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Theory of modulation effects in resonant-nuclear-disorientation experiments. III

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Earlier calculations of the effects of a resonant, frequency-modulated, rf field and spin-lattice relaxation on the emission of radiations from thermally oriented radioactive nuclei are extended. A purely magnetic interaction is assumed for the nuclei. Simple formulas, applicable for any nuclear spin, are derived for the effects of fast modulation on the nuclear-orientation parameters B_ν. Also an analytic expression is derived for static nuclear orientation in a magnetic field at high temperatures.

I. INTRODUCTION

Since the first observation[1] of the effect of a resonant rf field on the emission of radiations from oriented nuclei there has been considerable interest in the theory of these resonant-nuclear-disorientation (RND) experiments. There are two classes of RND experiments. In nuclear-orientation–NMR experiments, the resonance is detected via the resulting change in the anisotropy of the emitted radiations. In Mössbauer-effect–NMR experiments the change in the asymmetry of the Mössbauer-effect spectra of the daughter nuclei is observed.[2] The effects of a constant-frequency rf field on the radiations from nuclei which have been oriented at low temperatures in a static magnetic field are now well understood. In this case the radiation anisotropy may be completely destroyed by a sufficiently large rf field if nuclear spin-lattice relaxation is present.[3] If relaxation is not taken into account a "hard-core" anisotropy will result and this cannot be destroyed regardless of the intensity of the rf field.[4–6] So far most RND experiments have been performed on nuclei which have been oriented by hyperfine magnetic fields in ferromagnetic host metals. The main experimental advantages associated with the ferromagnetic hosts are the large magnitudes of the hyperfine magnetic fields and also the ferromagnetic enhancement of the rf magnetic field acting on the nuclei. However it should also be possible to perform such experiments on nuclei which have been oriented by an applied magnetic field ("brute-force" nuclear orientation). Here the absence of any rf enhancement should be largely compensated for by a reduction in the inhomogeneous broadening.

Because of off-resonant heating effects only small rf fields H_1 can be used so that, in general, the inhomogeneous broadening width will be considerably greater than the frequency width $\omega_1 = \gamma H_1$ for a single nuclear-spin packet. It is then necessary to employ a frequency-modulated rf field to obtain large reductions in the radiation anisotropy at resonance. Under these conditions calculations based on a constant rf frequency are not applicable. Calculations of the effects of a frequency-modulated rf field have been reported previously[8,9] (to be referred to as I and II, respectively). In these, it was assumed that during each modulation cycle individual nuclear-spin packets are resonated twice and undergo spin-lattice relaxation towards lattice equilibrium between these resonances. The dependence of the signal—the fractional destruction of the anisotropy—on H_1 and the modulation amplitude W and frequency ω were calculated. In I, a spin-temperature description of the relaxation was assumed so that the calculated dependences upon H_1 and ω will be only approximate although the dependence upon W should be exact. In II, the resonances of the spin packets were treated as single resonant passages[10,11] and also the Gabriel[12] theory of spin-lattice relaxation was used. This resulted in an exact quantum-mechanical treatment of the effect of a resonant-frequency-modulated rf field on nuclei which have been oriented in a static magnetic field. A general treatment was outlined and applied in some detail for spin-1 nuclei. We report here improvements in the formalism together with simple results, applicable for any nuclear spin.

II. THEORY

The polarization of radioactive nuclei in an axial magnetic field $\vec{H}$ produces a fractional change F in the intensity of radiation emitted at an angle θ to the direction of $\vec{H}$ given by

$$F = \sum_{\nu=1,2,\ldots} U_\nu F_\nu B_\nu P_\nu(\cos\theta) , \qquad (1)$$

where the F_ν and U_ν are angular-momentum coupling coefficients for the observed and preceding radiative transitions; the B_ν are nuclear-orienta-

tion parameters for the parent nuclei. If the nuclei are in thermal equilibrium we denote F by F^e and the B_ν by B_ν^e. The B_ν^e depend upon $X=\mu_N H/2kTI$.

