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Theory of Modulation Effects in Resonant-Nuclear-Disorientation Experiments. II

G. V. H. Wilson
Department of Physics, Royal Military College, Duntroon, A.C.T., Australia

and

J. A. Barclay and C. G. Don
Department of Physics, Monash University, Victoria, Australia
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An analysis is made of modulation effects in resonant-disorientation experiments on radioactive nuclei which have been polarized by hyperfine interaction at low temperatures. The degree of destruction of the γ- and β-radiation anisotropy is calculated by assuming that, because of the inhomogeneous broadening, the modulation results in individual nuclear-spin packets experiencing a series of resonant passages. The effect of each passage is characterized by the adiabatic parameter. Between passages the spin-lattice relaxation is assumed to follow the theory of Gabriel. The methods apply for any spin; detailed results are given for spin-1 nuclei. This is the first quantum-mechanical treatment of the effect of a resonant-frequency-modulated rf field on the radiations from oriented nuclei. It is shown that if the rf field is sufficiently large complete destruction of the radiation anisotropy is expected. This has not been observed in experiments on ferromagnetic metals and suggests that in these the nuclear interaction is more complicated than that of the nuclear magnetic moments with the static magnetic field and the enhanced applied rf field. The results of the calculations should apply for nonmagnetically ordered samples and possibly for ferromagnets with weak hyperfine interactions.

I. INTRODUCTION

We report here an improved theory of modulation effects in resonant-nuclear-disorientation (RND) experiments. In these experiments radioactive nuclei in a ferromagnetic host metal are polarized by hyperfine interaction at low temperatures (~ 0.01 °K) and the nuclear magnetic resonance is detected by observing the effect of a resonant rf field upon the β- or γ-radiation anisotropy. After the first such observation by Matthias and Holliday[1] on ^{60}Co nuclei in iron, Templeton and Shirley[2] showed how, because of the inhomogeneous broadening associated with NMR in ferromagnetic metals, it is essential to use a frequency-modulated rf field to obtain large reductions in the radiation anisotropy at resonance.

This technique has been applied to a wide variety of radioactive nuclei in ferromagnetic host metals. In general, the main aim of such experiments has been to accurately determine the resonant frequencies from which values of the hyperfine fields or the nuclear magnetic moments are obtained or to study spin-lattice relaxation through the time dependence of the anisotropy after the modulation is removed. There has been much less experimental study of the signal—the fractional destruction of the anisotropy—and its dependence upon the rf field and other experimental parameters. As was pointed out by Shirley[3] and Wilson[4] such studies can lead to much valuable information on the phenomenon of resonance and on the interactions of the nuclei. It is now apparent that for some alloy systems, such as ^{60}Co nuclei in iron, RND is easily observable, while for others the resonances have been observed only with considerable effort. We know of several unsuccessful careful searches for resonances with alloys which did not appear to be difficult candidates. From experimental studies at Berkeley and Monash it has been observed that for a given alloy system one cannot destroy all of the radiation anisotropy by just increasing the rf field. The limiting degree of destruction varies greatly from system to system in a nonobvious manner. Hence another reason for theoretical studies of the dependences of the signals upon the experimental parameters is to assist in understanding the feasibility of RND experiments on various alloy systems.

The first calculations of the destruction of radiation anisotropy from oriented nuclei by a resonant rf field were those of Shirley.[3] These calculations assumed that any inhomogeneous broadening is small in comparison with the rf power broadening and that each measurement is then made at constant rf frequency. Shirley showed that at resonance there will then be a hard-core level below which the anisotropy cannot be reduced. However, in the ferromagnetic alloys studied so far the inhomogeneous broadening has been far greater than the power broadening, so that it has been necessary to employ frequency modulation.

Shirley's theory is then not applicable because of the assumption of a static field in the Larmor frame. In our original modulation calculations[4] (to be referred to as I) the effect of the modulation upon the anisotropy was obtained by assuming that, in between being resonated twice each modulation cycle, individual nuclear-spin packets underwent spin-lattice relaxation. The relaxation was assumed to be describable in terms of a nuclear-spin temperature, and a simple relationship was assumed for the effect of each resonant passage upon the spin temperature. These calculations indicated the form of the dependence of the signal upon modulation amplitude and modulation frequency. Because of the arbitrary type of disorientation model assumed the predicted dependence upon H_1, the amplitude of the circularly polarized component of the rf field, cannot be regarded as accurate. In the present work the resonances of the spin packets are treated as in our recent study of single-passage NMR,[5,6] and the Gabriel[7] theory of spin-lattice relaxation is also used.

II. BASIC THEORY

The polarization of radioactive nuclei in an axial magnetic field $\vec{H}$ produces a fractional change F in the intensity of the radiation emitted at an angle θ to the direction of $\vec{H}$ given by[8]

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

where the F_ν and U_ν, respectively, are angular-momentum coupling coefficients for the observed and preceding radiative transitions. The B_ν are orientation parameters defined by

$$B_\nu=(2I+1)^{1/2}\sum_M(-1)^{I-M}C(II\nu;\, M-M)W(M) \quad , \tag{2}$$

where C is a Clebsch-Gordan coefficient and $W(M)$ is the probability of the state $|IM\rangle$. For γ emission, parity conservation causes the odd ν terms in Eq. (1) to be zero. For β emission both odd and even terms are present. If the nuclei are in thermal equilibrium then we denote F by F^e and the B_ν by B_ν^e. The B_ν^e are known functions of $X = \mu_B H/2kTI$.

