Ultrasonic Excitation of Nuclear Magnetic Energy Levels of Na^{23} in NaCl*†

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The nuclear magnetic levels of Na^{23} in a single crystal of NaCl placed in a strong magnetic field have been saturated by the pure quadrupole transition $\Delta m = 2$, caused by ultrasonic excitation. The observed transition rate has been compared with theoretical expressions to find that the electric field gradient generated at the nuclear site by the lattice distortion is very close to that expected from a simple classical model. Hence the large covalent and antishielding factor required to explain the spin-lattice relaxation time on the basis of the theory of Van Kranendonk is not found. Possible reasons for this discrepancy are discussed.

I. INTRODUCTION

THE most important mechanism for the nuclear spin-lattice relaxation in many solids is known to involve the presence of impurities.[1] However, in many crystals containing nuclei with quadrupole moments, the characteristic time (T_1) of this relaxation is found to be fairly short and independent of the purity of the sample. Pound[2] has proposed that this can be explained as a result of a quadrupole interaction $(Q \cdot \nabla E)$ and offers strong evidence for this in the case of Na^{23} in NaNO$_3$, for I^{127} in KI, and for all the nuclei in NaBr. Pound proposed that field gradients in crystals are modulated or generated by distortions of the lattice, these distortions being caused by thermal lattice waves. The time-varying quantity ∇E can therefore cause transitions between the various magnetic energy levels. The selection rules are $\Delta m = \pm 1$ and $\Delta m = \pm 2$.

A detailed theory of this relaxation mechanism has been formulated by Van Kranendonk[3] for the case of NaCl-type crystals. In this case the Na nucleus finds itself in a cubic environment, and thus ∇E must have a time average value of zero. In order to calculate the field gradient, Van Kranendonk assumed a model wherein the Na nucleus interacted with point charges placed at the positions of the six nearest neighbors. These point charges take the place of the neighboring ions and undergo the same motion. From this, one can calculate the interaction and hence the relaxation time. However, the electrons surrounding the Na nucleus of interest may also interact with the field of these charges,[4] and therefore the effective charge may be multiplied by some number. Van Kranendonk defines γ as this number, and it is a measure of the extent of

the shielding and antishielding of the nucleus due to these electrons. In the case of I^{127} in KI, Pound found T_1 to be 0.02 second, and the γ required to explain this is 10^3.

The energy stored in lattice waves of a frequency corresponding to Δm of ± 1 and ± 2 in reasonable magnetic fields and at room temperature is so small that the absorption and emission of these lattice waves (direct effect) can be neglected as an important mechanism in the relaxation. The important process must be one of a Raman nature wherein high-energy phonons are inelastically scattered according to $h\nu' \rightarrow h\nu'' \pm h\nu$ (or $\pm 2h\nu$), where $h\nu$ corresponds to the separation of adjacent nuclear magnetic energy levels. It is these last processes (indirect effect) upon which Van Kranendonk's theory is based and his values of γ calculated. He has pointed out that the γ of the direct effect need not be the same as that corresponding to the indirect effect,[5] and the difference will be discussed in Sec. V. The present experiment was undertaken in order to investigate the direct effect so as to study this model and to make a somewhat independent measurement of γ. We were able to observe the effect of transitions between magnetic energy levels when ultrasonics energy at a frequency corresponding to $\Delta m = \pm 2$ was introduced. The effect of the sound was determined by measuring the magnetization of the nuclear system using the pulse technique.[6] In this method the transient rf pulse following a short pulse of rf magnetic field at the Larmor frequency is proportional in magnitude to the static magnetization of the system which in turn is a function of the populations of the various states.

The possibility of affecting the nuclear magnetization in solids through the use of ultrasonics has already been mentioned by Kastler.[7] Altschuler[8,9] has also suggested that ultrasonic energy might interact with the nuclear spin system to a measurable extent. The first successful experiment in this field was carried out by Proctor and

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[1] N. Bloembergen, Physica 15, 386 (1949).

[2] R. V. Pound, Phys. Rev. 79, 685 (1950).

[3] J. van Kranendonk, Physica 20, 781 (1954).

[4] R. M. Sternheimer and H. M. Foley, Phys. Rev. 102, 731 (1956).

[5] J. van Kranendonk (private communication).

[6] E. L. Hahn, Phys. Rev. 77, 297 (1949).

[7] A. Kastler, Experientia 8, 1 (1952).

[8] S. A. Altschuler, Doklady Akad., Nauk U.S.S.R. 85, 1235 (1952).

[9] S. A. Altschuler, J. Exptl. Theoret. Phys. S.S.S.R. 1, 37 (1955).

Tanttila[10–12] who observed that the population difference of the two pure quadrupole levels of Cl³⁵ in NaClO₃ decreased when the sample was subjected to ultrasonic energy at the transition frequency. The essential difference between their experiment and this one is that here the nuclei are in a magnetic field and $\Delta m = \pm 2$ transitions are induced. In the NaClO₃ case there is no magnetic field and both $\Delta m = \pm 1$ and $\Delta m = \pm 2$ transitions are induced. With the sound at twice the Larmor frequency ($\Delta m = \pm 2$), magnetic fields generated by currents in the ultrasonic system could not affect the populations. In the experiment of Proctor and Tanttila this was a possible source of difficulty.

Because of the measurements of Pound, it might seem that KI would be the most interesting sample with which to perform this experiment. However, Watkins and Pound[13] have measured the absolute intensity of the nuclear magnetic resonance signal for I¹²⁷ in KI and found it to be only 0.3 of the expected value. They interpret this value of intensity as being due to static quadrupole interactions of the I¹²⁷ nuclei with field gradients produced by crystal dislocations. Since the spin of I¹²⁷ is 5/2, there will be five transitions in the nuclear magnetic resonance line. Of these, only the $\frac{1}{2}$ to $\frac{1}{2}$ transition will not be perturbed. The other four transitions are spread so much that only 10% of the signal is due to other than the $\frac{1}{2}$ to $\frac{1}{2}$ transition. Thus the largest effect we could expect in KI would be a 10% decrease in magnetization. For this reason we used NaCl, although the quadrupole moment of Na²³ is $\frac{1}{5}$ that of I¹²⁷.

