The Solid Effect

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Abstract. The present paper presents a tutorial on the solid effect (SE) as a mechanism for dynamic nuclear polarization (DNP). DNP is a method to orient nuclear spins in a solid. For this purpose, this solid is doped with a small amount of unpaired electron spins and a microwave field is used to transfer the orientation of the electron spins to the nuclear spins. Three different mechanism may be responsible for successful DNP: the Overhauser effect in metals and liquids, the SE and thermal mixing (TM) in insulators. The fundamental process of the SE are flip-flop transitions between the electron spins and the nuclear spins induced by the microwave field. In this paper the SE is approached in a similar way as in the description of cross polarization and coherence transfer between nuclear spins.

1 Introduction

Nuclear magnetic moments are small and brute force orientation of nuclear spins requires temperatures in the millikelvin range and magnetic fields of typically 10 T. Moreover, the nuclear spin–lattice relaxation time may then be excessively long, so the nuclear spins are still not oriented. Dynamic nuclear polarization (DNP) is a method to orient nuclear spins in a solid under easier conditions. For this method to work, this solid needs to contain a small amount of unpaired electron spins, through, e.g., doping with a radical. As the magnetic moment associated with these unpaired electron spins is much larger, these spins are easily oriented at liquid helium temperatures in a magnetic field of typically 3 T. Then a microwave field is used to transfer the orientation of the electron spins to the nuclear spins.

In the past the physical processes underlying this transfer have been extensively reviewed by Abragam and Goldman [1, 2]. Basically, three different mechanisms may be responsible for successful DNP: the Overhauser effect in metals and liquids, the solid effect (SE) and thermal mixing (TM) in insulators. In insulators the SE governs the polarization transfer if the concentration of electron spins is low and the mutual interactions between the electron spins can be ne-

glected. TM dominates the polarization transfer if the concentration of electron spins is high, while also the width of the ESR line is comparable with or larger than the NMR frequency. If the concentration of electron spins is high, but the ESR line still narrow, either one of the mechanisms, or even both, may play a role, depending on the precise circumstances. This paper concentrates on the mechanism of the SE, while TM is treated by Goldman [4].

The fundamental process of the SE is flip-flop transitions between the electron spins and the nuclear spins induced by the microwave field. In the classical description of the SE second-order perturbation theory – invoking the interaction of the electron spins with the microwave field and the dipolar interaction between the electron spins and the nuclear spins – is used to calculate the rate of these second-order transitions. Such an approach limits the description to weak microwave fields, while strong microwave pulses can be successfully used in DNP (see, e.g., [3, 6]). To avoid this limitation, in this paper the SE is approached in a similar way as in the description of cross polarization and coherence transfer between nuclear spins [9].

2 The Concept of Polarization

We define the polarization P of a set of N spins I as

$$P = -\frac{1}{NI} \mathrm{Tr} \left\{ \rho \sum_{i=1}^{N} I_z^i \right\}, \tag{1}$$

where ρ is the normalized density matrix, so its trace is equal to one. In thermal equilibrium a Boltzmann distribution is established and for $I = 1/2$ the polarization is given by

$$P_0 = \tanh\left(\frac{\hbar\omega_{0I}}{2k_BT}\right), \tag{2}$$

where $\hbar\omega_{0I}$ is the Zeeman splitting between the spin levels and T is the temperature.

For a good understanding of the concept of polarization it is useful to appreciate that it is basically equivalent to entropy [2]. To show this, we consider N equivalent spins $I = 1/2$ in an externally applied magnetic field while ignoring all their other interactions. Thus, the Hamiltonian is simply

$$\hat{\mathscr{H}} = \hbar\omega_{0I} \sum_{i=1}^{N} I_z^i.$$

This Hamiltonian has eigenstates $|m_1...m_N\rangle$, where $m_i = \pm 1/2$, and eigenvalues $E = \hbar\omega_{0I}m$, where $m = \sum_i m_i$. We consider all eigenstates corresponding to a fixed value of m. Then $N_- = (1/2)N - m$ is the number of spins for which $m_i = -1/2$, and $N_+ = (1/2)N + m$ is the number of spins for which $m_i = +1/2$.

