

## POLARIZED TARGETS : HOW?

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### INTRODUCTION

It is well known that an assembly of magnetic moments  $\mu$  embedded in a sample of bulk matter in thermal equilibrium at a temperature  $T$  will, when placed in a magnetic field  $H$ , orient themselves preferentially in the direction of the field. This orientation is not perfect : there is competition between the magnetic energy  $\mu H$  which tends to orient the moments parallel to the field and the thermal energy  $kT$ , which destroys the orientation. If  $N$  is the number of moments per unit volume, the magnetization  $M$  along the field will reach the value  $M = N\mu P$  where  $P$ , a number smaller than unity, is called the polarization. For weak polarizations,  $P$  is simply the ratio  $\mu H/kT$  of these two energies ; this is the celebrated Curie law. For nuclear spins  $I$  the magnetic moment is an operator  $\mu_n = \sigma_n \hbar I$  where  $\sigma_n$  is a constant, characteristic of the nuclear species. The nuclear polarization  $P_n$  is the ensemble average  $\langle I_z \rangle / I$ , taken over all the spins of the sample,  $Oz$  being the direction of the field.

For a spin  $I = 1/2$ ,  $P_n$  is given by :

$$P_n = \tanh \left( \frac{\sigma_n \hbar H}{2kT} \right) \quad (1)$$

which reduces to  $\mu H/kT$  when  $P_n$  is small.

For fields and temperatures easily obtainable in the laboratories the nuclear polarizations are exceedingly small (0.1 % for protons with  $H = 10$  kilogauss,  $T = 1^\circ \text{K}$ ).

Recent progress in the production of very high magnetic fields by means of superconducting coils and of very low temperatures by

means of the new  $^3\text{He}$ - $^4\text{He}$  refrigerators may open in the future new prospects for the so-called "brute force" method which aims at producing sizeable nuclear polarization through the sheer increase of the  $(H/T)$  ratio.

In the meantime we shall concern ourselves with polarizations obtainable by dynamical methods in "conventional" fields and temperatures ( $H \sim 20$  kilogauss,  $T \sim 1^\circ \text{K}$ ).

All methods of dynamic nuclear polarization in bulk matter stem from the remark that for "conventional" values of field and temperature the equilibrium polarization  $P_e^0$  of electronic spins localized on paramagnetic atoms or ions (given by (1), where  $\sigma_n$  is replaced by the electronic gyromagnetic ratio  $\sigma_e$ , three orders of magnitude greater than  $\sigma_n$ ) is large and may approach 100 %.

Dynamic methods use the magnetic couplings that exist between electronic and nuclear spins to transfer to the latter a polarization comparable in magnitude to the electronic polarization  $P_e$  and of the same sign or of opposite sign.

The first of these methods is due to Overhauser <sup>1)</sup> who predicted that in metals the saturation of the spin resonance of conduction electrons could lead to a nuclear polarization comparable to the electronic polarization but of opposite sign. (More accurately, to the polarization that the conduction electrons would exhibit if they obeyed Boltzmann rather than Fermi statistics).

Shortly afterwards, this prediction received an experimental confirmation <sup>2)</sup>. A detailed theoretical analysis <sup>3)</sup> showed that although this method could under certain conditions be extended to non-metallic substances and in particular to liquids containing in solution paramagnetic impurities, it did not apply to diamagnetic solids containing localized paramagnetic impurities, which is by far the most interesting case for the construction of polarized targets.

There exists however a different method, sometimes called the "solid effect" which is applicable to non-metallic solids at low temperatures.

The solid effect and the Overhauser effect are "orthogonal" in the sense that in substances where one of these two methods is operative the other is not, in general (metals, liquids, paramagnetic substances with strong exchange forces between the electronic spins, for the Overhauser effect ; fixed paramagnetic impurities for the solid effect).

Although proposed at a later date the solid effect is conceptually simpler than the Overhauser effect. It is also the only method that has been used successfully so far for dynamically polarized solid targets. In the following we shall concern ourselves with the solid effect only.

