PHYSICAL REVIEW VOLUME 101, NUMBER 6 MARCH 15, 1956

# Influence of Ultrasonic Energy on the Relaxation of Chlorine Nuclei in Sodium Chlorate*†

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(Received November 14, 1955)

An investigation of the direct and indirect thermal relaxation processes of $Cl^{35}$ in a single crystal of $NaClO_3$ has been made by using pulsed techniques. The temperature dependence of the indirect process has been measured at four temperatures ranging between room temperature and liquid nitrogen temperature. The experimental results are in good agreement with the theoretical results of Chang.

The direct process has been studied by introducing into the crystal ultrasonic energy at a frequency equal to the transition frequency between the two quadrupolar energy levels of the $Cl^{35}$ nucleus. The agreement between the theoretical dependence of the direct-process relaxation time as a function of the energy density of the transition-frequency lattice vibrations is poor.

The experiment, as done, has the basic weakness that the calculated energy density of the introduced lattice vibrations is a function of the phonon relaxation time, $T_p$, a quantity only poorly known in the most favorable cases. A different method for making the same type of study independent of the phonon relaxation time is discussed.

## I. INTRODUCTION

THE dominant mechanism responsible for thermal relaxation of nuclei in solids may in general be regarded as one of two kinds. For nuclei of spin $\frac{1}{2}$, the coupling of the spin system to the lattice is through paramagnetic impurities. For nuclei of spin 1 or greater, the spin system is coupled to the lattice via the nuclear electric quadrupole interaction with the electric fields generated by the lattice distortions. The former mechanism, by virtue of its nature, is hardly susceptible to a precise theoretical analysis and experiment check.[1] This is in contrast with the latter, about which several calculations[2,3] have already been made, in particular, those of Van Kranendonk[4] and Chang,[5] and about which this experimental work has been concerned.

The thermal relaxation time, resulting from the quadrupole interaction, is due to two processes: the direct process and the Raman, or indirect, process. The former represents the complete absorption or creation of a phonon $h\nu$ as a nuclear reorientation takes place between levels differing by energy $h\nu$. The indirect process, as we shall continue to call it in this paper, represents the change in frequency of a high-energy phonon $h\nu' \rightarrow h(\nu'' \pm \nu)$, as a nuclear orientation takes place. The general result of the calculations is that the latter process, although very temperature-dependent, is at room temperature about $10^9$ times as effective as the former. Consequently, a simple measurement of the thermal relaxation time $T_1$ is a measure of the relaxation time $T_{1i}$ due to the indirect process. The measurement of the relaxation time $T_{1d}$ resulting from the direct process, however, presents an experimental problem, which we have chosen (not wholly successfully) to solve in the following way. Since the rate of this process is proportional to the density of phonons in a unit frequency interval at the frequency $\nu$, it should be possible, by increasing the phonon density at that frequency with ultrasonic waves,[6–8] to cause the direct process to compete with the indirect one. The thermal relaxation time will be shortened as $T_{1d}$ is made effective by the ultrasonic waves. Furthermore, the spin system will show a saturation, or show populations characteristic of some temperature higher than that of the lattice. It is the latter phenomenon which we have observed.

In particular, we have (1) measured the thermal relaxation time as a function of temperature for $Cl^{35}$ in a single crystal of $NaClO_3$. These results will be compared to the calculations of Chang[5] for the indirect process. We have also (2) caused saturation of the pure quadrupole energy levels by ultrasonic waves at the transition frequency at the temperature of liquid nitrogen, for which the transition frequency was 30.57 Mc/sec. Our result shall be the relation between the energy density of the 30.57-Mc/sec lattice vibrations and the direct process relaxation time. It will turn out that the experiment is indecisive in the sense that the energy density of the 30.57-Mc/sec lattice vibrations is known only in terms of a quantity $T_p$, the 30.57-Mc/sec phonon relaxation time in a crystal combination involving sodium chloride and sodium chlorate glued together. No attempt was made to measure this relaxation time, estimates of it were made using information

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* This paper contains parts of a thesis presented by W. H. Tanttila to the Physics Department, University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

† This research was supported by the United States Air Force, through the Office of Scientific Research and Development Command.

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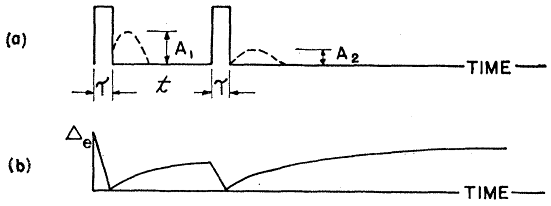

FIG. 1. (a) Following the first strong rf pulse of duration $\tau$ is a transient nuclear induction signal of amplitude $A_1$, proportional to the population difference between the two quadrupoles states at thermal equilibrium. After a time $t$, a second pulse of the same duration is applied and the induction signal of amplitude $A_2$ appears. The relation between $A_1$ and $A_2$ is given in Eq. (2). (b) The instantaneous population difference over the same interval as (a). $\Delta_e$ indicates the equilibrium population difference at the beginning of the rf pulse.

from the literature. Consequently an adequate comparison with Chang's result for the direct process cannot be made.

