For spin $\frac{3}{2}$, $\bar{I}_{x(y)} \propto (C_{\frac{3}{2}}{}^*C_{\frac{1}{2}}(\pm)C_{-\frac{3}{2}}{}^*C_{-\frac{1}{2}})\exp(i\omega t)$+complex conjugate, where $\omega=(E_{\frac{3}{2}}-E_{\frac{1}{2}})/\hbar=(E_{-\frac{3}{2}}-E_{-\frac{1}{2}})/\hbar$.

We solve the time-dependent Schroedinger equation in two intervals: during the pulse, in the presence of the rf field H_1, and following the pulse, where H_1 is zero. The effect of H_1 is then to induce only the transitions $\frac{3}{2}\rightleftharpoons\frac{1}{2}$ and $-\frac{3}{2}\rightleftharpoons-\frac{1}{2}$. Considering the Boltzmann surplus and assuming the system to be initially in the $\pm\frac{3}{2}$ state, the result (for $H_0=0$) is a time-independent induction signal following the pulse. We assume that the effect of the existence over the sample of differing ∇E (due to crystalline imperfections) or internal magnetic fields (due to dipolar interactions) is to dephase the precessing microscopic magnetization vectors and to cause the induction signals to decay in a time T_2. Figure 1 is a multiple exposure of decay signals in a $NaClO_3$ single crystal taken with and without an H_0. The decay envelope is Gaussian with T_2 equal to 425 μsec. A calculated T_2 of this order of magnitude results from a computation of the magnetic dipolar interaction of a Cl nucleus with the nuclear moments located within one lattice parameter.

To compute the Zeeman effects, we consider an H_0 applied at an angle θ_0 with respect to ∇E and an H_1 applied for a time t_w at an angle θ_1. The voltage induced in the coil for $t>t_w$ is then given by:

$$V(t)\propto\sin\theta_1\sin(\sqrt{3}\Omega_1t_w\sin\theta_1)\left[\frac{f-1}{f}\cos\left\{\frac{\Omega_0(3+f)\cos\theta_0}{2}t\right\}+\frac{f+1}{f}\cos\left\{\frac{\Omega_0(3-f)\cos\theta_0}{2}t\right\}\right],\quad(1)$$

where $\Omega_0=\gamma H_0$, $\Omega_1=\gamma H_1$, and $f=(1+4\tan^2\theta_0)^{\frac{1}{2}}$. The appearance, in general, of the two frequencies in square brackets in (1) arises from the mixing (in the presence of an H_0) of the $\frac{1}{2}$ and $-\frac{1}{2}m$ states, which splits the steady state resonance symmetrically into two pairs of lines.[2] Further calculations predict a spin-echo signal at 2τ (following the application of a second rf pulse at time τ). We have observed echoes and stimulated echoes in both the powders and single crystals. Hahn and Herzog (see following letter) report the behavior of the echoes as a function of H_0 and of crystal orientation.

In $NaClO_3$, ∇E lies along the symmetry axis of the molecule. The four molecules in a unit cell of the crystal are oriented with their symmetry axes along the body diagonals of the unit cube. [Direction cosines $(1/\sqrt{3}, 1/\sqrt{3}, 1/\sqrt{3}$; etc.)] The beat structure in Fig. 1 is that observed on the decay in a single crystal with H_1 and H_0 both applied along (0,0,1). In this orientation $\cos\theta_0=1/\sqrt{3}$ and $f=3$ for each of the four molecules in the unit cell. A single-beat frequency $\sqrt{3}\gamma H_0/2\pi$ is then predicted by Eq. (1) and is found to agree with that observed. Figure 2 shows the more complex pattern observed with H_1 along (0,0,1) and H_0 along $(1/\sqrt{2},1/\sqrt{2},0)$. The voltage predicted by (1) is here proportional to $2\cos(\Omega_0t)+1.6\cos(0.53\Omega_0t)+0.4\cos(1.9\Omega_0t)$, which agrees with the pattern of the observed decay. The echo exhibits a structure similar to that on the decay.