As in I if the center frequency, modulation amplitude, and modulation frequency are y, W, and ω, respectively, a nuclear-spin packet with resonant frequency x 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

$$t'=\pi|x-y-W|/W\omega \quad \text{(triangular waveform)} ,$$

$$t'=(2/\omega)\cos^{-1}[|x-y|/W] \quad \text{(sinusoidal waveform)}, \tag{3}$$

where t' varies from 0 to π/ω depending on the position of the packet x with respect to the modulation waveform. For each packet the rf field will only have a significant effect on the orientation when it is within a value $\simeq \omega_1=\gamma H_1$ about x. Because of the inhomogeneous broadening it will be necessary to use modulation amplitudes W which are far greater than ω_1. Hence for the rf field we only have to account for the effects on the orientation parameters during resonant passages. Between the passages only the static field H is significant and the rf may be neglected. We assume that the alloys used in RND experiments are sufficiently dilute so that the dominant relaxation process is spin-lattice relaxation with a characteristic time T_1. Because the actual passage times for the packets are far smaller than T_1 we can neglect the effect of relaxation during the passages. In our recent experimental and theoretical study[5,6] of radiative detection of single-passage NMR we have shown that for a single passage the final orientation parameters B_ν^f are simply related to the initial parameters B_ν^i by

$$B_\nu^f=K_\nu B_\nu^i \quad ,$$

where

$$K_\nu=P_\nu(\cos\alpha) \quad . \tag{4}$$

Here α is the angle through which the magnetization moves during the passage and is given correctly by a classical calculation. It is a known[5] function of the adiabatic parameter $A=\omega_1^2(d\omega/dt)^{-1}$. Equation (4) only holds if initially the nuclear ensemble has pure axial alignment with no x or y components of magnetization. If there was no inhomogeneous broadening, then after a passage there would be a unique precessing off-diagonal component of spin for all the nuclei, and to calculate the effect on the next passage it would be necessary to allow for the phase of the xy motion with respect to the rf field. However, because of the inhomogeneous broadening, there will be a random distribution of the phases of the various packets before every passage.[9] This is equivalent to an ensemble with axial alignment so that Eq. (4) will hold for all passages with coefficients K_ν given in terms of A.

Between passages we assume that the time dependence of the orientation parameters is given by the theory of Gabriel[7] so that

$$\Delta B_\nu(t/T_1)=\sum_{\nu'}\Delta B_{\nu'}(0)\,G_{\nu\nu'}(t/T_1) \quad , \tag{5}$$

where $\Delta B_\nu=B_\nu-B_\nu^e$. Analytic functions $G_{\nu\nu'}(t/T_1)$ have been given for spin 1 by Barclay and Gabriel[10] together with a recipe for calculating these for any spin. As in I the RND signal S is defined as the fractional destruction of the radiation anisotropy. Here we assume that all spin packets contribute the same signal, and we leave until Sec. V a discussion of the effects of the line shape, the modulation amplitude, and waveform. Hence the signal is given by

$$S=1-\frac{\omega^2}{2\pi^2 F^e}\int_0^{\pi/\omega}\oint F\,dt\,dt' \ , \tag{6}$$

where $\oint$ refers to an integration over a complete modulation cycle. By substituting into (6) the time dependence of F as derived from the above single-passage and relaxation theories one can determine the time dependence of the signal after applying the rf field, i.e., the destruction curve for the anisotropy. If it is assumed that S is unchanged after a complete cycle then the final steady-state signal may be obtained as a function of the various experimental parameters.

It is found that when the above assumptions are made, the signal may be regarded as depending on only two parameters, $\theta=\omega T_1$ and an rf-field saturation parameter $k=\gamma^2 H_1^2 T_1/2W$. The parameter k affords the interesting explanation of being half the usual saturation parameter $\gamma^2 H_1^2 T_1^2$ multiplied by a duty-cycle factor which is given by the ratio of the intrinsic width $(2/T_1)$ of a spin packet to the width $2W$ of frequencies used.

III. OUTLINE OF CALCULATIONS

From Eq. (6) it can be seen that the basis of the problem is to determine for each spin packet (i.e., each value of t') the time dependence of the fractional change F in radiation intensity over one modulation period. The signal S is then obtained by integration over the t' values. From Eq. (1) the only time-dependent terms in F are the orientation parameters B_ν. For a given packet we represent the orientation parameters before a passage which is followed by an interval t' as B_ν^0 so that

$$\Delta B_\nu^0=B_\nu^0-B_\nu^e \ .$$

Then after this passage $B_\nu=K_\nu B_\nu^0$ and

$$\Delta B_\nu=K_\nu\,\Delta B_\nu^0+B_\nu^e(K_\nu-1) \ . \tag{7}$$

Just before the next passage we represent the parameters by $B_\nu(t'-)$, and these are given in terms of B_ν^0 by the Gabriel equation (5) using Eq. (7) as the initial conditions so that

$$\Delta B_\nu(t'-)=\sum_{\nu'} G^a_{\nu\nu'}\left[K_{\nu'}\,\Delta B^0_{\nu'}+B^e_{\nu'}(K_{\nu'}-1)\right] \ , \tag{8}$$