II. LEVEL POPULATION AND ULTRASONIC EFFECT

The spin of Na²³ is $\frac{3}{2}$ and in a magnetic field the magnetic quantum number m may take values $\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, and $-\frac{3}{2}$. These give four nondegenerate energy levels (see Fig. 1), and the separation of adjacent levels is given as

$$\hbar\omega = \mu H_0/I, \tag{1}$$

where ω is the angular frequency of the emitted radiation, μ is the nuclear magnetic moment, I is the nuclear spin, and H_0 the external magnetic field strength. There are three transitions between these levels and they lie in a narrow range of frequency. That they do not necessarily satisfy Eq. (1) is a result of crystal imperfections, and this will be discussed in the last section. The range of frequency involved is narrow enough that the amplitude of a nuclear magnetic resonance signal will involve the contributions of each of the three transitions and will therefore, be proportional to the original nuclear magnetization. If $n_{\frac{3}{2}}$ is the population of the $m = \frac{3}{2}$ level, etc., then the signal is

10 W. Proctor and W. Tanttila, Phys. Rev. 98, 1854 (1955).
11 W. Proctor and W. Tanttila, Phys. Rev. 101, 1757 (1956).
12 W. Tanttila, thesis, University of Washington, 1955 (unpublished).
13 G. D. Watkins and R. V. Pound, Phys. Rev. 89, 658 (1953).
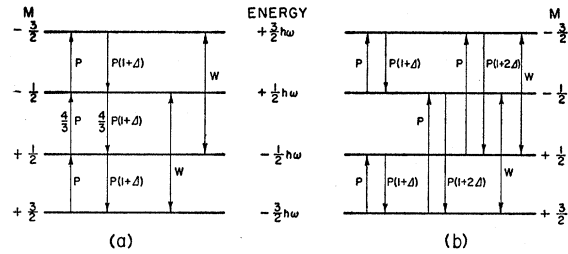
FIG. 1. Nuclear magnetic energy levels for $I = \frac{3}{2}$ showing thermal transitions (P) and ultrasonic transitions (W). (a) The case for relaxation due to magnetic dipole transitions; (b) the case for relaxation due to electric quadrupole transitions.

proportional to

$$\tfrac{3}{2}(n_{\frac{3}{2}} - n_{-\frac{3}{2}}) + \tfrac{1}{2}(n_{\frac{1}{2}} - n_{-\frac{1}{2}}).$$

A detailed study of these differences must thus be made.

The results of this study will depend upon the mechanism by which thermal equilibrium is established. We do not know in advance the exact mechanism involved, so we must treat two possible cases. The cases of interest are magnetic dipolar (impurity) interactions and quadrupolar interactions. In the first case thermally caused transitions can occur only between adjacent levels [see Fig. 1(a)]. Furthermore, downward transitions are more probable than upward transitions by a factor $e^{\hbar\omega/kT}$. Since ω lies in the radio-frequency region, this factor may be approximated by $1 + \Delta$, where $\Delta = \hbar\omega/kT$. Recalling that the matrix elements of the $m = \pm\frac{1}{2}$ to $m = \mp\frac{1}{2}$ transitions are $2/\sqrt{3}$ times larger than those of the other dipole transitions, we can write down the rates by which the population of the levels will change.

$$\dot{n}_{\frac{3}{2}} = -n_{\frac{3}{2}}[P+W] + n_{\frac{1}{2}}P[1+\Delta] + n_{-\frac{1}{2}}W,$$

$$\dot{n}_{\frac{1}{2}} = n_{\frac{3}{2}}P - n_{\frac{1}{2}}(P[(7/3)+\Delta]+W) + n_{-\frac{1}{2}}P$$
$$\times[(4/3)+(4/3)\Delta] + n_{-\frac{3}{2}}W,$$

$$\dot{n}_{-\frac{1}{2}} = n_{\frac{3}{2}}W + (4/3)n_{\frac{1}{2}}P - n_{-\frac{1}{2}}(P[(7/3)$$
$$+ (4/3)\Delta]+W) + n_{-\frac{3}{2}}P[1+\Delta], \tag{2}$$

$$\dot{n}_{-\frac{3}{2}} = n_{\frac{1}{2}}W + n_{-\frac{1}{2}}P - n_{-\frac{3}{2}}(P[1+\Delta]+W).$$

Here P is the upward thermal transition probability per second and W is the $\Delta m = \pm 2$ transition probability per second caused by ultrasonic vibrations. It is not necessary for our purpose to solve these equations completely. However, we must know the relation of the measurable quantity T_1 to the thermal transition probability P. If the populations of the four levels are initially equal, one expects that each will return to its equilibrium value with an exponential decay and a characteristic time T_1. By inspection, the trial solutions are ($W = 0$):

$$n_{\frac{3}{2}} = n_0(1+3\Delta) - \tfrac{3}{2}n_0\Delta e^{-\tau/T_1},$$

$$n_{\frac{1}{2}} = n_0(1+2\Delta) - \tfrac{1}{2}n_0\Delta e^{-\tau/T_1},$$

$$n_{-\frac{1}{2}} = n_0(1+\Delta) + \tfrac{1}{2}n_0\Delta e^{-\tau/T_1}, \tag{3}$$

$$n_{-\frac{3}{2}} = n_0 + \tfrac{3}{2}n_0\Delta e^{-\tau/T_1},$$

where n_0 is the equilibrium population of the $m=-\frac{3}{2}$ level. Upon substitution of (3) into (2) one finds that not only is (2) satisfied but

$$P=3/2T_1.$$

In performing the experiment to determine γ, the nuclear spin system is allowed to approach a steady state so that we may set $\dot{n}_{\frac{3}{2}}=\dot{n}_{\frac{1}{2}}=\cdots=0$ in Eq. (2) and obtain

$$(n_{\frac{1}{2}}-n_{-\frac{1}{2}})/n_0=(2P-W)\Delta/(2P+5W),$$
$$(n_{\frac{3}{2}}-n_{-\frac{3}{2}})/n_0=(6P+W)\Delta/(2P+5W).$$

Since the nuclear magnetization (M) is proportional to

$$3(n_{\frac{3}{2}}-n_{-\frac{3}{2}})+(n_{\frac{1}{2}}-n_{-\frac{1}{2}}),$$

and in the limit of $W=0$ becomes $10n_0\Delta$, we may write

$$\frac{M}{M_0}=\frac{1+W/10P}{1+5W/2P},$$

where $M=M_0$ for $W=0$. In terms of the pulse amplitude A and T_1 we have

$$\frac{A}{A_0}=\frac{1+WT_1/15}{1+5WT_1/3}. \tag{4}$$

Here A_0 is the amplitude with no ultrasonic waves present.

