THEORETICAL ASPECTS OF
NUCLEAR DYNAMIC POLARIZATION

M. BORGHINI

CERN, Geneva

1   INTRODUCTION

The basic facts involved in the principle of nuclear dynamic polari-
zation by "solid effect" having been given in one of the preceding
papers [1], we would like to enter here into some more details of the
theory with the specific purpose of seeing why solid effect does not
work in every case and what can be done to improve the present achie-
vements that are presented in other papers [2,3] : we shall see for
instance why solid H_2, solid HD and solid D_2 are not well polarized,
and why the polarized targets of lanthanum magnesium nitrate (LMN)
with longer nuclear relaxation times are better polarized than the
other ones, as is apparent in reference 2. We shall be able to see
also why the polarization of a LMN target decreases by a factor of
about two when it is bombarded by a few 10^{12} incident ionizing par-
ticles. The solid effect being a method to increase the thermal equi-
librium polarization of nuclear spins, it seems in order to begin by
discussing this one.

2   STATIC POLARIZATION ("brute force" polarization)

The polarization of an assembly of protons placed in a magnetic
field H and in contact with a thermal bath at a temperature T, is
given by :

M. BORGHINI

$$P_n = P_n(1/2) = 2 \coth\left(2 \times 10^{-7} \frac{H}{T}\right) - \coth\left(10^{-7} \frac{H}{T}\right) =$$

$$= \tanh\left(\frac{\mu_n H}{kT}\right) \simeq \tanh\left(10^{-7} \frac{H}{T}\right)$$

where H is expressed in gauss and T in degree Kelvin. However, this formula is valid only if there is no coupling between the spins of these protons and the orbital states of the molecules to which they belong : it is valid for instance for hydrogen atoms in lithium hydride LiH, in polyethylene $(CH_2)_n$, in the water of hydration of the lanthanum magnesium double nitrate LMN, and it is not valid, as is well known, for solid hydrogen : due to the exclusion principle, mo‹ lecules of hydrogen, H_2, may exist only as para-molecules, with a total nuclear spin I = 0 and rotational quantum number J = 0, 2, 4, ... or as ortho-molecules with I = 1 and J = 1, 3, 5, ... The fun‹ damental molecular rotational state being J = 0, then I = 0 ; in th‹ solid, molecules retain enough of their individuality so that this fact remains true, and, as well-known, solid hydrogen converts to a pure para-state with zero total nuclear spin :

$$P_n = P_n(0) = 0, \text{ independently of H and T.}$$

Of course, as one knows how to produce nearly pure ortho-hydrogen, and if it were possible to keep it in that state, the proton system would keep a polarization given by :

$$P_n = P_n(1) = \frac{3}{2} \coth\left(3 \times 10^{-7} \frac{H}{T}\right) - \frac{1}{2} \coth\left(10^{-7} \frac{H}{T}\right) \text{ bigger than } P_n(\cdot$$

but this does not seem possible. We would not have spoken of this p: blem if it were not to introduce another compound which presents ju‹ the opposite behaviour, and may become a good sample to use with th‹ new advanced techniques for producing high magnetic fields and very low temperatures ; namely methane, CH_4. Here, again, in the molecul‹ state, the exclusion principle connects the total nuclear spin and the rotational quantum numbers, but it is the state with maximum nu‹ clear spin I = 2 (meta-methane) which is the fundamental state, thu: excluding the poorer I = 1 and I = 0 ones. In the solid form, the fundamental state is not yet completely known [4], but contains more than the normal statistical weight of meta-methane, which means tha‹ the static polarization is higher than given by $P_n(1/2)$. For pure m‹ ta-methane :

$$P_n = P_n(2) = \frac{5}{4} \coth\left(5 \times 10^{-7} \frac{H}{T}\right) - \frac{1}{4} \coth\left(10^{-7} \frac{H}{T}\right) .$$