We have chosen to measure level populations by pulsed techniques, rather than by methods involving continuous observation of a line. Several papers,[9–12] have appeared in the literature dealing in particular with the induction decay transients of $Cl^{35}$ from $NaClO_3$. We refer the reader to the most comprehensive of these, by Bloom, Hahn, and Herzog,[12] and point out here only that the amplitude of the transient following a single pulse of rf flux at the transition frequency is a measure of the population difference between the two states involved at the instant that the pulse appears.

## II. LEVEL POPULATIONS

The thermal relaxation time $T_1$ was measured at several temperatures by a pattern of two pulses of variable spacing,[13] as shown in Fig. 1 (a), followed at a time $>T_1$ by another set. Figure 1 (b) plots the instantaneous population difference between the two pure quadrupole energy levels during the same interval. The instantaneous population difference $\Delta$ approaches the equilibrium value $\Delta_e$ at a rate given by the thermal relaxation time $T_1$:

$$\Delta(t)/\Delta_e = (1-e^{-t/T_1}), \tag{1}$$

if $\Delta(0)$ is zero, as it is following the first pulse. The pulse length $\tau$ is adjusted to produce the maximum induction transient amplitude, which occurs when the expectation value of the population excess is zero.

Referring again to Fig. 1, the heights $A$ of the transients pictured are proportional to the population differences at the beginning of the rf pulse; hence

$$A_2/A_1 = \Delta(t)/\Delta_e = (1-e^{-t/T_1}), \tag{2}$$

where $t$ is the time interval between the trailing edge of the first pulse and the beginning of the second. We have measured the ratio $A_2/A_1$ as a function of the interval $t$, with the results presented in Table I in Sec. IV.

We shall now consider the effect of ultrasonic waves at the transition frequency upon the level populations. If $N_{\frac{3}{2}}$ ($N_{\frac{1}{2}}$) represents the population in the upper (lower) energy level (where we have arbitrarily placed the $m=\pm\frac{3}{2}$ level higher in energy), the populations are governed by the following differential equations:

$$\dot{N}_{\frac{3}{2}} = N_{\frac{1}{2}}(W_{\frac{3}{2}\leftarrow\frac{1}{2}}+V) - N_{\frac{3}{2}}(W_{\frac{1}{2}\leftarrow\frac{3}{2}}+V), \tag{3}$$

$$\dot{N}_{\frac{1}{2}} = -N_{\frac{1}{2}}(W_{\frac{3}{2}\leftarrow\frac{1}{2}}+V) + N_{\frac{3}{2}}(W_{\frac{1}{2}\leftarrow\frac{3}{2}}+V). \tag{4}$$

$W_{\frac{3}{2}\leftarrow\frac{1}{2}}$ and $W_{\frac{1}{2}\leftarrow\frac{3}{2}}$ represent the natural transition probabilities between these states in the direction indicated and $V$ the additional transitional probability due to the presence of the acoustic excitation.

We have here made two assumptions: (i) that $W_{\frac{1}{2}\leftarrow\frac{3}{2}}$ and $W_{\frac{3}{2}\leftarrow\frac{1}{2}}$ are unaffected by the presence of the acoustic waves and (ii) that, following Lloyd and Pake,[14] the intensities we shall use are so great that $V$ is equally effective in making transitions upward or downward. If, furthermore, we make the additional usual assumption that $W_{\frac{1}{2}\leftarrow\frac{3}{2}} = W_{\frac{3}{2}\leftarrow\frac{1}{2}}e^{h\nu/kT}$, we arrive at the following equation describing the population difference:

$$\frac{d\Delta}{dt} = \frac{\Delta_0}{T_1} - \Delta\left(\frac{1}{T_1}+\frac{1}{T_{1b}}\right), \tag{5}$$

where, as usual, $T_1=(2W)^{-1}$ and where $T_{1b}$ has been introduced in an analogous fashion for $(2V)^{-1}$. $\Delta_e$ again is the normal equilibrium population difference $\frac{1}{2}N(h\nu/kT)$ and $N=N_{\frac{3}{2}}+N_{\frac{1}{2}}$, the total number of nuclei. Setting $d\Delta/dt=0$, Eq. (5) yields, for an equilibrium population with acoustic waves present,

$$\Delta_e' = \Delta_e(1+T_1/T_{1b})^{-1}. \tag{6}$$

Introducing this quantity into (5), we find that the population difference $\Delta$ approaches the equilibrium value given by (6) according to

$$d\Delta/dt = (\Delta_e'-\Delta)\left(\frac{1}{T_1}+\frac{1}{T_{1b}}\right). \tag{7}$$

