YU ISSN 0015-3206
FZKAAA 13 (4) 313 (1981)

NUCLEAR SPIN POLARIZATION IN DISTANT ENDOR EXPERIMENTS

M. PERIĆ and A. DULČIĆ

Ruđer Bošković Institute, P. O. B. 1016, 41001 Zagreb, Yugoslavia

Received 25 June 1981

UDC 538.9

Original scientific paper

Mechanism of nuclear spin polarization by forbidden electron-nuclear transitions is analysed in inhomogeneously broadened ESR line. The calculated spin distributions are related to the observed phenomena in distant ENDOR experiments.

1. Introduction

Distant electron-nuclear double resonance (ENDOR) can be observed when electron spin transitions are accompanied by polarizations of nuclear spins. So far, two mechanisms have been proposed which lead to nuclear spin polarization. Lambe et al.[1] have proposed forbidden transitions ($\Delta m_s = 1$, $\Delta m_I = 1$) as a process which polarizes Al^{27} nuclei in ruby crystal. Wenckebach et al.[2,3] have proposed a mechanism which depends on electron spin dipole-dipole interaction. The mathematical treatment of the latter mechanism relies on the use of spin temperature concept and the Provotorov equations[4]. The original treatment of Wenckebach et al. was later modified by Boroske and Möbius[5].

In their theoretical treatment of nuclear spin polarization and its impact on electron spin susceptibilities χ' and χ'', Lambe et al.[1] did not note that nuclear spin polarizations might be different for the two spin packets that undergo forbidden transitions. Detailed knowledge of the mechanisms of nuclear polarization is necessary for a correct description of the distant ENDOR effect. We have carried out a calculation of the spin distributions taking into account the mentioned differences. The results are at some variance with those of Lambe et al.

2. *Calculation of spin distributions*

When the width of the inhomogeneous electron spin resonance (ESR) line is larger than the nuclear Zeeman frequency ω_N, both, allowed ($\Delta m_s = 1$, $\Delta m_I = 0$) and forbidden ($\Delta m_s = 1$, $\Delta m_I = 1$) transitions can occur. Using the notation of Portis[6], the ESR line shape is given by a function $h(\omega' - \omega_0)$, where ω_0 is the centre frequency. This function is normalized with

$$\int_0^\infty h(\omega' - \omega_0)\, d\omega' = 1. \tag{1}$$

The lineshape of an individual spin packet centred at some frequency ω is given by function $g(\omega - \omega')$ with the normalization condition

$$\int_0^\infty g(\omega - \omega')\, d\omega' = 1. \tag{2}$$

If microwave field at frequency ω is applied to such a spin system, allowed transitions will occur for the spin packet whose shape function is $g(\omega - \omega')$. These transitions do not lead to a change in nuclear spin quantum number, and thus are unimportant for the nuclear polarization. Forbidden transitions occur for those spin packets which would have their allowed transitions at $\omega \pm \omega_N$. Taking

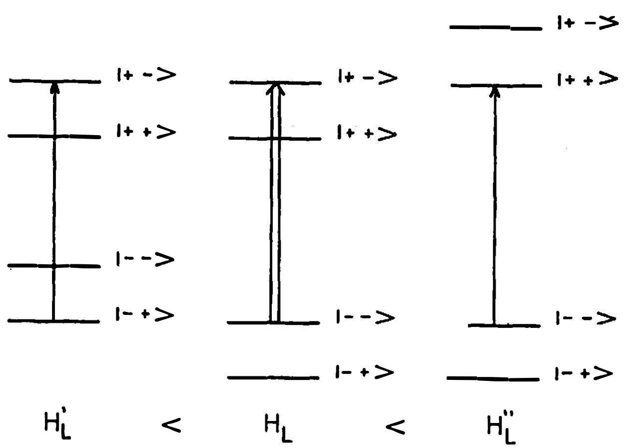

Fig. 1. Energy levels of electron-proton spin systems in the spin packets corresponding to different local magnetic fields. The spin eigenfunctions are denoted with the signs of m_s and m_I the quantum numbers of the electron and nuclear spins. The double arrow indicates allowed transition. The single arrows indicate forbidden transitions.

into account that forbidden transitions are less probable than the allowed, we can represent the corresponding shape function with $g'(\omega \pm \omega_N - \omega')$ whose normalization condition would be

$$\int_0^\infty g'(\omega \pm \omega_N - \omega')\,\mathrm{d}\omega' = g' \tag{3}$$

where $g' \ll 1$.

