Theory of Modulation Effects in Resonant Nuclear Disorientation Experiments

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An analysis is made of modulation effects in "resonant nuclear disorientation" experiments on radioactive nuclei which have been polarized by hyperfine interaction at low temperatures in ferromagnetic host metals. The inhomogeneously broadened nuclear magnetic resonance is detected through the destruction of the γ radiation anisotropy by a resonant-frequency-modulated rf field. It is shown that to a good approximation the observed line shape is determined solely by the modulation amplitude and the distribution of hyperfine magnetic fields; for large rf fields, the signal amplitude depends separately upon the modulation amplitude and frequency. For finite rf field intensities, the signal amplitude also depends upon a parameter k which is closely related to the saturation behavior which would be observed in the absence of inhomogeneous broadening. At high modulation frequencies, the dependence of the signal amplitude upon k is easily calculated, and this should permit experimental determinations of k values. Independent determinations should also be possible from studies of the time rate of destruction of the γ radiation anisotropy immediately after applying a resonant rf field.

1. INTRODUCTION

Recently there have been several reports[1–3] of observations of the nuclear magnetic resonances of dilute traces of radioactive nuclei in ferromagnetic metals. In such "resonant nuclear disorientation" (RND) experiments the effect of a resonant rf field on the anisotropy of γ radiation from nuclei polarized by hyperfine interaction at low temperatures ($\sim 0.01°K$) was observed.

The polarization of radioactive nuclei in an axial magnetic field **H** at a low temperature T produces a fractional change F in the intensity of γ emission at an angle Θ to the direction of **H** given by[4]

$$F=\sum_{\text{even }\nu}[U_\nu F_\nu B_\nu P_\nu(\cos\Theta)]-1\,, \qquad (1)$$

where the B_ν are functions of $\beta=\mu H/kTI$ and describe the orientation of the parent nuclei; the F_ν and U_ν, respectively, are angular-momentum coupling coefficients for the observed and preceding radiative transitions. If a sufficiently intense, linearly polarized rf field is applied perpendicular to **H** then at the nuclear magnetic resonance (NMR) frequency, as is well known in magnetic resonance theory, substantial disorientation of the polarized nuclei will occur. The subsequent reduction in the anisotropy of the γ radiation leads to a very sensitive method of detecting the magnetic resonance by simply measuring, at a fixed angle Θ, the γ radiation intensity as a function of the radio frequency. A review of this technique has been recently given by Shirley,[5] who shows that in addition to the very accurate determinations of hyperfine interaction fields and nuclear moments the method is also of considerable fundamental interest. This is so because the detection of resonance by the observation of statistical tensors of order higher than first is closely related to the nature of the absorption of energy from a resonant field and of the nuclear magnetic relaxation. It also should lead to criteria for the validity of the spin-temperature concept.

Another possibility of observing RND is afforded by the asymmetry of a hyperfine-split Mössbauer spectrum due to the polarization of the parent nuclei by hyperfine interaction at low temperatures.[6–9] The intensity of one transition of the Mössbauer nucleus is proportional to

$$P(m)=\Big[\sum_{M_I=-I}^{I}C(M_I,m)e^{-M_I\mu H/kTI}\Big]\Big/\sum_{M_I=-I}^{I}e^{-M_I\mu H/kTI}\,, \qquad (2)$$

where H is the hyperfine field acting at the parent nucleus of spin I, and the $C(M_I,m)$ are coupling coefficients representing the branching probability of a parent nucleus in the state M_I decaying to the initial state m of the observed Mössbauer transition. At present there has not yet been a report of RND detected by this technique although it should be applicable at

[1] E. Matthias and R. J. Holliday, Phys. Rev. Letters **17**, 897 (1966).
[2] J. E. Templeton and D. A. Shirley, Phys. Rev. Letters **18**, 240 (1967).
[3] J. A. Barclay, W. D. Brewer, E. Matthias, and D. A. Shirley, in *Hyperfine Interactions and Nuclear Radiation*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968).
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[5] D. A. Shirley, in *Hyperfine Interactions and Nuclear Radiation*, edited by E. Matthias and D. A. Shirley (North-Holland Publishing Co., Amsterdam, 1968).
[6] J. G. Dash, R. D. Taylor, P. P. Craig, D. E. Nagle, D. R. F. Cochran, and W. E. Keller, Phys. Rev. Letters **5**, 152 (1960).
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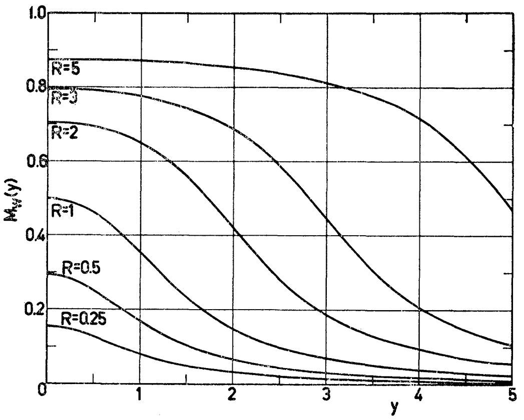

FIG. 1. Modulation-broadened line shapes for a Lorentz distribution of hyperfine fields plotted for various values of R, the ratio of modulation width to the width at half-height of the hyperfine field distribution.

considerably higher temperatures than those necessary to observe anisotropy of γ radiation.

In the first observation of RND by Matthias and Holliday[1] the axial intensity (i.e., $\Theta=0°$) of γ radiation from ^{60}Co nuclei polarized in iron at $\sim 0.03°K$ was measured. Although, due to the nuclear alignment, the axial intensity was 16% lower than the isotropic intensity observed at 1°K, the rf field caused only a small ($\sim 2\%$) increase in the intensity at resonance. Templeton and Shirley[2] showed that this small effect was due to inhomogeneous broadening. In the ferromagnetic sample the distribution of hyperfine fields causes the NMR resonance width to be far greater than the intrinsic width associated with the nuclear relaxation processes. Consequently an rf field with a well-defined frequency can only disorient a very small fraction of the nuclei. In order to observe significant resonant destruction of the radiation anisotropy it is necessary to employ frequency modulation of the rf field. The modulation amplitude needs to be comparable with the inhomogeneously broadened line width and the modulation frequency should be comparable or fast compared with the reciprocal of the nuclear spin-lattice relaxation time T_1.