Hence we find a thermal relaxation time $T_1'$ while the

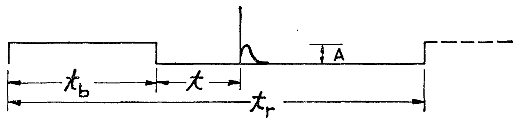

FIG. 2. Schematical representation of pulse applications to the $NaClO_3$ crystal. The ultrasonic excitation is applied at the nuclear transition frequency for a time $t_b$. After a time $t$ following the cessation of the ultrasonic pulse, an inspecting rf pulse is applied. Following the inspecting pulse is a nulcear induction signal of amplitude $A$ which is proportional to the population difference. The repetition period is $t_r$.

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[9] M. Bloom and R. E. Norberg, Phys. Rev. **93**, 638 (1954).

[10] E. L. Hahn and B. Herzog, Phys. Rev. **93**, 639 (1954).

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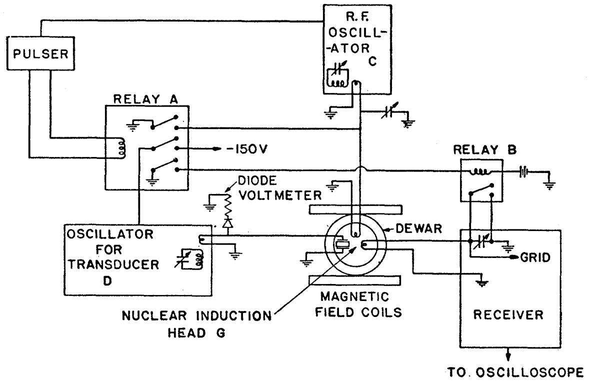

FIG. 3. A block diagram of the equipment.

acoustic waves are present, given by

$$\frac{1}{T_1'}=\frac{1}{T_1}+\frac{1}{T_{1b}}. \tag{8}$$

The method we have used to measure the effectiveness of the acoustic wave is indicated in Fig. 2. The rf pulse, of negligible duration, follows a long ultrasonic pulse, of duration $t_b$, by a time $t$. The repetition period for this pattern is $t_r$.

If the beginning of the cycle is regarded to be the end of the rf pulse, when the population $\Delta$ is zero, the population at the beginning of the rf pulse may be written by inspection of Fig. 2 as

$$\Delta=\{\Delta_e(1-e^{-(t_r-t_b-t)/T_1})e^{-t_b/T_1'} +\Delta_e'(1-e^{-t_b/T_1'})\}e^{-t/T_1}+\Delta_e(1-e^{-t/T_1}). \tag{9}$$

The induction transient following the rf pulse is to be compared for various intensities of the acoustic wave. The maximum transient is obtained for zero acoustic intensity, or

$$\Delta_{\max}=\Delta_e(1-e^{-t_r/T_1}). \tag{10}$$

We have measured the ratio $\Delta/\Delta_{\max}$ for various intensities. This ratio is given by dividing (10) into (9)

$$\frac{\Delta}{\Delta_{\max}}=(1-e^{-t_r/T_1})^{-1}\left\{\left[(1-e^{-(t_r-t_b-t)/T_1})e^{-t_b/T_1'} +\frac{1}{1+T_1/T_{1b}}(1-e^{-t_b/T_1'})\right]e^{-t/T_1} +(1-e^{-t/T_1})\right\}, \tag{11}$$

which may be put into the form

$$\frac{A}{A_{\max}}=\frac{\Delta}{\Delta_{\max}}=C_1\left\{1-C_2\left[1-\frac{1}{1+x} C_3\frac{1}{1+1/x}e^{-xt_b/T_1}\right]-C_4e^{-xt_b/T_1}\right\}, \tag{12}$$

where the following constants have been introduced in (12) to facilitate the computations:

$$x=T_1/T_{1b},\quad C_2=e^{-t/T_1},\quad C_4=e^{-t_r/T_1}.$$
$$C_1=(1-e^{-t_r/T_1})^{-1},\quad C_3=e^{-t_b/T_1}, \tag{13}$$

A plot of $\Delta/\Delta_{\max}$ *vs* $x^{-1}$ appears in Sec. IV.