## A FEW FACTS ABOUT MAGNETIC RESONANCE 4)

Larmor frequency

The behaviour of nuclear magnetic moments in magnetic fields (d-c or r-f) can be described either classically or quantum-mechanically whichever is more convenient. We shall consider spins 1/2 only, a simplifying but by no means essential restriction. Quantum-mechanically, the Larmor frequency of a nuclear spin in a d-c field  $H_0$ ,  $\omega_n = \sigma_n H_0$  is the energy difference between the two orientations of this spin in the field  $H_0$  expressed in frequency units :

$$\omega_n = \frac{\Delta E}{\hbar} = \frac{2\mu_n H_0}{\hbar} .$$

Classically it is the angular frequency of the free precession of the nuclear magnetization  $\vec{M}$  around the field  $\vec{H}_0$ . At thermal equilibrium the magnetization is aligned along  $\vec{H}_0$  and the precession cannot be observed. On the other hand it will become observable if by means such as say a sudden change in the orientation of  $\vec{H}_0$ , or by other means to be described shortly,  $\vec{M}$  is brought to make a finite angle with  $\vec{H}_0$ .

Magnetic resonance

A sample of bulk matter in thermal equilibrium in a d-c field  $H_0$  will have an equilibrium nuclear magnetization  $\vec{M}_0 = \chi \vec{H}_0$ . If a rotating r-f field of amplitude  $H_1$  and frequency  $\omega$  in the neighbourhood of the nuclear Larmor frequency  $\omega_0$  is applied to the sample at right angle to  $H_0$ , the nuclear magnetization of the sample will change appreciably even if  $H_1$  is several orders of magnitude smaller than  $H_0$ .

This is easily understood in a simple-minded quantum-mechanical language : the r-f field induces transitions (emission and absorption of photons of frequency  $\omega$ ) between the two energy levels  $I_z = \pm 1/2$  of the nuclear spin, separated by  $\hbar \omega_0$ . The resonance condition  $\omega \approx \omega_0$  is simply the conservation of energy. In thermal equilibrium the lower level is more populated than the higher, there will be more upward than downward transitions, whence a net absorption of r-f energy by the system of nuclear spins and a decrease of the total nuclear magnetization.

This approach disregards an important feature of the r-f field, namely its coherence, preserved in the classical description. It is convenient to analyze the phenomenon in a frame of reference rotating at the frequency  $\omega$  of the r-f field. In that frame the r-f field appears as a small d-c field of amplitude  $H_x = H_1$  whereas the rotation of the frame is taken into account by adding to  $H_0$

a fictitious field of magnitude  $H_f = -\omega/\sigma$ . The nuclear spins in the rotating frame "see" a so-called d-c effective field  $\underline{H}_{\text{eff}}$  with components :

$$H_{\text{eff}}^z = H_0 - \frac{\omega}{\sigma} = \frac{\omega_0 - \omega}{\sigma} \quad \text{and} \quad H_{\text{eff}}^x = H_1 \quad .$$

Far from resonance  $\underline{H}_{\text{eff}}$  is practically parallel to  $H_0$  and the nuclear magnetization  $\underline{M}_0$ , aligned along  $\underline{H}_0$ , has no reason to change. Near resonance  $\underline{H}_{\text{eff}}$  can make a large angle with  $\underline{H}_0$  and the nuclear magnetization will tend to precess around  $\underline{H}_{\text{eff}}$  rather than  $\underline{H}_0$ . Going back to the laboratory frame we see that the nuclear magnetization acquires a transverse component precessing at the frequency  $\omega$ , a feature which did not appear in the quantum-mechanical treatment above. Needless to say, a more sophisticated quantum-mechanical treatment where the statistical behaviour of the nuclear spins is described by a statistical operator with off-diagonal matrix elements restores the proper picture.

### Spin-lattice relaxation

The establishment of thermal equilibrium which leads to the value (1) for the nuclear polarization is not instantaneous. The time constant associated with this process which provides some measure of the strength of the coupling between the spins and the other degrees of freedom of the sample is represented in the literature by the symbol  $T_1$  and called the spin-lattice relaxation time<sup>4)</sup>. Depending on the nature of the sample, its physical state, its temperature, its purity, etc., the nuclear relaxation time varies between very large limits. The shortest times observed are of the order of microseconds or even less, the largest, of the order of hours, days or more, are often limited only by the impurities content of the sample. Whatever the relaxation mechanism and there are many, its effect is to establish an inequality among the populations of the nuclear spin energy levels. When a resonant r-f field is applied to the sample, resonance and relaxation are competing processes, the former striving to equalize the populations between which the r-f transition takes place, the latter attempting to maintain between them the Boltzmann ratio  $\exp(-\hbar\omega_0/kT)$ .