In RND experiments, as in conventional magnetic resonance experiments,[10–12] the true line shape (in this case the distribution of hyperfine fields) is only obtained if the modulation amplitude is small compared with the linewidth. However, the signal-to-noise ratio is then often poor. Hence it is important to understand the dependences of the resonance amplitude and modulation broadening upon the modulation amplitude. In Sec. 2 these dependences are given for Gaussian and Lorentz line shapes together with methods for correcting observed line shapes for modulation broadening. In Sec. 3 the effects of finite modulation frequency are summarized for the case of a large rf field amplitude and in Sec. 4 we then show how the dependence of the resonance amplitude upon modulation frequency for smaller rf field amplitudes depends strongly upon the causes of the intrinsic linewidth which would be observed if inhomogeneous broadening were absent.

[10] G. V. H. Wilson, J. Appl. Phys. 34, 3276 (1963).
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[12] G. V. H. Wilson, J. Appl. Phys. 36, 3505 (1965).

2. EFFECTS OF THE MODULATION AMPLITUDE FOR FAST MODULATION

A. Calculation of Resonance Amplitudes and Modulation-Broadened Line Shapes

In this section we assume that the modulation frequency $\omega/2\pi$ is sufficiently large so that we may neglect the reorientation of nuclei during those intervals of the modulation period when they are not being resonated by the rf field; i.e., we assume that $\omega T_1 \gg 1$. We also assume that the rf field is sufficiently intense so that all nuclei which are resonated during the modulation period are sufficiently disoriented so that their γ radiation anisotropy (or in the case of a Mössbauer-effect RND experiment, the asymmetry of the Mössbauer spectrum of the daughter nuclei) may be neglected.

In both of the RND experiments described above there is, in the absence of the rf field, a fractional change F in the observed radiation intensity upon cooling the specimen from a temperature at which the nuclear orientation is negligible to a low temperature T. For a single hyperfine field H,

$$F(H,T)=[I(H,T)-I(H,\infty)]/I(H,\infty). \qquad (3)$$

In a γ radiation anisotropy experiment $I(H,T)$ is the γ radiation intensity at a fixed angle Θ to the alignment axis; in the Mössbauer experiment $I(H,T)$ is the intensity of one of the lines of the hyperfine-split Mössbauer spectrum of the daughter nuclei. Allowing for inhomogeneous broadening we have

$$F(T)=\int_0^\infty F(H,T)p(H)dH,$$

where $p(H)$ is the normalized distribution of hyperfine fields. From now on we consider this in terms of the distribution $P(\nu)$ of NMR frequencies $\nu=\mu H/hI$ so that:

$$F(T)=\int_0^\infty F(\nu,T)P(\nu)d\nu,$$

where

$$\int_0^\infty P(\nu)d\nu=1.$$

If the center frequency and modulation amplitude of the frequency modulation are y and W, respectively, then from the above assumptions it follows that all nuclei which resonate at frequencies between $y-W$ and $y+W$ will be effectively completely disoriented. We define the RND signal $S(y)$ as the fractional reduction of $F(T)$ so that

$$S(y)=\int_{y-W}^{y+W}F(\nu,T)P(\nu)d\nu\bigg/\int_0^\infty F(\nu,T)P(\nu)d\nu.$$

Generally the fractional width of the inhomogeneous broadening $P(\nu)$ is small and $F(\nu,T)$ may be regarded as independent of ν over the width of the line so that

$$S(y)=\int_{y-W}^{y+W}P(\nu)d\nu \tag{4}$$

and the fractional destruction of F is equal to the fraction of nuclei being influenced by the rf field.

If the rf field is not intense enough to effectively completely disorient the resonated nuclei then, provided $\omega T_1\gg 1$, all nuclei with resonance frequencies in the range $y\pm W$ will be disoriented to the same extent so that $S(y)=cM_W(y)$, where c is a constant which is less than unity, and

$$M_W(y)=\int_{y-W}^{y+W}P(\nu)d\nu. \tag{5}$$

The function $M_W(y)$ is the observed line shape and if the resonance is symmetric about $y=0$ then $M_W(0)$ is proportional to the signal amplitude, normalized so that $M_W(0)\to 1$ as $W\to\infty$. Equation (5) should also still represent the effect of the modulation amplitude if $\omega T_1\gg 1$ and there is a hard-core value of the radiation anisotropy which cannot be removed no matter how intense is the rf field. Shirley[5] has shown that because the γ radiation anisotropy is given by statistical tensors of higher order then the first, coherence between the nuclear magnetic precession and the rf field at resonance leads to such an effect for a simple model in which relaxation and inhomogeneous broadening are neglected.

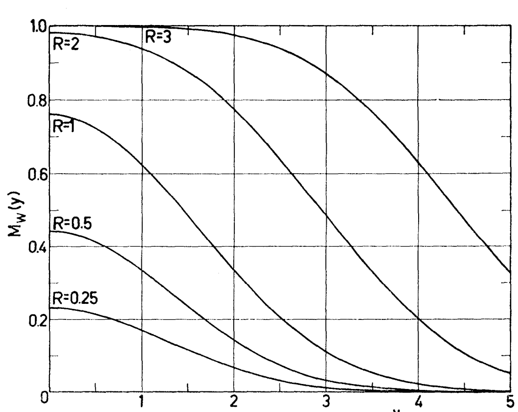

FIG. 2. Modulation-broadened line shapes for a Gaussian distribution of hyperfine fields plotted for a various values of R, the ratio of modulation width to the width at half-height of the hyperfine field distribution.

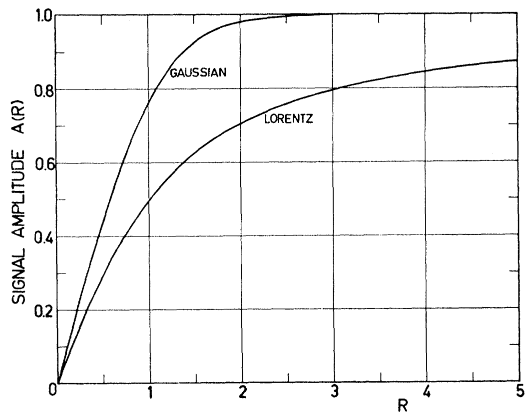

FIG. 3. Dependence of the signal amplitudes for Lorentz and Gaussian hyperfine field distribution upon R, the ratio of modulation width to the width at half-height of the hyperfine field distribution.