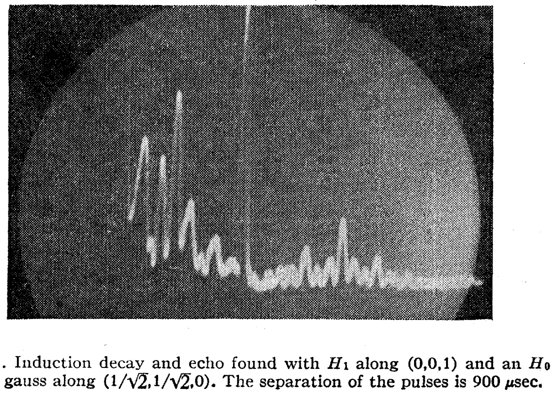

FIG. 2. Induction decay and echo found with H_1 along (0,0,1) and an H_0 of 12 gauss along $(1/\sqrt{2},1/\sqrt{2},0)$. The separation of the pulses is 900 μsec.

The single crystals of $NaClO_3$ were loaned by the Bell Telephone Laboratories. We are grateful to E. L. Hahn and B. Herzog for discussions of their results and have also benefited from conversations with C. P. Slichter and D. McCall. Much of our rf equipment was designed by H. W. Knoebel and L. S. Kypta.

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[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[2] C. Dean, thesis, Harvard University (unpublished); Phys. Rev. **86**, 607 (1952).

Anisotropic Relaxation of Quadrupole Spin Echoes

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By the pulsed nuclear induction method[1] we have observed the free Larmor precession of Cl^{35} and Cl^{37} nuclear moments, due only to the pure crystalline electric field gradient in single and powdered crystals of $NaClO_3$. When a small constant magnetic field H_0 is applied to the single crystal, the echo relaxation time due to spin-spin coupling is modified by the variation of the Zeeman splitting as the magnitude and direction of H_0 normal to the cubic axis of a $NaClO_3$ single crystal is varied. We refer the reader to the preceding letter by Bloom and Norberg which discusses their independent observations of the free quadrupole precession and theory of the Zeeman splitting.

The formation of nuclear signals following two rf pulses, as shown in Fig. 1, can be explained by the analogous mechanism of spin echo formation in large magnetic fields.[1] The chlorine quadrupole moment Q, with spin $I=\frac{3}{2}$, is aligned by an electric field gradient q which is assumed to be axially symmetric about the molecular bond (z axis) joining Na to Cl. The single quadrupole resonance transition frequency $\omega=eqQ/2\hbar$ is replaced in general by four separate resonance frequencies[2] as the degeneracy of the $m=\pm\frac{1}{2}$ and $m=\pm\frac{3}{2}$ states is removed by H_0. In the unit cell there are four chlorine nuclei with their z axes of quantization oriented along the body diagonals of the sub-cubic cells. There are two nonequivalent directions of Na-Cl axes with respect to H_0, and a pair of chlorine nuclei is assigned to each of these directions denoted by + and −. Using a quantum-mechanical treatment applied in an earlier paper,[3] we obtain the solution for free precession in agreement with that given by Bloom and Norberg. The spin echo signal, described by a similar solution, appears symmetric about the time $t=2\tau$, where τ is the separation between pulses. The observed signal is given by $V=V_++V_-$, where

$$V_\pm\propto\sin^3(\sqrt{3}\omega_1t_w\sin\theta_\pm)\cos(\sqrt{3}\omega_1t_w\sin\theta_\pm)\times\left\{\left(\frac{\beta_\pm-1}{\beta_\pm}\right)\cos[(\omega_0\cos\theta_\pm)(3+\beta_\pm)(t-2\tau)/2]+\left(\frac{\beta_\pm+1}{\beta_\pm}\right)\cos[(\omega_0\cos\theta_\pm)(3-\beta_\pm)(t-2\tau)/2]\right\}\times\exp\left\{-[(t-2\tau)^2/T_2{}^2+t^2/(T_2')^2(H_0,\theta_\pm)]\right\}.$$