If the r-f field is so strong that the transition probability  $W$  is much larger than the relaxation rate  $1/T_1$ , the populations of the two levels between which the transition takes place become equal and the resonance is said to be saturated.

### Line width, local field, spin diffusion

The interaction between two nuclear moments at a distance  $r$  from each other is given by the dipole-dipole Hamiltonian :

$$\mathcal{H}_d = \frac{\sigma\sigma'\hbar^2}{r^3} \left\{ \underline{I} \cdot \underline{I}' - \frac{3(\underline{I} \cdot \underline{r})(\underline{I}' \cdot \underline{r})}{r^2} \right\} \quad (2)$$

Its effect is to broaden the energy levels of a system of many nuclear spins and thus also the resonance line. It is convenient, if not quite accurate, to introduce the concept of local field which is the field produced at the site of a nuclear spin by its neighbours. The local field is in general of the order of a few gauss and thus usually much smaller than the applied d-c field  $H_0$ . The local field varies from site to site in a random way, whence the broadening of the resonance.

If the nuclear polarization is very weak, for every spin that "sees" a local field, say parallel to the applied field, there will be another spin whose local field is equal but opposite and the resonance line will be symmetrical with respect to the central frequency. On the other hand for high polarizations the spins will "see" more local fields of one sign than of the other and the line will become asymmetrical.

Another effect of the interaction (2) is the spin-diffusion. This interaction contains operators such as  $I_+ I'_-$  whereby neighbouring spins can exchange their orientations by "flip-flops" that conserve energy if  $\sigma = \sigma'$ . A local inhomogeneity in the nuclear polarization will diffuse through the sample by means of these "flip-flops". The probability  $W$  per unit time of a "flip-flop" between, say, two neighbouring protons, is in general of the order of  $10^{-4} \text{ s}^{-1}$ . For dimensional reasons it is clear that the diffusion coefficient  $D$  will be of the order of  $Wa^2$ , where  $a$  is the distance between neighbouring spins, that is of the order of  $10^{-12}$ ,  $10^{-13}$ .

### Electronic spins

Most of what has been said above applies to electronic spins and to electron spin resonance. The main changes are :

- a. much larger Larmor frequencies which in "conventional" fields fall into the microwave range ,
- b. much shorter relaxation times.

At very low temperatures, the relaxation mechanism is due to the direct process, absorption or emission of a single phonon of energy  $\hbar\omega_0$ . For this process the lifetimes  $\tau_+$  and  $\tau_-$  of the ground and excited electron spin state are proportional respectively to  $\bar{n} + 1$  and  $\bar{n}$  where according to Planck's law :

$$\bar{n} = \left[ \exp\left(\frac{\hbar\omega_0}{kT}\right) - 1 \right]^{-1} . \quad (3)$$

From (1) we get :

$$\left. \begin{aligned} \frac{1}{\tau_+} \propto (\bar{n} + 1) &= \frac{1 + P_0}{2P_0} & \frac{1}{\tau_-} \propto \bar{n} &= \frac{1 - P_0}{2P_0} \\ \frac{1}{T_e} &= \frac{1}{\tau_+} + \frac{1}{\tau_-} \propto \frac{1}{P_0} \end{aligned} \right\} \quad (4)$$

For very low temperatures  $P_0 \rightarrow 1$ , and the electron relaxation time tends toward a finite limit which is simply the lifetime of the upper state.

c. for many paramagnetic ions, large anisotropy of the Larmor frequency.

#### Elementary theory of the solid-effect

Consider an assembly of nuclear spins  $I = 1/2$  embedded in a diamagnetic solid that contains a few paramagnetic impurities with spins  $S = 1/2$ .