The existence of a hard-core effect for an inhomogeneously broadened line has not yet been demonstrated.

In Figs. 1 and 2 the line shapes $M_W(y)$ which would be observed for Lorentz and Gaussian hyperfine field distributions, respectively, are shown. We take for the normalized distributions

$$P(\nu)=[\pi(1+\nu^2)]^{-1}\ \text{(Lorentz)} \tag{6}$$

and

$$P(\nu)=e^{-(\nu^2/\pi)}/\pi\ \text{(Gaussian)}. \tag{7}$$

The line shapes are shown for various values of R, the ratio of the modulation width $(2W)$ to the width of the field distribution $P(\nu)$ at half-height. For (6) $R=W$ and for (7) $R=W(\pi\ln 2)^{-1/2}\approx 0.6776W$. For small R, as is obvious from (5), the observed line shape is proportional to $P(\nu)$ but the signal amplitude is small:

$$[M_W(y)]_{W\to 0}\to 2WP(y). \tag{8}$$

In Fig. 3 the signal amplitude $A(R)=M_W(0)$ for the Lorentz and Gaussian distributions is plotted against R. As expected smaller modulation amplitudes are necessary with a Gaussian distribution since less nuclei experience fields in the "wings" of the distribution. In dilute alloys one expects a Gaussian distribution of fields and Fig. 3 shows that then R should be $\gtrsim 1$ to effectively obtain complete disorientation.

B. Moments of the Modulation-Broadened Line Shapes

It is interesting to note that Eq. (5), which accurately represents the modulation-broadened signal for a RND experiment, was first used[13] as an approximation to the modulation broadening for the phase-sensitive detection of a conventional magnetic resonance experiment. In order to derive expressions for the moments of the broadened line shapes we firstly define the normalized

[13] M. M. Perlman and M. Bloom, Phys. Rev. 88, 1290 (1952).

modulation-broadened line shape:

$$K(y)=M_W(y)\Big/\int_{-\infty}^{\infty}M_W(y)dy=M_W(y)/(2W). \quad (9)$$

Equation (5) may be rewritten as

$$M_W(y)=\int_{-W}^{W}P(y+x)dx, \quad (10)$$

where $x=\nu-y$ and a Taylor expansion leads to

$$K(y)=\sum_{m=0}^{\infty}a_mP^{(2m)}(y), \quad (11)$$

where $P^{(2m)}(y)$ refers to the $(2m)$th derivative of $P(y)$ with respect to y and $a_m=W^{2m}/(2m+1)!$. Let S^n and σ^n denote the nth moments of the observed line shape $S(y)$ and true line shape $P(\nu)$, respectively. Then

$$S^n=\int_{-\infty}^{\infty}K(y)y^ndy, \quad \sigma^n=\int_{-\infty}^{\infty}P(y)y^ndy \quad (12)$$

and from (11)

$$S^n=\sum_{m=0}^{\infty}a_m\int_{-\infty}^{\infty}y^nP^{(2m)}(y)dy.$$

After n partial integrations, assuming that σ^n is finite, we obtain

$$S^n=\sum_{m=0}^{n/2}\frac{W^{2m}n!}{(2m+1)!(n-2m)!}\sigma^{n-2m} \quad (n \text{ even}). \quad (13)$$

For odd n the limit in the sum must be changed to $\frac{1}{2}(n-1)$. Equation (13) may be used to correct the moments of any order of the observed line shape for modulation broadening. The second moment is often used as a measure of the width of the line shape and (13) leads to the following expression relating the second moment of the observed and true line shapes:

$$S^2=\sigma^2+\tfrac{1}{3}W^2, \quad (14)$$

as first obtained by Perlman and Bloom[13] in their approximate treatment of modulation broadening in conventional magnetic resonance experiments.

For sufficiently large values of W the Taylor expansion (11) will diverge and the above derivation of the correlation equation (13) is then invalid. However, as for conventional magnetic resonance detection,[11] in the case of RND experiments the method of Flynn and Seymour[14] will always apply and also leads to Eq. (13).[15]

C. Correction of Modulation-Broadened Line Shapes

The amplitude W of the frequency modulation is easily measured so that by using (13) moments of the line shape may be accurately corrected for modulation broadening. As in conventional magnetic resonance experiments[10] we may also correct the observed line shape for modulation broadening to obtain the distribution of hyperfine fields by either a series method or correction of Fourier coefficients.

In the series method the Taylor expansion (11) is inverted to express $P(y)$ in terms of derivatives of the observed line shape:

$$P(y)=\sum_{i=0}^{\infty}k_iK^{(2i)}(y). \quad (15)$$

Then by comparison with (11),

$$\sum_{i=0}^{\infty}\sum_{m=0}^{\infty}k_ia_mD^{2(m+i)}=1,$$

where D is the differential operator. By equating coefficients of powers of D a set of linear equations is obtained and the first four solutions (k_0 to k_3) lead to

$$P(y)=K(y)-W^2K^{(2)}(y)/6+7W^4K^{(4)}(y)/360 -7W^6K^{(6)}(y)/2160+\cdots. \quad (16)$$

By tabulating the observed line shape the derivatives may be determined from the central differences and the calculation of $P(y)$ using (16) is very simple. However, the series is only sufficiently rapidly convergent for $R\lesssim 0.5$ so that this simple method can only be applied in cases where the distortion is not too great.

In the Fourier coefficient correction method we expand $P(y)$ in the range $-Y\leqslant y\leqslant Y$:

$$P(y)=a_0+\sum_{i=1}^{\infty}\left(a_i\cos\frac{\pi iy}{Y}+b_i\sin\frac{\pi iy}{Y}\right). \quad (17)$$

Substituting this into Eq. (10) leads to

$$K(y)=a_0+\frac{Y}{W\pi}\sum_{i=1}^{\infty}\left(\frac{a_i}{i}\cos\frac{\pi iy}{Y}+\frac{b_i}{i}\sin\frac{\pi iy}{Y}\right)\sin\frac{\pi iW}{Y}, \quad (18)$$

so that in the range $-Y\leqslant y\leqslant Y$ the Fourier coefficients

[14] C. P. Flynn and E. F. W. Seymour, Proc. Phys. Soc. (London) **75**, 337 (1960).