The second possibility is that the relaxation is entirely quadrupolar. In this case both $\Delta m=\pm1$ and

±2 thermal transitions are allowed with the exception of $\frac{1}{2}\leftrightarrow\frac{1}{2}$. Furthermore, we assume that the probability of $\Delta m=+1$ is equal to that of $\Delta m=+2$ since the averaged matrix elements are equal, and that the increase in downward probability over the upward value for a particular transition is proportional to the energy of the transition [see Fig. 1(b)]. Then the expressions for the rate of change of the populations become:

$$\dot{n}_{\frac{3}{2}}=-n_{\frac{3}{2}}(2P+W)+n_{\frac{1}{2}}P[1+\Delta]$$
$$+n_{-\frac{1}{2}}(P[1+2\Delta]+W),$$
$$\dot{n}_{\frac{1}{2}}=n_{\frac{3}{2}}P-n_{\frac{1}{2}}(P[2+\Delta]+W)+n_{-\frac{1}{2}}(P[1+2\Delta]+W),$$
$$\dot{n}_{-\frac{1}{2}}=n_{\frac{3}{2}}(P+W)-n_{-\frac{1}{2}}(P[2+2\Delta]+W)$$
$$+n_{-\frac{3}{2}}P[1+\Delta],$$
$$\dot{n}_{-\frac{3}{2}}=n_{\frac{1}{2}}(P+W)+n_{-\frac{1}{2}}P-n_{-\frac{3}{2}}(P[2+3\Delta]+W). \tag{5}$$

In a manner similar to that used in the dipolar case, one finds

$$T_1=\frac{1}{2P}, \quad \frac{M}{M_0}=\frac{P+W/5}{P+W}, \quad \frac{A}{A_0}=\frac{1+\frac{2}{5}WT_1}{1+2WT_1}. \tag{6}$$

This last expression will hold only if there are no appreciable transitions between the $m=+\frac{1}{2}$ and the $m=-\frac{1}{2}$ levels through dipolar processes in the time allowed, in the experiment, for steady state to be established.

To relate the ultrasonic transition probability W to the intensity of sound, we calculate the field gradients accompanying sound waves in NaCl and find the interaction between these gradients and the Na²³ nuclear quadrupole moment. In part, we base the calculation of the field gradients on the model of Van Kranendonk. In this model, the cubic symmetry of the field of the six point charges is destroyed by the motion of the lattice points in a sound wave (see Fig. 2). We first consider the case of a compressional wave propagating in the x direction. Then the position of lattice point 1 may be written $S_1=\xi \sin\omega\tau$, of lattice point 2 as $S_2=\xi \sin(\omega\tau-ka)+a$ where k is the propagation constant of the sound, and of 3 as

$$S_3=\xi \sin(\omega\tau-2ka)+2a.$$

Thus we find the result

$$\frac{1}{2}(S_3-S_1)\approx-\xi ka \cos\omega\tau+a \quad \text{if} \quad ka\ll1.$$

The symmetry is no longer cubic, and we can calculate the field at the Na nucleus (position 2). If b is the nuclear separation in the x direction and a the separation in the y and z directions, then the potential at a point $r=(x,y,z)$ due to the six charges is

$$V=e(a^{-3}-b^{-3})(y^2+z^2-2x^2)+4e(a^{-1}+\tfrac{1}{2}b^{-1}),$$

to second-order terms in x, y, and z if $r\ll a$ and $r\ll b$. Using the result $a-b=\xi ka \cos\omega\tau$, we get the result that the magnitudes of the components of the field
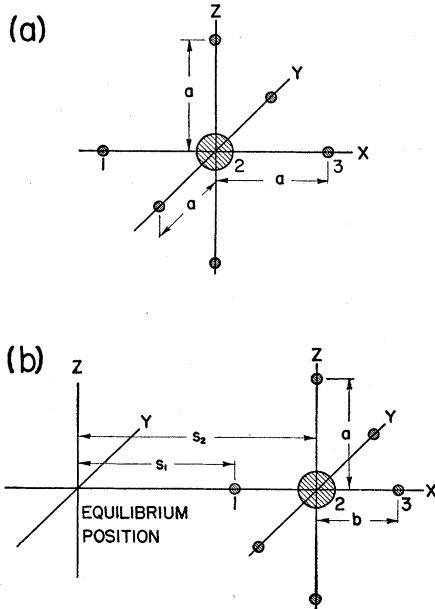
FIG. 2. The six-point charge model showing the positions of the nucleus of interest (position 2) and the six nearest neighbors. (a) With cubic symmetry. (b) Showing the distortion caused by the displacement of the lattic points by sound.

gradient at the nucleus are

$$V_{xx}=12ek\xi/a^3; \quad V_{yy}=V_{zz}=-6ek\xi/a^3; \quad V_{xy}, \text{ etc.}=0. \quad (7)$$

This result also holds for the case of compressional waves with the x axis along the (110) direction.

It is not necessary to carry out this calculation in the case of arbitrary angles between sound direction, crystal orientation and magnetic field because of the simplicity of the model. To simplify the calculations and yet adhere reasonably closely to the physical situation, we shall assume that a sound wave will create an axially symmetric electric field with the symmetry axis in the direction of the sound propagation. Also, we shall require this gradient to agree with the results of the six-point charge model in form. So the field gradient (q) in the sound direction is taken as

$$q=12\gamma ek\xi/a^3.$$

γ includes all the factors not included in the the model, such as Poisson's ratio and the effects of next nearest neighbors. The most important of these factors is expected to be the shielding effects resulting from the electrons bound to the Na⁺ ion.