Assume for simplicity (but quite realistically) values of  $H$  and  $T$  such that to a good approximation the electronic spins  $S$  are completely polarized, say all "up" and the nuclear spins  $I$  completely unpolarized, as many "up" as "down". The dipolar interaction (2) (where  $I'$  is replaced by  $S$ ) permits simultaneous reversals of  $S$  and  $I$  in opposite directions, or flip-flops and also reversals in the same direction which we shall call flip-flips. However in such reversals the total energy of the spin system changes by an amount  $h(\omega_S \pm \omega_I)$  and the process will not occur unless the missing energy is supplied by the crystalline lattice, usually in the form of one or several phonons. It is precisely those simultaneous reversals that are responsible for the classical mechanism of nuclear relaxation by paramagnetic impurities. The rate of these processes can be very small at low temperatures ( $1/T_n \sim 10^{-3} \text{ s}^{-1}$  is a typical value for polarized targets materials). On the other hand the reversal of an electronic spin alone, caused by its coupling to the lattice occurs at a much higher rate:  $1/T_e$  ( $1/T_e \sim 10^3 \text{ s}^{-1}$  is a typical value). Suppose now that an external source of microwave energy at a frequency  $\Omega = \omega_S \pm \omega_I$  is capable of inducing either flip-flops ( $\Omega = \omega_S - \omega_I$ ) or flip-flips ( $\Omega = \omega_S + \omega_I$ ). Assume also that the electronic line-width  $\Delta\omega_S$  is much smaller than the nuclear frequency  $\omega_I$  so that when the flip-flops occur ( $\Omega = \omega_S - \omega_I$ ), flip-flips are impossible because they are off-resonance with the driving frequency  $\Omega$ , and vice-versa. In principle the simplest way of inducing such flip-flops (flip-flips) which has not been tried so far, is to use a hypersonic generator at the microwave frequency  $\Omega$ , and to modulate at that frequency the dipolar interaction (2) 5).

In practice a microwave magnetic field is used. A flip-flop is then a forbidden transition in first approximation but, as for the nuclear relaxation process, it becomes allowed through the dipolar interaction which scrambles the electronic and nuclear states. Assume then that we drive, say, forced flip-flops and that the strength of the source is such that the rate at which they occur is much greater than the nuclear relaxation rate  $1/T_n$ . We shall show that it is possible in that way to force "up" all the spins I.

Consider first a spin I that is up. The spins S being all up, the spin I could only do a flip-flip which is forbidden as being off-resonance. On the other hand a spin I that is down may do a flip-flop with a spin S that is up, ending in a situation where I is up and S is down. This spin S, which has come down, is a danger for all the I spins that are up, since it could bring one of them down through a forced flip-flop. Fortunately, before any harm is done, its powerful relaxation mechanism will have brought this spin S to its "up" position of thermal equilibrium and the cycle can start again until all the I spins are up.

It is easy to see that if the source frequency  $\Omega = \omega_S + \omega_I$  drives flip-flips rather than flip-flops, the I spins will all go "down" with a polarization opposite to that of the S spins.

It is also easy to see that for an incomplete electronic polarization  $|P_e| < 1$ , these processes lead to a nuclear polarization  $P_n = \pm P_e$ .

This very simple model of the solid effect spells out some of the requirements for a polarized target material. It should be possible to dope it with paramagnetic impurities. The electronic line width should be sufficiently narrow to forbid the simultaneous occurrence of forced flip-flips and flip-flops which would cancel each other. This precludes large concentrations of electronic spins S which would lead to a broadening of the electronic resonance through dipolar S-S coupling. On the other hand for small electronic concentrations, each electronic spin S must "service" a large number  $N_I/N_S$  of nuclear spins.

In order to be effective it must be able after each forced flip-flop (flip-flip) to flip back into its thermal equilibrium position before any of the  $N_I/N_S$  nuclear spins of its sphere of influence has flipped through a nuclear relaxation mechanism. The condition for this is clearly :

$$f = \left( \frac{N_I}{T_n} \right) / \left( \frac{N_S}{T_e} \right) \ll 1 \quad . \quad (5)$$

It can be shown that this condition is always verified in reasonably high fields if the nuclear relaxation of the spins I has no other origin than their couplings with the spins S <sup>6)</sup>. If however

other nuclear relaxation mechanisms, sometimes called leakage relaxation, are present, caused either by couplings with another species of electronic spins  $S'$  with a Larmor frequency  $\omega_{S'} \neq \omega_S$ , or by a purely nuclear mechanism, the condition (5) may be violated and the nuclear polarization  $P_N$  could be much smaller than  $P_e$ .

