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Radiative Detection of Single- and Multiple-Pulse Magnetic Resonance of Oriented Radioactive Nuclei

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Observations by radiative detection of pulse magnetic resonance of oriented ^{60}Co nuclei in iron are reported. Multiple-pulse techniques are used to observe free-induction decays and spin echoes.

Radiative detection of the magnetic resonance of oriented radioactive nuclei by the observation of the effects of a resonant rf field upon the anisotropic distribution of the γ radiation was suggested by Bloembergen and Temmer.[1] The main advantage of radiative detection is that far less nuclei are required as compared with conventional NMR techniques in which the emf induced in the rf coil by the precessing nuclei is detected. Also Shirley[2] pointed out that the effects of resonant fields on the emission of radiation by nuclei are of fundamental interest. Using a model in which the spins of the resonated nuclei are assumed to be evenly distributed around the well-known[3] precessional cone in the Larmor frame, Shirley showed that the dependence of the resonant change in γ-radiation anisotropy upon rf frequency should exhibit structure associated with the various multipole terms in the angular distribution of the emitted radiation.

The first observation of NMR by radiative detection was by Matthias and Holliday[4] using ^{60}Co nuclei oriented by magnetic hyperfine interaction in iron at a low temperature (~ 0.03 K). At the resonant frequency of 165.5 MHz only a small (~ 1%) change in the γ-radiation anisotropy was observed and this was later shown by Templeton and Shirley[5] to be due to the spread (~ 0.1 T) in the hyperfine fields associated with inhomogeneous line broadening. With a single rf frequency ω, only nuclei in the frequency range $\omega \pm \gamma H_1$ will be significantly affected by the rf field, where H_1 is the amplitude of the circularly polarized rf field at the nuclei. With the largest cw rf fields which may be used without intolerable heating of the metallic samples this frequency range is much smaller than the inhomogeneous linewidth. Templeton and Shirley showed that large changes (~ 60%) in the anisotropy may be obtained by employing frequency-modulated rf fields using modulation parameters chosen so that most of the nuclei are resonated at intervals which are short in comparison with the nuclear spin-lattice relaxation time T_1. With use of this technique, accurate measurements of magnetic hyperfine interactions and T_1 values for a wide variety of dilute ferromagnetic alloys have been reported and have recently been reviewed by Stone.[6] In such experiments, each nucleus experiences a series of many fast passages and the effects of coherent spin motion in the rf field are not observable.[7] We recently reported[8] the application of radiative detection to single-pulse experiments using short (~ 2-10 μsec) pulses of high (~ 1 kW) rf power. Values of $\omega_1 = \gamma H_1$ which were comparable with the inhomogeneous width were applied without detectable off-resonant heating. Large signals were observed indicating the feasibility of using fixed-frequency rf pulses. We report here improved results obtained with faster pulse rise times which permit, for the first time, the radiative detection of coherent spin rotations in the

Larmor frame and of transverse phase effects in multiple-pulse experiments.

The sample was prepared by diffusing a few microcuries of ^{60}Co activity into the surface of a 200-μm-thick disk of iron. The diffusion temperature and time were 830°C and 4 min, respectively, leading to an expected mean diffusion depth ~0.7 μ.m. The estimated number of ^{60}Co nuclei in the sample is ~5×10^{13}, leading to an average fractional concentration ~5×10^{-5} in the diffusion layer. Single-passage resonance[9,10] experiments on this sample indicated a small electric quadrupole interaction with energy P such that $P/h\sim10$ kHz, which is negligible in comparison with the interaction of the nuclei with the rf fields used in these experiments. The sample was cooled to 9 mK in an adiabatic-demagnetization cryostat and a 0.1-T dc field was applied to produce a common axis of nuclear orientation. A gated rf synthesizer together with a 250-MHz band-width amplifier capable of producing 1-kW rf pulses with a 40-nsec rise time was coupled to a coil in the cryostat to provide the necessary rf field.

The normalized distribution of γ radiation from axially oriented nuclei may be written as[11]

$$W(\theta)=1+\sum_{\text{even }\nu}A_\nu B_\nu(\beta)P_\nu(\cos\theta), \tag{1}$$

where θ is the angle between the direction of emission and the orientation axis. The A_ν contain angular-momentum coupling coefficients and the $B_\nu(\beta)$ describe the orientation of the parent radioactive nuclei; for the thermal polarization of nuclei of spin I in a magnetic field H, then $\beta=\mu H/kTI$. In our experiments an axial ($\theta=0$) γ-radiation detector was used. In the presence of an rf field the spin motion is best considered by transformation to the Larmor frame of reference which rotates about the z axis at the rf frequency ω. In this frame an effective field,

$$\vec{H}_{\text{eff}}=[(\omega_0-\omega)/\gamma]\hat{z}+H_1\hat{x}, \tag{2}$$

acts on the nuclei where $\omega_0=\gamma H_0$ and H_0 is the dc field on the nuclei. If the rf is switched on sufficiently rapidly in comparison with a time $2\pi/\gamma H_{\text{eff}}$, the nuclear magnetization $\vec{M}$ will then precess in the Larmor frame about $\vec{H}_{\text{eff}}$ with a cone angle $\theta_c=\arctan[\omega_1/(\omega-\omega_0)]$. At resonance, $\vec{M}$ precesses in the y-z plane about the field $H_1\hat{x}$ with frequency ω_1. The 90° and 180° pulses of conventional NMR are then obtained for pulse widths of $\pi/2\omega_1$ and π/ω_1, respectively. The radiative detection signal S_2, or fractional change in radiation anisotropy, immediately after a resonant pulse of width