θ is the angle between H_0 and the molecular axis, $\omega_0=\gamma H_0$, $\omega_1=\gamma H_1$, $\beta_\pm=(1+4\tan^2\theta_\pm)^{\frac{1}{2}}$, γ is the gyromagnetic ratio, and H_1 is the rf field. In terms of the angle φ which H_0 makes with respect to the 001 direction, $\cos\theta_\pm=\sqrt{\frac{2}{3}}\cos(\varphi\pm\pi/4)$ and $\sin\theta_\pm=[1-\frac{2}{3}\cos^2(\varphi\pm\pi/4)]^{\frac{1}{2}}$. We infer from our observations that T_2' for each of the + and − groups is nearly the same. The total width of the echo at half-maximum is given by T_2 seconds (0.5 millisecond for Cl^{35}), which is equivalent to a static local magnetic dipole field inhomogeneity of $\Delta H\approx2.6$ gauss for an assumed Gaussian distribution. For each setting of τ, with the spins initially at thermal equilibrium, the maximum of the echo amplitude is observed to be proportional to $\exp[-(2\tau)^2/T_2'^2(H_0,\varphi)]$

which describes the shape of the envelope of the echo maxima. The time constant T_2' is observed to be a function of φ and H_0 (see the polar plot in Fig. 2).[4] It appears that the Zeeman splitting modifies the extent to which time-varying local fields and spin-spin flipping are effective in destroying the phase coherence necessary for echo formation. The thermal relaxation times T_1 ($\sim$35 milliseconds) for both chlorine isotopes are independent of H_0 and play no role in the anisotropy of relaxation. A polar plot similar to that in Fig. 2 is obtained for Cl^{37}. Within experimental error, it appears that the T_2' values may be larger by a factor $1.3 \sim \gamma Cl^{35}/\gamma Cl^{37}$ for large values of H_0. Except for the difference in magnetic moments, this is a rough indication that the relaxation due to the fluctuating local field distribution is approximately the same for both chlorine isotopes in spite of the difference in their abundance. As the overlap (due mainly to T_2) among the four quantum levels diminishes with increasing Zeeman splitting (a similar situation occurs for the sodium nuclei), there is less chance that a spin-spin flip with an accompanying change in dipole field will take place between like nuclear neighbors. T_2' has a particularly sensitive dependence on H_0, (a) when $1/T_2 \sim \gamma H_0$, and (b) when any of the possible resonance transitions cross or coincide as φ is varied. There are eight possible simultaneous resonance frequencies. Four are given by: $\omega(\pm) = eqQ/(2\hbar)+F$ and $\omega'(\pm) = eqQ/(2\hbar)-F$, where $F=(\gamma H_0/\sqrt{2}) \times \{\sqrt{3}\cos(\varphi-\pi/4) \pm [2-\cos^2(\varphi-\pi/4)]^{\frac{1}{2}}\}$. Another set of four frequencies is obtained by substituting $+\pi/4$ for $-\pi/4$ in F. When $\varphi=0°$, the eight resonances coalesce to three and the probability for coupling is a maximum, giving the shortest T_2' for a given H_0. In the region $0° < \varphi < 45°$, T_2' becomes the largest because eight separate resonance transitions exist. At $\varphi = 45°$ there are six resonances and a decrease in T_2' takes place. The plot repeats these conditions periodically with increasing φ. The round lobes arise from the effect of static line width or broadening of each of the Zeeman levels. At large H_0, where $\gamma H_0 > 1/T_2$, the magnitude of T_2' approaches a constant value.

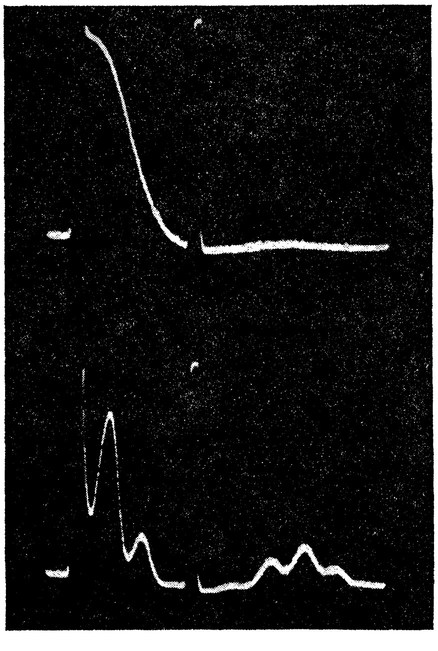

FIG. 1. Oscillographic display of free quadrupole precession of Cl^{35} in a single $NaClO_3$ crystal upon application of two rf pulses at the condition $\sqrt{3}\omega_1 t_w = \pi/2$. The total length of each sweep is 2.4 milliseconds. The upper photograph indicates the free precession after the first pulse and an almost completely attenuated echo in the absence of a magnetic field. The lower photograph indicates an echo and tail with accompanying Zeeman beat pattern for an applied $H_0 = 5.3$ gauss at $\phi = 0°$ with all other conditions the same as in the upper photo.