This value of q can be used to calculate the transition probability, and the first step is to find the matrix elements connecting states for $\Delta m=\pm2$. These are given by Pound,[2] namely

$$H'_{m,m\pm2}=\frac{3}{8}\frac{eqQ}{2I(2I-1)}[(I\mp m)(I\mp m-1)$$

$$\times(I\pm m+1)(I\pm m+2)]^{\frac{1}{2}}\sin^2\theta e^{\pm2i\varphi}. \quad (8)$$

θ and φ are the polar angles of the symmetry axis with respect to the magnetic field. In terms of the sound amplitude, for $I=\frac{3}{2}$, the magnitude of $H'_{m,m\pm2}$ is given by

$$H'_{m,m\pm2}=\frac{3\sqrt{3}}{2}\frac{e^2Q\gamma k\xi}{a^3}\sin^2\theta e^{\pm2i\varphi}. \quad (9)$$

From first-order perturbation theory, one finds for a harmonic perturbation that the transition probability per second is $W=|H'|^2/4\hbar^2\delta$, where δ is the line width in frequency of the effect. One consequently finds

$$W(\theta)=\frac{27e^4Q^2\gamma^2k^2\xi^2}{16\hbar^2a^6\delta}\sin^4\theta. \quad (10)$$

However, in our experiment sound waves generated by a quartz transducer cemented to the sample underwent reflection at the irregular surfaces of the sample, and were scattered into an isotropic distribution. In such a sound system, one has some sort of stationary wave pattern which is very complex. But one can say that over small volumes whose diameters are a few wavelengths the direction of particle motion and the phase of the motion are constant. The sample as a whole,
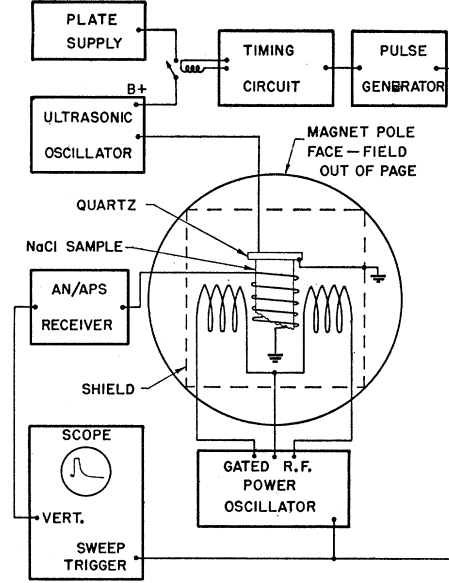

FIG. 3. Block diagram of apparatus.

however, has an isotropic distribution of these volumes with respect to their sound directions. This fact allows us to write the mean ultrasonic transition probability per second for the whole sample as $W=(\frac{1}{4}\pi)\oint W(\theta)d\Omega$. Also, the mean peak value of ξ^2 can be written in terms of the energy density ($\mathcal{E}$) in the crystal as $\xi^2=2\mathcal{E}/\rho\omega^2$. The angular frequency of the sound is denoted by ω and the crystal density by ρ. The value of W may then be written

$$W=\frac{9e^4Q^2\gamma^2\mathcal{E}}{5\rho\hbar^2c^2a^6\delta}.$$

Here c is the velocity of sound in NaCl. By the experimental procedures described in the next two sections, we were able to measure W and $\mathcal{E}$ so as to determine γ.

III. APPARATUS AND TECHNIQUES

The apparatus and techniques used in this experiment were similar to those used by Proctor and Tanttila in most respects. The apparatus consists of two groups (see Fig. 3): that used to measure the nuclear magnetization and the ultrasonic generating equipment. The nuclear magnetization was measured in a steady magnetic field of 4220 oersteds at a frequency of 4.75 Mc/sec by the pulse technique described by Hahn.[6] A nuclear induction head of the type described by Weaver[14] with perpendicular transmitter and receiver coils was used. This is shown in Fig. 4. A short pulse (50 μsec) of radio-frequency magnetic field was generated in the transmitter coil at the Larmor frequency (4.75 Mc/sec). This induced a transient rf nuclear signal in the receiver coil. The magnitude of this was

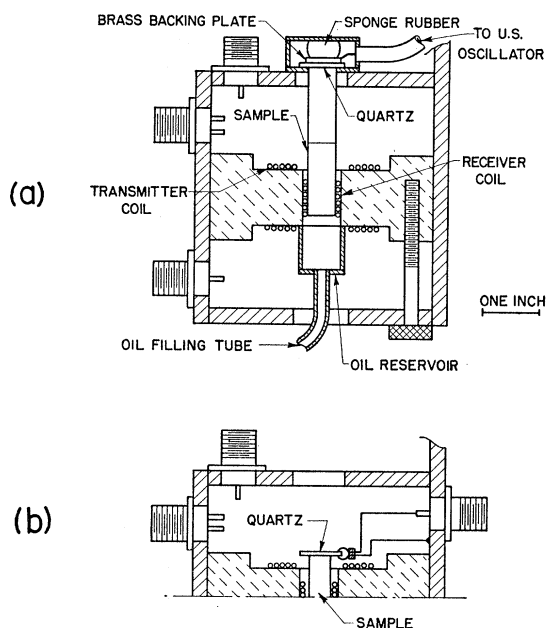[14] H. E. Weaver, Phys. Rev. 89, 923 (1953).

FIG. 4. The nuclear induction head with the sound system and sample. The oil level in the reservoir could be raised to come in contact with the sample allowing sound energy to escape. (a) Halite sample. The ultrasonic system was shielded from the nuclear magnetic resonance system. (b) Optical quality sample.

proportional to the nuclear magnetization just before the pulse.[6] The transmitter is described elsewhere,[15] and the receiver was an AN/APS-15 radar i.f. strip altered to work in the 5-Mc/sec region.