Fig. 1. shows the energy levels and transitions involved in the three spin packets. Forbidden transitions are followed by relaxation processes. Thus transition $|--\rangle$ to $|++\rangle$ is followed by electron spin relaxation $|++\rangle$ to $|-+\rangle$ and nuclear spin relaxation $|-+\rangle$ to $|--\rangle$. When stationary state is achieved, one has equal rates for the two relaxation transitions. Let us use the same notation for electron spins as Lambe et al.[1]:

$N(\omega') = h(\omega' - \omega_0)$ for the distribution function of electrons in local fields;

$N^+(\omega')$ and $N^-(\omega')$ for those parts of $N(\omega')$ which have spin up and down, respectively. $N^+(\omega') + N^-(\omega') = N(\omega')$;

$n(\omega') = N^-(\omega') - N^+(\omega')$ for the difference in electron spin populations.

At variance with Lambe et al., we put an index for the populations of nuclear spins since those populations may depend on ω'. Thus we use:

$M^+_{\omega'}$, and $M^-_{\omega'}$, for the fraction of nuclei with spin up and down, respectively. $M^+_{\omega'} + M^-_{\omega'} = 1$.

$m_{\omega'} = M^+_{\omega'} - M^-_{\omega'}$ for the difference in nuclear spin populations.

One can easily prove that

$$N^-(\omega')\,M^-_{\omega'} - N^+(\omega')\,M^+_{\omega'} = \frac{1}{2}\,[n(\omega') - N(\omega')\,m_{\omega'}], \tag{4}$$

$$N^-(\omega')\,M^+_{\omega'} - N^+(\omega')\,M^-_{\omega'} = \frac{1}{2}\,[n(\omega') + N(\omega')\,m_{\omega'}]. \tag{5}$$

For the spin packet whose allowed transition is at $\omega' \sim \omega + \omega_N$, one has

$$\frac{n^0(\omega + \omega_N) - n(\omega + \omega_N)}{T_{1e}} = \frac{1}{4}\,\pi\,\gamma^2 H_1^2\, g'(0)\,[N^-(\omega + \omega_N)\,M^+_{\omega+\omega_N} - N^+(\omega + \omega_N)\,M^+_{\omega+\omega_N}]. \tag{6}$$

The equality of the relaxation rates in the stationary state implies that

$$\frac{m_{\omega+\omega_N} - m^0_{\omega+\omega_N}}{T_{1N}} = \frac{1}{4}\,\pi\,\gamma^2 H_1^2 \int g'(\omega + \omega_N - \omega')\,[N^-(\omega')\,M^-_{\omega'} - N^+(\omega')\,M^+_{\omega'}]\,\mathrm{d}\omega'. \tag{7}$$

The amplitude at the centre of the spin packet is T_{2e}/π. For a forbidden transition we can multiply it by the factor g'. Using Eq. (4) and the saturation parameter $S = \left(\frac{1}{2}\gamma H_1\right)^2 T_{1e} T_{2e}$, we can rewrite Eq. (6) for $\omega' = \omega + \omega_N$ in the form

$$n^0(\omega + \omega_N) - n(\omega + \omega_N) = \frac{S g'}{2}\left[n(\omega + \omega_N) - N(\omega + \omega_N)\, m_{\omega+\omega_N}\right]. \qquad (8)$$

In the integration of Eq. (7) one may approximate $n(\omega')$ and $N(\omega')$ by $n(\omega + + \omega_N)$ and $N(\omega + \omega_N)$, respectively.

The result is

$$\frac{m_{\omega+\omega_N} - m^0_{\omega+\omega_N}}{T_{1N}} = \frac{\pi}{T_{1e}T_{2e}}\frac{S g'}{2}\left[n(\omega + \omega_N) - N(\omega + \omega_N)\, m_{\omega+\omega_N}\right]. \qquad (9)$$

The two coupled Eqs. (8) and (9) give solutions:

$$m_{\omega+\omega_N} = \frac{m^0 + a_{\omega+\omega_N}\dfrac{n^0(\omega+\omega_N)}{N(\omega+\omega_N)}}{1 + a_{\omega+\omega_N}} \qquad (10)$$

$$n(\omega + \omega_N) = \frac{n^0(\omega+\omega_N) + \dfrac{S g'}{2}\dfrac{N(\omega+\omega_N)\, m^0 + a_{\omega+\omega_N}\, n^0(\omega+\omega_N)}{1 + a_{\omega+\omega_N}}}{1 + \dfrac{S g'}{2}}. \qquad (11)$$

where

$$a_{\omega'} = \frac{\pi T_{1N}}{T_{1e}T_{2e}}\,\frac{\dfrac{S g'}{2}}{1 + \dfrac{S g}{2}}\, N(\omega'). \qquad (12)$$

