B^B) \ln (1 - p_B^B) \right].
\]

For the restricted trace \( T^{AF}(p') \) we find

\[
T^{AF}(p') = \frac{1}{2} ND^2 \left[ \frac{1}{4} - \frac{1}{12} (5(p_{zA}^A)^2 - (p_{xA}^A)^2) + \frac{1}{24} (2(p_{zB}^B)^2 - (p_{xA}^B)^2)^2 \right] +
\]

\[
+ \frac{1}{2} ND^2 \left[ \frac{1}{4} - \frac{1}{12} (5(p_{zB}^B)^2 - (p_{xA}^B)^2) + \frac{1}{24} (2(p_{zA}^A)^2 - (p_{xA}^A)^2)^2 \right] +
\]

\[
+ \frac{1}{2} NC^2 \left[ \frac{1}{16} (p_{zA}^A - p_{zB}^B)^2 - \frac{1}{8} (p_{xA}^A - p_{xB}^B)^2 -
\]

\[
- \frac{1}{8} ((p_{zA}^A)^2 - (p_{zB}^B)^2)^2 - \frac{1}{32} ((p_{zA}^A)^2 - (p_{zB}^B)^2)^2 + \frac{1}{8} (p_{zA}^A p_{zB}^B - p_{zB}^B p_{zA}^A)^2 \right].
\]
where $D^2$ was defined above and

$$C^2 = \frac{1}{N} \sum_{i \neq j} A_{ij}^2$$

(4.15)

The latter sum converges rapidly with the 6th power of the distance between the $i$-th and $j$-th spin. We have calculated it in the same manner as the sum $D^2$ and found it to be given by

$$C^2 = (2\pi)^2 \times 6.013 \times 10^6 \text{ s}^{-1}.$$  

(4.16)

5. Calculation of the phase diagram.

Now we have obtained expressions for the restricted traces occurring in the equations (3.17) and (3.18), we can solve these equations for each value of the effective fields $\Delta$ and $\omega_1$ and for each of the three possible phases. Subsequently, we can determine which phase is most favourable, i.e. has the highest energy, by inserting the solutions of equations (3.17) and (3.18) in expression (3.14) for the energy.

In our previous paper, where we used the molecular field approximation, we were able to perform this task analytically for all cases, except for the antiferromagnetic phase when $\Delta = 0$. In the present treatment, using the restricted trace approximation, the more complex equations to be solved render such analytical solutions impossible, except for some very special cases. Therefore, we solved the problem numerically, using the Newton-Revson method for non-linear equations [8].

Figure 4 shows the phase diagram resulting from this calculation, as a function of the effective fields $\Delta$ and $\omega_1$, for the case that $\rho^0 = 0.4$. Upon comparison with the results of the molecular field approximation presented in figure 3, one sees an important difference. The

![Phase diagram](image_url)

Fig. 4. — $\omega_1 - \Delta$ phase diagram of the nuclear spin system in Ca(OH)$_2$ for $T \ll 0$ and $B_0$ parallel to the crystalline c-axis and according to the restricted trace approximation. The initial polarization is $\rho^0 = 0.4$. ADRF-1 is the path of the ADRF as used by Sprenkels. ADRF-2 is a proposed path avoiding a metastable ferromagnetic phase.
latter approximation yields an antiferromagnetic phase only if $\Delta = 0$, while under those circumstances it is still degenerate with the ferromagnetic phase. On the other hand, in the restricted trace approximation this degeneracy is lifted. Thus, as long as $\Delta$ is small, the antiferromagnetic phase is favourable for all values of $\omega_1$.

It is interesting to note, that our observation that short range correlations favour the antiferromagnetic phase with respect to the ferromagnetic phase, also follows from the following simple argument originating from J.-F. Jacquinot [9].

Using a classical description like the molecular field approximation, the energy of the ferromagnetic as well as the antiferromagnetic phases is determined by terms of the type $A_{ij} I^i_z I^j_z$ only. Contributions to the energy originating in terms of the type $A_{ij} (I^i_x I^j_x + I^i_y I^j_y)$ are neglected. In a quantum mechanical treatment, one may not always neglect these latter terms. Consider e.g. an antiferromagnetic state, where half the spins has $\langle I^i_z \rangle = + \frac{1}{2}$, while the other half has $\langle I^i_z \rangle = - \frac{1}{2}$. If we neglect terms of the type $A_{ij} (I^i_x I^j_x + I^i_y I^j_y)$, this state is degenerate with a second state where all spins are inverted. If however, we take this latter term into account it mixes both states, leading to one with a higher energy and one with a lower energy, thus rendering one of these mixed states more favourable than each of the two original states. On the other hand, ferromagnetic states do not show this type of degeneracy. So in that case, the extra terms do not lead to such a qualitatively different result between a quantum mechanical and a classical description. Then, if a classical description yields the same energy for an antiferromagnetic and a ferromagnetic phase, one may expect that in a quantum mechanical description, the extra contribution to the energy originating in the term $A_{ij} (I^i_x I^j_x + I^i_y I^j_y)$, should favour the antiferromagnetic phase.

