AN ULTRASONIC EXPERIMENT ON
SODIUM CHLORIDE

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AN ULTRASONIC EXPERIMENT ON SODIUM CHLORIDE

by

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ABSTRACT

When a sodium chloride crystal is placed in a magnetic field H_o, the sodium nuclei, having a spin 3/2, find their energy level split into four sub-levels. The separation, in frequency, between neighboring levels is

$\gamma H_o / \hbar$ where γ is the gyromagnetic ratio. Ultrasonic energy has been used to make $\Delta m = \pm 2$ transitions between these levels. These transitions tend to equalize the populations of the four levels. The effectiveness of the ultrasonic energy in producing $\Delta m = \pm 2$ transitions has been measured by using pulsed nuclear induction. This method determined the population difference between adjacent levels during the ultrasonic excitation.

The effectiveness of the ultrasonic energy in causing transitions has been measured with longitudinal waves propagated in the $[100]$, the $[110]$, and the $[111]$ crystal directions. The experimental results are compared with theoretical predictions. The results indicate that the ionic quadrupole polarization is independent of the direction of the ultrasonic waves.

TABLE OF CONTENTS

INTRODUCTION

The spin-lattice relaxation between the spin levels
of the sodium nucleus in a magnetic field is brought about
by the interaction of the quadrupole moment of the nucleus
and the time varying electric field gradient at the site
of the nucleus. The time varying electric field gradient
is generated by the thermal lattice vibrations which bring
about relative motion between the ions in the crystal.
One may modulate the time varying electric field gradient
with ultrasonic energy of such frequency as to cause $\Delta m = \pm 1$
or $\Delta m = \pm 2$ transitions, where m is the magnetic quantum
number.

Proctor and Robinson[1] were the first to produce $\Delta m = \pm 2$
transitions between the sodium spin levels in sodium chlor-
ide. Later more work of this nature was done by Kraus[2] and
also Jendrasiak[3].

Kraus[2] has written a theory for the ultrasonic tran-
sition probability. He uses van Kranendonks'[4] model of the
lattice; a sodium atom surrounded by point charges, γe,
situated at the neighboring lattice points. There has been
some question as to whether the γ appearing in van Kranend-
onks'[4] and Kraus'[2] model possesses tensor properties. By
comparing the effectiveness of the ultrasonic energy in
producing transitions in each of the three crystal direc-
tions one can, with the aid of Kraus'[2] theory, establish,

within experimental limits, three components of the γ tensor.

Since the ultrasonic energy density in the expression for the ultrasonic transition probability derived by Kraus is difficult to measure, the ratios of the three components of the γ tensor to each other are determined rather than their absolute values.

THEORY

When the sodium chloride crystal is placed in a magnetic field the energy level of the sodium spin 3/2 nucleus is split into four Zeeman levels as shown below:

m = - 3/2 ─────────

m = - 1/2 ─────────

─ ─ ─ ─ ─

m = + 1/2 ─────────

m = + 3/2 ─────────

FIGURE 1

m is the magnetic quantum number and may take any of the $(2I+1)$ values in the series I, $I-1$, $I-2$, ..., $-(I-1)$, $-I$. The nuclei, at room temperature, assume a Boltzman distribution and the number in each level is given by;

$$N_m = C \exp (-E_m/KT)$$

where E_m is the energy of the (m) level, K is Boltzman's constant, C is a constant and T is the absolute temperature of the sodium chloride crystal.

We are interested in the population difference, Δ_o , between two adjacent levels. The energy of a given level is;

$$E_m = - g \mu_o H_o m$$

where $\mu_o = e \hbar/2Mc$ and M is the mass of the proton and c the velocity of light and $g = \mu/\mu_o I$.

Let us find Δ_o between m = 3/2 and m = 1/2,

$$\frac{N_{3/2}}{N_{1/2}} = \frac{C \exp (g \mu_o H_o 3/KT2)}{C \exp (g \mu_o H_o/KT2)}$$

$$= \exp (g \mu_o H_o/KT)$$

but $g = \mu/\mu_o I$ and here I = 3/2

$$\frac{N_{3/2}}{N_{1/2}} = \exp (2 \mu H_o/3KT)$$

expanding

$$\frac{N_{3/2}}{N_{1/2}} = 1 + 2 \mu H_o/3KT$$

and we see that

$$(N_{3/2} - N_{1/2}) = N_{1/2} \, 2 \mu H_o/3KT$$

If this calculation is extended to the other levels we find that the population difference between any two adjacent levels is equal to $N_{1/2} \, 2 \mu H_o/3KT$.