where

$$G^a_{\nu\nu'}=G_{\nu\nu'}(t'/T_1) \ . \tag{9}$$

After this passage

$$\Delta B_\nu(t'+)=K_\nu\,\Delta B_\nu(t'-)+B_\nu^e(K_\nu-1) \ , \tag{10}$$

and the values of ΔB_ν after one complete waveform are given by the Gabriel expression using (10) as the initial conditions. The final result is

$$\Delta B_\nu(2\pi/\omega)=\sum_{\nu'\nu''} G^a_{\nu''\nu'}G^b_{\nu\nu''}K_{\nu''}\left[K_{\nu'}\Delta B^0_{\nu'}+B^e_{\nu'}(K_{\nu'}-1)\right]+\sum_{\nu''} G^b_{\nu\nu''}B^e_{\nu''}(K_{\nu''}-1) \ , \tag{11}$$

where

$$G^b_{\nu\nu''}=G_{\nu\nu''}((2\pi-\omega t')/\omega T_1) \ . \tag{12}$$

Hence during one modulation cycle the time dependence of the orientation parameters is

$$\begin{aligned}\Delta B_\nu&=\sum_{\nu'}\left[K_{\nu'}\Delta B^0_{\nu'}+B^e_{\nu'}(K_{\nu'}-1)\right]G_{\nu\nu'}(t/T_1), && 0<t<t'\\ \Delta B_\nu&=\sum_{\nu''}\Delta B_{\nu''}(t'+)G_{\nu\nu''}([t-t']/T_1), && t'<t<2\pi/\omega\end{aligned} \tag{13}$$

where $\Delta B_{\nu''}(t'+)$ is given in terms of the ΔB_ν^0 by Eqs. (8) and (10).

The above equations for the time dependence of the ΔB_ν may be used to determine both the transient destruction curves and the steady-state signals. The transient curves, giving the time dependence of the radiation anisotropy after the application of the frequency-modulated rf field, are obtained from Eq. (11), which gives the change in ΔB_ν over one modulation cycle. This is applied over many cycles to give the complete transient destruction curve. For fast modulation ($\theta\gg 1$) this is particularly meaningful and also simple to perform. Only terms of first order in t'/T_1 and $1/\omega T_1$ need to be retained, and Eq. (11) gives a series of first-order differential equations for the time dependence of the ΔB_ν.

To obtain the steady-state signals and their dependence upon ωT_1 and the rf-field saturation parameter k (via the K_ν) one puts $\Delta B_\nu(2\pi/\omega)=\Delta B_\nu^0$ in Eq. (11). These linear equations are then solved to give the ΔB_ν^0, and the signal is obtained by substituting the time dependences, Eqs. (13), into Eq. (6) and integrating over both modulation cycles and t' values. These calculations are best carried out on a computer, except for the important practical case of fast modulation where the dependence of the signal upon k may be obtained analytically.

IV. RESULTS FOR SPIN-1 NUCLEI

A. Introduction

For nuclei with spin I the B_ν are nonzero only for $\nu\le 2I$ so that for spin 1 we only need to consider B_1 and B_2. The Gabriel factors for spin 1 are[10]

$$
\begin{aligned}
G_{11} &= \tfrac{1}{2}(1-\cosh X)e^{-\alpha t/T_1} + \tfrac{1}{2}(1+\cosh X)e^{-\beta t/T_1} \;, \\
G_{12} &= \tfrac{1}{6}\sqrt{3}\,\sinh X(e^{-\beta t/T_1} - e^{-\alpha t/T_1}) \;, \\
G_{21} &= -3G_{12} \;, \\
G_{22} &= \tfrac{1}{2}(1+\cosh X)e^{-\alpha t/T_1} + \tfrac{1}{2}(1-\cosh X)e^{-\beta t/T_1} \;,
\end{aligned}
\tag{14}
$$

where

$$\alpha = 2 + 1/\cosh X, \quad \beta = 2 - 1/\cosh X \;.$$

We obtain from (11) expressions for the changes in B_1 and B_2 over one modulation cycle:

$$
\Delta B_1(2\pi/\omega) = \Delta B_1^0(G^a_{11}G^b_{11}K_1^2 + G^a_{21}G^b_{12}K_1K_2) + \Delta B_2^0(G^a_{12}G^b_{11}K_1K_2 + G^a_{22}G^b_{12}K_2^2) + B_1^e[G^a_{11}G^b_{11}K_1(K_1-1) + G^a_{21}G^b_{12}K_2(K_1-1) + G^b_{11}(K_1-1)] + B_2^e[G^a_{12}G^b_{11}K_1(K_2-1) + G^a_{22}G^b_{12}K_2(K_2-1) + G^b_{12}(K_2-1)] \tag{15}
$$

and

$$
\Delta B_2(2\pi/\omega) = \Delta B_1^0(G^a_{11}G^b_{21}K_1^2 + G^a_{21}G^b_{22}K_1K_2) + \Delta B_2^0(G^a_{12}G^b_{21}K_1K_2 + G^a_{22}G^b_{22}K_2^2) + B_1^e[G^a_{11}G^b_{21}K_1(K_1-1) + G^a_{21}G^b_{22}K_2(K_1-1) + G^b_{21}(K_1-1)] + B_2^e[G^a_{12}G^b_{21}K_1(K_2-1) + G^a_{22}G^b_{22}K_2(K_2-1) + G^b_{22}(K_2-1)] \;. \tag{16}
$$