Figure 1 shows $P_n(0)$, $P_n(1/2)$, $P_n(1)$, $P_n(2)$ as a function of $H/T \times 10^{-7}$. With H = 100 kG and T = 0.02° K, the polarization of normal hydrogen is 46 % whereas it is 73 % for meta-methane. Expres‹ sed in another way, it would require a field about two times smalle› or a temperature two times higher to obtain the same polarization a‹
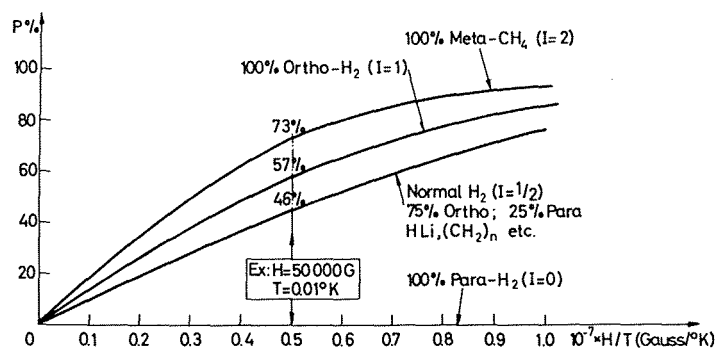
Fig. 1 Static polarization of protons in various samples (theoretical).

in normal hydrogen compounds.

Before we can obtain such polarized targets, we have to rely on dynamic polarization, with its unique feature that the direction of the polarization with respect to the magnetic field can be reversed by a slight change in the microwave frequency only.

3 DYNAMIC POLARIZATION

3.1 Notations

We deal with solid samples containing nuclear spins I and unpaired electronic spins S, placed in a static magnetic field H_0 along a direction Oz and in a liquid helium bath at a temperature T_0. Let N_n and N_e be the respective numbers of nuclear and electronic spins per unit volume, ω_n and ω_e their Larmor pulsations ($\omega_n = 2\pi f_n = \sigma_n H_0$, $\omega_e = 2\pi f_e = \sigma_e H_0$, f_n and f_e being the Larmor frequencies), T_n and T_e their spin lattice relaxation times, P_n^0 and $P_e^0 = P_0$ their thermal equilibrium polarizations. We shall have to introduce a special set of lattice vibration modes $M(\omega_e)$ interacting with the electronic spins S by one phonon exchange processes, with a frequency within the electronic resonance line ; let N_M be their number. We suppose also that the solid sample experiences a microwave magnetic field H_1, normal to H_0, with a pulsation ω .

We shall make the simplifying assumption that we are dealing with spins 1/2, both nuclear and electronic, although the consideration of higher spins presents a number of interesting features.

It has already been recalled [1] how, by inducing "flip-flips" or "flip-flops", one can polarize the nuclear spins, and how these "forbidden" processes are partially allowed by the action of the dipole-dipole interaction between the spins S and the spins I ; we have to introduce a parameter to describe this, the so-called dipolar mixing parameter ϵ : if we consider one spin S and one spin I^i, separated by a distance r_i, the ratio of the flip-flip or flip-flop probabilities to a pure electronic flip probability will be given by :

$$\frac{4\epsilon_i^2}{(1 + \Sigma_i \epsilon_i^2)^2}$$

where

$$\epsilon_i^2 = \frac{9}{16}\left(\frac{\gamma_e \hbar}{r_i^3}\right)^2 H_o^{-2} \sin^2 \theta_i \cos^2 \theta_i$$

θ_i being the angle between the direction Oz of the field and the direction of the vector joining S to I^i.

We have thus to introduce the relevant factor $f = \Sigma_i \epsilon_i^2$. The denominator $(1 + f)^2$ coming from the normalization of the wave function is not an aesthetical one, and will have an importance on some of the forthcoming conclusions.

3.2   Discussion

We may turn now towards the discussion of dynamic polarization : this can deal with the dependence of the dynamic polarization on the frequency ω and the amplitude H_1 of the applied microwave field with the maximum polarizations attainable in given conditions, and with the polarization time constants, but we shall mainly be interested in looking for the maximum steady state polarizations in given samples.

This theory can be divided into a few parts according to the nature and the width of the electronic resonance line : we are going to suppose here that this line is homogeneous, i.e. that the electron spins have all the same Larmor frequency, the broadening of their energy levels coming mostly from the electronic dipole-dipole interactions ; this case may be complicated enough so that we do not consider various inhomogeneous systems.