We assume the density matrix to provide equipartition over these eigenstates, while it is zero elsewhere. Then the polarization Eq. (1) reduces to

$$P = \frac{2m}{N} = \frac{N_- - N_+}{N}. \tag{3}$$

There is considerable degeneracy, to each eigenvalue correspond

$$\binom{N}{N_+} = \frac{N!}{N_-!N_+!}$$

eigenstates. Thus, to the polarization Eq. (3) corresponds an entropy

$$\frac{S}{Nk_B} = \frac{1}{N}\ln\left(\frac{N!}{N_-!N_+!}\right)$$

$$\approx \ln 2 - \frac{1}{2}[(1+P)\ln(1+P) + (1-P)\ln(1-P)],$$

where we insert the Sterling approximation. Hence we may interpret a high polarization $|P|$ as low entropy and the process of polarizing nuclear spins as a reduction of their entropy. Also we see that flip-flop transitions conserve entropy.

3 The Solid Effect

3.1 Processes Involved in the Solid Effect

A schematic overview of the processes involved in the SE is shown in Fig. 1. Most nuclear spins are far away from the electron spins and their interaction with these electron spins is negligible. Still we wish to polarize just those spins. This is achieved in two steps. First, the microwave field induces flip-flop transitions between the electron spins and the nuclear spins near the former. Thus, the electron spin polarization is transferred to these near nuclear spins. Next, this polarization is transported further away from the electron spins by means of flip-flop transitions between the nuclear spins. The latter process is generally described as a diffusion process and hence called "nuclear spin diffusion". Unfortunately, the so-called local nuclear spins, i.e., those nearest to the electron spins, are excluded from nuclear spin diffusion. Their interaction with the electron spins is very strong, enabling a fast transfer of polarization from the electron spins to these local nuclear spins. However, this strong interaction also shifts the nuclear magnetic resonance (NMR) frequency of these local nuclear spins, thus inhibiting flip-flop transitions between them and the nuclear spins further away.

Stated in a colloquial way, the relation between polarization and entropy tells us that the polarization of an electron spin can be transferred to the nuclear spins
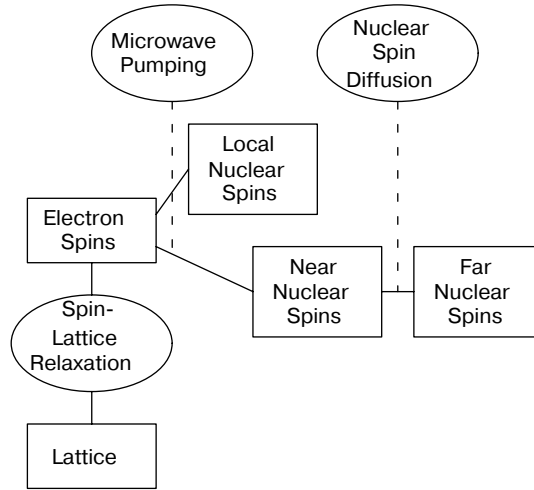
Fig. 1. Overview of the processes involved in DNP.

only once. But there are many nuclear spins which we wish to polarize. To enable this, the electron spin has to be repolarized. This is achieved by the electron spin–lattice relaxation process.

Thus, DNP occurs in three steps. First, the electron spins are polarized via electron spin–lattice relaxation. Next, this polarization is transferred to the nearby nuclear spins by means of the microwave field. Finally, nuclear spin diffusion transports the polarization to the far nuclear spins. Inevitably, all these processes have to counter nuclear spin–lattice relaxation, which is not shown in Fig. 1.

