SPIN-TEMPERATURE MODEL OF NUCLEAR DYNAMIC POLARIZATION USING FREE RADICALS

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We present a spin-temperature model, valid at low temperature, of nuclear dynamic polarization using electronic spin systems with g-factor anisotropy and hyperfine structure. Predictions for the maximum polarization corresponding to some free radicals are compared with experiment.

Sizable dynamic polarizations of protons have recently been obtained in solid samples containing free radicals as paramagnetic centers.[1-3] Although the g tensors of these radicals have small anisotropies by current standards, for example,[4] $g_{\max}-g_{\min}\simeq 10^{-3}\text{-}10^{-2}$, the corresponding frequency spread in the high fields used for such dynamic polarizations, for example 25 kG, is not at all negligible compared with the other sources of broadening of their resonance line. Furthermore, these radicals exhibit often quite important hyperfine structures,[4] and the over-all linewidth is not smaller than the resonance frequency of the nuclei which are polarized. In order to predict the maximum polarizations that can be expected from a given radical species, as defined by the parameters of its spin Hamiltonian, some previous considerations,[5] which assumed a narrow line, are thus no longer applicable.

We present here a model of saturation and dynamic polarization which takes into account anisotropy and hyperfine structure, and which is valid at low temperatures.

We consider a dielectric solid, at a temperature T_0, containing diluted unpaired electronic spins S_i, with $S=\frac{1}{2}$, located in a strong magnetic field H_0 and in a high-frequency field H_1 of frequency ω, with $H_1 \ll H_0$. We assume first that there are no nuclei other than those which interact by hyperfine coupling with the spins S. The spin Hamiltonian of the system reads, by neglecting the small Zeeman and quadrupolar contributions from the "hyperfine nuclei" K_j,

$$\hbar\mathcal{H}=\sum_i \vec{S}_i\cdot \mathrm{g}_i\beta\cdot\vec{H}_0+\sum_{ij}\hbar\vec{S}_i\cdot \mathsf{A}_{ij}\cdot\vec{K}_j +\sum_i \vec{S}_i\cdot \mathrm{g}_i\beta\cdot\vec{H}_1\cos\omega t+\mathcal{H}_{SS'},$$

where g_i and A_{ij} are, respectively, the g tensor and the hyperfine tensors relative to spin S_i; $\mathcal{H}_{SS}$ are the spin-spin interactions among spins S.

We shall consider cases where the broadening of the electronic resonance line due to $\mathcal{H}_{SS}$ is much smaller than its broadening coming from anisotropy and hyperfine interactions. This allows one to avoid using the "high-temperature approximation",[6] and thus to evaluate realistic upper limits for the nuclear polarization in strong fields at low temperatures; besides this, such a condition is satisfied in many experimental situations. We shall be concerned here only with the limiting case of saturating hf fields. It can be shown by extending Provotorov's quantum-mechanical derivation of cross relaxation[7] that, in the high-temperature approximation and in the limit of strong hf field, the spin system can be described as having a single temperature in a suitable reference frame, when cross relaxation is fast. Here we want to draw some conclusions from the assumption that this remains valid even at low temperatures. In other words, we apply Redfield's spin-temperature hypothesis[8] to the case of spin systems with spectral distributions, by assuming that the cross relaxation[9] between the various spin packets is faster than spin-lattice relaxation, which is a reasonable assumption at low temperatures. Performing the transformation $U=\exp(-i\omega t\sum_i\vec{S}_i\cdot\hat{\omega}_i)$ on the system, where $\hat{\omega}_i$ is the unit vector in the direction $\mathrm{g}_i\beta\cdot\vec{H}_0$, in order to make the main part of $\mathcal{H}$ time independent, and keeping the main secular terms alone, the transformed Hamiltonian reads

$$\hbar\mathcal{H}^*=\sum_i\hbar(\omega_i-\omega)\vec{S}_i\cdot\hat{\omega}_i +\sum_{ij}\hbar(\hat{\omega}_i\cdot\mathsf{A}_{ij}\cdot\vec{K}_j)\vec{S}_i\cdot\hat{\omega}_i,$$

with $\hbar\omega_i=|\mathrm{g}_i\beta\cdot\vec{H}_0|$. The density matrix describing the system is $\rho_0=\exp(-\alpha_0\mathcal{H})/\mathrm{Tr}\exp(-\alpha_0\mathcal{H})$, with $\alpha_0=\hbar/kT_0$, before the application of the hf field, and becomes $\rho^*=\exp(-\alpha\mathcal{H}^*)/\mathrm{Tr}\exp(-\alpha\mathcal{H}^*)$. Assuming that the various parts of the Hamiltonian have the same relaxation towards the lattice,[10] the stationary value of α is given by $\mathrm{Tr}\rho^*\mathcal{H}^*=\mathrm{Tr}\rho_0\mathcal{H}^*$. By using the fact that $S=\frac{1}{2}$, and by neglecting α_0 with respect to α, since we are interested here in situations where high "cooling" is possible, and writing $\Delta_i = \omega_i - \omega$, $\overline{\omega} = \sum_i \omega_i$, and $\Delta = \overline{\omega} - \omega$, this equation becomes