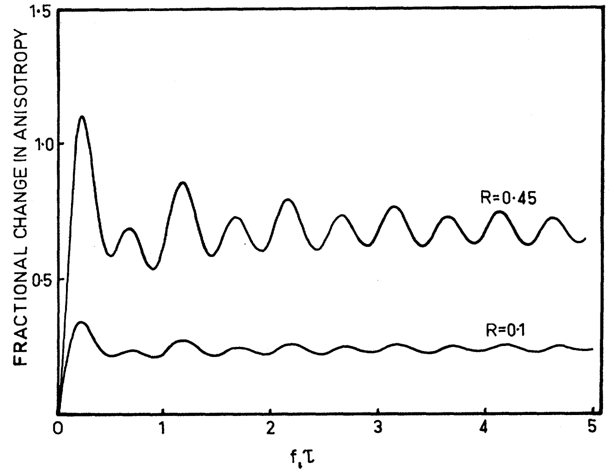

FIG. 1. Calculated dependence of the fractional change in γ-radiation anisotropy upon the width of a single pulse for two values of $R=\omega_1/\Delta$.

τ will be

$$S_2=1-P_2(\cos\omega_1\tau) \tag{3}$$

for the case of a dominant $\nu=2$ term in the angular distribution (1). Hence signals varying between 0 and 1.5 with an oscillation frequency of $2\omega_1$ are expected as a function of pulse width. However the inhomogeneous broadening will result in a z component of $\vec{H}_{\text{eff}}$ for all nuclei except those for which $\omega=\omega_0$. We have shown,[12] allowing for this, that the expected signal will then be

$$S_2=1-\int_{-\infty}^{\infty}P(\omega_0-\overline{\omega}_0)P_2(\cos\alpha)\,d(\omega_0-\overline{\omega}_0), \tag{4}$$

where $P(\omega_0-\overline{\omega}_0)$ is the normalized resonant frequency distribution with a half width at half-maximum Δ and

$$\cos\alpha=1-2\sin^2\theta_c\sin^2\tfrac{1}{2}\gamma H_{\text{eff}}\tau. \tag{5}$$

The dependence of the calculated signal immediately after a pulse upon $f_1\tau$ (where $f_1=\omega_1/2\pi$) for two values of $R=\omega_1/\Delta$ is shown in Fig. 1. It is seen that oscillations in signal with varying pulse width are still expected for quite small values of R; the amplitude is lower but the oscillation frequency is still close to $2f_1$. One interesting feature is that, as R increases, the average of the signal over one period tends to the hard-core signal of 0.75 as introduced by Shirley.[2]

In each single-pulse experiment the γ-radiation anisotropy was monitored as a function of time for 200 sec after the application of an rf pulse of width τ. During this time the anisotropy decayed back to its original value because of the spin-lat-

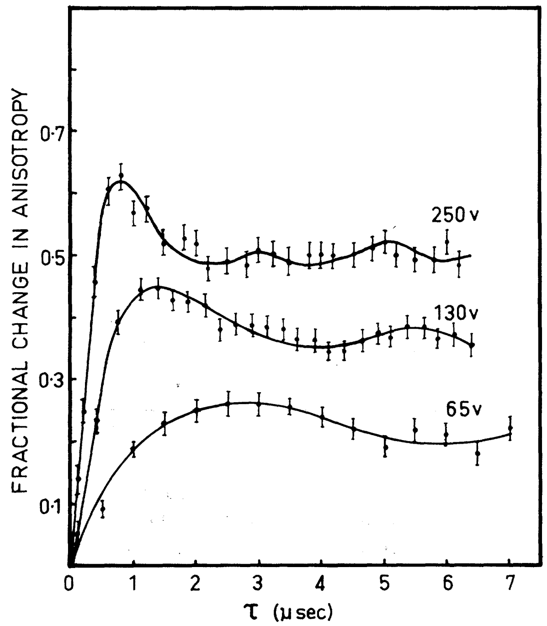

FIG. 2. Observed dependence of the fractional change in γ-radiation anisotropy upon the width of a single pulse for ^{60}Co nuclei in iron at 0.01 K for three values of the peak rf voltage.