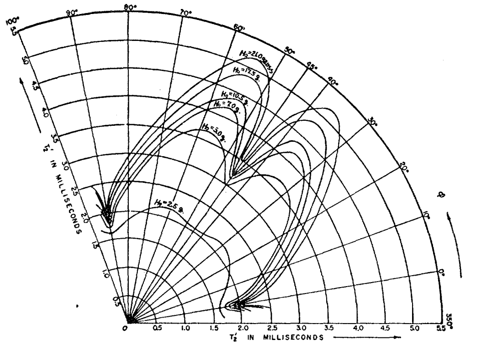

FIG. 2. T_2' for Cl^{35} in $NaClO_3$ as a function of H_0 and φ. In and near the critical regions ($\phi = 0°$, 45°, and 90°), repeated measurements indicate the plotted quantitative behavior of T_2' within ±5 percent. Other regions of the plot are less accurate, to approximately ±10 percent.

We have been able to predict the general shape of the plots in Fig. 2 by considering all the possibilities for resonance coupling between a chlorine nucleus and all nearest neighbors. The net T_2' is then determined by all possible spin flips and accompanying dipole field fluctuations.[5] In a typical resonance formula, account is taken of the level broadening. The strengths of the local fields and transition probabilities are included by evaluating the squares of the matrix elements involving the Zeeman level wave functions.

One of us (ELH) wishes to acknowledge the benefit of early discussions with Dr. W. G. Proctor regarding physical features of quadrupole precession. We thank Dr. M. Bloom and Dr. R. E. Norberg for informative communications about their work. We thank Dr. T. Wang for his assistance and interest in the measurements, and Professor C. H. Townes for clarifying discussions. The $NaClO_3$ crystal in our experiment was kindly provided by Dr. A. L. Schawlow of the Bell Laboratories.

[1] E. L. Hahn, Phys. Rev. **80**, 580 (1950).

[2] B. T. Feld and W. E. Lamb, Phys. Rev. **67**, 28 (1945); C. Dean, thesis, Harvard University (unpublished).

[3] E. L. Hahn and D. E. Maxwell, Phys. Rev. **88**, 1070 (1952).

[4] The echo envelope lifetime T_2' referred to here accounts only for the incoherence of Larmor precession due to local dipole fields which fluctuate in time. It does not include static line broadening, whereas in steady state resonance measurements, "T_2" includes both of these effects. The time duration of any echo (or induction tail) would also be expected to depend upon both of these effects. However, we observe no significant change in this lifetime as T_2' changes with H_0. It appears, therefore, that as the rate of spin-spin flipping increases, for example, as $H_0 \rightarrow 0$, the otherwise static dipole fields of these coupled neighbors are averaged to a lower value, and the net observed lifetime of the individual signals tends to remain the the same. A rigorous analysis of this effect is being considered.

[5] The estimate of eqQ for Na would correspond to a frequency of $\lesssim 1$ Mc/sec [C. H. Townes and B. P. Dailey, J. Chem. Phys. **20**, 35 (1952)]. If the condition $\gamma\hbar H_0 \sim eqQ$ for the Na nuclear moment in our experiment is obeyed, the Na spin axis of quantization will no longer be along the molecular axis, and the Na dipole field at the Cl nucleus will be modified. We have not taken this possibility into account in our semi-empirical prediction of the anisotropy. Further investigation of this question is under way.

The Primeval Cosmic Abundance of Deuterium

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NO definite answer has yet been given to the problem of the primeval cosmic abundance of deuterium. In stars deuterium has never been detected; in the sun an upper limit for the amount of deuterium was given in 1932 by Menzel[1] as 1.6×10^{-6} times the amount of hydrogen and more recently by Class[2] as 2.5×10^{-8} times the amount of hydrogen.

Moreover, it has been shown[3] that in a sufficiently hot star the deuterium is consumed very rapidly by nuclear reactions. The reaction starts in the center of the star, but convection currents