3.2 The Hamiltonian

We continue considering the polarization transfer between the electron spins and the nuclear spins. Recall that we treat the SE, so the mutual interactions between the electron spins play no role. Thus, this process is conveniently described considering a single electron spin $S = 1/2$ surrounded by N_i nuclear spins $I = 1/2$. The Hamiltonian for such a system is then given by

$$\hat{\mathscr{H}} = \omega_{0S}S_z + 2\omega_{1S}S_x\cos\omega t + \omega_{0I}\sum_{i=1}^{N_I}I_z^i + \sum_{i=1}^{N_I}\mathbf{S}\cdot\mathbf{A}^i\cdot\mathbf{I}^i.$$

Here the first term represents the Zeeman interaction of the electron spin with the externally applied magnetic field, the second term the interaction of this spin with the microwave field and the third term the Zeeman interaction of the nuclear spins. The following term is the hyperfine interaction between the electron spin and the nuclear spins. Finally, we ignore the dipolar interactions between the nuclear spins yielding nuclear spin diffusion.

We transform the electron spin operators in the Hamiltonian to a frame of reference which rotates about the z-axis with the microwave frequency using the operator $\exp(i\omega S_z t)$. Next we truncate the Hamiltonian – which corresponds to averaging the Hamiltonian over a time of the order $2\pi/\omega$. In the following step we apply the operator $\exp(i\theta S_{y'})$ to tilt the electron spin operators about the y'-axis in the rotating frame over an angle θ defined by

$$\sin\theta = \frac{\omega_{1S}}{\sqrt{\Delta^2 + \omega_{1S}^2}}, \tag{4}$$

where $\Delta = \omega_{0S} - \omega$ is the detuning of the microwave field with respect to the resonance frequency of the electron spin. Thus, as depicted in Fig. 2 the effective frequency vector with components Δ and ω_{1S} in the rotating frame and with a length

$$\omega_{\text{eff}} = \sqrt{\Delta^2 + \omega_{1S}^2}$$

defines the $\tilde{z}$-axis in the tilted rotating frame. As a result, the Hamiltonian has the shape

$$\hat{\mathcal{H}}' = Z + V_{\tilde{z}}\cos\theta + V_{\tilde{x}}\sin\theta,$$

where

$$Z = \omega_{\text{eff}}S_{\tilde{z}} + \omega_{0I}\sum_{i=1}^{N_I} I_z^i \tag{5}$$

is the Zeeman term and

$$V_\mu = \omega_{0I}\sum_{i=1}^{N_I}(A_{zz}^i S_\mu I_z^i + A_{zx}^i S_\mu I_x^i + A_{zy}^i S_\mu I_{zx}^i),$$
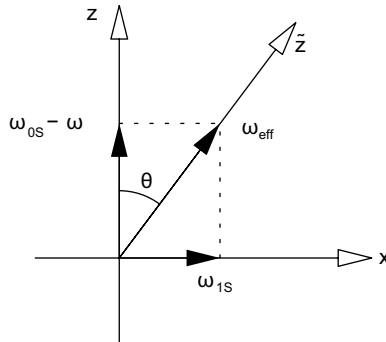
where $\mu = \tilde{z}$ or $\tilde{x}$.

Fig. 2. Effective frequency vector and its components in the rotating frame of reference.

3.3 Polarization Transfer

In the SE polarization transfer between the electron spin and the nuclear spins occurs when the Hartmann–Hahn condition [5]

$$\omega_{\text{eff}} = \sqrt{\Delta^2 + \omega_{1S}^2} = \omega_{0I} \tag{6}$$

for flip-flop transitions between the electron spin and the nuclear spins is satisfied. Thus, we require that the effective frequency ω_{eff} of the electron spin in the tilted rotating frame is equal to the NMR frequency ω_{0I} in the laboratory frame of reference. In strong magnetic fields the NMR frequency ω_{0I} is much larger than any component of the hyperfine tensor for any nuclear spin. If the Hartmann–Hahn condition Eq. (6) is fulfilled, this is also true for ω_{eff}. This allows a further truncation of the Hamiltonian – now corresponding to averaging over a time of the order $2\pi/\omega_{0I}$ – to