B. Steady-State Signals for Fast Modulation

As in I, to obtain the largest possible signal amplitudes it is necessary to minimize reorientation of the nuclei between their resonant passages by employing fast modulation ($\theta \gg 1$). For such fast-modulation calculations, terms of order $(t/T_1)^2$ and higher may be neglected in the relaxation between passages so that for spin-1 nuclei we use

$$
\begin{aligned}
G_{11}(t) &= 1 - t/T_1 \;, \\
G_{12}(t) &= \sinh X\, t/\cosh X\, T_1\sqrt{3} \;, \\
G_{21}(t) &= -3G_{12}(t) \;, \\
G_{22}(t) &= 1 - 3t/T_1 \;.
\end{aligned}
\tag{17}
$$

In all RND experiments reported so far the adiabatic parameter A has been $\ll 1$ when $\theta \gg 1$. Some interesting results obtained for fast modulation and large A are given in Secs. IV D and IV E but here we assume that $A \ll 1$. Under these conditions the angle of deflection after one passage is given accurately by[11]

$$\alpha = (2\pi A)^{1/2} \;. \tag{18}$$

We then have, to first order in A,

$$K_1 = 1 - \pi A \;, \quad K_2 = 1 - 3\pi A \;. \tag{19}$$

By substituting Eq. (17) into (11) and assuming that B_1 and B_2 are unchanged over one cycle we obtain two linear equations in the steady-state values B_1^∞ and B_2^∞. The solutions of these are

$$B_1^\infty = \frac{B_1^e(1+\pi k+\delta^2) - \pi k\delta B_2^e}{(1+\pi k)^2 + \delta^2} \tag{20}$$

and

$$B_2^\infty = \frac{B_2^e(1+\pi k+\delta^2) + \pi k\delta B_1^e}{(1+\pi k)^2 + \delta^2} \;, \tag{21}$$

where $\delta = \sqrt{\tfrac{1}{3}}\tanh(X)$ and where k has been obtained in terms of A for a triangular waveform. The dependence upon temperature via δ is not very strong. For small δ the high-temperature limits are obtained as

$$B_1^\infty = B_1^e(1+\pi k)^{-1} \tag{22}$$

and

$$B_2^\infty = B_2^e(1+\pi k)^{-2} \;. \tag{23}$$

The high-temperature dependence upon k of the fractional reduction of the signals S_1 and S_2 corresponding to B_1 and B_2, respectively, is shown in Fig. 1.

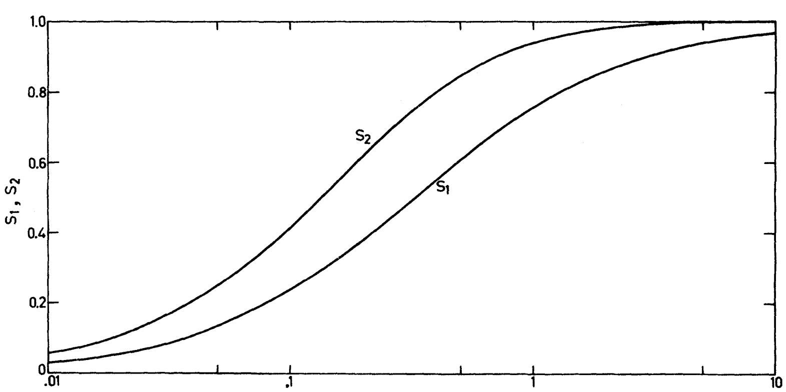

FIG. 1. Dependence of the fractional reductions S_1 and S_2 in the orientation parameters B_1 and B_2, respectively, upon the rf-field parameter k for fast modulation and high temperatures.

The above shows that for fast modulation B_1 and B_2 are reduced by the rf field to an extent determined solely by k. For $k \gg 1$ the radiation anisotropy as given from these calculations will be completely destroyed; i.e., for the simple interaction of a frequency-modulated rf field with oriented nuclei no "hard-core effect" (whereby not all of the anisotropy can be destroyed) is expected.

C. Transient Solutions for Fast Modulation

To determine the orientation parameters as functions of time after the rf field is switched on (or after the modulation is switched on) one simply obtains differential equations for B_1 and B_2 from Eqs. (11) and (17) as described in Sec. III. In general the time dependences of B_1 and B_2 each contain two exponential terms with time constants $T_1/\{2(1+\pi k) \pm [(1+k)^2 + 3\delta^2]^{1/2}\}$. At high temperatures ($X \ll 1$) one obtains

$$B_1 = B_1^\infty + (B_1^e - B_1^\infty) e^{-t/T_1^\dagger} \quad , \tag{24}$$

$$B_2 = B_2^\infty + \tfrac{1}{2}\pi k\{-3\delta B_1^e e^{-t/T_1^\dagger} + [\delta B_1^e + 2B_2^e(1+\pi k)] e^{-3t/T_1^\dagger}\}/(1+\pi k)^2 \quad , \tag{25}$$

where

$$T_1^\dagger = T_1/(1+\pi k) \quad . \tag{26}$$

The factor $(1+\pi k)^{-1}$ in $T_1^\dagger$ indicates that the approach to the new steady state in the presence of the rf field will be faster than the natural relaxation of the nuclei in the absence of the rf field. The high-temperature results for B_1 showing a reduction factor $(1+\pi k)$ in both B_1^∞ and $T_1^\dagger$ are identical to those obtained in I. This is as expected because the Gabriel theory for B_1 at high temperatures is equivalent to a spin-temperature approach. However, such an equivalence is never true for B_2 or higher-order parameters, so that even at high temperatures we now obtain two exponential terms in B_2 instead of the one predicted using the assumptions of a spin temperature.