In frequency-modulated RND experiments each nuclear-spin packet will experience two passages through resonance per modulation cycle. The time interval between these passages will alternate between t' and $(2\pi/\omega - t')$, where t' varies from 0 to π/ω depending on the position of the packet in the frequency range of the modulation waveform. Expressions for t' are given in I for triangular and sinusoidal waveforms. As in II, if initially the nuclear ensemble for each packet has pure axial alignment with no x or y components of spin, the orientation parameters B_ν^f immediately after a single passage are related to the parameters B_ν^i immediately before by

$$B_\nu^f = K_\nu B_\nu^i \ . \tag{2}$$

The K_ν are simply calculated in terms of the adiabatic parameter, $A=\omega_1^2(d\omega/dt)^{-1}$ using

$$K_\nu = P_\nu(\cos\alpha) \ , \tag{3}$$

where α is the angle through which the nuclear magnetization moves during the passage. The assumption of pure axial alignment for each spin packet before every passage requires that the modulation is sufficiently slow so that coherence effects of successive passages on the spin packets may be neglected. The main mechanism for decoherence will be the inhomogeneous broadening.

Between passages we assume that the time dependence of the orientation parameters is given by the theory of Gabriel[12] so that

$$\Delta B_\nu(t/T_1) = \sum_{\nu'} \Delta B_{\nu'}(0)\, G_{00}^{\nu\nu'}(t/T_1) \ , \tag{4}$$

where $\Delta B_\nu = B_\nu - B_\nu^e$ and $t=0$ refers to the time immediately after the last passage. Analytic functions $G_{00}^{\nu\nu'}(t/T_1)$ have been given for spin-1 nuclei[13] and were used in II. We derive below and apply formulas for the case $t \ll T_1$ for any spin.

The signal S_ν is defined as the fractional reduction of the parameter B_ν so that

$$S_\nu = 1 - \frac{\omega^2}{2\pi^2 B_\nu^e} \int_0^{\pi/\omega} \oint B_\nu \, dt\, dt' \ , \tag{5}$$

where $\oint$ refers to an integration over a complete modulation cycle.

Using Eqs. (2)–(4) we obtained in II a general expression for the change in the B_ν over one modulation cycle. This can be used to derive the transient dependences of the B_ν upon the time after switching on the rf; however here we are concerned with the steady-state signals which are obtained by putting the changes over one cyle equal to zero. It then follows that

$$\sum_{\nu'} \alpha_{\nu\nu'} \Delta B_{\nu'}^\infty = \sum_{\nu'} \beta_{\nu\nu'} B_{\nu'}^e \qquad (\nu = 1, 2, \ldots, 2I) \tag{6}$$

where

$$\alpha_{\nu\nu'} = \delta_{\nu\nu'} - \sum_{\nu''} G_{00}^{\nu\nu''}(2\pi/\omega - t') K_{\nu''} G_{00}^{\nu''\nu'}(t') K_{\nu'} \ ,$$

$$\beta_{\nu\nu'} = \sum_{\nu''} G_{00}^{\nu\nu''}(2\pi/\omega - t')\, K_{\nu''} G_{00}^{\nu''\nu'}(t')(K_{\nu'} - 1)$$
$$+ G_{00}^{\nu\nu'}(2\pi/\omega - t')(K_{\nu'} - 1) \ . \tag{7}$$

Here B_ν^∞ refers to the limiting steady-state value averaged over a complete modulation cycle. All sums over ν', ν'' are from 1 to $2I$. The formal solution of Eq. (6) is

$$\Delta B_\nu^\infty = \sum_{\nu'} (\alpha^{-1}\beta)_{\nu\nu'} B_{\nu'}^e \ . \tag{8}$$

The signals S_ν involve an average over all spin packets and hence over t' so that

$$S_\nu = -\langle \Delta B_\nu^\infty \rangle_{t'} / B_\nu^e \ ,$$

where

$$\langle \Delta B_\nu^\infty \rangle_{t'} = \sum_{\nu'} \langle (\alpha^{-1}\beta)_{\nu\nu'} \rangle_{t'} B_{\nu'}^e \ . \tag{9}$$

A procedure for the calculation of the Gabriel factors for any spin has been outlined by Barclay and Gabriel.[13] Also the factors K_ν are simply computed so that, for both slow and fast modulation, the dependences of the signals upon the various experimental parameters may be computed. These were calculated analytically in II for the special case of spin-1 nuclei.