[15] For this rigorous derivation of Eq. (13) we use the correction equation (Refs. 11 and 14)

$$S^n=\sum_{p=0}^{n}\frac{n!}{p!(n-p)!}M_p(\psi)\sigma^{n-p}, \quad \text{(i)}$$

where $M_p(\psi)$ is the pth moment of the response $\psi(y)$ to a δ-function resonance at $y=0$. Then for RND experiments

$$\psi(y)=1, \quad |y|\leqslant W$$
$$=0, \quad |y|>W$$

and

$$M_p(\psi)=\frac{1}{2W}\int_{-\infty}^{\infty}\psi(y)y^pdy$$
$$=W^p/(p+1), \quad (p \text{ even})$$
$$=0, \quad (p \text{ odd}) \quad \text{(ii)}$$

and substitution of (ii) into (i) leads to Eq. (13).

a_i, b_i of $P(y)$ are related to the corresponding coefficients α_i, β_i of the observed curve by

$$\alpha_i = q_i a_i, \quad \beta_i = q_i b_i, \tag{19}$$

where $q_i = (Y/W\pi i)\sin(\pi i W/Y)$. These simple relationships hold for any modulation amplitude. In using this method to correct line shapes for modulation broadening the parameter Y should be chosen to avoid cases where $\sin(\pi i W/Y) \approx 0$ since the coefficients a_i, b_i as given by (19) are then ratios of small, inaccurately known quantities.

3. EFFECTS OF THE FINITE MODULATION FREQUENCY

A. Basic Assumptions

In Sec. 2 it was assumed that $\omega T_1 \gg 1$. When this is not so, nuclei with a given resonant frequency can partially reorient during those intervals of the modulation cycle when they do not experience a resonant rf field. Consequently when averaged over all nuclei and over a complete modulation cycle there is never complete disorientation no matter how intense the rf field is. The signal amplitude and observed line shape then strictly depend upon both the modulation frequency and waveform as well as upon the modulation amplitude. However, we will show that to a fairly good approximation the line shape depends only upon modulation amplitude and the signal amplitude is given by $M_W(0)$ as in Sec. 2 multiplied by a function of $\theta = \omega T_1$.

Templeton and Shirley[2] could not detect any disorientation with a resonant rf field and no frequency modulation so that, because of the inhomogeneous broadening, only a very small fraction of the nuclei interact with the rf field. This is reasonable since the intrinsic NMR linewidth $1/T_2$ is certainly very much smaller than the observed inhomogeneous broadened linewidths which are of order 1 Mc/sec. Consequently we may treat the case of a finite modulation frequency in terms of small groups of nuclei being resonated for an infinitesimal fraction of the modulation period. In between these disorientations each such group of nuclei will partially reorient and we assume that this may be described in terms of a spin temperature which varies with time as

$$\frac{d(1/T_S)}{dt} = \frac{1}{T_1}\left(\frac{1}{T} - \frac{1}{T_S}\right). \tag{20}$$

The assumption of a nuclear spin temperature during the absence of a resonant rf field is certainly valid if the spin-lattice relaxation time T_1 is much greater than the characteristic time T_2' for the decoherence in the transverse nuclear magnetization as caused by nuclear spin-spin interactions. The mass of the thin foil samples used in RND experiments[1–3] is typically about 10^{-4} g and, for a half-life $\tau_{1/2}$ of 1 year 10 μCi of activity leads to a concentration of the active element of order 1 part in 10^5. Assuming that T_2' varies inversely with concentration[16] then, from measurements of T_2' in more concentrated alloys,[17] we expect $T_2' \sim 0.2$ to 5 sec for the RND experiments. This estimate is for $\tau_{1/2} = 1$ year and will be inversely proportional to $\tau_{1/2}$. At present, RND experiments have only been reported for cases where $T_1 \sim 10$–50 sec. Hence in typical RND experiments on elements with $\tau_{1/2} \gtrsim 1$ year there will be a high enough concentration of active nuclei for $T_2' \ll T_1$ and the assumption of a spin temperature should be valid. The assumption (20) of exponential relaxation of T_S seems reasonable, since for the magnetized samples used there will be no domain-wall effects, and a unique T_1 is then usually observed in ferromagnetic metals.[17]

In experiments on nuclei with shorter half-lives, weaker spin-spin interactions, or at higher temperatures where T_1 is shorter, there will certainly be cases where $T_2' \gg T_1$ and then the transverse relaxation time T_2 will effectively be equal to T_1. The assumption of a nuclear spin temperature would then be invalid but (20) may well be a fair approximation to the reorientation of the nuclei in terms of an effective spin temperature T_S.

In the presence of the frequency-modulated rf signal, the fractional change in intensity of the observed radiation between a temperature where the nuclear orientation is negligible and a low temperature T is

$$\begin{aligned}\bar{F} &= \left(\int_0^{y-W} + \int_{y+W}^{\infty}\right) P(\nu)F(\nu,T)d\nu \\ &\qquad + \int_{y-W}^{y+W} P(\nu)\frac{\omega}{2\pi}\oint F(\nu,T_S)dt\,d\nu \\ &= F(T) + \int_{y-W}^{y+W} P(\nu)\frac{\omega}{2\pi} \\ &\qquad \times \oint [F(\nu,T_S) - F(\nu,T)]dt\,d\nu, \end{aligned} \tag{21}$$

where $F(T)$ and $F(\nu,T)$ are defined in Sec. 2 A and $\oint$ refers to an integration over one complete modulation cycle. The RND signal is then given by

$$\begin{aligned} S(y) &= [F(T) - \bar{F}]/F(T) \\ &= \int_{y-W}^{y+W} P(\nu)\frac{\omega}{2\pi}\oint [F(\nu,T) - F(\nu,T_S)]dt\,d\nu \Big/ \\ &\qquad \int_0^{\infty} P(\nu)F(\nu,T)d\nu, \end{aligned} \tag{22}$$

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[16] M. Weger, E. L. Hahn, and A. M. Portis, J. Appl. Phys. 32, 124S (1961).

[17] V. Jaccarino, N. Kaplan, R. E. Walstedt, and J. H. Wernick, Phys. Letters 23, 514 (1966); M. B. Salamon, J. Phys. Soc. Japan 21, 2746 (1966); N. Kaplan, V. Jaccarino, and R. T. Lewis, J. Appl. Phys. 39, 500 (1968).