## III. APPARATUS AND TECHNIQUES

A block diagram of the apparatus is given in Fig. 3. All parts indicated in that diagram, except the gated oscillator *D*, which provides radiofrequency energy for the quartz transducer located in the head *G* and the relays, formed an apparatus for examining the transient signals of pulsed transitions between pure quadrupole energy levels. The reader is referred to Bloom, Hahn, and Herzog[12] for general circuit details, and in particular for details of the transmitters, of which we have used two, the grated oscillators *C* and *D*. The receiver was an AN/APS-15 radar 30-Mc i.f. strip, with a very few changes; its input circuit is indicated in Fig. 3. The receiver coil was placed at right angles to the transmitter coil and the static magnetic field, $H_0$, was applied perpendicular to the axes of both coils. The signal maximum appeared $\sim(\gamma H_0)^{-1}$ second after the cessation of transmitter pulse.

The experiment was done at liquid nitrogen temperature for two reasons: the thermal relaxation time is comparatively long, 0.94 sec, so that the ultrasonically induced transitions could be more easily observed, and the nuclear induction signal would be enhanced above that at room temperature. Figure 4 shows the arrange-

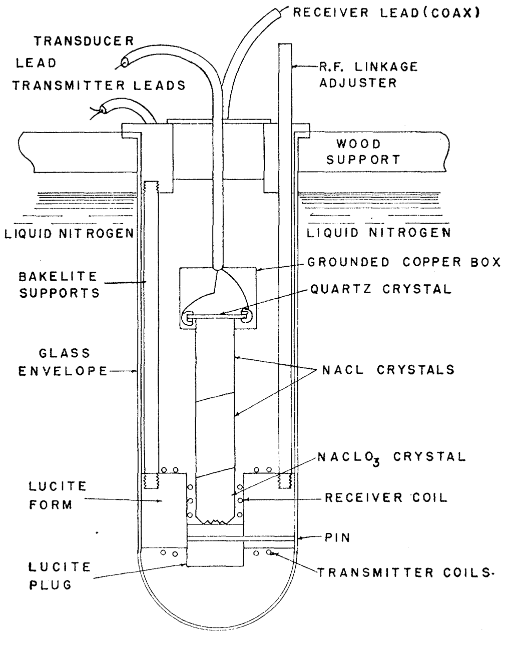

FIG. 4. The arrangement of the transducer and nuclear induction head.

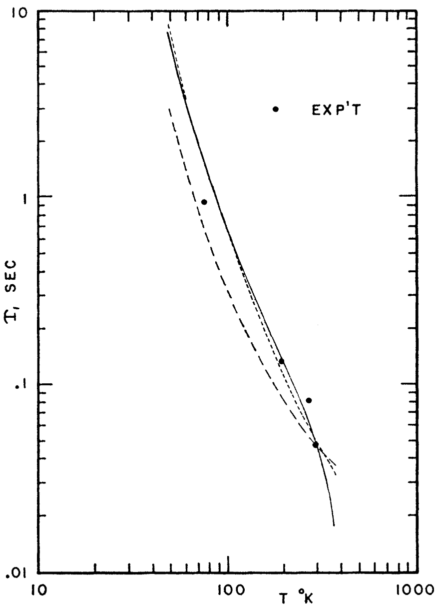

FIG. 5. The circles show the experimentally observed relation between the thermal relaxation time and the temperature for $NaClO_3$ crystals. The lines represent the theoretical predictions of Chang using various assumptions.[5]

ment of the parts in the nuclear induction head for doing experiments at this temperature.

The ultrasonic energy was transmitted from the quartz transducer into the sodium chlorate crystal through two sodium chloride crystals of combined length 7 cm and of diameter of 1.26 cm. The $NaClO_3$ crystal, of the same diameter and of length 1 cm, rested on a Lucite plug in the assembly and supported the NaCl crystals and the quartz transducer. The quartz crystal, at the top of the upper sodium chloride crystal, was cemented to it by placing a small amount of high-vacuum grease at the interfaces and pressing the polished faces of the crystals together until the grease film between the crystals became continuous. The excess grease was carefully wiped off. The other crystal interfaces were similarly joined. The ultrasonic energy entered the sodium chlorate in the (1,0,0) direction.

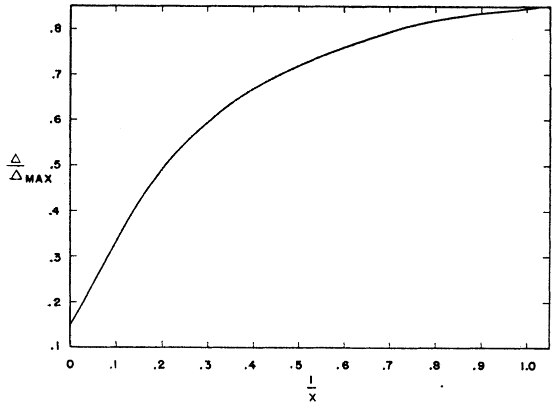

FIG. 6. The predicted relation between the quantities $\Delta/\Delta_{\max}$ and $1/x$, where $\Delta$ is the population difference with ultrasonic excitation present and $\Delta_{\max}$ is the population difference without the ultrasonic present. $x = T_1/T_{1b}$, where $T_1$ is the thermal relaxation time without the ultrasonic excitation present and $T_{1b}$ is the contribution to the relaxation due to the ultrasonic excitation.