For the spin packet, whose allowed transition is at $\omega' \approx \omega - \omega_N$, one obtains analogously:

$$m_{\omega-\omega_N} = \frac{m^0 - a_{\omega-\omega_N}\dfrac{n^0(\omega-\omega_N)}{N(\omega-\omega_N)}}{1 + a_{\omega-\omega_N}} \qquad (13)$$

$$n(\omega - \omega_N) = \frac{n^0(\omega-\omega_N) - \dfrac{S g'}{2}\dfrac{N(\omega-\omega_N)\, m^0 - a_{\omega-\omega_N}\, n^0(\omega-\omega_N)}{1 + a_{\omega-\omega_N}}}{1 + \dfrac{S g'}{2}}. \qquad (14)$$

In Eqs. (10), (11), (13) and (14) we have used the notation m^0 for $m^0_{\omega\pm v_N}$.

When forbidden transitions are weak, we have $\alpha \frac{n^0}{N} \ll m^0$ and very small changes are induced in the nuclear spin polarizations at both spin packets. Appreciable saturation of forbidden transitions implies $\alpha \frac{n^0}{N} \gg m^0$. One should note that m^0 is three orders of magnitude smaller that $\frac{n^0}{N}$ so that α can still be lower than unity. We obtain accordingly:

$$m_{\omega+\omega_N} = \frac{a_{\omega+\omega_N}}{1 + a_{\omega+\omega_N}} \frac{n^0(\omega+\omega_N)}{N(\omega+\omega_N)} \tag{15}$$

$$n(\omega+\omega_N) = \frac{1 + \frac{a_{\omega+\omega_N}}{1+a_{\omega+\omega_N}} \frac{Sg'}{2}}{1 + \frac{Sg'}{2}} n^0(\omega+\omega_N) \tag{16}$$

$$m_{\omega-\omega_N} = -\frac{a_{\omega-\omega_N}}{1 + a_{\omega-\omega_N}} \frac{n^0(\omega-\omega_N)}{N(\omega-\omega_N)} \tag{17}$$

$$n(\omega-\omega_N) = \frac{1 + \frac{a_{\omega-\omega_N}}{1+a_{\omega-\omega_N}} \frac{Sg'}{2}}{1 + \frac{Sg'}{2}} n^0(\omega-\omega_N). \tag{18}$$

Nuclear spins which take part in the two forbidden transitions are polarized in the opposite directions. The net spin polarization of distant nuclei is

$$M = \frac{n^0}{N}\left(\frac{a_{\omega+\omega_N}}{1+a_{\omega+\omega_N}} - \frac{a_{\omega-\omega_N}}{1+a_{\omega\infty\omega_N}}\right) \tag{19}$$

where we have used the fact that $\frac{n^0}{N}$ is independent of the frequency. This polarization is positive for $\omega < \omega_0$ and negative for $\omega > \omega_0$. At $\omega = \omega_0$, there is no polarization.

Eqs. (16) and (18) show that $n < n^0$ which means that holes are burnt in the corresponding electron spin packets. For $\omega < \omega_0$ the resulting distribution of $n(\omega)$ is shown in Fig. 2.

When saturating radiofrequency (*rf*) field of frequency ω_N is switched on, one can put $m_{\omega+\omega_N} = 0$ in Eq. (8). The result is

$$n(\omega+\omega_N) = \frac{1}{1+\frac{Sg'}{2}} n^0(\omega+\omega_N). \tag{20}$$

For the spin packet at $\omega' \approx \omega - \omega_N$, one obtains from an equation analogous to Eq. (8)

$$n(\omega - \omega_N) = \frac{1}{1 + \frac{S g'}{2}} n^0 (\omega - \omega_N). \tag{21}$$

Thus, when *rf* saturation is present, the ratio $\frac{n}{n^0}$ is the same at both frequencies. However, this ratio is lower than in the absence of the saturating *rf* field. The corresponding changes are shown in Fig. 2.