This homogeneous electronic line can be narrow or not with respect to the nuclear frequency, $\Delta\omega_e \ll \omega_n$. In the first case, the theory can be extended rather far into the description of actual situations in particular in the case of LMN, doped with neodymium. In the se-

cond case, one deals with a more complicated problem which involves the direct action of the microwave field H_1 on the electronic spins. This requires going into a rotating frame of reference [1] and attributing various temperatures to various parts of the transformed Hamiltonian : in this case, the theory of dynamic polarization has been derived [5] only under the so-called "high temperature" approximation, meaning in fact "low polarization" assumption. We are interested here, of course, in high polarizations only but, as the analysis of the general case, even with the above restriction, leads to an interesting physical insight into the situation, qualitative explanations or predictions can nevertheless be made and we are going to describe the general case here.

3.3 Narrow electronic resonance line

The spin system can be described by the expectation values of the z-components of the various spins only : with spins 1/2, the density matrix of the spin system reads :

$$\rho = \Pi_j(\tfrac{1}{2} + P_e S_z^j) \; \Pi_i(\tfrac{1}{2} + P_n^i I_z^i) \quad .$$

We have introduced only one P_e as the electronic system is homogeneous, and various P_n^i because we have not yet introduced nuclear spin diffusion. In some cases, spin diffusion is such that P_n^i is uniform at least in the major part of the sample, $P_n^i = P_n^{i'} = P_n$, and P_n has a single relaxation time T_n ; in other cases, the various P_n^i may be different, but the mean value $P_n = \overline{P_n^i}$ has anyhow a single relaxation time T_n.

It can be shown that the maximum dynamic polarization is given by "something like" :

$$P_n^{max} = \frac{P_o}{1 + \dfrac{N_n}{N_e}\dfrac{T_e}{T_n}} \tag{1}$$

where the relevant term $(N_n/N_e)(T_e/T_n)$ expresses the fact that the electrons should not be depolarized by having to polarize too many nuclei. We said "something like" because this formula is strictly valid in some very particular cases ; the exact formulation depends strongly on the precise character of spin diffusion, on the existence of "phonon bottle-neck" as we shall define it, on the presence of nuclear extra relaxation processes, etc, but formula (1) will give a sufficient basis for this general discussion.

We shall consider three different cases : i) where there is no extra relaxation processes (no "leakage"), i.e. no other electronic spins than the relevant spins S, and no intrinsic nuclear mechanisms ;

ii) where extra relaxation processes are present ; iii) where the
electronic relaxation is limited by "phonon bottle-neck" as we
shall see.

3.3.1 No "leakage", no "phonon bottle-neck".

We have to say something about the direct action of one spin S on
one spin I^i : the electronic relaxation process with a rate $1/T_e$
induces a relaxation rate for I^i given by :

$$\frac{1}{T_n^i} = \frac{1}{T_e} \frac{4\,\epsilon_i^2}{(1+f)^2}\,(1 - P_o^2)$$

as discussed in reference 1 : ϵ_i^2 varies as r_i^{-6} so that $1/T_n^i$ is ma-
ximum for the nuclei close to the spin S, and decreases very rapid-
ly. We suppose now that spin diffusion is fast with respect to the
fastest $1/T_n^i$, so that at each time $P_n^i = P_n^{i\,\prime} \equiv P_n$, which has then a
single relaxation time given by :

$$\frac{1}{T_n}\bigg)_{fast} = \overline{\frac{1}{T_n^i}} = \frac{N_e}{N_n} \frac{1}{T_e} \frac{4f}{(1+f)^2}\,(1 - P_o^2)$$

so that

$$\frac{N_n}{N_e} \frac{T_e}{T_n}\bigg)_{fast} = \frac{4f}{(1+f)^2}\,(1 - P_o^2) \leqslant 1 - P_o^2 \leqslant 1 \quad .$$