Our result, that for larger values of $\Delta$, the ferromagnetic phase still becomes more favourable than the antiferromagnetic phase, can be understood completely by using the molecular field approximation only. The parallel susceptibility is much larger for a ferromagnet than for an antiferromagnet. Therefore, the former gains more energy than the latter when a parallel effective field is applied, eventually rendering it more favourable. Equivalently, for small values of $\Delta$ but increasing values of $\omega_1$, the spin system remains antiferromagnetic, because the transverse susceptibilities of both ordered phases are the same.

6. Comparison with experiments and conclusion.

We now compare our calculations with experimental results obtained by Sprenkels et al. [2]. His experiments were performed under the conditions described in section 1. However, the ADRFs were not always complete. I.e. first the parallel effective field $\Delta$ was reduced to a value $\Delta_0$ which was not necessarily equal to zero. Subsequently, the transverse effective field $\omega_1$ was turned off. The development of the effective fields during such an ADRF is indicated in figure 4 as ADRF-1. After each of these ADRFs, the NMR signal was recorded. From this signal the average polarization in the z-direction

$$\bar{p}_z = \frac{1}{N} \sum_i p^i_z$$

and the energy of the nuclear spin system was determined, using the methods described in reference [4]. The results for $\bar{p}_z$ as a function of $\Delta_0$ are shown in figure 5 for the case that $p^0 = 0.7$. For each of the values of $\Delta_0$, also the decay of the energy of the nuclear spin system after the ADRF was recorded. For all values of $\Delta_0$ shown in figure 5, an analysis of this decay leads to the conclusion that the nuclear spin system was ferromagnetic.
In order to compare these experimental results with the theoretical treatment presented above, we calculate the phase diagram for \( \rho^0 = 0.7 \). We take into account that in the experiment of Sprenkels, the shape of the sample is such that demagnetizing fields can not be neglected. For his sample, \( A^0 = 2 \pi \cdot 32.12 \times 10^3 \text{s}^{-1} \) [2]. As a result, the phase transitions are shifted to lower values of \( \Delta \) than shown in figure 4, where \( A^0 = 0 \). We find that a phase transition between the ferromagnetic and antiferromagnetic phase should occur at \( \Delta = 2 \pi \cdot 0.4 \times 10^3 \text{s}^{-1} \). Hence, the two ADRFs to \( \Delta_0 = 0 \) shown in figure 5, should have lead to an antiferromagnetic phase. However, this theoretical prediction is in strong contradiction with the experimentally observed decay of the energy of the nuclear spin system, from which Sprenkels deduced that the nuclear spin system was really ferromagnetic.

In order to get more information about this disagreement between experiment and theory, we use the restricted trace approximation in the way described above, to calculate \( \bar{\rho}_z \) for both the antiferromagnetic and ferromagnetic phase. The results are also plotted in figure 5. Clearly, the experimental results at \( |\Delta_0| > 2 \pi \cdot 0.4 \times 10^3 \text{s}^{-1} \) agree with the predictions for a ferromagnetic phase and hence they are consistent with the analysis of the decay of the energy after the ADRF. Unfortunately, there are insufficient data at \( |\Delta_0| < 2 \pi \cdot 0.4 \times 10^3 \text{s}^{-1} \) to obtain similar extra support for the existence of a ferromagnetic phase at these lower values of the longitudinal effective field.

However, the consistency between the observed decay of the energy and \( \bar{\rho}_z \) at higher values of \( |\Delta_0| \), does confirm that it is correct to use the decay of the energy to conclude whether the nuclear spin system is ferromagnetic or not. Hence, Sprenkels conclusion that the nuclear spin system is ferromagnetic at \( \Delta_0 = 0 \) must be correct. In this way, these determinations of \( \bar{\rho}_z \) still yield extra support for our observation that at \( \Delta_0 = 0 \) experimentally a ferromagnetic phase is observed, while theoretically an antiferromagnetic phase is predicted.

The explanation of this contradiction may be found in the short time scale of the experiment. After the ADRF, the nuclear spin system heats up with the so-called nuclear dipolar relaxation time, which in the experiment of Sprenkels is about 80 s. So, on a time scale...
of this order of magnitude, the temperature rises to above the critical temperature. On the other hand, the phase transition from a ferromagnetic to an antiferromagnetic phase is first order and it takes a finite time to change from a macroscopic domain structure to a microscopic sublattice structure. In Sprenkels case, the domains are very large — he estimates a thickness of the order of \(10^3\) atomic layers. Then, this phase transition might take too long compared to the heating of the nuclear spin system. Hence, the ferromagnetic phase is observed, though in fact it is metastable.

If this explanation is correct, one may avoid this problem and really observe the antiferromagnetic phase as follows. Then, the ADRF is performed using a very strong rf field, as indicated in figure 4 by ADRF-2. So, one does not pass through an intermediate ferromagnetic phase that would persist as a metastable stable after finishing the ADRF.

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