The rf magnetic field pulse length was adjusted so that the $\frac{3}{2}$, $-\frac{3}{2}$, $\frac{1}{2}$, $-\frac{1}{2}$, population differences were zero
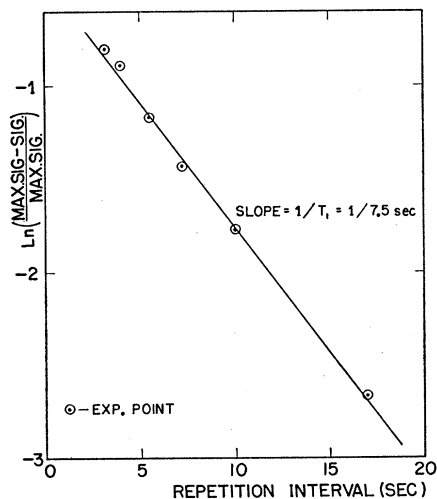

FIG. 5. The points correspond to the amplitude of the nuclear magnetic resonance pulse for various repetition intervals between these pulses and with no ultrasonic excitation. The solid line, fitted to these points, is a theoretical line for the case of the spin-lattice relaxation time $T_1 = 7.5$ seconds.

[15] Bloom, Hahn, and Herzog, Phys. Rev. **97**, 1699 (1955).

immediately following the pulse. Then if the next pulse occurs at a time $\Delta\tau$ later and the ultrasonics is not applied, the population differences will be given by Eq. (3) as

$$n_{\frac{3}{2}}-n_{-\frac{3}{2}}=3n_0\Delta(1-e^{-\Delta\tau/T_1}), \quad n_{\frac{1}{2}}-n_{-\frac{1}{2}}=n_0\Delta(1-e^{-\Delta\tau/T_1}),$$

and thus the pulse size as

$$A=A_{\max}(1-e^{-\Delta\tau/T_1}). \tag{11}$$

If the time between pulses is varied, T_1 can be obtained from the size of the nuclear signal. In Fig. 5, a plot of experimental points of $\log_e(1-A/A_{\max})$ is made against $\Delta\tau$. From Eq. (11), this should be a straight line of slope $-1/T_1$.

Two NaCl samples were used in this experiment with different arrangements for each. The first sample was a rod of halite obtained from the University of Washington Geology Department, 1.5 cm in diameter and 3 cm long. This was cemented to an identical crystal which in turn was cemented to an X-cut quartz transducer [Fig. 4(a)]. This transducer was outside the head and in a pillbox like shield, and thus the sample was
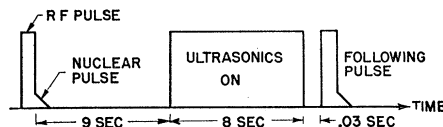

FIG. 6. The time sequence of events in the saturation of levels by ultrasonic transitions. Nine seconds after the preceding nuclear magnetization measurement, ultrasonic excitation is applied at twice the Larmor frequency for 8 seconds. After a delay of 0.03 second, the magnetization is again measured.

well shielded from the ultrasonic circuits. This shielding permitted the possibility of an experiment with $\Delta m = \pm 1$ which was not performed. The second sample, a piece of optical quality NaCl crystal measuring 1 cm by 1.5 cm by 1.5 cm and purchased from Harshaw Chemical Company, was cemented directly to the quartz, as shown [Fig. 4(b)]. In both cases the cement used was a mixture of talc and waterglass, and the joints were baked at about 90°C for a few hours.

The oscillator was turned on for a period of 8 seconds; then after a delay of 0.03 second the population difference was measured. This cycle was repeated every 17 seconds. This sequence is shown in Fig. 6. The pulse heights observed were recorded as a function of the voltage and the frequency of the rf across the quartz. From these data we were able to determine the line width (δ) and the ultrasonic transition probability W.

The value of $\mathscr{E}$ was determined from the voltage across the quartz. If P_s is the power delivered to the sample for a given voltage across the quartz then in the steady state

$$V'\mathscr{E}=P_sT_\rho, \tag{12}$$

where T_ρ is the sound attenuation coefficient (phonon relaxation time) for NaCl and V' the volume of the

sample. In the next section, an experiment is described by which T_p was measured. The value of P_s was determined by measuring, in addition to the applied voltage V, the equivalent resistance R^{eff} for a loaded quartz plate.[16] If one connects the loaded or unloaded crystal across the capacitor terminals of a Boonton Q meter with a coil of inductance L and Q of Q_0, then the registered Q will be a minimum at the series resonance frequency. Here the value of Q will be

$$Q=Q_0Q'/(Q_0+Q'), \quad \text{where} \quad Q'=R^{eff}/\omega L.$$

Thus it is a simple matter to obtain R^{eff} in both the loaded case $(Q_l, R_u^{eff}+R_l^{eff})$ and the unloaded case (Q_u, R_u^{eff}). The power to the quartz will then be

$$P_q=V^2/(R_u^{eff}+R_l^{eff}).$$

But this will be divided between the load (R_l) and the internal resistance of the quartz and its circuits (R_u). So the power to the sample is given as

$$P_s=R_l^{eff}P_q/(R_u^{eff}+R_l^{eff});$$

TABLE I. Values of the acoustic parameters of the samples (resistances in ohms).

	R_u^{eff}	$R_u^{eff}+R_e^{eff}$	R_e^{eff}	k (watts/volt²)	Volume of sample (cc)
Halite sample	1330	1520	190	8.2×10^{-5}	9.1
Optical sample	1250	1390	140	7.2×10^{-5}	1.75

in other terms,

$$P_s=kV^2, \quad (13)$$

where

$$k=R_l^{eff}/(R_u^{eff}+R_l^{eff})^2.$$

The values obtained from the two cases are listed in Table I.

IV. EXPERIMENTAL RESULTS

The value of T_1 for the two samples were both found to be 7.5 ± 0.5 seconds. These values of T_1, determined by the method outlined in the last section, and all data in this experiment were taken at room temperature. A plot of a typical experimental run is shown in Fig. 5. The uncertainty in T_1 involves primarily the measurement of the nuclear pulse height, and such errors amounted to 5% of the total height. Very little differences in T_1 could be found for any of a varied group of samples tested.