If spin diffusion is not so fast, then obviously :

$$\left(\frac{N_n T_e}{N_e T_n}\right) < \frac{N_n}{N_e} \frac{T_e}{T_n}\bigg)_{fast} \leqslant 1 - P_o^2 \leqslant 1 \quad .$$

According to formula (1), P_n^{max} is thus never smaller than $P_o/2$. The
exact solutions, taking into account the fact that $1 - P_o^2$ should be
written in fact as $1 - P_o P_e$, are shown in figure 2 for the case of
fast relaxation : one sees immediately the favourable effect of the
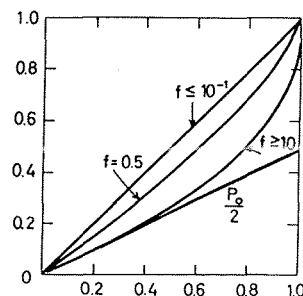factor $1 - P_o^2$ which goes quickly to zero as P_o approaches 1 [6].

Fig. 2 Dynamic nuclear polarization P_n(max.) vs static electronic po-
larization P_o (no "leakage", no phonon bottle-neck)($f = \Sigma\,\epsilon^2$ dipolar
parameter).

3.3.2   "Leakage", no "phonon bottle-neck".

We suppose now that there exist extra relaxation mechanisms for the nuclear spins, for instance their coupling with the rotation of the molecules, like for ortho-hydrogen, or simply their interaction with other paramagnetic centres, as for example with defects created by irradiation : one says that there is a "leakage". In that case the total nuclear relaxation rate $1/T_n^*$ can be much larger than in the preceding cases :

$$\frac{1}{T_n^*} \text{ possibly } \gg \frac{1}{T_n} \text{ and even } \gg \left.\frac{1}{T_n}\right)_{fast}$$

so that $(N_n/N_e)(T_e/T_n^*)$ can have any value smaller or bigger than one, and P_n^{max} may become very small.

This is the case in solid deuterium for example : electronic centres can be atoms produced in a gas discharge before condensation at low temperature [7] ; the density of such atoms is not very high and N_e/N_n is at most 2×10^{-6} ; T_e being about 1 ms whereas T_n^* is some 10 s :

$$\frac{N_n}{N_e} \frac{T_e}{T_n^*} \simeq 50 \qquad ;$$

with $P_o = 50 \%$ ($T_o = 1.2^\circ$ K, $H_o = 8$ kG), formula (1) gives $P_n^{max} \simeq 1 \%$ which is in agreement with experiment.

The same explanation holds for solid hydrogen where the rotation of ortho-molecules relaxes rapidly the nuclear spins, and in which even smaller concentrations of atoms can be obtained. In solid HD, nuclear relaxation times T_n as long as 10^4 s have been obtained [8], but the electronic relaxation times of impurities created by irradiation are of the order of 1 s ; their concentration remaining low, quite small polarizations are expected.

One should mention the fact that, if the "leakage" is due to paramagnetic impurities, $1/T_n^*$ is proportional to $1 - P_o'^2$ where P_o' is the polarization of these impurities and :

$$\frac{N_n}{N_e} \frac{T_e}{T_n^*} \sim 1 - P_o'^2$$

can be appreciably reduced by going to higher fields and/or lower temperatures.

3.3.3   No "leakage" but "phonon bottle-neck".

We come now to the "phonon bottle-neck" case : it happens sometimes, when N_e and $1/T_e$ are large, that the vibration modes $M(\omega_e)$ interacting with the electronic spins are not able to transfer rapidly enough the amount of energy that these spins have to release in the

presence of microwave fields ; $\langle Z_e \rangle$ being the electronic Zeeman
energy and $\langle E_M \rangle$ the energy of these modes, σ the phonon bottle-
neck parameter is defined as :

$$\sigma = \left. \frac{\partial}{\partial t} \right)_M \langle Z_e \rangle \Big/ \left. \frac{\partial}{\partial t} \right)_L \langle E_M \rangle$$

and may be very large compared to unity ; $\partial/\partial t)_M$ means the energy
exchange rate between spins S and modes $M(\omega_e)$, $\partial/\partial t)_L$ the energy
exchange rate between modes $M(\omega_e)$ and the rest of the lattice. It
can be shown then that the effective electronic relaxation rate is
smaller than $1/T_e$ and becomes :