The sodium chloride crystals were introduced to conduct the ultrasonic energy from the transducer whose leads unavoidably generated magnetic fields. Sodium chloride was chosen because of its good acoustic conductivity.[15] In order to minimize further the stray rf fields at the sodium chlorate the quartz crystal was surrounded by a copper box which was connected to the outer lead of a coaxial cable. The underside of the silver-plated quartz was in turn connected to the copper box.

The experiment was planned with the idea of having an isotropic distribution of standing waves in the sample. Not only would one be able to increase the energy density of the acoustic waves, but the isotropic distribution as a geometric pattern, could be more perfectly achieved than a traveling or unidirectional standing-wave pattern. For this reason the connections between the two sodium chloride crystals, as well as between the sodium chloride and the sodium chlorate, were made at slight angles with respect to the quartz face. Moreover, the bottom surface of the sodium chlorate crystal was made uneven and made contact with the Lucite plug at only a few points. These measures were taken so that the acoustic waves which suffered many reflections might have random directions.

The quartz crystal used was of square cross section, three-fourths of an inch on the side, silver-coated using DuPont Silver 4666, baked on at a temperature of 850–900°F for 20 min. The crystal was operated at its third harmonic and tuned broadly at 30.42 Mc/sec; the half-width at half-maximum was about 1.5 Mc/sec.

The whole nuclear induction head was placed between two large coils lying on either side of the Dewar. It was found, however, that the splitting of the levels was accomplished satisfactorily by the earth's field.

The purpose of the relays shown in Fig. 3 was to short circuit the transmitter and receiver coils during the ultrasonic excitation period. In order to be sure that leakage magnetic flux from any source was not causing transitions when the relays were closed, repeated experiments were performed in which the sodium chloride crystals were separated from each other by several layers of tissue paper. This provided the quartz with essentially the same loading and consequently the current to the quartz transducer remained unchanged. No nuclear saturation effect was observed under these conditions. A further possible spurious effect, the generation of a temperature gradient in the sample crystal by the ultrasonic energy during the interval $t_b$, was not likely since the nuclear saturation manifested itself in a very narrow frequency

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[15] J. K. Galt, Phys. Rev. 73, 1460 (1948).

TABLE I. Measured thermal relaxation time $T_1$ of $Cl^{35}$ in crystalline $NaClO_3$ as a function of temperature.

| Temperature °K | $T_1$ milliseconds |
|---|---|
| 77 | 940±100 |
| 194 | 132±13 |
| 273 | 81±8 |
| 300 | 46±5 |

band while the loaded quartz crystal resonance was broad.

The technique of preparing the apparatus for taking data was as follows: Liquid nitrogen was poured slowly into the Dewar containing the assembly of Fig. 4 in order to avoid cooling the crystals too rapidly. After about an hour the assembly approached thermal equilibrium. The oscillator $C$ was put into operation and the nuclear induction signal located and maximized. Then oscillator $D$ was turned on with the associated relays. With the variac which controlled the voltage on the screen and plate of oscillator $D$ set at the maximum value (80 v), and with the gate lengths adjusted properly, the maximum diminution of the nuclear signal was established by adjusting the frequency of oscillator $D$ to the transition frequency. The amplitude of the transient nuclear induction signal appearing on the oscilloscope at a given time after the rf pulse was recorded. Immediately after this measurement the frequency of the oscillator generating acoustic energy was turned slightly away from the transition frequency and the unattenuated signal appearing on the oscilloscope recorded. With the variac set to a new voltage (70 v), the same measurements were repeated. The voltage on the variac was dropped in steps of 10 volts down to 30 volts, at which the diminution was only barely detectable. After these measurements the oscilloscope was used, as a part of the crystal diode peak detector, to measure the voltage across the quartz crystal for each of the former variac settings.

At the completion of one set of readings, similar data was taken in the same manner three more times and the average results of the measurements were computed. The above procedure was followed for two different sodium chlorate crystals.