In addition to the spin-lattice relaxation time T_1, we measured the value of the phase memory time T_2. The transient nuclear pulse has an exponential decay with a time constant (T_2) of about 140 ± 15 μsec. Since the full width at half-maximum of the nuclear magnetic line width $(\Delta\nu)$ is approximately $1/\pi T_2$, we have $\Delta\nu=2.3\pm0.2$ kc/sec. The nuclear magnetic line width

[16] W. P. Mason, *Electromechanical Transducers and Wave Filters* (D. Van Nostrand Company, Inc., New York, 1948), second edition.
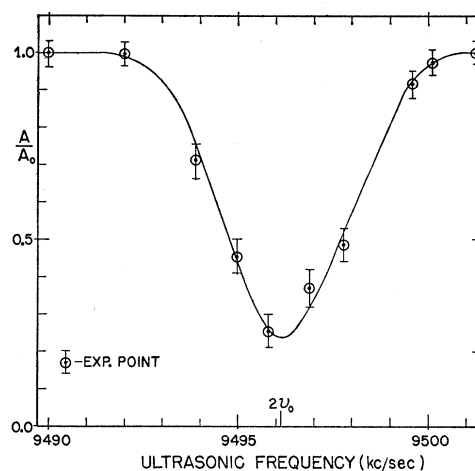

FIG. 7. The points are the values for various ultrasonic frequencies of the ratio of the nuclear magnetic resonance pulse amplitude with a fixed level of ultrasonic power and a 17-sec repetition rate to the amplitude with no ultrasonic excitation. This shows a line width of 4 kc/sec for the effect, ν_0 is the nuclear magnetic resonance frequency.

itself has been measured for these samples and the value obtained is also 2.3 kc/sec.[17] This value is to be compared to the width of the ultrasonic effect. The ratio A/A_0 was measured at a constant ultrasonic power as a function of frequency. Typical data are shown in Fig. 7. It is seen that the full width at half-maximum of the effect was 4.0 kc/sec for this case. This value of line width was found for all levels of ultrasonic power in both the halite and the optical crystal cases.

To determine γ, we observed the ratio A/A_0 at ultrasonic frequencies exactly twice the nuclear magnetic resonance frequency. This was done for various ultrasonic power levels, and the data obtained are shown in Fig. 8. By the results of II, W is proportional to V^2,
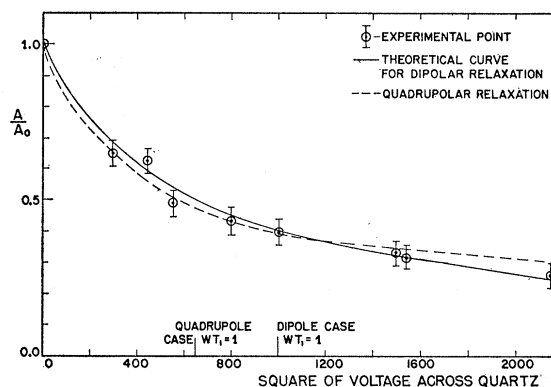
FIG. 8. The ratio of the nuclear magnetic resonance pulse amplitude with ultrasonic power to the amplitude with no ultrasonic power is shown by the points for several values of the mean square rf voltage across the quartz plate. The solid line is the fitted theoretical curve for the case that the relaxation mechanism is magnetic dipolar. The dashed line is the fitted theoretical curve for electric quadrupole relaxation.

[17] R. Schumacher (private communication).

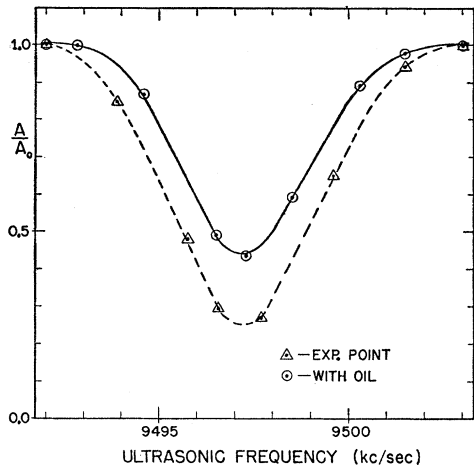FIG. 9. The dashed curve fits experimental points showing the relation of pulse height to ultrasonic frequency (similar to Fig. 7). The solid curve is identical to the dashed curve except that the lower end of the halite sample is in contact with castor oil and sound energy was thus allowed to escape the sample.

and thus we may write A/A_0 from Eq. (6) as

$$\frac{A}{A_0} = \frac{1+\frac{2}{5}\alpha V^2}{1+2\alpha V^2}, \quad (14)$$

for the pure quadrupole relaxation case. This expression, normalized by setting $\alpha V^2 = 1$ for the experimental value of $A/A_0 = 7/15$, is shown as the dashed line in Fig. 8. The solid curve represents the similar expression obtained in the magnetic dipole relaxation case. This expression is

$$\frac{A}{A_0} = \frac{1+\beta V^2/15}{1+5\beta V^2/3}, \quad (15)$$

where we have normalized the curve by setting $\beta V^2 = 1$ for $A/A_0 = \frac{2}{5}$. The basis for this plan in normalizing is that the values $7/15$ and $\frac{2}{5}$ are near the center of the A/A_0 values, and both curves fit the data reasonably well without attempting any sort of best fit. The agreement of the data with both curves is good enough that it is not possible to distinguish between the two relaxation mechanisms, and so one value of γ is found corresponding to the possibility of dipolar relaxation and another to quadrupolar. In the case of the optical crystal, it was felt that a curve of A/A_0 vs power would not give any new information. Thus only one point was taken. The purpose of using two samples was mainly to show that the line width was not sample-dependent.

The results of the analysis of the data are listed in Table II. The value of P_s was obtained through the use of Eq. (13) and the values listed in Table I. Use of Eq. (12) then gives us $\mathscr{E}$ except for the factor T_ρ. This has been measured to be 0.36 millisecond in the halite sample by a method to be described below.