$$\frac{1}{T_e^*} \simeq \frac{1}{T_e} \frac{1}{\sigma + 1} \simeq \frac{1}{T_e \sigma} \ll \frac{1}{T_e} \quad \text{if} \quad \sigma \gg 1$$

whereas T_n is generally not changed, because of the small energy
of the nuclear spins, so that the factor $(N_n/N_e)(T_e/T_n)$ becomes :

$$\frac{N_n}{N_e} \frac{T_e^*}{T_n} \simeq \frac{4f}{(1 + f)^2} \sigma(1 - P_0^2)$$

which can be much larger than one when $f\sigma$ is larger.

In fact, the exact theoretical treatment is more complicated and
involved evolution equations for P_e, P_n, and for the temperatures
of the modes $M(\omega_e)$ as well as for the modes $M(\omega_e + \omega_n)$ and $M(\omega_e - \omega$
responsible for the relaxation by forbidden transitions [6], and so-
me results are presented in figures 3 and 4 with $f\sigma'$ as a significa
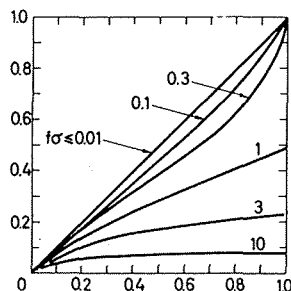parameter $(\sigma = \sigma' P_0)$.

Fig. 3 Dynamic nuclear polarization vs static electronic polarization
(no "leakage" but phonon bottle-neck) (f : dipolar parameter ; σ : pho-
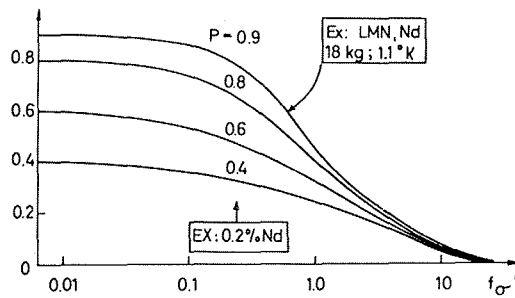non bottle-neck parameter).

Fig. 4 Maximum proton polarization vs dipolar phonon bottle-neck parameter $f\sigma'$ (P_o : static electronic polarization).

As shown by C.D. Jeffries and collaborators [9], phonon bottle-neck exists in LMN,Nd at the fields and temperatures used for polarized targets : σ', deduced from electronic relaxation measurements, is roughly proportional to the Nd ion concentration and is of the order of a few hundreds ; f, deduced from nuclear relaxation measurements and the crystalline structure of LMN is of the order of 5×10^{-4} at 18 kG, so that $f\sigma'$ has typically values ranging from 0.1 to 0.5. One sees that the maximum polarization P_n^{max} is not far from P_o but is rather sensitive to the value of σ', i.e. of the neodymium concentration C ; as the nuclear relaxation time T_n is inversely proportional to C, one expects that the maximum polarization decreases when T_n is shorter, which is in fact observed in actual polarized targets [2]. We thus suggest that by having relaxation times of the order of 100 mn instead of 10-15 mn, the corresponding polarizations should become higher.

3.3.4 "Leakage" and "phonon bottle-neck".