Experimentally the most important case is that of fast modulation ($\omega_m T_1 \gg 1$) and we now obtain simple expressions for this. Here it may be assumed that $t/T_1 \ll 1$ and, using the theory of Barclay and Gabriel,[13] we have, to first order in t/T_1,

$$G_{00}^{\nu\nu'}(t/T_1) = \delta_{\nu\nu'} - (U_0^{(\nu)} | \overline{M} | U_0^{(\nu')})t$$
$$= \delta_{\nu\nu'}[1 - \nu(\nu+1)t/2T_1]$$
$$- \nu(\nu+1) N_{\nu\nu'} t/2T_1 \ , \tag{10}$$

where

$$N_{\nu\nu'} = [a(I,\nu)\delta_{\nu',\nu-1} - a(I,\nu')\delta_{\nu,\nu'-1}]\tanh X \tag{11}$$

with

$$a(I,\nu) = [(2I+1+\nu)(2I+1-\nu)/(4\nu^2-1)]^{1/2} \ . \tag{12}$$

Equation (10) may be substituted into (7) to obtain the signals for fast modulation for any spin and adiabatic parameter. However, since A varies inversely with ω we may generally assume that A is of the same order at t/T_1. To first order in A

$$K_\nu = 1 - \nu(\nu+1)\pi A/2 \ .$$

For a triangular waveform, $A=\gamma^2 H_1^2 \pi/2\omega W$, so that

$$1 - K_\nu = \pi^2 \nu(\nu+1)\kappa/2\omega T_1$$

where $\kappa = \gamma^2 H_1^2 T_1/2W$ is the rf saturation parameter for modulation width $2W$. To first order in t/T_1 and $(1-K_\nu)$ Eq. (8) then becomes

$$\Delta B_\nu^\infty = -\pi\kappa \sum_{\nu'} (\Gamma^{-1})_{\nu\nu'} B_{\nu'}^e \ , \tag{13}$$

where

$$\Gamma = (1+\pi\kappa)E + N \ , \tag{14}$$

with E the unit matrix and N the matrix $N_{\nu\nu'}$. Under these conditions there is no longer any dependence upon t' so that all spin packets covered by the waveform now contribute the same signal. The signals may easily be computed by inversion of the matrix Γ. For spin 1, inversion of the 2×2 matrix leads to the same analytic expressions for B_1^∞, B_2^∞ as were derived in II.

To obtain analytic expressions for the ΔB_ν^∞ for fast modulation and high temperatures we rewrite Eq. (13) in a recursive form

$$\Delta B_\nu^\infty = -\frac{\pi\kappa}{(1+\pi\kappa)} B_\nu^e - \frac{\tanh X}{(1+\pi\kappa)} \times [a(I,\nu)\Delta B_{\nu-1}^\infty - a(I,\nu+1)\Delta B_{\nu+1}^\infty] \tag{15}$$

(valid for $\nu = 1, 2, \ldots, 2I$, noting that $\Delta B_0^\infty = 0$). At high temperatures, $X \ll 1$, the $\Delta B_{\nu+1}$ term may be neglected being smaller by order X^2 than the B_ν^e and $\Delta B_{\nu-1}$ terms. It then follows directly for $\nu = 1$ and by induction, using expression (A7) of the Appendix, for all ν that

$$B_\nu^\infty / B_\nu^e = (1+\pi\kappa)^{-\nu} \tag{16}$$

which is spin independent. Equation (16) also shows that under the special conditions of fast modulation and high temperatures the concept of a spin temperature is still preserved in the presence of the modulated rf field. This certainly will not be so at lower temperatures or with slow modulation.