D. Effect of Large Adiabatic Parameters

In Secs. IV B and IV C we have assumed that the adiabatic parameter A has become small when $\theta \gg 1$. Due to the term $(d\omega/dt)^{-1}$ in A, as the modulation frequency ω is allowed to increase A mu t always finally become small. However, in some favorable experiments it may well be possible to have large values of A while still keeping $\theta \gg 1$ so that each passage produces a large change in the B_ν parameters with little reorientation between successive passages.

We first derive the signals for the special case of $A = \infty$ and then consider the approach to these signals for finite but large A. For $A = \infty$ all passages are perfectly adiabatic so that $\alpha = \pi$ and

$$K_\nu = \begin{cases} +1 & (\nu \text{ even}) \\ -1 & (\nu \text{ odd}) \, . \end{cases}$$

In Fig. 2 the dependences upon θ of S_1 and S_2 are shown for $X = 0.01$ (high-temperature behavior) and $X = 10$ (low-temperature behavior). The curves for S_1 and S_2 are almost identical so that only one is given for each value of X. As expected from I the signals do not depend strongly upon the temperature. A surprising feature of the curves is that the limiting signal for fast modulation ($\theta \gg 1$) is significantly lower than the value of unity which would correspond to complete resonant destruction of the anisotropy. The incomplete destruction results because, unlike the effect with smaller adiabatic parameters, perfectly adiabatic passages cannot change the magnitudes of the B_ν coefficients. The effect of this is easiest to see for the case of high temperatures where the relaxation of B_1 is uncoupled from that of B_2. Packets on the edge of the waveform have their B_1 values reversed twice in succession followed by relaxation for a whole modulation period. When $\theta \gg 1$ both B_1 and B_2 have magnitudes equal to their equilibrium values and so do not contribute to the destruction of the anisot-

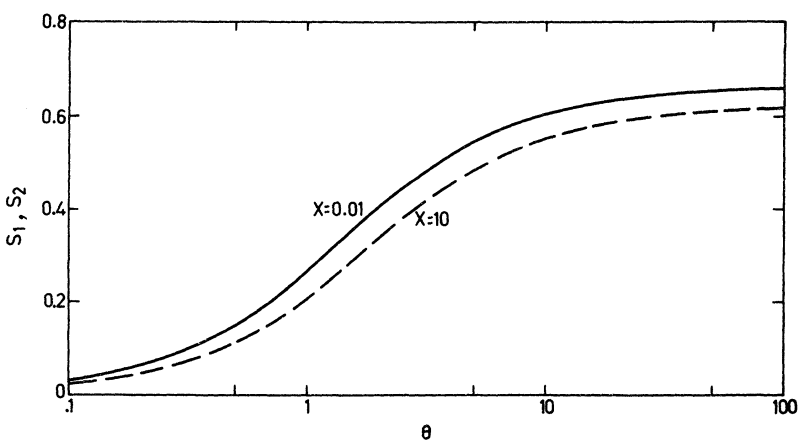

FIG. 2. Dependence of the signals S_1 and S_2 (indistinguishable) upon θ ($=\omega T_1$) for $X = 0.01$ and $X = 10$ for adiabatic passages.

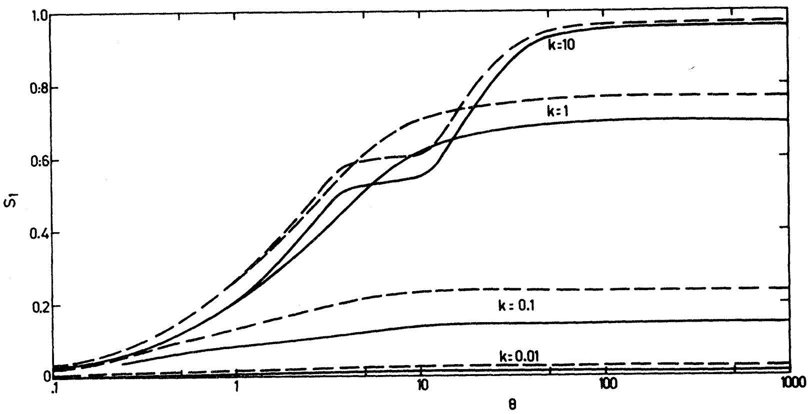

FIG. 3. Dependence of S_1, the fractional reduction in B_1, upon θ $(=\omega T_1)$ for various values of the rf-field parameter k and $X=0.01$ (dashed curves) and $X=10$ (continuous curves).

ropy. However, packets at the center of the waveform produce the greatest signal of unity. At high temperatures the average fast-modulation signals when averaged over all packets are $S_1=S_2=\frac{2}{3}$. The corresponding signals for any temperature for spin-1 nuclei are

$$S_1=1-(\delta^2+1)(\delta-\tan^{-1}\delta)/\delta^3$$

and (27)

$$S_2=1-[(\delta^2+1)\tan^{-1}\delta-\delta]B_1^e/\delta^2B_2^e\ .$$

These depend only weakly upon X so that the fast-modulation signals are close to $\frac{2}{3}$ at all temperatures.