The two conditions, narrow electron resonance and short electronic relaxation time, are well met by impurities of rare earth ions. These ions have a largely unquenched orbital moment which ensures a strong coupling between the orientation of the electronic magnetic moments and the lattice. On the other hand a large orbital magnetism implies a strong magnetic anisotropy which makes it imperative to use single crystals. It is not surprising that the polarized targets materials successfully used so far are single crystals of rare earth ions.

By far the best results have been obtained so far from double nitrates  $(La)_2(Mg)_3(NO_3)_{12} \cdot 24H_2O$  where a small fraction of lanthanum has been replaced by neodymium (cerium and dysprosium have also been tried) and where the protons to be polarized are those of the water molecules.

#### Very low temperatures (below 1° K)

Assuming for simplicity that there is no leakage relaxation we see that dynamic polarization is essentially a competition between a "forced" nuclear flip caused by forced electron nuclear flip-flops (or flip-flips) driven by the microwave source and a "natural" nuclear flip caused by "natural" flip-flops and flip-flips resulting from the coupling of the electron nuclear spin system with the lattice vibrations. Increasing the rate of the first type of process by raising the microwave power or decreasing the second by lowering the temperature should increase the nuclear polarization. It would seem however that at least at the microwave driving frequencies currently used (4 mm wavelength), there is little to be gained by going to temperatures below 1° K since both the equilibrium electron polarization which is practically unity and the electron relaxation rate which is practically the lifetime of the upper electronic level change very little.

Not so however the nuclear relaxation rate which is the rate of "natural" flips. In order to flip "naturally" a nuclear spin must find an electron willing to flip-flop or flip-flip with it, with the help of a phonon or more generally of the lattice. The probability of this process is proportional to  $(N_+/\tau_+ + N_-/\tau_-)$  where  $N_+$  and  $N_-$  are the populations of the electron levels and  $\tau_+$  and  $\tau_-$  their lifetimes given by (4) (for the direct process). When the temperature goes to zero the population  $N_+$  of the excited state and the inverse lifetime  $1/\tau_-$  of the ground state go to zero and so does :

$$\frac{1}{T_n} \propto \left( \frac{N_+}{\tau_+} + \frac{N_-}{\tau_-} \right) .$$

Using (1) and (4) it is easily found :

$$\frac{1}{T_n} \propto \frac{1 - P_o P_e}{P_o}$$

where for the sake of generality it was assumed that the electronic polarization  $P_e = N_- - N_+$  was not necessarily the equilibrium polarization  $P_o$  given by (1).

If  $P_e = P_o$  :

$$\frac{1}{T_n} \propto \frac{(1 - P_o^2)}{P_o} \quad (6)$$

$1 - P_o^2$  decreases very rapidly with  $T$ , a fact which opens up interesting possibilities for the use of the new refrigerators in dynamic polarization also.

At such low temperatures as provided by these refrigerators the coupling with paramagnetic impurities may be the only nuclear relaxation mechanism for non metallic diamagnetic solids. In fields large enough for the nuclear equilibrium polarization to be sizeable, the electronic polarization  $P_o$  would be so near unity as to make the nuclear relaxation time and the establishment of the nuclear equilibrium polarization forbiddingly long. On the other hand the time for the establishment of a dynamic polarization, or polarization time, independent of  $P_o$ , could conceivably be kept within reasonable limits.

#### Dynamic polarization and spin diffusion

The probabilities of a flip-flop (flip-flip) "forced" or natural, decrease very rapidly with the distance  $r_{IS}$  (we call  $\Gamma/r^6$  and  $C/r^6$  their values at a distance  $r = r_{IS}$ ). One would thus expect a broad distribution of the relaxation and polarization times for the various spins  $I$ , depending on their distance to the nearest spin  $S$ . These variations are smoothed out to a large extent by the nuclear spin diffusion. The "information" of polarization or relaxation collected by spins  $I$  in the immediate vicinity of the spins  $S$  is carried by diffusion to all the other spins  $I$ . A spin diffusion coefficient  $D$  as small as  $10^{-13}$  will still carry this information over  $100 \text{ \AA}$  in a time of the order of ten seconds which is very much faster than the rate of direct flip-flops, "forced" or "natural", between an electron and a nuclear spin separated by  $100 \text{ \AA}$ . The role of spin diffusion in relaxation and polarization processes is thus essential.