For lower temperatures it is necessary to invert the $2I\times 2I$ matrix Γ in Eq. (13). However if the temperature is not too low approximate expressions for ΔB_1^∞, ΔB_2^∞ may be obtained by neglecting the admixture of $\nu \geq 3$ terms in the relaxation of B_1 and B_2 and simply inverting the appropriate 2×2 matrix. The result is

$$B_1^e = \frac{B_1^e(1+\pi\kappa+\delta^2) - \pi\kappa\delta B_2^e}{(1+\pi\kappa)^2+\delta^2} \ , \tag{17}$$

$$B_2^e = \frac{B_2^e(1+\pi\kappa+\delta^2) + \pi\kappa\delta B_1^e}{(1+\pi\kappa)^2+\delta^2} \ ,$$

where

$$\delta = \tanh X[\tfrac{1}{15}(2I+3)(2I-1)]^{1/2} \ . \tag{18}$$

These equations show that the effects of temperature and spin are not strong. If other parameters are kept constant then decreasing the temperature or increasing the spin will reduce the signals a little. In actual experiments the effect of simply reducing the temperature will normally be to increase the signal because of the resulting increase in T_1 and corresponding increase in κ.

III. CONCLUSIONS AND COMPARISON WITH EXPERIMENT

The theory given above is an exact quantum-mechanical treatment of the effects of a frequency-modulated, resonant, rf field on the emission of radiations from nuclei which have been thermally oriented by a purely magnetic interaction. So far, most of the reported RND experiments have been on nuclei in ferromagnetic host metals although "brute-force" experiments should now be possible. In an experimental study[11] of ^{60}Co nuclei in iron it has been shown that the effects of single passages on the B_ν parameters are describable in terms of a single rotation but that the angle is considerably smaller than would apply for a simple pure magnetic interaction. Recently Callaghan *et al.*[14] have suggested that this discrepancy may be associated with small quadrupole interactions (comparable with μH_1) for the nuclei in the ferromagnetic hosts. Hence, because of the assumption of a pure magnetic interaction, one does not expect detailed agreement between the present calculations and experiments on ferromagnetic metals. The calculated effects do however show some broad similarities to those observed. As the modulation parameter ωT_1 becomes small the signals[9,15] tend towards zero. Under these conditions of slow modulation, small signals are expected since between passages individual spin packets are able to substantially return to lattice equilibrium by relaxation.

For fast relaxation, $\omega T_1 \gg 1$, the calculated signals, Eqs. (13) and (14) depend only on the saturation parameter κ, the nuclear spin I and the temperature via $X = \mu_N H/2kTI$; there is no significant dependence upon ω. The lack of dependence on ω is because, as ω increases, there is a cancellation between the effects of the decrease in the adiabatic parameter and the increase in the number of passages per unit time. The observed signals[9,15] are independent of ω over a wide range; however for very fast modulation ($\omega \gtrsim \omega_1$) the experimental signals again become small. It has been suggested[15,16] that this can be qualitatively explained in terms of sidebands. For a frequency-modulated wave the frequency separation of the sidebands is so that for $\omega \gg \omega_1$ only an insignificant fraction of the nuclei will experience a resonant rf field. The two treatments of the modulation effects in terms of single passages of sidebands are equivalent time-domain and frequency-domain descriptions except that we have neglected coherence effects of successive passages. To apply a sideband treatment it would be

necessary to start with the response of a single spin packet to the combined effects of relaxation and a fixed rf frequency and then to sum over *all* the sidebands. A suitable starting theory would be that of Spanjaard and Hartman-Boutron.[3] An advantage of such a treatment is that it would be valid for all values of the modulation frequency.

After allowing for the rf enhancement in ferromagnetic alloys it is found that much larger values of H_1 are experimentally required than are expected via the dependence upon κ in the theory. This corresponds to the difference between the effects of single passages as calculated assuming pure magnetic interactions and as observed for ferromagnetic alloys.