$$\hat{\mathscr{H}}'' = Z + V_{\tilde{z}z}\cos\theta + V_{\pm}\sin\theta, \tag{7}$$

where Z is given by Eq. (5) and

$$V_{\tilde{z}z} = \sum_{i=1}^{N_I} A_{zz}^i S_{\tilde{z}} I_z^i$$

shifts the energy levels. Finally,

$$V_{\pm} = \frac{1}{4}\sum_{i=1}^{N_I}(A_{z+}^i S_+ I_-^i + A_{z-}^i S_- I_+^i)$$

is the flip-flop term causing polarization transfer. It is written using the step operators $S_{\pm} = S_{\tilde{x}} \pm \mathrm{i}S_{\tilde{y}}$ and $I_{\pm}^i = I_x^i \pm \mathrm{i}I_y^i$ and the tensor elements $A_{z\pm}^i = A_{zx}^i \pm \mathrm{i}A_{zy}^i$ of the hyperfine interaction.

The Hamiltonian Eq. (7) can now be used to calculate the polarization transfer to the nuclear spins, following the same method as used to calculate coherence transfer or cross polarization between two species of nuclear spins [9]. The situation is complicated by the fact that the nuclear spins are many and nonequivalent. This problem can be solved by an appropriate transformation of the matrix representation of the Hamiltonian. For a full treatment of this method see ref. 7. This approach has the advantage that coherent effects as observed using pulsed methods for DNP (see, e.g., [8]) can also be understood.

In many cases it is sufficient to use the first-order perturbation theory. Then the rate of the polarization transfer is found to be given by

$$W_{\pm}(\omega) = 2\pi\sum_{i=1}^{N_I}\left|\frac{1}{4}A_{z+}^i\right|^2\frac{\omega_{1S}^2}{\omega_{0I}^2}f(\omega + \omega_{0I}\cos\theta). \tag{8}$$
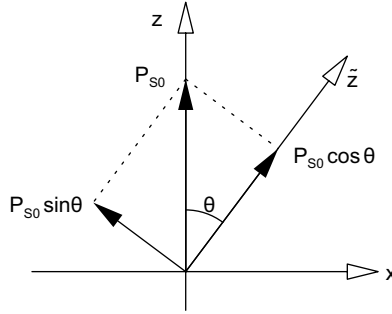
Fig. 3. Component of the electron spin polarization which is available for transfer to the nuclear spins.

Here $f(\omega)$ is the ESR line shape and the Hartmann–Hahn condition Eq. (6) is conveniently written as $\omega_{0S} = \omega + \omega_{0I}\cos\theta$. Furthermore, we combine Eqs. (4) and (6) to yield $\sin\theta = \omega_{1S}^2 / \omega_{0I}^2$.

Actually, not the full electron spin polarization is transferred to the nuclear spins, but only the component along the effective field vector. In standard DNP the electron spins are simply in thermal equilibrium with the lattice before the polarization transfer starts, so the polarization vector is oriented along the z-axis of the laboratory frame of reference, and hence also the z-axis of the rotating frame of reference. As shown in Fig. 3, its component along the effective frequency vector is equal to $P_{S0}\cos\theta$, where P_{S0} is the thermal-equilibrium value Eq. (2) of the electron spin polarization. As a result, the rate equation for the polarization transfer has the shape

$$\frac{\partial}{\partial t}(P_S \cos\theta - P_I) = -W_{\pm}(P_S \cos\theta - P_I). \tag{9}$$