Actually, the nuclear spins that are nearest to the impurities "see" a sizeable electronic field  $h_e$  produced by the impurity

and their Larmor frequency may be appreciably different from that of a neighbouring spin  $I$  farther removed from  $S$ . The nuclear flip-flop between these two spins does not conserve energy and the spin diffusion is quenched.

We use a crude model where  $D$  is zero inside a sphere of radius  $b_0$ , called the diffusion barrier, and is constant outside. The radius  $b_0$  is defined approximately by the condition  $h_e(b_0) = \Delta H$  where  $\Delta H$  is the nuclear line width.

If  $(C + \Gamma)$  is not too large (moderate electronic relaxation rates and moderate driving powers) it is reasonable to assume that outside the diffusion barrier the flipping information reaches every nuclear spin through spin diffusion faster than through a direct electron-nuclear flip. The nuclear polarization is then uniform outside the small sphere of radius  $b_0$  and we can assume a single relaxation time  $T_n$  and a single polarization time  $\tau_p$  which are averages of  $C/r^6$  and  $(\Gamma + C/r^6)$  outside the diffusion barrier.

An elementary calculation <sup>7)</sup> gives :

$$\frac{1}{T_n} = \frac{4\pi N_S C}{b_0^3} \quad \frac{1}{\tau_p} = \frac{4\pi N_S (\Gamma + C)}{b_0^3} . \quad (7)$$

The maximum nuclear polarization  $P_n$  will be given by :

$$P_n = \pm P_e \frac{\Gamma}{C + \Gamma} = P_e \frac{T_n}{\tau_p + T_n} . \quad (8)$$

If on the other hand  $C + \Gamma$  is large (large driving power for instance), there may still be large nuclear inhomogeneities in the nuclear polarizations outside the diffusion barrier and up to a radius  $b$  such that :

$$\frac{C + \Gamma}{b^6} = \frac{D}{b^2} . \quad (9)$$

Beyond  $b$ , spin diffusion maintains a uniform polarization and the formulae (7) and (8) are still valid but with  $b_0$  replaced by  $b$ . We call this case the diffusion limited relaxation (and polarization) rate. Because of the non linear dependence of  $1/T_n$  and  $1/\tau_p$  on  $C$  and  $\Gamma$ , the average probabilities for "forced" and "natural" nuclear flips are no more additive and  $T_n$  has no other simple physical interpretation than that given by the last formula (8).

As for the constant  $1/\tau_p$  which is the observed rate of growth of the dynamical polarization it has in the diffusion limited range a dependence on  $\Gamma$  and therefore on the driving power  $\mathcal{P}$ , much slower than linear since according to (9) it goes like  $(C + \Gamma)^{1/4}$ .

It should be borne in mind that these theories are crude approximations and that the qualitative agreement with experiment, actually observed in most cases, is quite gratifying.

Dynamic polarization viewed as a cooling of nuclear spins

We have so far kept to the assumption that  $\omega_n \gg \Delta \omega_S$  which implied that when driving, say, flip-flops, no flip-flips were induced and furthermore that the electron resonance and the electronic polarization were unaffected. When this condition is not fulfilled a complicated situation arises which I am happy to let my friend Borghini deal with to morrow and I shall be content to introduce the concept of spin-temperature in the rotating frame <sup>8)</sup> and more generally the concept of dynamic polarization as a "cooling" of nuclear spins <sup>8-12)</sup>.