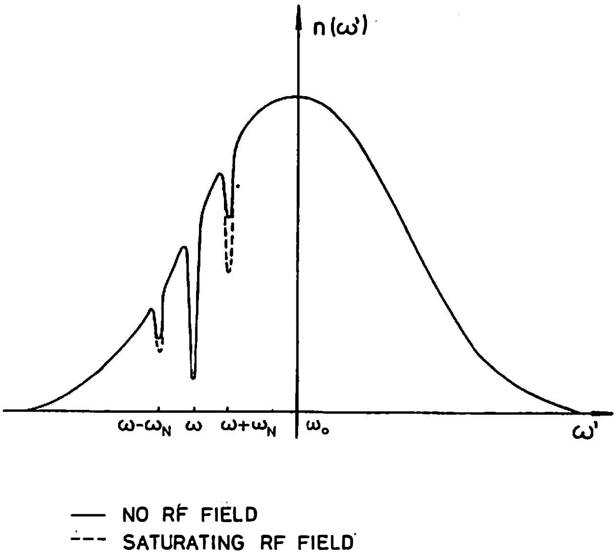

Fig. 2. Distribution of $n(\omega') = N^-(\omega') - N^+(\omega')$ with the holes burnt by microwave field in various spin packets in the absence of a *rf* field (full line) and in the presence of saturating *rf* field (dashed line).

3. *Discussion*

The present results appear to be somewhat different from those calculated by Lambe et al. and shown in Fig. 8 of Ref. 1. However, the resulting behaviour of electron spin susceptibilities χ' and χ'' is qualitatively the same as that found by Lambe et al. The imaginary part χ'' should exhibit increase when *rf* field is turned on since flipping of nuclear spins speeds up overall relaxation rate and enables more forbidden transitions. Since the increase in $\frac{n}{n^0}$ at $\omega + \omega_N$ is greater than that at $\omega - \omega_N$, the change in χ' is more affected by the higher frequency spin packet. Thus, the dispersive part of the electron spin susceptibility decreases as has been verified experimentally[1].

The above treatment is idealized in the sense that it does not take nuclear spin diffusion into account. It has been assumed implicitly that the electron spins are very far from each other while forbidden transitions affect nuclei at some moderate distance from the corresponding electron spins. Thus, polarized nuclei form two distinct groups. Spin difussion would establish a steady state where polarization is partially transfered from one polarized group to the rest of the distant nuclei and from there to the nuclei and from there to the other group. The values of $m_{\omega \pm \omega_N}$ as calculated in Eqs. (15) and (17) are thereby reduced. Upon inspection of Eq. (8) one finds that $n(\omega + \omega_N)$ is reduced, too. The same holds for $n(\omega - \omega_N)$. In the case when spin diffusion is much faster than the rate of forbidden transitions, the degree of polarization of all the distant nuclei is the same and equals that given by Eq. (19). Such an assumption has been made by Lambe et al. Thus, their solutions appear to hold in the special case of very fast spin diffusion. In reality, the spin polarizations and distributions are inbetween those calculated by Lambe et al. and our solutions given by Eqs. (15—18).

References

1) J. Lambe, N. Laurence, E. C. McIrvine and R. W. Terhune, Phys. Rev. **122** (1961) 1161;
2) W. Th. Wenckebach, T. J. B. Swanenburg and N. J. Poulis, Physica **46** (1970) 303;
3) W. Th Wenckebach, L. A. H. Schreurs, H. Hoogstraate, T. J. B. Swanenburg and N. J. Poulis, Physica **52** (1971) 455;
4) B. N. Provotorov, Zh. Eksper. Teor. Fiz. **41** (1961) 1582; Soviet. Phys. JETP **14** (1962) 1126;
5) E. Boroske and K. Möbius, J. Mag. Res. **28** (1977) 325;
6) A. M. Portis, Phys. Rev. **91** (1953) 1071.

SPINSKA POLARIZACIJA JEZGARA U EKSPERIMENTIMA S UDALJENOM ELEKTRONSKO NUKLEARNOM DVOSTRUKOM REZONANCIJOM

M. PERIĆ i A. DULČIĆ

Institut »Ruđer Bošković«, P. P. 1016, 41 001 Zagreb

UDK 538.9

Originalni znanstveni rad

Analiziran je mehanizam spinske polarizacije jezgara putem zabranjenih elektronsko nuklearnih prijelaza u nehomogeno proširenoj liniji elektronske spinske rezonancije. Izračunate spinske razdiobe povezane su sa fenomenima opaženim u eksperimentima s udaljenom elektronsko nuklearnom dvostrukom rezonancijom.