## IV. EXPERIMENTAL RESULTS

The method of measuring the thermal relaxation time, outlined in II, gave the results presented in Table I. These data are plotted in Fig. 5, in which a comparison in made with the theory of Chang.[5]

For measuring $T_{1b}$, the parameters $t_b=0.25$ sec, $t=0.10$ sec, $t_r=0.87$ sec, and $T_1=0.94$ sec were used. The constants of Eqs. (13) then are $C_1=1.66$, $C_2=0.899$, $C_3=0.767$, $C_r=0.397$, and Eq. (12) becomes

$$\frac{\Delta}{\Delta_{\max}}=1.66\left\{1-0.899\left[1-\frac{1}{1+x}-\frac{0.767}{1+1/x}e^{-0.266x}\right]-0.397e^{-0.266x}\right\}.$$

This function appears in Fig. 6; observed ratios $\Delta/\Delta_{\max}$ were used to find $x=T_1/T_{1b}$. Our data, for each of two crystals, are presented in Table II. The errors in the values $x$ and $1/x$, not listed in Table II, were obtained from an examination of Fig. 6 and appear in Figs. 7(a) and (b), where the ratio $x=T_1/T_{1b}$ for each crystal is plotted against the data in the second column of Table II. The best straight line to these data has been drawn through the points. The information contained in this figure represents all of the results of our measurements on $T_{1b}$.

Interpretation of the voltage across the crystal, in terms of an energy density per unit volume of the ultrasonic waves, so that a comparison with theory may be made, depends upon an analysis of the efficiency of the transducer, and a knowledge of the phonon mean lifetime at this frequency. Since the appropriate phonon mean lifetime is not well known, we express the energy density as given in Table II and Figs. 7(a) and 7(b) in terms of it.

The analysis of the transducer efficiency depends on knowledge of the internal resistance, $R_c$, of the quartz crystal, operating at its third harmonic. Using a $Q$-meter, we obtained the value 80 kilo-ohms.

In order to calculate the power into the specimen the equivalent circuit for a quartz crystal given by Van Dyke[16] and Mason[17] and shown in Fig. 8 was used.

TABLE II. Energy densities and induced relaxation times.

| Rms volts across quartz crystal | (Energy density in ergs/cm³) $\times T_p$ | Crystal I<br>$A/A_{\max}$ | Crystal I<br>$1/x$ | Crystal I<br>$x$ | Crystal II<br>$A/A_{\max}$ | Crystal II<br>$1/x$ | Crystal II<br>$x$ |
|---|---|---|---|---|---|---|---|
| 24.4 | 885 | 0.31±0.02 | 0.09 | 11.1 | 0.30±0.03 | 0.085 | 11.8 |
| 21.0 | 652 | 0.37±0.02 | 0.12 | 8.3 | 0.36±0.06 | 0.115 | 8.7 |
| 18.0 | 480 | 0.45±0.04 | 0.17 | 5.9 | 0.48±0.06 | 0.19 | 5.3 |
| 14.5 | 311 | 0.57±0.03 | 0.27 | 3.7 | 0.59±0.07 | 0.29 | 3.4 |
| 11.5 | 196 | 0.76±0.03 | 0.60 | 1.66 | 0.74±0.08 | 0.55 | 1.8 |
| 8.65 | 111 | 0.83±0.03 | 0.65 | 1.16 | 0.84±0.05 | 0.95 | 1.05 |

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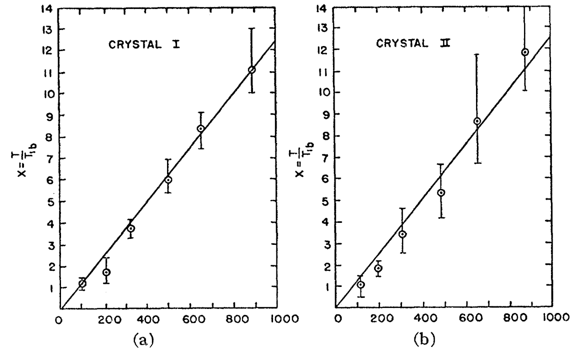
[16] K. S. Van Dyke, Proc. Inst. Radio Engrs. **16**, 742 (1928).

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



(a) (b)

FIG. 7. (a) The relation between $x=(T_1/T_{1b})$ (ordinate) and $T_p^{-1}$ times the energy density in ergs/cm$^3$ for crystal I (abscissa). $T_p$ is the phonon relaxation time. (b) The same data for crystal II.

Since the high-vacuum grease was rigidly frozen at 77°K, the compliance $C_2$ was ignored,[18] and at resonance the reactance of $L_1$ and $C_1$ cancels. $Z_0$ is reflected to the input side of the transformer through the impedance transformation[19] $4\phi^2/9$.