We can now turn to the effect of radiation damage in LMN targets : it is easy to calculate the effect of an extra relaxation term $1/T_n'$ in a sample suffering from phonon bottle-neck as LMN,Nd ; $1/T_n'$ can in turn be related to a number of incident particles at minimum ionization hitting the target, by making use of nuclear relaxation measurements made in a 7 kG field on a LMN crystal irradiated by a source of strontium-90 [10] ; this was done for the curves presented in figure 5 and figure 6 ; the number N_i of incoming particles is of course not given with a high precision, as we have, in particular, in order to go from 7 kG to 18 kG supposed the relaxation rate of the paramagnetic defects to be proportional to H_o^3, which may not be absolutely correct. The right order of magnitude is nevertheless obtained. We should stress that, in order to compare irradiation effects in various targets, one has to use the complete set of equations and to take into account the relevant values of H_o, f and τ' which are generally different for these targets.
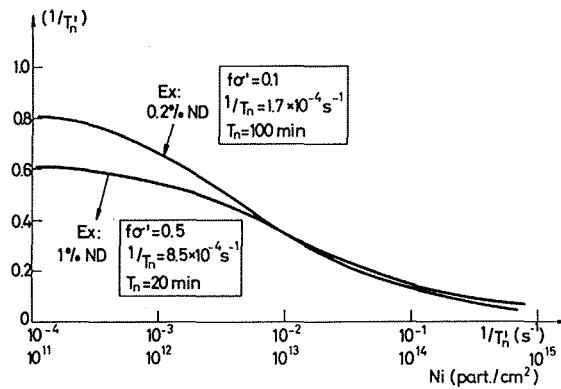
Fig. 5 Impurity effect (ex. radiation damage) on polarization in
LMN,ND. Max. proton polarization vs extra relaxation rate or n° of
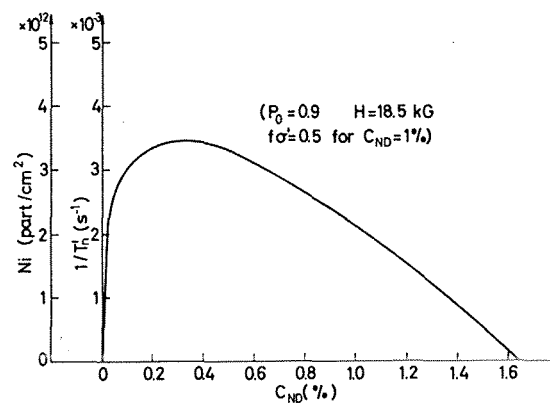incident particles (min. ioniz.).

Fig. 6 Impurity effect (resp. radiation damage) reducing max. proton
polarization to 0.5 vs ND concentration in LMN,ND.

We would like to end this section on the narrow electronic lines b;
saying that we do not think that dynamic polarization works well i:
rare earths salts because they have rather short relaxation times
it is true that T_e is short, for example, 100 μs but, because of
phonon bottle-neck, the effective T_e^* is much longer, 10 to 50 ms
for example, which is of the same order as for other kinds of para-
magnetic centres, like free radicals for instance. This has some
consequence on the search for new polarized materials : one should

be more interested in having electron spins with a narrow resonan-
ce line, as in LMN,Nd, than having a particularly strong coupling
with the lattice, provided their concentrations can be made large
enough. For instance, polarizations in frozen liquids containing
free radicals [11,12] are presently limited by the broadening of
the electronic lines, and will be increased when narrower lines
are found. This leads us to the case of an arbitrary electronic
resonance line.

3.4 Arbitrary electronic resonance line

It has already been stated in reference 1 how solid effect can be
viewed as a cooling of the electronic spins in a frame $R(\omega)$ defi-
ned by the transformation $U = \exp\left(i\omega t \sum_j S_z^j\right)$ rotating with the
frequency ω of the applied RF field, and that this description,
which gives trivial results when the electronic resonance line is
narrow becomes necessary when it is not. Keeping to the assumption
that we deal with spins $1/2$, we are not only going to see why the
nuclear dynamic polarization is reduced in the case of a broad re-
sonance line, but also to show that this analysis can lead to a
new polarization scheme, using two RF fields of different frequen-
cies, which can give, at least in principle, nuclear polarizations
higher than the electronic polarization P_0 which is the limit for
the ordinary solid effect.