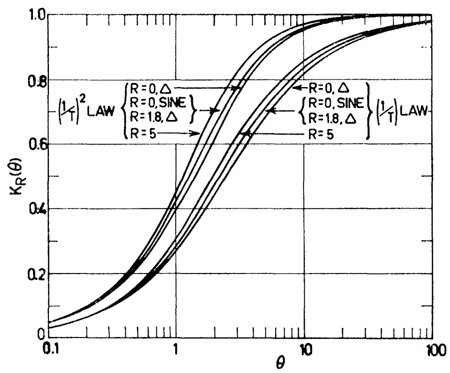

FIG. 4. Curves of $K_R(\theta)$ against θ $(=\omega T_1)$ for $1/T$ and $1/T^2$ temperature dependences of the γ radiation anisotropy and sinusoidal and triangular modulation waveforms. A Gaussian distribution of hyperfine fields is assumed. The function $K_R(\theta)$ gives the effect of modulation frequency upon the signal amplitude for a modulation ratio R.

and as in Sec. 2 A we assume that the fractional inhomogeneous broadening is small so that

$$S(y)=\int_{y-W}^{y+W} P(\nu)\frac{\omega}{2\pi}\oint f(T_S)dtd\nu\,, \tag{23}$$

where

$$f(T_S)=[F(\nu_0,T)-F(\nu_0,T_S)]/F(\nu_0,T) \tag{24}$$

and ν_0 is the center frequency of the resonance. The problem is now reduced to determining, for each group of nuclei (i.e., each resonant frequency ν), the dependence of their spin temperature over a modulation cycle and substituting this into (23) to determine the signal amplitude and line shape. Each such group of nuclei with resonant frequency $y-W\leqslant\nu\leqslant y+W$ will be resonated twice during each modulation cycle. The time interval between these disorientations will alternate between t' and $(2\pi/\omega-t')$, where

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

and (25)

$$t'=(2/\omega)\arccos(|\nu-y|/W) \quad \text{(sinusoidal waveform)}.$$

B. Complete Disorientation Model

We first consider a simple model in which the nuclei are effectively completely disoriented whenever they are resonated. If a given group of nuclei is resonated at $t=0$ then by (20) the time dependence of their spin temperature until their next disorientation is given by

$$1/T_S=T^{-1}(1-e^{-t/T_1}) \tag{26}$$

and the integral over 1 cycle in (23) is given by substituting (26) into

$$\oint f(T_S)dt=\int_0^{t'} f(T_S)dt+\int_0^{2\pi/\omega-t'} f(T_S)dt \tag{27}$$

and in terms of the dimensionless quantities $\theta=\omega T_1$ and $z=(\nu-y)/W$ the signal is

$$S(y)=W\int_{-1}^{1} P(y+zW)\rho(z,\theta)dz\,, \tag{28}$$

where

$$\rho(z,\theta)=\frac{1}{2\pi}\left[\int_0^{\omega t'} f(T_S)d\alpha+\int_0^{2\pi-\omega t'} f(T_S)d\alpha\right] \tag{29}$$

and

$$1/T_S=T^{-1}(1-e^{-\alpha/\theta}). \tag{30}$$

For small modulation amplitudes $P(y+zW)$ may be Taylor expanded to obtain

$$S(y)=2WP(y)\int_0^1 \rho(z,\theta)dz\,, \tag{31}$$

from which it follows that for small modulation amplitudes the true line shape is obtained regardless of the modulation frequency which then simply contributes a term $K_0(\theta)$ to the resonance signal amplitude where

$$K_0(\theta)=\int_0^1 \rho(z,\theta)dz. \tag{32}$$

For larger modulation amplitudes the effect of the modulation frequency upon the signal amplitude will depend upon the modulation amplitude and we write

$$S(0)=K_R(\theta)A(R)\,,$$

so that $K_R(\theta)$ is the ratio of the signal amplitude which would be observed with $\theta=\omega T_1$ to that with a modulation frequency sufficiently high for reorientation during the cycle to be neglected.

When the fractional change $F(T)$ in the radiation intensity due to nuclear orientation is proportional to $1/T$ (e.g., the Mössbauer experiment at sufficiently high temperatures or, somewhat roughly, the γ radiation anisotropy in the "linear region") or to $1/T^2$

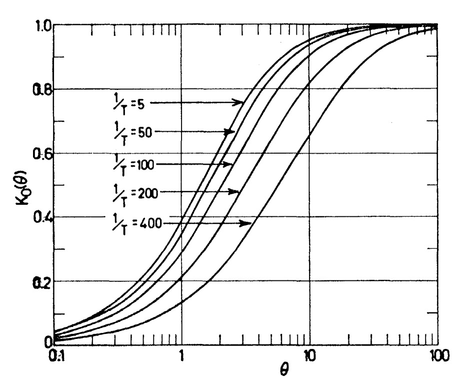

FIG. 5. Curves of $K_0(\theta)$ against θ $(=\omega T_1)$ for the detection of axial γ radiation from ^{60}Co nuclei in an iron host at various low temperatures. The function $K_0(\theta)$ gives the effect of modulation frequency upon the signal amplitude for small modulation amplitudes.

(e.g., the γ radiation anisotropy at sufficiently high temperatures), $\rho(z,\theta)$ may be calculated analytically from (29), (30) as

$$\rho(z,\theta)=(\theta/2\pi)(2-e^{-\omega t'/\theta}-e^{(\omega t'-2\pi)/\theta}) \quad (1/T \text{ law})$$

and

$$\rho(z,\theta)=(\theta/2\pi)[3+\tfrac{1}{2}(e^{-2\omega t'/\theta}+e^{2(\omega t'-2\pi)/\theta}) -2(e^{-\omega t'/\theta}+e^{(\omega t'-2\pi)/\theta})], \quad (1/T^2 \text{ law}) \quad (33)$$

where $\omega t'$ is given by (25). For a triangular modulation waveform (31) may also be integrated, leading to

$$K_0(\theta)=(\theta/\pi)[1+(\theta/2\pi)(e^{-2\pi/\theta}-1)] \quad (1/T \text{ law})$$

and

$$K_0(\theta)=\frac{2\theta}{\pi}\left[1+\frac{\theta}{2\pi}(e^{-2\pi/\theta}-1)\right] -\frac{\theta}{2\pi}\left[1+\frac{\theta}{4\pi}(e^{-4\pi/\theta}-1)\right](1/T^2 \text{ law}). \quad (34)$$