Still with the assumption  $\omega_n \gg \Delta \omega_S$  consider the behaviour of the electronic spins  $S$  in the frame rotating at the frequency  $\Omega = \omega_S - \omega_I$ . In that frame, as explained earlier, the main part of the effective Hamiltonian of the spins  $S$  is static and given by :

$$\begin{aligned} \mathcal{H}_{\text{eff}} &= - \sigma_S \hbar S_z \cdot H_{\text{eff}} = \hbar(\Omega - \omega_S) S_z - \hbar \sigma_S H_1 S_x \\ &= - \hbar \omega_I S_z - \hbar \sigma_S H_1 S_x \end{aligned} \quad \left. \vphantom{\mathcal{H}_{\text{eff}}} \right\} \quad (10)$$

If the microwave field  $H_1$  is not too large so that  $|\omega_I| \gg |\sigma_S H_1|$  we can say in first approximation that in the rotating frame the  $S$  spins "think" that they have a Larmor frequency  $\omega_I$ . Since however their polarization along  $Oz$  is still given by  $\tanh(\hbar \omega_S / 2kT)$  rather than  $\tanh(\hbar \omega_I / 2kT)$  the spins  $S$  must also "think" that in the rotating frame they have a temperature  $T_S = T \omega_I / \omega_S$ , lower by three orders of magnitude than that of the sample.

Since no r-f field is applied anywhere near the nuclear frequency  $\omega_I$  the nuclei should be viewed in the laboratory frame. The combined effect of the part  $- \hbar \sigma_S H_1 S_x$  of the Hamiltonian (10) and of the I-S dipolar couplings is to establish a thermal contact between the electrons viewed in the rotating frame and the nuclei still in the laboratory frame. The reason this contact is effective is that now electrons and nuclei have the same Larmor frequency  $\omega_I$  and are thus on "speaking terms".

If this contact is much stronger than the thermal contact between the lattice and the nuclei the latter will reach in the laboratory frame the same low temperature than that of the electrons in the rotating frame namely  $T_S = T \omega_I / \omega_S$  positive or negative depending on the sign of  $\omega_I / \omega_S$ . (There is nothing inconsistent in the concept of a negative temperature for a system of spins whose energy spectrum has an upper bound).

If we choose  $\Omega = \omega_S + \omega_I$  we reverse the sign of the electronic temperature in the rotating frame, therefore also the sign of the nuclear temperature in the laboratory frame and the sign of the nuclear polarization.

It should be realized that the language just used which at first sight may smack of science-fiction actually does nothing but para-

phrase mathematical equations.

So far the new language of spin temperature although quite consistent has not brought anything new. Its usefulness stems from the fact that when line broadening mechanisms such as spin-spin couplings are important, and the condition  $|\omega_I| \gg \Delta\omega_S$  no more fulfilled, by introducing the concept of a local field that accounts for the spin-spin interaction, this language can be generalized so as to handle this more complex situation in a satisfactory way, as will be discussed to-morrow by Dr Borghini.

The only point I wish to emphasize is the double role of the driving microwave field viewed in the rotating frame : by giving to the electronic spins in the rotating frame an effective Larmor frequency  $\omega_I$  it cools them by a factor of the order of  $\omega_S/\omega_I$  and it puts them on speaking terms with the nuclear spins. This suggests some new methods of dynamic polarization, listed in the literature, which I shall not describe here (10,13).

Dr Jeffries will describe in great detail the only one successful so far (11).

## CONCLUSION

I have attempted at some length to explain to non-specialists the physics behind the dynamic polarization method known as the solid effect. I shall not discuss any of the theoretical and practical problems connected with the making and the use of polarized targets since a large part of the Conference will be devoted to these problems.

Let me simply mention one rather farfetched idea. As I have explained earlier an r-f field of frequency  $\omega$  near the nuclear Larmor frequency  $\omega_I$  would give to the nuclear polarization a sizeable transverse component precessing at the frequency  $\omega$ . This makes it possible to modulate the amplitude of a reaction involving strong interactions at the same frequency.

Thus, to mention a crazy gedankene experiment, the coherent forward amplitude for the scattering of neutral K mesons which can be considered as an off-diagonal matrix element between  $K_L$  and  $K_S$  could be modulated at a frequency of the order of :

$$\omega_K = \frac{m(K_L) - m(K_S)}{\hbar c^2}$$

and thus drive a resonant transition between the two states  $K_L$  and  $K_S$ . (A target with a nuclear spin  $I > 1/2$  would be necessary). In view of the great line-width of  $K_S$ , comparable to  $\omega_K$ , a resonance experiment of that type does not make much sense anyway but it is an amusing speculation.

Perhaps more realistic uses of such possibilities will appear in the future.

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