Let us start first with only one RF field with a frequency ω, and
suppose that there is only a homogeneous system of electronic
spins. When this field is applied within the electronic resonance
line, the spin system can no longer be described by the electronic
polarization alone, but rather by two different temperatures in
the rotating frame $R(\omega)$: one for the effective Zeeman energy
$Z_e^* = \sum_j \hbar(\omega_e - \omega)S_z^j$, another for the electronic dipolar energy, mo-
re precisely for the part $\mathcal{H}_{SS}^0$ of it which commutes with Z_e^*. Without
entering into any details, let us just say that, because of energy
conservation, the RF field provides a thermal contact between these
two reservoirs : when a photon of energy $\hbar\omega$ produces a flip of an
electronic spin with an energy change $\hbar\omega_e$, the remaining energy
$\hbar(\omega - \omega_e)$ has to be exchanged with the dipolar interactions through
a fast rearrangement of the relative orientations of all the spins.
As a consequence, it can be shown that the cooling of the Zeeman
part is smaller than the ratio $\omega_e/(\omega_e - \omega)$ corresponding to no con-
tact with the dipolar part so that the electronic polarization is
made smaller than its thermal equilibrium value P_0. When nuclei are
present and when ω is near $\omega_e \pm \omega_n$, the RF field furthermore provi-
des the necessary thermal contact between the two preceding reser-
voirs and the nuclear Zeeman energy Z_n which should be described by
its own temperature in the rotating frame ; this contact cools Z_n,
and as Z_n is not affected by the transformation U, the nuclear po-

larization is enhanced by the inverse ratio of the new temperature to the initial (lattice) one. The final results depend on the various heat capacities of these three reservoirs and on the strength of their interactions with the lattice (relaxation rates) as well as on the strength of the thermal contacts provided by the RF field

To be more specific, supposing again a fast nuclear spin diffusion, the enhanced nuclear polarization is given by :

$$P_n = \frac{P_o(W^+T_n - W^-T_n) + P_o \dfrac{\omega_n(\omega - \omega_e)}{a\omega_L^2} W_o T_e (W^+T_n + W^-T_n)}{\left[1 + (1 + k)(W^+T_n + W^-T_n)\right]\left[1 + \dfrac{(\omega_e - \omega)^2 + a\omega_L^2 + k\omega_n^2}{a\omega_L^2} W_o T_e\right]}$$

with $k = (N_n/N_e)(T_e/T_n)$ and $\omega_L^2 = \gamma_e^2 H_L^2$, where H_L is a local field due to the electronic spin-spin interactions, related to the second moment of the electronic resonance line by $H_L^2 = 1/3 \ \Delta H^2$; a is number representing the ratio of the relaxation rates for the dipolar energy and for the electronic Zeeman energy : it varies between 2 (when there is no correlation between the relaxation of two neighbouring electronic spins) and 3 (when there is a complete correlation) ; we shall take a = 2 in the following. W^+ and W^- are the transition probabilities for the forbidden transitions, W_o the probability for the pure electronic transitions ; with the hypothesis of a fast spin diffusion, one can write the "saturation" parameters WT as $W^+T_n = S^+ \sim f(\omega - \omega_n)$, $W^-T_n = S^- \sim f(\omega + \omega_n)$, $W_o T_e = S_o \sim f(\omega)$ where $f(\omega)$ represents the shape of the electronic resonance line, having its maximum value for $\omega = \omega_e$.

We have introduced the factor $k = (N_n/N_e)(T_e/T_n)$ only for the sake of completeness and to discuss formula (2) we shall suppose that it is negligibly small. The first term of the numerator and the first factor of the denominator represent the ordinary solid effec if the electronic resonance line is narrow, and with a single RF field, only one of the saturation parameters S can be non zero ; then $P_n^{max} = P_o$ or $P_n^{max} = -P_o$ according to whether S^+ or S^- are larger than unity. If the electronic resonance line is broad, S^+, S^- and S_o are simultaneously non zero : with low RF power, P_n is smaller than P_o as a result of the competition between positive and negative polarizations described by the term $W^+T_n - W^-T_n$ (so-called "differential effect") ; in the limiting case of strong RF irradiation, S^+, S^- and S_o are much larger than unity and P_n is given by :

$$P_n = P_o \frac{\omega_n(\omega - \omega_e)}{(\omega_e - \omega)^2 + 2\omega_L^2}$$

with a maximum value as a function of ω equal to :

$$P_n^{max} = P_o \frac{\omega_n}{2\sqrt{2}\;\omega_L} \tag{3}$$

and as we have supposed $\omega_L > \omega_n$, P_n^{max} again is smaller than P_o ; for instance, the polarization obtained in a field of 25 kG with a broad resonance line corresponding to a local field H_L of 50 G is given by $P_n^{max} \simeq 0.26\;P_o$.