In Fig. 4 curves of $K_R(\theta)$ are plotted against θ for both $1/T$ and $1/T^2$ dependences of $F(T)$. For $R=0$ and a triangular waveform Eqs. (34) are plotted; for the other cases the curves were computed by numerical integration of (28) and (29). For $R=0$ the Gaussian line shape (7) was used for $P(\nu)$; for large R (in practice $R>3$) it may be shown from (28) that the signal amplitude does not depend upon the line shape $P(\nu)$. It is obvious from Fig. 4 that for typical modulation amplitudes ($R\sim0.5$ to 2), $K_R(\theta)$ is almost independent of the modulation amplitude so that to a fairly good approximation the signal amplitude depends separately upon modulation frequency and amplitude:

$$S(0)\approx K_0(\theta)A(R). \quad (35)$$

In Fig. 5 curves of $K_0(\theta)$ against θ are given for the detection of axial ($\Theta=0$) γ radiation from ^{60}Co nuclei aligned by hyperfine interaction in iron at various low temperatures. A triangular modulation waveform is assumed. These were computed from the known nuclear orientation parameters[2] U_ν, F_ν, μ, and H. For $1/T=5$ then $F(T)\propto 1/T^2$ and the curve in Fig. 5 is identical to the corresponding curve in Fig. 4, which applies to any case in which the γ radiation anisotropy is proportional to $1/T^2$. For $1/T\sim50$–100 the γ anisotropy is very approximately linear in $1/T$ and the curves in Fig. 5 are similar to the curve in Fig. 4 for a $1/T$ temperature dependence.

Similar calculations showed that to a very good approximation the observed line shape is the same for either a sinusoidal or triangular waveform. Also, as $\theta\rightarrow0$ the observed line shape tends to $M_W(y)$ as would also be observed for a large θ and, to a fairly good approximation, it may be regarded as independent of θ, i.e., it is effectively dependent only upon $P(\nu)$ and the modulation amplitude:

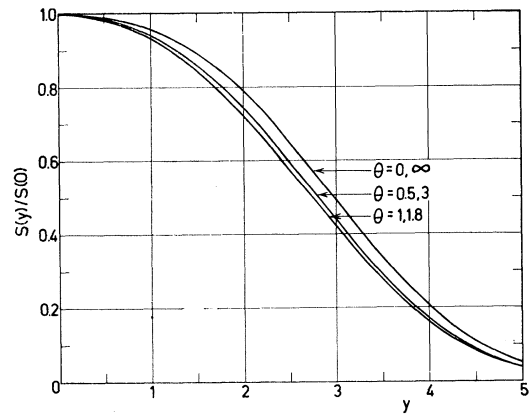

FIG. 6. Modulation-broadened line shapes for $R=2$ and a Gaussian distribution of hyperfine fields plotted for several values of θ ($=\omega T_1$) and showing the weak dependence of the line shape upon the modulation frequency. A $1/T$ law for the γ radiation anisotropy is assumed.

$$S(y)\approx K_0(\theta)M_W(y). \quad (36)$$

This is illustrated in Fig. 6, where the line shape for a $1/T$ law and Gaussian $P(\nu)$ is plotted for $R=2$ and several values of θ. The dependence upon θ is weak and also the curves for sinusoidal and triangular waveforms agree to far higher accuracy than could be shown in the figure.

4. EFFECTS OF THE FINITE rf FIELD AMPLITUDE

A. Introduction

For sufficiently high modulation frequencies the complete disorientation model (CDM) must become invalid since the duration of each disorientation is proportional to $1/\omega$ and the rf field could only completely disorient the nuclei instantly if it had an infinite amplitude. In order to allow for finite rf field amplitudes we now assume that while the rf field is resonating a group of nuclei the disorientation is given in terms of an effective spin temperature T_S which satisfies

$$1/T_S=(1/T_i)e^{-t/\tau}, \quad (37)$$

where $t=0$ at the beginning of the disorientation when $T_S=T_i$. It is well known[18] that in the presence of a strong resonant rf field there is a non-Boltzmann distribution of the nuclear spin populations so that these cannot be described in terms of a spin temperature. However, here we are simply assuming that, for a noninhomogeneously-broadened group of nuclei, the time dependence of their γ radiation anisotropy during disorientation is $F(\nu,T_S)$, where T_S is given by (37). In Sec. 4 C it is shown that this assumption may be easily tested experimentally.

[18] See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, London, 1961), Chap. V.

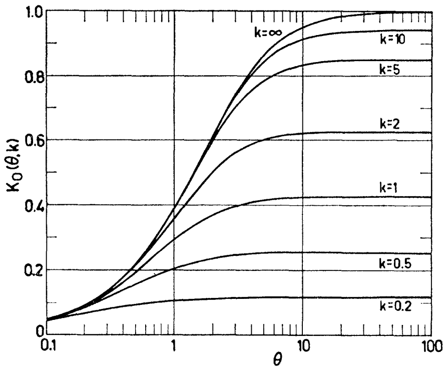

FIG. 7. Curves showing the dependence $K_0(\theta,k)$ of the signal amplitude upon θ ($=\omega T_1$) and the parameter k for $1/T^2$ temperature dependence of the γ radiation anisotropy. A small modulation amplitude is assumed.

If a triangular waveform is used then the duration of the disorientations will be the same for all nuclei. If K is the ratio of $1/T_S$ before and after each disorientation we define a parameter k by

$$K=e^{-k/\theta}. \tag{38}$$

For a given rf field amplitude H_1, k/θ should be proportional to the duration of each disorientation, i.e.,

$$k/\theta \propto \Omega/(\omega W),$$

so that

$$k \propto \Omega/(T_1 W), \tag{39}$$

where Ω is the width of the resonance which would be obtained in the absence of inhomogeneous broadening. The inverse dependence of k upon W means that as the modulation amplitude is increased there is a reduction in the effective rf field amplitude. In choosing the modulation amplitude in an RND experiment to achieve the largest possible signal amplitude it will be necessary to obtain a compromise between this effect and the dependence of $M_W(0)$ upon W as given in Fig. 3.