These results suggest interesting possibilities for a system with which it is possible to apply a large enough rf field on the nuclei so that large-A values result for values of $\theta\gg1$. Then if θ is kept constant and the rf field is increased from zero, all of the anisotropy should first be destroyed with only $\frac{2}{3}$ destruction for larger rf fields. To study this we calculated the steady-state value of B_1 for spin-1 nuclei at high temperatures with $\theta\gg1$, assuming also that $K_1=-1+\epsilon$ where $\epsilon\ll1$ so that the passages are almost adiabatic. The result is

$$B_1^0/B_1^e=(\pi-\omega t')/(\pi+\epsilon\theta)\ .$$

The result depends on the term $\epsilon\theta$. If $\epsilon\theta\ll\pi$ so that the small ϵ dominates over the large θ then, as expected, the results for truly adiabatic passage follow. Then $B_1^0/B_1^e=1-\omega t'/\pi$, and averaging over all t' values leads to $S_1=\frac{2}{3}$. However, if the modulation frequency is increased, then ϵ as well as θ must increase, and one will always be able to finally make $\epsilon\theta\gg1$, for which complete destruction of the anisotropy will follow.

E. General Results

In addition to the above analytic results for fast modulation the steady-state signals for spin-1 nuclei were computed for a variety of values of θ and X using the theory of Secs. II and III. The dependence of S_1 upon θ for various values of k for $X=0.01$ and $X=10$ is shown in Fig. 3. Again as expected the temperature dependence is weak. The curves show well the complications for large A as described in Sec. IV D. For $k=10$ the signal is very similar to that for $A=\infty$ when θ is $\lesssim 10$. For higher values of θ there is an increase in the signal to the fast-modulation limit as in Fig. 1. In Fig. 4 similar curves for S_2 with $X=0.01$ and a

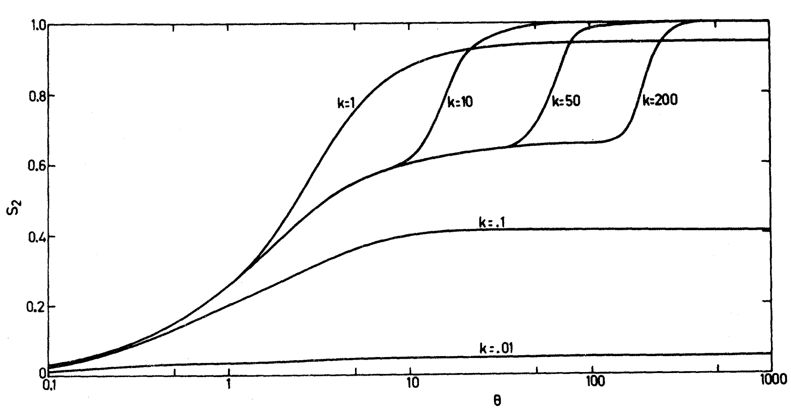

FIG. 4. Dependence of S_2, the fractional reduction in B_2, upon θ $(=\omega T_1)$ for various values of the rf-field parameter k and $X=0.01$. The effect of large X is similar to that shown in Fig. 3 for S_1.

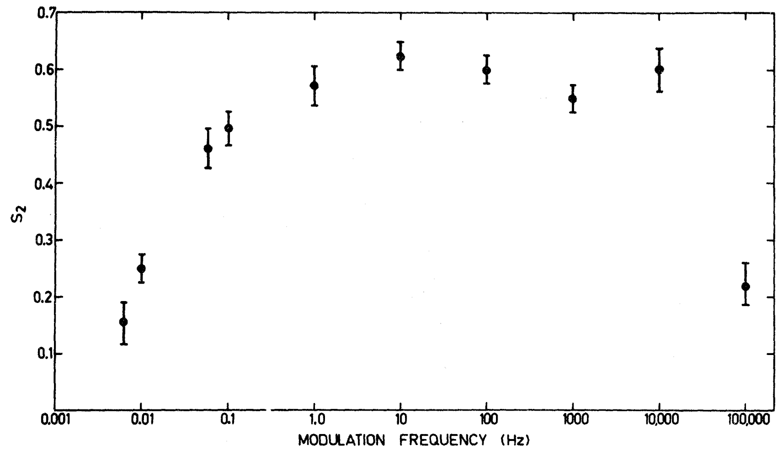

FIG. 5. Dependence of S_2, the fractional reduction in the γ-radiation anisotropy, upon modulation frequency for a single crystal of ^{60}Co in iron with an applied rf field of 2.7 mG with a temperature range 0.02–0.008 °K.

greater variety of k values are shown. The behavior for large rf fields (large k) is well illustrated. Here when $\theta \lesssim k$ the signal for adiabatic passages results with a break towards the fast-modulation limit for larger θ. That this change should occur at $\theta \sim k$ is not surprising since the motion becomes almost adiabatic for $A \approx \pi$ and for a triangular waveform $k/\theta = A/\pi$. Figure 4 also shows how it is possible, for $\theta \lesssim k$ and constant, to observe an initial increase followed by a decrease in the signal as the rf field is increased.