$$\tfrac{1}{2}\sum_i \Delta_i \tanh\tfrac{1}{2}\alpha\Delta_i + \tfrac{1}{2}\sum_{ij} A_{ij}{}'K_j \times \mathcal{B}(K_j; \tfrac{1}{2}\alpha A_{ij}{}'K_j) \simeq \tfrac{1}{2}\Delta \tanh\tfrac{1}{2}\alpha_0\overline{\omega}, \qquad (1)$$

with $A_{ij}{}' = |\hat{\omega}_i \cdot \mathsf{A}_{ij}|$ and $\Delta_i, A_{ij}{}' \ll \omega$; $\mathcal{B}(K;x)$ being the Brillouin function

$$\mathcal{B}(K;x) = (2K+1)(2K)^{-1}\coth[(2K+1)x/2K] - (2K)^{-1}\coth(x/2K).$$

Equation (1) defines the value of α, i.e., of the common spin temperature.

In order to go further into practical applications, one has to relate Δ_i and $A_{ij}{}'$ to the angles defining the orientation of the free radical molecules with respect to $\vec{H}_0$: If we consider completely disoriented solids, as in the experiments quoted above, these angles take random values, and $\sum_i X_i$ becomes

$$(2\pi)^{-2}\int_0^{2\pi}\int_0^{2\pi} X(\theta,\varphi)\,d\varphi\,\sin\theta\,d\theta;$$

one has

$$\hbar\Delta(\theta,\varphi) = g(\theta,\varphi)\beta H_0 - \omega, \quad g(\theta,\varphi) = (g_1{}^2\cos^2\theta + g_2{}^2\sin^2\theta\cos^2\varphi + g_3{}^2\sin^2\theta\sin^2\varphi)^{1/2}$$

and a similar formula for $A(\theta,\varphi)$.

We turn now to nuclear dynamic polarization: We consider that the solid contains nuclear spins I, with resonant frequency ω_n, coupled with the spins S through dipole-dipole interactions. We suppose that ω_n is not much larger than the electronic linewidth, and we keep on considering the limiting case of saturating hf fields. As we have shown previously,[6] the nuclei may acquire the same temperature as the electronic spins, in which case the nuclear polarization is given by $P_n = \mathcal{B}(I; \alpha\omega_n I)$, where α is defined by Eq. (1).[11]

Table I. Calculated polarizations for two free radicals at 1.2°K.

Radical	H_0 (kG)	P_{opt} (protons) (calc)	P_{opt} (deuterons) (calc)
DDPH[a] (^{14}N)	25	+0.72	+0.18
		−0.76	−0.20
	50	+0.93	+0.32
		−0.97	−0.40
DPPH (^{15}N)	25	+0.74	+0.19
		−0.79	−0.21
	50	+0.95	+0.35
		−0.98	−0.43
PR[b] (^{14}N)	25	±0.62	±0.14
	50	±0.91	±0.29
PR (^{15}N)	25	±0.64	±0.15
	50	±0.92	±0.31

[a] DPPH = 1, 1-diphenyl-2-picrylhydrazyl. $g_1 \simeq 2.005$, $g_2 = g_3 \simeq 2.010$ at 1.6°K [L. S. Singer and C. Kikuchi, J. Chem. Phys. 24, 170 (1955)]. $A_1(^{14}\text{N}) \simeq 20$ G, $A_2 = A_3(^{14}\text{N}) \simeq 2$ G; $A_1{}'(^{14}\text{N}) \simeq 21$ G, $A_2{}' = A_3{}'(^{14}\text{N}) \simeq 4$ G (see Ref. 4).

[b] PR = porphyrexide. $g_1 \simeq 1.9997$, $g_2 \simeq 2.0047$, $g_3 \simeq 2.0097$ [M. Borghini, S. Mango, and O. Runolfsson, to be published]. $A_1(^{14}\text{N}) \simeq 27$ G, $A_2 + A_3$ small (neglected).

Examples of the polarization obtained by using the present model, optimized with respect to the hf frequency, are shown in Table I for two free radicals, diphenylpicrylhydrazyl and porphyrexide.[12] The theoretical values are higher than the experimental ones, which are of the order of 35% at most.[1,3] There are many reasons why these calculated optimum polarizations cannot be achieved in a given sample, coming either from the electron spin temperature not being as low as calculated by Eq. (1), because of relaxation mechanisms, or from this temperature not being completely transmitted to the nuclei, because of the regime of spin diffusion and heat-transfer properties of the samples.

The preceding considerations should be taken as giving the maximum polarizations that can be expected in a sample by using a given paramagnetic species.[13]

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[1] R. J. Wagner and R. P. Haddock, Phys. Rev. Letters 16, 1116 (1966).

[2] A. Moretti, A. Yokosawa, F. W. Markley, and R. C. Miller, to be published.

[3] M. Borghini, S. Mango, O. Runolfsson, and J. Vermeulen, in Proceedings of the International Conference on Polarized Targets and Ion Sources, Saclay, France, 1966 (La Documentation Français, Paris, France, 1967), p. 387.