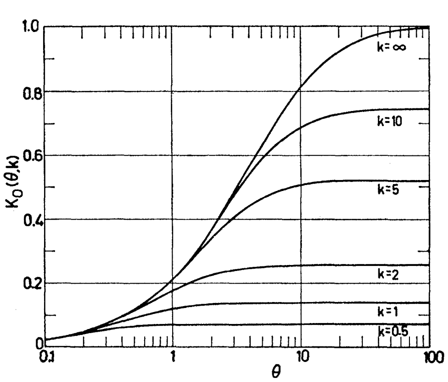

FIG. 8. Curves showing the dependence $K_0(\theta,k)$ of the signal amplitude upon θ ($=\omega T_1$) and the parameter k for the detection of axial γ radiation from ^{60}Co nuclei in an iron host at a temperature given by $1/T=200°K^{-1}$. A small modulation amplitude is assumed.

One of the most important results of Sec. 4 is to indicate how values of k may be obtained from RND experiments so that the dependence of the intrinsic linewidth Ω upon temperature and possibly rf field amplitude may be studied. For a system of nuclei obeying the Bloch equations[19] the imaginary part of the complex nuclear susceptibility in the presence of saturation is given by[20]

$$\chi''(\nu)=2\pi^2\nu_0\chi_0T_2^2(\nu-\nu_0)/\left[1+4\pi^2T_2^2(\nu-\nu_0)^2+\gamma^2H_1^2T_1T_2\right] \tag{40}$$

so that the intrinsic width of the resonance is

$$\Omega=(2\pi)^{-1}(1/T_2^2+\gamma^2H_1^2T_1/T_2)^{1/2} \tag{41}$$

and when $\gamma^2H_1^2T_1T_2\gg1$ then

$$\Omega=\gamma H_1T_1/2\pi T_2. \tag{42}$$

For NMR in solids where there are strong spin-spin interactions the behavior at large rf field amplitudes is often well described by Redfield's theory.[21] The imaginary part of the susceptibility is then given by

$$\chi''(\nu)=\frac{\pi\nu_0\chi_0(H_1^2+2H_l'^2)}{\left[4\pi^2(\nu-\nu_0)^2+\gamma^2(H_1^2+2H_l'^2)\right]T_1H_1^2\nu}, \tag{43}$$

where $2H_l'^2$ is the square of the effective spin-spin width of the NMR line. The intrinsic width is then

$$\Omega=\gamma(H_1^2+2H_l'^2)^{1/2}/(2\pi)$$

and for

$$H_1\gg\sqrt{2}H_l', \quad \Omega=\gamma H_1/(2\pi). \tag{44}$$

Hence there is a difference by a factor of T_1/T_2 in the intrinsic widths as given by the equations of Bloch and Redfield. When $T_2'\gg T_1$ so that $T_2=T_1$ the two theories should lead to indistinguishable results for RND experiments. From observations of the temperature dependence of k Eq. (39) enables the temperature dependence of Ω to be determined. The width should be temperature-independent except when the Bloch result applies and also $T_2\neq T_1$. In conventional NMR experiments at room temperature it has been found that for cobalt[22] (where $T_2\ll T_1$) Redfield's theory fits well whereas for iron[23] and nickel[24] (where $T_2=T_1$) the results are well explained by the Bloch equations when modified[25] for fast passage and inhomogeneous broadening.

[19] F. Bloch, Phys. Rev. **70**, 460 (1946).
[20] Reference 18, Chap. III.
[21] A. G. Redfield, Phys. Rev. **98**, 1787 (1955).
[22] A. C. Gossard and A. M. Portis, Phys. Rev. Letters **3**, 164 (1959); A. M. Portis and A. C. Gossard, J. Appl. Phys. **31**, 205 (1960).
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[24] D. L. Cowan and L. W. Anderson, Phys. Rev. **139**, A424 (1965).
[25] A. M. Portis, Phys. Rev. **100**, 1219 (1955).

B. Steady-State Solution

For an rf field with given modulation amplitude, modulation frequency, and center frequency a steady state will result in which, for each group of nuclei, the spin temperatures before and after each modulation cycle are equal (i.e., the reorientation between rf pulses is equal to the disorientation caused by them). By applying the relaxation equations (20) and (37) to this steady state it follows that just after the rf pulse preceding the interval t' in (29) the spin temperature T_a of a group of nuclei is given by

$$\frac{1}{T_S}=\frac{K}{T}\,\frac{1+(K-1)e^{-(\omega t'-2\pi)/\theta}-Ke^{-2\pi/\theta}}{1-K^2e^{-2\pi/\theta}}. \tag{45}$$

Then during the interval t' the spin temperature of the group is

$$\frac{1}{T_a}=\frac{1}{T}+\left(\frac{1}{T_a}-\frac{1}{T}\right)e^{-\omega t/\theta} \tag{46}$$

and during the interval $2\pi/\omega-t'$ the spin temperature of the group is

$$\frac{1}{T_S}=\left\{K\left[\frac{1}{T}+\left(\frac{1}{T_a}-\frac{1}{T}\right)e^{-\omega t'/\theta}\right]-\frac{1}{T}\right\}e^{-\omega t/\theta}+\frac{1}{T}. \tag{47}$$

The calculation of line shapes and signal amplitudes is now the same as that for the CDM of Sec. 3 B except that Eq. (30) must now be replaced by (46) and (47) for the integrations in (29).

In Fig. 7 and 8 the calculated dependence of the signal amplitude upon modulation frequency and k are shown for ^{60}Co in iron with $1/T=5$ and 200, respectively. A small modulation amplitude is assumed. For $1/T=5$ the γ radiation anisotropy from ^{60}Co nuclei polarized in iron is accurately proportional to $1/T^2$ and Fig. 7 will apply to the polarization of any nuclei in any ferromagnetic host when the temperature is sufficiently high for a $1/T^2$ law to be obeyed. Calculations for finite modulation amplitudes yielded results similar to those from the CDM calculations—i.e., the line shape is hardly affected by the modulation frequency and, to a fairly good approximation, the signal amplitude is separately dependent upon the modulation frequency and the modulation amplitude. A comparison between Fig. 5 and Figs. 7 and 8 shows that, for any value of k, if $\theta \ll k$ the function $K_0(\theta)$ is the same as that from the CDM calculations. This is expected since for sufficiently slow modulation the duration of each disorientation will be large enough to completely disorient each group of nuclei. As θ is increased significant deviation from the CDM curves occurs at $\theta \approx k$ and finally $K_0(\theta)$ approaches a limiting value. Here the modulation is so fast that in the steady state all nuclei have the same spin temperature T_l, which is effectively constant during each modulation