From the expressions given by Mason,

$$Z_0=\rho vA, \quad 2\phi=DKA/2\pi l_t,$$

one can calculate the impedance of the network in cgs units. In the above expressions, $\rho$ is the density of the NaCl crystal, $v$ is the velocity of 30.57-Mc/sec waves in NaCl, $A$ is the area of the NaCl-quartz contact surface, $D$ is the piezoelectric constant relating stress generated by the piezoelectric effect to the applied surface charge, $K$ is the dielectric constant of quartz, and $l_t$ is the quartz crystal thickness. In the above circuit, as represented, it is necessary to divide each of the impedances, except $R_c$ which was measured in ohms, by $1.11\times10^{-12}$ in order to express them in ohms. Using the values $D=13.85\times10^4$,[17,18] $K=4.55$,[17,18] $A=1.24$ cm$^2$ (measured), $l_t=(0.0262$ cm) (measured), $\rho=2.19$,[20,21] and $v=5.1\times10^5$,[20] one gets for the reflected impedance of the sodium chloride rod, $504\times10^3$ ohms. The power $P$ into the NaCl rod at 30.57 Mc/sec then becomes

$$E_0^2\times504K(80K+504K)^{-2}. \tag{14}$$

In order to calculate the energy density of the 30.57-Mc/sec acoustic waves in the $NaCl-NaClO_5$ crystal combination it is necessary to consider the losses of energy at this frequency. These losses are due to (1) phonon-phonon collisions (2) leakage through points of contact and (3) radiation to the air. We have shown that (2) and (3) are negligible. Considering (1), the energy in the combination is governed by

$$dE/dt=P-E/T_p, \tag{15}$$

where $E$ is the total energy in the crystals, $T_p$ is the phonon relaxation time for the crystal combination, and $P$ is the ultrasonic input power. The phonon relaxation time is the average time that it takes for a number of 30.57-Mc/sec phonons to be lost to phonons of other frequencies by phonon-phonon collisions. This time will likely be governed by the phonon relaxation time in the sodium chloride crystal since it represents a volume 7 times as great as the volume of the sodium chlorate.

Under steady-state conditions, $dE/dt=0$, so that the energy density becomes

$$U=(P/V)T_p. \tag{16}$$

If one uses a crystal volume 9.9 cm$^3$, the energy density becomes

$$U=1.48E_0^2T_p \text{ ergs/cm}^3. \tag{17}$$

From Figs. 7(a) and 7(b) giving the dependence of $x=T_1/T_{1b}$ on the energy density, one can find the dependence of the induced relaxation time, $T_{1b}$, on the energy density. The relation can be expressed as $x=k$ (energy density), where $k$ is a constant. Examination of Figs. 7(a) and 7(b) gives

$$k=[(12.5\times10^{-3})/T_p]\text{cm}^3/\text{erg}. \tag{18}$$

From Figs. 7(a) and 7(b), the error $k$ due to our method of observation of the saturation can be easily estimated as about 10% by drawing a variety of straight lines associated with the points and passing through zero. Also, we feel that there is a considerable uncertainty in our determination of the internal resistance of the quartz, since two measurements differed by 10%. The magnitude of the resistance, however, is not surprising in view of crystal resistances at high frequencies given by other investigators.[16,22] Use of Eq. (12) shows that a 10% error in $T_1$ reflects a 4% error in $x$. Taken altogether, the result (18) is uncertain by about 15%.

Values for $T_p$ are only poorly known. Galt[15] gives attenuations for 30-Mc/sec ultrasonic waves in NaCl crystals of 0.004 cm$^{-1}$ for longitudinal waves at room temperature. Since the phonon mean free path is proportional to $1/T$ at high temperatures,[23] we find that $T_p\cong5$ milliseconds at 77°K. Hence $k$ becomes 2.5 cm$^3$/erg. That is, 0.4 erg/cm$^3$ at the transition frequency gives the same relaxation rate as all the thermal motions existing at liquid nitrogen temperatures. In order to get a relaxation rate by the direct process equal to the total relaxation rate at room temperatures, it would be necessary to increase the energy density of the 30.57-Mc/sec phonons by a factor approximately equal to the ratio of the relaxation time at room temperature to that at liquid nitrogen temperature. This factor is 940/46; hence the energy density necessary to meet this requirement is 8 ergs/cm$^3$

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[18] W. P. Mason and H. J. McSkimin, J. Acoust. Soc. Am. **19**, 464 (1947).

[19] We are grateful to Dr. Mason for pointing out to us that the impedance transformation $4\phi^2$ appropriate for the fundamental becomes $4\phi^2/9$ for the third harmonic.

[20] F. C. Rose, Phys. Rev. **49**, 50 (1936).

[21] A. Henglein, Z. Physik Chemie **115**, 97 (1925).

[22] E. M. Terry, Proc. Inst. Radio Engrs. **16**, 1486 (1928).

[23] Berman, Simon, and Wilks, Nature **168**, 277 (1951).

at the monochromatic frequency 30.57 Mc/sec. When the above values are averaged over the line width of the Cl$^{35}$ resonance (1.2 kc/sec) the results become 0.3 erg sec/cm$^3$ kc and 7 erg sec/cm$^3$ kc, for liquid nitrogen temperature and room temperature, respectively.