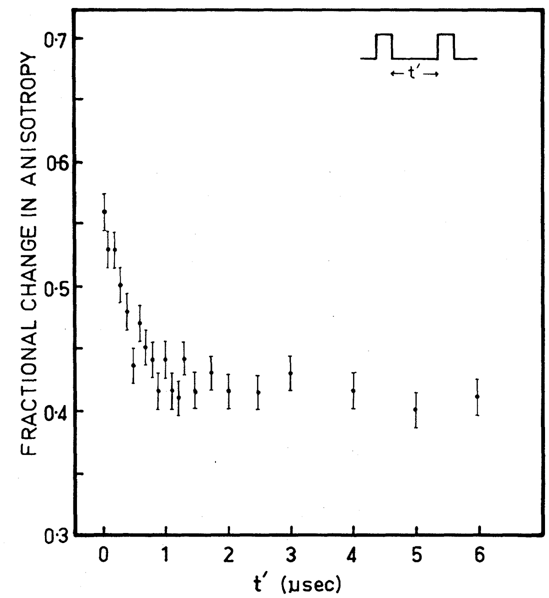

FIG. 3. Free-induction decay: dependence of the fractional change in γ-radiation anisotropy upon pulse interval in a two-pulse experiment on ^{60}Co nuclei in iron at 0.01 K with a peak rf voltage $V = 259$ V and pulse width of 0.3 μsec.

tice relaxation. No off-resonant heating was detectable in experiments using rf frequencies a few MHz above or below the resonant frequency. The signal immediately after the pulse was determined from a single-exponential fit to the data. The observed dependence of the signal upon τ for three values of V, the peak rf voltage, is shown in Fig. 2. The oscillations, at a frequency which is proportional to the rf voltage, are obvious and correspond to a value $f_1 \simeq 225$ kHz for the largest voltage used; from low-rf field, cw, frequency-modulated experiments a value $\Delta/2\pi = 0.5$ MHz was obtained so that the curves in Fig. 2 correspond to values of R of $\simeq 0.45$, 0.23, and 0.1. Comparison with Fig. 1 shows that the observed oscillations are somewhat weaker than those in the calculated signals. We expect that this is due to neglect of the $\nu = 4$ term and of a distribution of H_1 values in the calculations. More detailed calculations are in progress.

Because of the great power of more sophisticated multiple-pulse sequences in studying nuclear interactions and relaxation processes we have made a study of the radiative detection of phasing effects in the transverse plane. In these experiments the γ anisotropy immediately after the pulse sequence is determined. The nuclei are then precessing rapidly (165.5 MHz for Fe^{60}Co) and transverse phase effects are not directly observable unless a detector at $\theta \neq 0$ is used and the anisotropy monitored as a function of time. This would be extremely difficult and so we use the last pulse to rotate the spin pattern. The resulting distribution of z-spin components then depends on whether or not there was coherence in the transverse plane before the last pulse. Ideally, to observe the free-induction decay (FID), a 90°-90° sequence would be used. However, because of the limited values of R presently available larger effects are observed using pulses with smaller average turning angles. Figure 3 shows the dependence upon pulse interval of the signal immediately after a pair of 0.3-μsec pulses. For a zero interval the sequence is equivalent to a single 0.6-μsec-wide pulse. The dependence of the signal upon interval is due to the transverse dephasing of the spins between pulses and the partial rotation of transverse components out of the transverse plane by the second pulse; it is thus an observation of the FID for $< 10^{14}$ nuclei.

The rationale[12] behind the radiative detection of spin echoes is similar to that for the FID except that a triple-pulse sequence is used. Figure 4

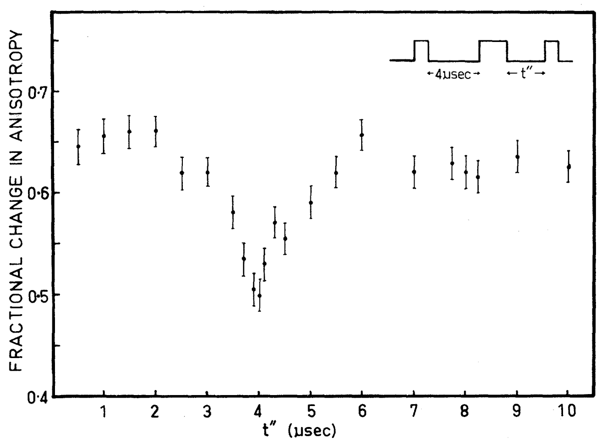

FIG. 4. Spin-echo experiment: dependence of the fractional change in γ-radiation anisotropy upon the second-pulse interval in a three-pulse experiment on ^{60}Co nuclei in iron at 0.01 K with a peak rf voltage $V = 250$ V. Pulse widths were 0.8, 1.6, and 0.8 μsec.

shows the signal after a "90°-180°-90°" sequence as a function of the second pulse interval. The echo is observed when this interval equals the first interval which was held at 4μsec. If the pulses were true 90° and 180° pulses, i.e., if $R \gg 1$, and there were no inhomogeneous rf broadening, the signal would vary from the Shirley hard-core value of 0.75 off the echo to zero at the echo. With our conditions the echoes were found not to depend greatly on the widths used and similar results were obtained for a "90°-90°-90°" sequence.

With the introduction of pulse techniques to experiments employing radiative detection, detailed studies of spin-spin interactions in very dilute alloys are now possible. Experiments on this and on the study of the electric quadrupole interactions are now in progress. The extension to larger rf fields to improve the coherence of the rotations is also being investigated.

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