4 Summing up: the Well-Resolved and the Differential Solid Effect

The Hartmann–Hahn condition Eq. (6) has two solutions for the detuning

$$\Delta_{\pm} = \pm\sqrt{\omega_{0I}^2 - \omega_{1S}^2}$$

and hence it is generally satisfied for two values of the tilting angle θ,

$$\cos\theta_{\pm} = \pm\frac{\sqrt{\omega_{0I}^2 - \omega_{1S}^2}}{\omega_{0I}}.$$

As is seen from Eq. (9), for $\cos\theta_{+}$, positive electron spin polarization is transferred to the nuclear spins, while for $\cos\theta_{-}$, negative electron spin polarization is transferred to the nuclear spins. Fortunately, the two effects do not compen-
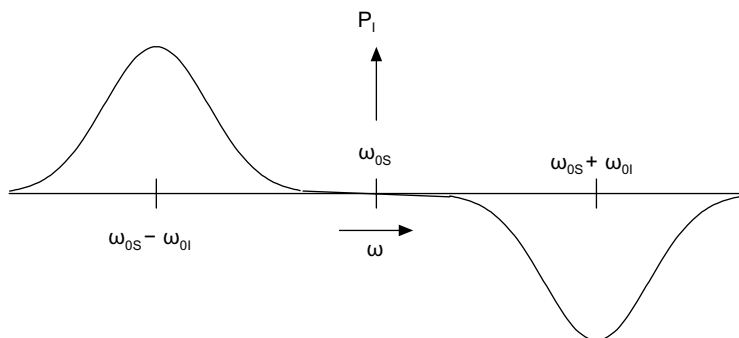
Fig. 4. Nuclear polarization as a function of the microwave frequency in the case of the well-resolved solid effect.

sate each other completely because the rate Eq. (8) of the polarization transfer is maximal at different microwave frequencies $\omega_+ = \omega_{0S} - \omega_{0I}\cos\theta_+$ and $\omega_- = \omega_{0S} + \omega_{0I}\cos\theta_-$.

In fact, when the ESR line is narrow compared with $\omega_{0I}\cos\theta_+$, positive and negative polarization transfers occur in two completely separated frequency regions. This case is known as the "well-resolved solid effect" and Fig. 4 shows the resulting nuclear polarization as a function of the microwave frequency. However, if the ESR line width is not narrow compared with $\omega_{0I}\cos\theta_+$, positive and negative polarization transfers compensate each other partly. This case is known as the "differential solid effect" and Fig. 5 shows how this compensation affects the resulting nuclear polarization as a function of the microwave frequency.
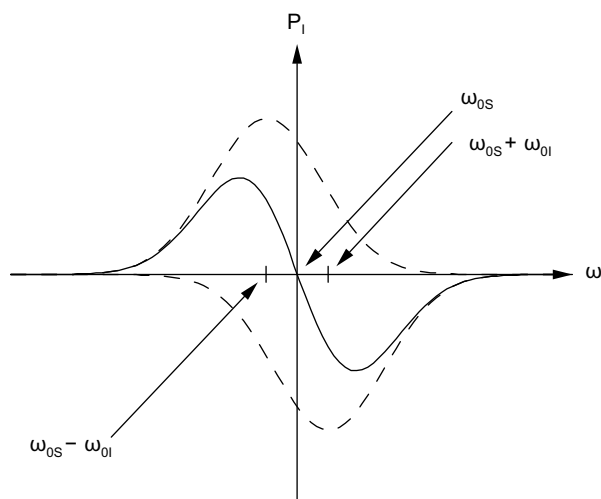

Fig. 5. Nuclear polarization as a function of the microwave frequency in the case of the differential solid effect.

At this point an important remark needs to be made. For a given ESR line width the cancellation of positive and negative polarization is more pronounced for nuclear spins with a small NMR frequency ω_{0I} than for nuclear spins with a large NMR frequency. Thus, nuclear spins with a large gyromagnetic ratio reach a higher polarization than those with a small gyromagnetic ratio. In practical situations, this may render the differential solid effect to be hard to distinguish from TM, which predicts a similar effect [1].

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