We shall now remark that formula (3) would give a polarization P_n^{max} larger than P_o if $2\sqrt{2}\omega_L$ was smaller than ω_n but then the e-lectronic resonance line would be narrow and $S_o(S^+ + S^-)$ would always be zero. However, by applying two RF fields, one with a frequency ω_1 near ω_e to produce the maximum cooling of the electronic spins in their rotating frame, the other one with a frequency $\omega_2 = \omega_e \pm \omega_n$ to provide the thermal contact between these spins and the nuclear ones*, one can reach polarizations given by equation (3) which could be higher than P_o**. To take a definite example, paramagnetic defects are produced in irradiated ^{6}LiH with a resonance line having a second moment $\overline{\Delta H^2} \simeq 210\;G^2$ so that $H_L \simeq 8.5\;G$ [13] ; with a static magnetic field of 25 kG, formula (3) gives :

$$P_n^{max} \simeq 1.6\;P_o \quad.$$

The extension of this spin temperature theory outside the "high temperature" approximation domain is difficult and has not yet been made : it is not clear how to define two different energy reservoirs, one corresponding to the Zeeman part Z_e of the Hamiltonian, the other one corresponding to the dipolar interactions $\mathcal{H}_{SS}^o$; the form of the dipolar energy relaxation equation when the electronic polarization is large has not been derived, and furthermore, cooperative phenomena between electronic spins may occur in the rotating frame of reference.

Notes and References

* One can also use one microwave source only with its frequency jumping continuously from ω_1 to ω_2 in a time short compared with the electronic relaxation time T_e.

** In the case of LMN,Nd at low temperatures, one has to take care of the fact that, in the case of a phonon bottle-neck with a parameter σ, the coefficient a should be multiplied by $\sigma + 1$ so that equation (3) becomes $P_n^{max} = P_o \omega_n / (2\sqrt{2}(\sigma + 1)\omega_L)$; this is because, whereas the relaxation rate of Z_e is lengthened by phonon bottle-neck, the relaxation rate of $\mathcal{H}_{SS}^o$ which has a much smaller heat capacity is not. As, in LMN,Nd, σ is of the order of a few hundreds, despite the smallness of ω_L, small polarizations would be produced by this method. The fact that high polarizations are obtained in LMN,Nd comes obviously from S_o remaining zero when S^+ or S^- are made non zero.

1) A. Abragam, "Polarized targets : how ?", these Proceedings, p. 27.
2) H.H. Atkinson, "Technology of present high energy targets", these Proceedings, p. 41.
3) D. Garreta, "Description of low energy targets", these Proceedings, p. 283.
4) For references, see for example, M. Borghini, "Choice of substances for polarized proton targets", CERN Report 66-3, 1966.
5) See A. Abragam and M. Borghini, Progr. in Low Temp. Phys. (C.J. Gorter, ed.), 1964, IV, chap. VIII.
   M. Borghini, Phys. Letters, 1966, 20, 228.
6) M. Borghini, Phys. Rev. Letters, 1966, 16, 318.
7) G.A. Rebka Jr and M. Wayne, Bull. Am. Phys. Soc., 1962, 7, 538 and private communication.
8) W.N. Hardy and J.R. Gaines, to be published.
9) See C.D. Jeffries, "Dynamic nuclear orientation", (John Wiley and sons, New York, 1965).
10) W.N. Hardy and G. Shapiro, private communication.
11) R.J. Wagner and R.P. Haddock, Phys. Rev. Letters, 1966, 16, 1116
12) M. Borghini, S. Mango, O. Runolfsson and J. Vermeulen, these Proceedings, p. 387.
13) F.E. Pretzel, G.V. Gritton, C.C. Rushing, R.J. Friauf, W.B. Lewis and P. Waldstein, J. Phys. Chem. Solids, 1962, 23, 325.