The calculations indicate that, for small X and intermediate modulation, the effect of the modulated rf field on the nuclei should be describable in terms of a spin temperature. This may be investigated by Mössbauer-effect–NMR. Such a study by Cain[2,17] on ^{57}CO nuclei in iron at 70 mK ($X \sim 0.1$) showed that this is correct for signals $S_1 \lesssim 0.2$. For larger rf fields some deviation from a spin-temperature description was observed. Also, as in the nuclear-orientation–NMR experiments the observed signals were considerably weaker than the calculated signals.

APPENDIX: HIGH-TEMPERATURE EXPRESSIONS FOR B_ν^e

The equilibrium orientation parameters B_ν^e are defined as[18]

$$B_\nu^e = (2I+1)^{1/2}\,\mathrm{Tr}\,\{U_0^{(\nu)}\rho(X)\}\ , \tag{A1}$$

where $U_0^{(\nu)}$ is the $q=0$ component of a normalized irreducible tensor operator of rank ν and

$$\rho(X) = e^{-2XI_z}/\mathrm{Tr}\{e^{-2XI_z}\}\ . \tag{A2}$$

We shall make use of the following relations for normalized irreducible tensor operators $U_q^{(k)}$:

$$\mathrm{Tr}\{U_{q_1}^{(k_1)}\,T_{q_2}^{(k_2)}\,U_{q_3}^{(k_3)}\} = (-1)^{2I}\,\frac{\langle I\|T^{(k_2)}\|I\rangle}{(2I+1)^{1/2}}\,[(2k_1+1)(2k_2+1)(2k_3+1)]^{1/2} \times \begin{pmatrix} k_1 & k_2 & k_3 \\ -q_1 & -q_2 & -q_3 \end{pmatrix}\begin{pmatrix} k_1 & k_2 & k_3 \\ I & I & I \end{pmatrix}\ , \tag{A3a}$$

and especially

$$\mathrm{Tr}\{U_0^{(k)}I_z\,U_0^{(k-1)}\} = \frac{k}{2}\left(\frac{(2I+1+k)(2I+1-k)}{(4k^2-1)}\right)^{1/2} = \frac{k}{2}\,a(I,k) \tag{A3b}$$

which leads to

$$\mathrm{Tr}\{U_0^{(k)}(I_z)^{k'}\} = 0 \quad \text{for} \quad k' < k \tag{A4}$$

and

$$\mathrm{Tr}\{U_0^{(k)}(I_z)^{k}\} = \mathrm{Tr}\{U_0^{(k)}I_z\,U_0^{(k-1)}\}\,\mathrm{Tr}\{U_0^{(k-1)}(I_z)^{k-1}\}\ . \tag{A5}$$

The derivation of the formulas (A3a), (A4), (A5) is most easily performed by using the Liouville formalism (see, e.g., the Appendix of Ref. 12).

A Taylor-series expansion of $\rho(X)$ then leads to the following expression for B_ν^e in the high-temperature limit ($X \to 0$):

$$B_\nu^e = [X^\nu(-2)^\nu/\nu!\,]\,\mathrm{Tr}\{U_0^{(\nu)}(I_z)^\nu\}/(2I+1)^{1/2}\ , \tag{A6}$$

where (A4) was used. From this we get with (A5) and (A3b) the recursion relations

$$B_\nu^e = -Xa(I,\nu)B_{\nu-1}^e \quad (X \to 0;\ \nu = 1,2,\ldots,2I)\ , \tag{A7}$$

which finally lead to ($B_0^e = 1$)

$$B_\nu^e = (-X)^\nu\left(\frac{(2I+1+\nu)!}{(2I+1)(2I-\nu)!\,(2\nu+1)!!\,(2\nu-1)!!}\right)^{1/2} \quad (\nu = 1,2,\ldots,2I)\ , \tag{A8}$$

$[(2\nu+1)!! = 1\cdot 3\cdot 5\cdots(2\nu+1)]$, representing the high-temperature form of the equilibrium orientation parameters (A1).

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