[4] See, for instance, H. Fisher, in Landolt-Börnstein Data and Functional Relationships in Science and Technology. New Series, edited by K.-H. Hellwege and A. M. Hellwege (Springer-Verlag, Berlin, Germany, 1965), Group II: Atomic and Molecular Physics, Vol.

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[5] M. Borghini, Phys. Rev. Letters 16, 318 (1966).

[6] See A. Abragam and M. Borghini, Progress in Low-Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, The Netherlands, 1964), Vol. IV. To deal with spin-spin interactions $\mathcal{H}_{SS}$ would require the introduction of the relaxation equation for $\langle \mathcal{H}_{SS}{}^* \rangle$ which is still unknown at low temperatures.

[7] B. N. Provotorov, Zh. Eksperim. i Teor. Fiz. 42, 882 (1962) [translation: Soviet Phys.–JETP 15, 611 (1962)].

[8] A. Redfield, Phys. Rev. 98, 1787 (1955); A. Abragam, The Principles of Nuclear Magnetism (Oxford-Clarendon Press, Oxford, England, 1961).

[9] N. Bloembergen, S. Shapiro, P. L. Pershan, and J. O. Artman, Phys. Rev. 114, 445 (1959).

[10] In fact, the hfs contribution to $\langle \mathcal{H}^* \rangle$ should be multiplied by $[1+(T_e/T_j)]$, where T_e and T_j are the spin-lattice relaxation times of spins S and spins K_j, respectively. In order to simplify the exposition and to avoid the introduction of adjustable parameters, we assume here that $T_e \ll T_j$.

[11] This supposes that the relaxation of spins I is not too fast with respect to the electronic relaxation; in fact, a term proportional to the thermal capacity of spins I should be added to $\langle \mathcal{H}^* \rangle$. In the case of strong "leakage" and fast spin diffusion,[5] it takes the form $I(N_n/N_e)(T_e/T_n)\omega_n \mathcal{B}(I;\alpha\omega_n I)$, where N_n and N_e are the number of spins I and S, respectively, T_n being the relaxation time of spins I.

[12] For radicals with axial symmetry, it can be shown that $P_{\mathrm{opt}}{}^{\mathrm{pos}}$ is slightly larger or smaller than $|P_{\mathrm{opt}}{}^{\mathrm{neg}}|$ according to $g_\parallel - g_\perp$ being positive or negative. The difference goes to zero when the left-hand side of Eq. (1) can be developed to the first order in α. For porphyrexide, although the hyperfine interactions produce a very asymmetric electron resonance line, the optimum positive and negative polarizations have equal absolute values because the three principal g values are almost equally spaced.

[13] One can see from Table I that the isotopic replacement of ^{14}N atoms by ^{15}N atoms does not increase appreciably the maximum values of the polarizations; however, if practical polarizations are limited by a fast relaxation of the ^{14}N atoms coming from their quadrupole interactions,[10] their replacement by ^{15}N should increase these polarizations by greater factors.

SECOND-HARMONIC GENERATION BY A RESONANT SPIN SYSTEM

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We wish to report the first observations of second-harmonic generation at microwave frequencies by a resonant two-level spin system. In particular, second harmonics were generated in ruby in a strong electromagnetic field at 2 kMc/sec when two spin states of the ground state of Cr^{3+} were split by 2 or 4 kMc/sec, independently from the location of the other spin states. As we shall see, harmonic waves are probably generated by a two-quantum absorption and single-quantum emission by the spin system, energy being conserved between the initial and final states.

This effect is quite different from the one reported by different authors[1-4] on the generation of a second harmonic by a resonant three-level spin system. In this case three equally separated spin states operate a frequency mixing (doubling) for a frequency which couples two successive states, provided that all the transitions are quantum-mechanically allowed. Except for some very special cases (e.g., $S=1$ in cubic symmetry), these three equally spaced levels may be obtained at very special field and angle values, so that the very presence of the harmonic signal is strongly dependent upon the angle. Often, no more than one line is detected in this case.

We have used a system of two re-entrant cavities resonating at 2 and 4 kMc/sec, respectively. The cavities were coupled in points of maximum rf magnetic field by a ruby single crystal. The size of the crystal was approximately 4 mm × 4 mm × 10 mm and the Cr^{3+} concentration about 0.1 % for one specimen and about 0.02 % for another specimen. Either no or a very weak 4-kMc/sec signal was obtained when the coupling was through the rf electric field of the cavities. The 2-kMc/sec cavity (pump cavity) was fed by up to 1-kW peak power ($\frac{1}{2}$-μsec pulse width and repetition rate from 200 to 1000 pps), well filtered from its harmonics by a low-pass filter at 2 kMc/sec. The signal from the second cavity (signal cavity), filtered by a 60-dB bandpass filter, was detected by a superheterodyne receiver. Upon substitution of the 4-kMc/sec bandpass filter between the signal cavity and the receiver with a low-pass filter at 2 kMc/sec, a very strong signal at 2 kMc/sec was detected. The new