From the value of $W/\mathscr{E}$ one can determine γ through

Eq. (10). The remaining constants in Eq. (10) are known from other sources and are listed in Table III. The results of these calculations are: for the halite sample, $\gamma = 2.15 \pm 0.6$, dipole case; $\gamma = 2.67 \pm 0.8$, quadrupole case; for the optical sample $\gamma \approx 0.9$, dipole case; $\gamma \approx 1.1$, quadrupole case. The differences in the two cases (approximately a factor of two) is a generous estimate of the errors involved. The values for the optical smple could most likely have very large errors since only one experimental measurement was taken and the phonon relaxation time was not measured in this sample.

Attempts have been made by Huntington[18] and Galt[19] to determine the value of T_ρ for NaCl at frequencies near 10 Mc/sec. In their experiments the attenuation of a pulsed sound wave, passing a given distance through a sample, was observed. This attenuation so slight that only an order of magnitude value for T_ρ could be found. These values are listed in Table IV along with our results. In our technique, one makes use of the relation between A/A_0 and the energy density of sound in the sample as given by the experimental points in Fig. 8. Since W is proportional to the energy density, we may write $WT_1 = \alpha V^2 = \eta \mathscr{E}$, where η is some constant. Therefore we can write

$$A/A_0 = f(\eta \mathscr{E}) = f(\eta P_s T_\rho), \quad (16)$$

where $f(\eta \mathscr{E})$ is obtained from experimental points. If we hold P_s constant and vary the frequency of ultrasonics, then we find a curve of the type shown in Fig. 7. The minimum value of A/A_0 will be given by Eq. (16). If we were to change T_ρ, then the curve obtained should be changed. In Fig. 9 is shown a plot of A/A_0 against frequency under normal conditions (dashed) and with 2 square cm area of the lower sample immerged in castor oil (solid curve). The level of the oil in the reservoir of Fig. 4 could be raised to contact the sample and the sound energy in the sample would then radiate into the castor oil. It could not return to the sample because of the large sound attenuation in castor

TABLE II. Energy density and related quantities in the sample when $WT_1 = 1$.

Sample	V^2 (volts^2)	P_s (watts)	Energy (ergs)	$\mathscr{E}$ (ergs/cc)	W (sec^{-1})
Halite dipole case	1000	8.2×10^{-2}	295	32.4	1/7.5
Halite quadrupole case	650	5.3×10^{-2}	190	21.0	1/7.5
Optical dipole case	1250	9.0×10^{-2}	323	184	1/7.5
Optical quadrupole case	810	5.9×10^{-2}	212	121	1/7.5

[18] H. B. Huntington, Phys. Rev. 72, 311 (1947).
[19] J. K. Galt, Phys. Rev. 73, 1460 (1948).

oil.[20] Under these conditions we must replace T_ρ in Eq. (16) by some time T' which includes the loss by radiation. The time T' is given by $1/T' = 1/T_\rho + 1/T_r$. Tanttila[11] has shown that

$$T_r = -\frac{\lambda}{c} \frac{\text{(total area)}}{\text{(contact area)}} \frac{1}{1-R},$$

where λ is the mean sound path between successive collisions with the surface area. R is the sound reflection coefficient[21] of NaCl to castor oil, and the value of $1-R$ is determined in Appendix A to be $1-R=0.45$. Thus by using the experimental shape of the A/A_0 curve in Fig. 8 together with the data in Fig. 9, we may solve for T_ρ. This has been done in Appendix B, with the result listed earlier.

The accuracy with which λ and the contact area are known determine mostly the accuracy with which T_ρ is known. These items contribute a maximum error of about 20% to our value of T_ρ. This reflects an error of about 10% in γ. The other important source of error in γ results from our not being able to measure the effective loaded and unloaded impedances of the quartz any better than 10%, and the differences between these impedances to even less precision. An estimate of the error in γ would therefore be about 30%. This includes errors introduced by uncertainties in measuring A/A_0, those introduced by the drift of the magnetic field during the experiment, and the error which results from using a steady state analysis when actually steady state is not attained in the 17-second repetition interval. This last reflects about a 3% error in γ.

V. DISCUSSION

From the data obtained in this experiment, it was not possible to identify the relaxation mechanism. However, the sample independence of the value of T_1 seems to indicate that the quadrupole mechanism is the more important. If this is the case we should be able to compute the values of γ required to explain this magnitude of T_1. Van Kranednonk[5] finds that $\gamma \approx 50$ for this case but points out that this γ, which he calls γ_2, is theoretically not the same as the quantity measured in our experiment, which he calls γ_1. The value of

TABLE III. Properties of NaCl.

Q_{Na}	10^{-25} cm²	a
P	2.165 grams/cc	b
A	2.813×10^{-8} cm	b
C	4.75×10^5 cm/sec	c

a Perl, Rabi, and Senitzky, Phys. Rev. **98**, 611 (1956).
b C. O. Hodgman, editor, *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, 1953), thirty-fifth edition.
c See reference 19.

[20] P. Vigoureux, *Ultrasonics* (John Wiley and Sons, Inc., New York, 1951).
[21] L. E. Kinsler and A. R. Frey, *Fundamentals of Acoustics* (John Wiley and Sons, Inc., New York, 1950).

TABLE IV. Phonon relaxation time.

Huntington's value[a]	0.4×10^{-3} sec
Galt's value[b]	$(0.5$ to $1.0) \times 10^{-3}$ sec
Our value	$(0.36 \pm 0.10) \times 10^{-3}$ sec

a See reference 18.
b See reference 19.

γ_1 is a measure of the actual first derivative of the electric field gradient with respect to the internuclear separation, while γ_2 is a measure of the second derivative. The ratio γ_1/γ_2 may then be about 20. This would indicate that the field gradient changes in quite a different way, with distortion of the lattice, than the six-point model would predict. Considering the approximate nature of the model and of the relaxation theory this discrepancy may not be unreasonable.