V. EFFECTS OF WAVEFORM AND MODULATION AMPLITUDE

In the above we have assumed that the modulation amplitude is greater than the inhomogeneous broadened linewidth so that all nuclei are resonated. Also in calculating the signal equal weighting was assumed whereas there is actually a distribution of resonant frequencies. As in I if we allow for the finite modulation amplitude then

$$S(y) = \int_{y-w}^{y+w} P(x)\left(1 - \frac{\omega}{2\pi F^e} \oint F(t)\,dt\right) dx \ , \qquad (28)$$

where $P(x)$ gives the normalized distribution of resonant frequencies. Here $S(y)$ gives the dependence of the signal upon the center frequency; i.e., $S(y)$ is the observed resonance line shape. The observed signal amplitude will be $S(0)$. The integration over x in Eq. (28) corresponds to that over t' in Eq. (6) with t' and x related by Eq. (3).

For fast modulation and a triangular waveform, Eq. (28) reduces to

$$S(y) = M(y)\, S(\theta, k) \ , \qquad (29)$$

where $S(\theta, k)$ is the signal amplitude as calculated in Secs. IV A–IV E and $M(y)$ is the fraction of nuclei being resonated within the modulation waveform. We define R as the ratio of the modulation width ($2W$) to the full width at half-height of the frequency distribution $P(x)$. Then in terms of R, θ, and k the signal amplitude is $A(R)S(\theta, k)$, where

$$A(R) = M(0) = \int_{-W}^{W} P(x)\,dx \ . \qquad (30)$$

Curves for $A(R)$ are given in I for Lorentz and Gaussian resonances. As in I the observed line shape and signal amplitude will always satisfy Eqs. (29) and (30) to a good approximation regardless of R and θ. This results in a considerable simplification so that the observed line shape is $M(y)$, which is determined only by the modulation amplitude and the inhomogeneous broadening distribution $P(x)$. The signal amplitude is then the product of $A(R)$, which is easily calculated from Eq. (30), and $S(\theta, k)$, which is calculated as in Sec. IV and does not depend upon the line shape. Actually this is only strictly correct for a triangular waveform. For a sinusoidal waveform one should allow for the variation in the adiabatic parameter with x but, as in I, the effect of this will always be small.

VI. COMPARISON WITH EXPERIMENT

In our studies[5] of single-passage NMR of ^{60}Co nuclei in iron we showed that the effect of such passages on the orientation parameters is considerably less than that expected. By comparing the changes in the anisotropies of both β and γ radiation we have shown[6] that single passages result in a rotation of the nuclear magnetization, the angle being less than that calculated in terms of A. This means that the usual description of the resonance experiments in terms of the static fields on the nuclei together with an enhanced rf field is inadequate, and there must be an additional effect which reduces the signals. Since the present modulation theory is based on the effect of resonant passages, it is expected that the observed signals from oriented nuclei in ferromagnets will also be smaller than those predicted.

The dependence of the γ-signal amplitude upon modulation frequency for the same single-crystal sample of ^{60}Co in iron is shown in Fig. 5 for an

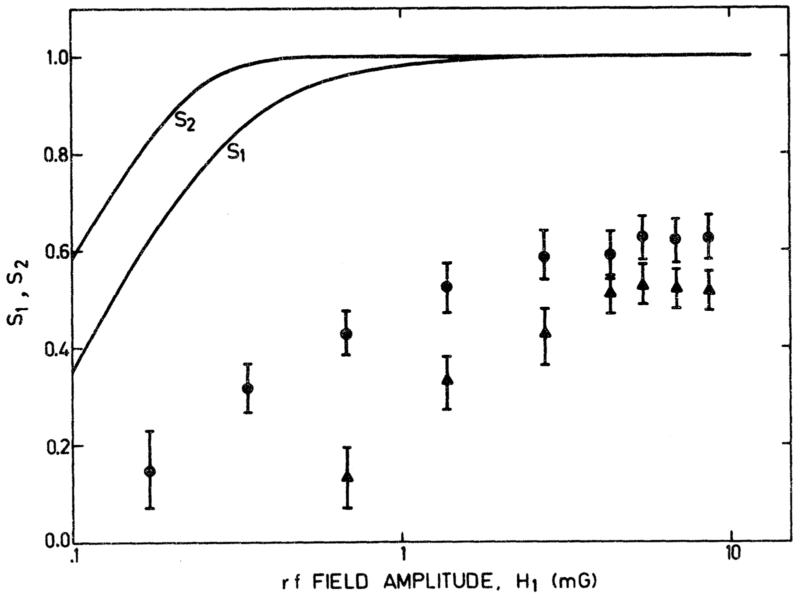

FIG. 6. Dependence of the fractional reductions in the γ-radiation (closed circles) and β-radiation (closed triangles) anisotropies for a single crystal of ^{60}Co in iron upon the applied rf field H_1 for a modulation frequency of 10 Hz and a modulation width of $\pm$ 500 kHz, with a temperature range 0.02–0.008 °K. The curves are calculated from Eqs. (20) and (21).

applied rf field $H_1 = 2.7$ mG over the temperature range 0.02–0.008 °K. The signals did not have a noticeable temperature dependence. The drop in signal at low values of θ and the lack of any appreciable dependence on θ over a wide range are obvious. The decrease in signal at high modulation frequencies (large θ) is similar to that previously observed except it occurs at higher frequencies.[12] This can be explained with a sideband model of modulation. The difference in frequencies suggests that the point of decrease is a measure of the instability of the oscillator rather than the width of the power-broadened spin packet. If the intrinsic width could be measured using a highly stable oscillator, this would be an excellent way of determining the actual value of the enhanced rf field.