## V. DISCUSSION

The main theoretical conclusions with which the results of this experiment are to be compared are those of Chang.[5] His analysis was an attempt to calculate $T_{1i}$ and $T_{1d}$ for the Cl$^{35}$ nuclei using the specific model NaClO$_3$ in zero magnetic field. Van Kranendonk,[4] on the other hand, has calculated the quadrupole relaxation time for the indirect process only, in cubic lattices of the NaCl type, for which the magnetic interaction of nuclei is large compared to the quadrupole interaction with the lattice. His results, consequently, are of less direct interest to us. There are no other papers explicitly devoted to this problem.

The field gradient tensor $V_{ij}$ at the Cl nucleus has been assumed by Chang to be the sum of each of the individual tensors due to the neighboring Na and O atoms. The latter tensors were assumed to have rotational symmetry about the line connecting the Na to the Cl nucleus, and the $zz$ component was assumed to vary in a linear fashion with the distance between Cl and the appropriate neighbor. All the tensor components were then calculable in terms of the positions of the neighbors. Upon assuming a Debye spectrum of lattice waves, expressions for the direct and indirect transition probabilities as a function of temperature were obtained. The latter depend further upon the assumed temperature dependence of $q$ and of the thermal expansion coefficient of the ClO$_3$ group. Curves, dotted, dashed, and solid, based on specific assumptions,[5] are given in Fig. 5 together with the experimental thermal relaxation times. The reader is referred to the calculation of Chang for further details.

The general agreement is gratifying.

The direct transition probability is given by[5]

$$W_d=\frac{\pi^3kT}{20Mh^4}(eqQ)^4\left(\frac{4}{v_T^5}+\frac{1}{v_L^5}\right), \tag{20}$$

where $v_T$ and $v_L$ are the velocities of the transverse and longitudinal waves in the crystal, and the other symbols have their usual meanings. Upon assumption of a common mass $M$ for all the nuclei in the molecule, $W_d$ is seen to depend wholly upon well known constants. The above calculation leads, at room temperatures, to a ratio of the indirect to direct relaxation times of $0.9\times10^9$. Hence, if ultrasonic waves were introduced into the crystal at room temperature, an energy density of ultrasonic waves given by

$$0.9\times10^9\times8\pi\frac{\nu^2}{v^3}kT\times10^3 \text{ erg sec/cm}^3\text{ kc} \tag{21}$$

would give a direct relaxation time equal to the indirect one. The expression (21) yields $4\times10^{-3}$ and $3\times10^{-2}$ erg sec/cm$^3$ kc for longitudinal and transverse waves, respectively.

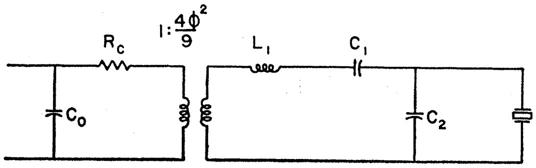

FIG. 8. The equivalent circuit of the quartz transducer.

The discrepancy between these values, and the value obtained from extrapolation of the experimental results, 7 erg sec/cm$^3$ kc is to be noted. We have little confidence in the phonon relaxation times we have used so that the above value cannot be taken too seriously. However, the major part of the discrepancy probably lies in the theory.

A number of points remain to be discussed. First, a negligible inefficiency of the acoustic transitions results from the weak Zeeman splitting of the degenerate quadrupole energy level. The widths of the levels are given by Hahn and Herzog[10] to be 2.6 gauss which agrees with our observations. Since the earth's magnetic field is equal to about 1 gauss, the levels overlapped considerably.

The question arises whether or not dipole-dipole interaction between the Cl$^{35}$ nucleus and its neighbors will contribute to the relaxation process. The matric element responsible in magnetic transitions is, however, of the order of (line width)/(transition frequency) smaller than for quadrupole transitions.[24] Hence the magnetic relaxation processes would be expected to be about $10^{-9}$ as effective as the quadrupole ones.

An alternate experiment would be to set up in the sodium chlorate crystal unidirectional standing waves. This type of experiment would be difficult but feasible. The difficulties involved would be in obtaining sodium chlorate crystals completely free of fractures and in providing parallel faces with extremely good precision, since the wavelength of the 30.57-Mc/sec ultrasonic waves in sodium chlorate is about 0.1 mm. The advantage of this method would be that the amplitude of the standing wave could be determined directly without a knowledge of the phonon relaxation time. This would be true, as well, for an experiment in which pure travelling waves were used; the energy density in this case, however, would be much lower.

There is another advantage to an experiment involving unidirectional standing waves. By the application of a magnetic field strong enough to lift the degeneracy of the quadrupole energy levels, the effectiveness of the ultrasonic waves on the various transitions could be studied.

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