The differences in these values for γ may be explained in other ways. The relaxation time (7.5 sec) may for example be due entirely to dipolar interactions. Recently Yosida and Moriya[22] have shown that the observed chemical shift in some alkali halides can be explained on the basis of a small amount of covalent binding in these predominantly ionic crystals. This covalency also gives rise to quadrupolar relaxation effects which are found to be only an order of magnitude too weak in the KI and KBr cases. With this theory, perhaps, Van Kranendonk's model with its very large γ's (10^3 for I^{127} in KI; 10^4 for Br^{79,81} in KBr) is no longer required. It is noted that a similar discrepancy was found by Proctor and Tanttila[11] in the case of Cl in NaClO₃. They found that approximately the same factor ($\sim 10^3$) more ultrasonic energy was required than was predicted from theory.

Although there is a difference between theory and experiment as to the magnitude of the effect there seem to be no important difficulties in explaining the line width. The nuclear magnetic line width observed for Na²³ in NaCl was 2.3 kc/sec. The value expected, due to nuclear dipole interactions, calculated by use of the Van Vleck formula[23] is $\Delta\nu = 850$ cycles/sec. This apparent discrepancy has been noted in other crystals and has been explained in terms of imperfections in the crystal lattice giving rise to random but permanent electric field gradients which interact with the nuclear quadrupole moment.[13,24] In a similar manner we can explain the difference in the ultrasonic line width (4 kc/sec) and the nuclear magnetic resonance line width. The permanent electric field gradients produce quadrupole interactions which perturb, in the first order, the energy levels as m^2. Hence a transition in which m changes, as is always the case for the ultrasonic resonances $\Delta m = \pm 2$, will have a frequency displaced from ν_0, the pure dipole resonance frequency. On the other hand, the nuclear magnetic resonance line

[22] K. Yosida and T. Moriya, J. Phys. Soc. Japan **11**, 33 (1956).
[23] J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).
[24] F. Reif, Phys. Rev. **100**, 1597 (1955).

consists of three transitions; two are of the type in which (m) changes and these will be spread just as the $\Delta m = \pm 2$ transitions. The third, $m = \frac{1}{2}$ to $m = -\frac{1}{2}$, transition will have only dipolar broadening and will weight the nuclear magnetic resonance line toward the center frequency.

The 4 kc width of the ultrasonic effect is then a measure of the number of crystal imperfections. Dislocations are expected to be the most important of these,[13] and Robinson[25] has shown the average field gradient caused by dislocations to be approximately $q \sim 6 e \gamma \zeta^{\frac{1}{2}} / a^2$, where ζ is the number of dislocations per square cm. This calculation is based on a very simple model, one which would be expected to give too large a value to q. The line width is set equal to twice the pure quadrupole interaction energy $eqQ/2$; then

$$\Delta \nu \sim 6 e^2 \gamma Q \zeta^{\frac{1}{2}} / a^2 h,$$

and from our data $\zeta \sim 10^{10}$ dislocations/cm^2. This compares reasonably with the values found from other means.[26]

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APPENDIX A. EFFECTIVE REFLECTION COEFFICIENT

Kinsler and Frey[21] give for the reflection coefficient at a boundary between two media the expression

$$1 - R = \frac{4 \rho_1 c_1 \rho_2 c_2 \cos\theta_1 \cos\theta_2}{(\rho_2 c_2 \cos\theta_1 + \rho_1 c_1 \cos\theta_2)^2},$$

and Snell's law gives $\sin\theta_1 / \sin\theta_2 = c_1/c_2$, where θ is the angle between the sound direction and the normal to

[25] W. A. Robinson, thesis, University of Washington, 1956 (unpublished).
[26] W. Shockley et al., editors, Imperfections in Nearly Perfect Crystals (John Wiley and Sons, Inc., New York, 1952).

the boundary. The subscript 1 refers to quantities in NaCl and 2 refers to castor oil. If we combine the two and make the substitution $x = \cos\theta_1$, we have

$$1 - R = \frac{4 \rho_1 c_1 \rho_2 c_2 x [1 - (c_2/c_1)^2 (1 - x^2)]^{\frac{1}{2}}}{(\rho_2 c_2 x + \rho_1 c_1 [1 - (c_2/c_1)^2 (1 - x^2)]^{\frac{1}{2}})^2}.$$

We must now average this quantity over all possible solid angles. This average gives

$$\langle 1 - R \rangle_{Av} = \frac{1}{2\pi} \oint [1 - R(\theta_1)] d\Omega$$

$$= 4z \int_0^1 \frac{x [1 - n^2 (1 - x^2)]^{\frac{1}{2}}}{(x + z [1 - n^2 (1 - x^2)]^{\frac{1}{2}})^2} dx,$$

where $n = c_2/c_1$ and $z = \rho_1 c_1 / \rho_2 c_2$. We measured ρ_{oil} to be 0.86 grams/cc and c_{oil} is known to be 1.5×10^5 cm/sec[19] at room temperature. This gives $n = 0.32$ and $z = 7.9$ in the case of sound going from NaCl into castor oil.

We note that the quantity within the radical varies little as x goes from 0 to 1, so we may write

$$\langle 1 - R \rangle_{Av} \approx 4z \int_0^1 \frac{x \, dx}{(z + x)^2} \approx 0.45.$$

APPENDIX B. PHONON RELAXATION TIME

The time (T_r) associated with radiation into oil may be calculated from the following data: $\lambda \sim 3$ cm, total area $= 32$ cm^2, contact area ~ 2 cm^2. These give $T_r = 0.23 \times 10^{-3}$ sec. Equation (16) states that $A/A_0 = f(\eta P_s T)$, and from Fig. 9 we have

$$A/A_0 = 0.27 \quad \text{for} \quad T = T_\rho,$$

$$A/A_0 = 0.43 \quad \text{for} \quad T = T'.$$

From Fig. 8, we have

$$\eta P_s T_\rho / \eta P_s T' = 2150/850 = 2.6 \quad \text{or} \quad T_\rho = 2.6 T'.$$

But $1/T' = 1/T_\rho + 1/T_r$, so that $T_\rho = (2.6 - 1) T_r$. The result is therefore that $T_\rho = 0.36 \times 10^{-3}$ second.