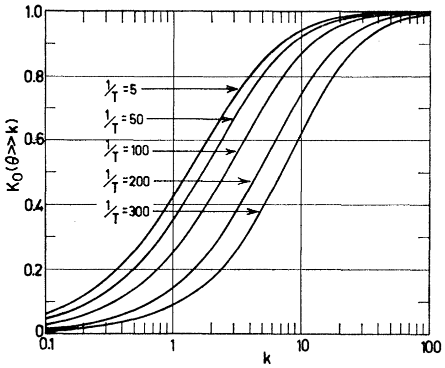

FIG. 9. Dependence upon the parameter k of the signal amplitude of the fast modulated resonance from ^{60}Co nuclei in iron at various temperatures. These curves are independent of line shape, modulation amplitude, and waveform. For any nuclei aligned in any host similar curves may be easily calculated from Eq. (48).

cycle. By expanding (45) for large θ it follows that

$$K_0(\theta \gg k)=\frac{F(\nu_0,T)-F(\nu_0,T_l)}{F(\nu_0,T)}, \tag{48}$$

where

$$T_l=T(1+k/\pi). \tag{49}$$

In Fig. 9 plots showing the dependence of the signal amplitude upon the parameter k for ^{60}Co in iron at high modulation frequencies ($\theta \gg k$) are given. These curves are very simply calculated from (48) and (49) and the condition $\theta \gg k$ is easily satisfied in carrying out RND experiments. If for any reason (e.g., hard-core effect) the orientation of the groups of nuclei experiencing a resonant rf field do not decay to zero as assumed in (37) then the curves of Figs. 6–8 may well still be valid if multiplied by an appropriate factor which is less than unity.

C. Transient Solutions for Fast Modulation

Shirley and Templeton[2] showed how, by destroying the nuclear orientation with a frequency-modulated resonant rf field and then measuring the γ radiation anisotropy as a function of time after the center frequency is moved off resonance, the spin-lattice relaxation time T_1 may be determined unambiguously. Here we show that the parameter k may be determined simply and unambiguously by measuring the γ radiation anisotropy as a function of time after the center frequency is moved from off resonance onto the resonance.

We assume that the modulation frequency is sufficiently high so that $\theta \gg 1$ (a condition very easily satisfied in practice) and expand the exponentials in (46) and (47), neglecting all terms of magnitude $<1/\theta^2$. However, now, instead of assuming a steady state, an expression for the change in $1/T_S$ over 1 modulation cycle is obtained:

$$\delta(1/T_S)=\frac{2\pi}{\theta}\left(\frac{1}{T}-\frac{1}{T_S}\right)-\frac{2k}{\theta T_S}. \qquad (50)$$

The two terms on the right-hand side give the reorientation and disorientation which occur during 1 modulation cycle. Since these are independent of t' it follows that all nuclei with ν between $y-W$ and $y+W$ have the same spin temperature. Since it is assumed that θ is large (50) may be written as a differential equation:

$$\frac{d(1/T_S)}{dt}=-\frac{(\pi+k)}{\pi T_1 T_S}+\frac{1}{T_1 T}, \qquad (51)$$

so that if a resonant rf field is applied at $t=0$ the reciprocal of the effective spin temperature will decay exponentially from $1/T$ to $1/T_l$ with a time constant:

$$T_1'=T_1(1+k/\pi)^{-1}. \qquad (52)$$

The published curve of Templeton and Shirley[2] showing the destruction and recovery of ^{60}Co nuclear orientation upon entering and leaving the resonance illustrates very well the shorter time constant T_1 during disorientation. The exponential decay of $1/T_S$ as given by (51) is in fact equivalent to the assumption (37) of exponential decay of $1/T_S$ for each group of nuclei as for fast modulation since the rates of disorientation are then the same for all groups of nuclei being resonated. Hence this assumption may be easily tested experimentally from the time dependence of the γ-radiation anisotropy after entering the resonance. The curve of Templeton and Shirley is to within experimental error quite a good fit to an exponential.

5. CONCLUSIONS AND APPLICATIONS TO EXPERIMENTS

When the modulation is sufficiently fast ($\theta\gg 1$) the modulation broadening in RND experiments is given accurately by Eq. (5) and the dependence of the observed line shape and signal amplitude upon modulation amplitude for Gaussian and Lorentz hyperfine field distributions is as given in Sec. 2 A. The moments of observed line shapes may be easily corrected for modulation broadening using Eq. (13). If the modulation broadening is not too great, the series method of Sec. 2 C may be used to determine the hyperfine field distribution from the observed line shape. For larger modulation amplitudes the Fourier method must be used and care must then be taken in the analysis to avoid "zeros" in $\sin(\pi i W/Y)$.

If the modulation is not fast then, to an accuracy which would generally be quite adequate in most experimental analyses, the observed line shapes are the same as for fast modulation but the signal amplitude is reduced by a factor $K_0(\theta)$. For large rf field intensities $K_0(\theta)$ may be calculated for various θ using the CDM method of Sec. 3 B, where the only assumption made is that of exponential decay of a nuclear spin temperature between complete disorientations. By measuring the signal amplitude as a function of modulation frequency these calculations may be easily checked and this may well be the simplest method of determining fast spin-lattice relaxation times.

For weaker rf field intensities, if the disorientation may also be described in terms of an effective nuclear spin temperature, then $K_0(\theta)$ will also be a function of the parameter k as in Section 4 B. For fast modulation ($\theta\gg 1$), $K_0(\theta)$ is very easily calculated as a function of k from Eqs. (48) and (49) and the known temperature dependence of the γ radiation anisotropy. Values of k may be obtained experimentally either from the signal amplitude or by applying Eq. (52) to measurements of the time dependence of the γ radiation anisotropy after entering the resonance. From the temperature dependence of k, the temperature dependence of Ω, the width of the noninhomogeneously broadened resonance, may be obtained. This is of fundamental interest in understanding saturation and spin-spin interactions in very dilute alloys. It would also be interesting to study the dependence of k upon the rf field intensity.

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