In Fig. 6 the dependence of the β and γ signals on applied H_1 is shown together with the theoretical curves for B_1 and B_2 calculated from Eqs. (20) and (21) by assuming that the rf field is enhanced by a factor equal to the ratio of the hyperfine and applied magnetic fields. The modulation width ($2W$) used was 1 MHz, and since the resonance width was 800 kHz then $A(R) = 1$, and there is a very significant discrepancy between theory and experiment. In particular the observed fast-modulation signals are never greater than about 0.52 for B_1 and 0.63 for B_2, whereas according to the theory given complete destruction corresponding to unity signals should be possible. Obviously this discrepancy must have the same origin as that for the single-passage studies. A better understanding would be invaluable because it appears to be the crucial factor in determining the feasibility of an RND experiment for a given alloy system. Previously[5] we have suggested that the discrepancy could be due to the effect of the magnetic field exerted on the electrons by the oriented nuclei. To obtain agreement with our single-passage experiments we had to assume an anisotropic exchange damping of the localized disturbance of the electronic magnetization by each nucleus. However, Smith[13] has shown that agreement may be obtained with isotropic damping having a range of a few lattice parameters as is usual for ferromagnetic metals. Thus the back-field concept appears capable of explaining the discrepancy. For NMR experiments in nonmagnetically ordered samples there will be no such effects of the back fields so that the results of this paper may then be applicable.

VII. CONCLUSIONS

A theory has been outlined to indicate the effects of a frequency-modulated resonant rf field on the radiation anisotropies from oriented nuclei. As in single-passage experiments the observed effects for ^{60}Co nuclei in iron are significantly smaller than those predicted. This is of fundamental importance in understanding NMR of oriented nuclei; it may well be due to the back field. The theory is an exact quantum-mechanical treatment of the effect of a resonant rf field on nuclei in a static magnetic field and predicts that complete destruction of the anisotropy is possible. This is in contrast with the results of calculations for the case of nonmodulated rf fields with no inhomogeneous broadening; here Shirley[3] showed that incomplete destruction is obtained in the tensor quantities B_ν for $\nu \geq 2$.

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Soft-Sphere Model for Nuclear Quadrupole Resonance: Rare-Earth Trichlorides under Hydrostatic Pressure*

David H. Current,† C. L. Foiles, and Edward H. Carlson‡
Department of Physics, Michigan State University, East Lansing, Michigan 48823
(Received 14 January 1972)

Nuclear quadrupole resonance of Cl^{35} in five hexagonal rare-earth trichlorides under hydrostatic pressure up to 5×10^3 kg/cm^2 showed a decrease in frequency ν with increase in pressure. The normalized pressure coefficients $\nu_0^{-1}\,(\partial\nu/\partial P)_T$ varied smoothly between the extremes $(-5.586\pm 0.020)\times(10^{-6}$ cm^2/kg) and $(-3.855\pm 0.016)\times(10^{-6}$ cm^2/kg) for $CeCl_3$ and $GdCl_3$, respectively. The negative sign suggested a model with a significant overlap contribution to the electric field gradient and a soft-sphere model was developed in analogy to the Born-Mayer model of inter-ionic repulsive forces. This model proved adequate to explain the systematic variations in ν_Q with compound and was consistent with the pressure dependence of ν. The use of pressure data as a critical test for the model must await reliable compressibility data for the compounds. Pressure data for monoclinic $ErCl_3$ and $YbCl_3$ are also presented.

I. INTRODUCTION

Nuclear quadrupole resonance (NQR) measures the electric field gradient (EFG) at a nucleus whose quadrupole moment is known (and nonzero).[1-3] The EFG is a traceless second-rank tensor characterized by a magnitude q with sign, by an asymmetry parameter $0\le\eta\le 1$ that describes departure from cylindrical symmetry, and by the orientation of its principal axes in space. The EFG components can be expressed in spherical-tensor notation as

$$q_m=\frac{1}{e}\int\frac{\rho_c(r)Y_2^m(\theta,\ \phi)}{r^3}\,d^3r\ , \qquad (1)$$

where ρ_c is the charge density in the neighborhood of the nucleus, e is the charge of an electron, and Y_2^m is a spherical harmonic. From Eq. (1), two features clearly emerge: (a) Only those components of ρ_c having the symmetry of $Y_2^m(\theta,\ \phi)$ can contribute to the EFG. This requirement explicitly eliminates any contribution from the spherically symmetric part of ρ_c. (b) The weighting function r^{-3} significantly decreases the importance of distant charge density. The practical consequence of these features is a domination of the EFG at the nucleus of a given ion by the outer, distorted electron cloud of that same ion.

Models for the mechanisms whereby distortions are introduced into the spherical ions have been proposed, but have not led to very satisfactory descriptions of the experimental results. The basic model[1] is the point-ion model in which the ith ion is replaced by an appropriate point charge z_ie, where z_i is the valence of ion i. Each ion gives a cylin-