The energy difference between two adjacent levels is;

$$E_{3/2} - E_{1/2} = (-g \mu_o H_o 3/2) - (-g \mu_o H_o/2)$$

$$= -g \mu_o H_o$$

The selection rule for governing magnetic dipole transitions between levels is $\Delta m = \pm 1$. Therefore a quantum of energy can excite transitions between the energy levels if it has the same magnitude as the level spacing;

$$h \nu_o = g \mu_o H_o$$

where ν_o is the frequency of the electromagnetic radiation supplying the quanta of energy.

If a magnetic dipole μ is placed in a magnetic field H_o the dipole precesses about the direction of the applied field. The rate of precession is the well known Larmor angular frequency;

$$\omega = \gamma H_o 2\pi$$

where γ is the gyromagnetic ratio of the dipole. This same effect takes place with the nuclear magnetic moment μ . Since $\gamma = \mu / I h$ we see that this frequency is just;

$$\nu_o = 2 \mu H_o / Ih = g \mu_o H_o / h$$

In general the nuclear magnetic moments are precessing at random phase with respect to each other. If a R.F. magnetic field H_1 is applied perpendicular to H_o the assemblage of u's can be made to rotate in phase and by placing a coil around the sample with the coil's axis perpendicular to both H_1 and H_o a small voltage will be induced in the coil. The magnitude of the induced voltage will be directly proportional to Δ , the population difference of the

levels. There would be 0 voltage if the levels were equal in population. This method of detecting population differences is called Pulsed Nuclear Induction[5]. In short the method is this: The sample is placed inside a detecting coil whose axis is perpendicular to the axis of the H_1 - transmitting coil and then this combination inserted into H_0 such that the three components; the detecting coil, H_1, and H_0 are mutually perpendicular. The R.F. magnetic field is turned on for a short time and the voltage induced by the precessing nuclear spins is detected, amplified and observed on an oscilloscope.

We are concerned with the mechanisms by which the population of the levels are equalized. There are three. (1) The R.F. pulse causing $\Delta m = \pm 1$ transitions, (2) spin-flip process, and (3) ultrasonic energy causing $\Delta m = \pm 2$ transitions.

The frequency of the R.F. pulse is equal to the frequency difference between adjacent Zeeman levels. Since the lower energy levels are more populated than the upper levels there will be a net upward transfer of nuclei as a result of the R.F. excitation. Once a nucleus reaches a higher state it will remain there a finite length of time. Mathematically this can be written;

$$\Delta = \Delta_0 (1 - exp - t/T_1)$$

where Δ is the instantaneous population difference at a

time t following the R.F. pulse. T_1 is the spin lattice
relaxation time and is the time required for all but 1/e
of the nuclei to return to equilibrium. Δ_o is the thermal
equilibrium population difference.

The spin-flip goes about in this manner: A nucleus
in the m 3/2 state may go to the m 1/2 state with a si-
multaneous transition of any one of the following, $-3/2 \rightarrow$
$-1/2$, $-1/2 \rightarrow 1/2$, and $1/2 \rightarrow 3/2$. Since this process
takes place via a magnetic dipolar interaction between spin
systems and doesn't depend on the lattice vibrations it con-
serves energy of the spin system. There is therefore no
gain in the macroscopic magnetization but merely a redis-
tribution of that magnetization in the spin system.

Ultrasonic energy applied to the NaCl crystal at a
frequency corresponding to the frequency difference between
levels separated by 2 in the magnetic quantum number causes
transitions between these levels. These transitions come
about by means of the interaction of the quadrupole moment
of the sodium nucleus and the time varying electric field
gradient at the site of the nucleus. The electric field
gradient is modulated by the application of ultrasound to
the crystal. This interaction causes a population equal-
ization of the levels. By the application of enough ultra-
sound one can essentially equalize the population of the
levels.

Kraus[6], taking these three mechanisms into account,

arrives at this equation;

$$(A_0/A)^2 = 1 + 8 W_{[a]} T_{1[a]}/5$$

where A_0 is the amplitude of the free induction signal with no ultrasound, A is the amplitude at a certain ultrasonic energy density and $W_{[a]}$ is the ultrasonic transition probability corresponding to the amplitude A. The subscript $[a]$ denotes a dependence on the crystal direction.

$$W_{[a]} = \frac{e^4 Q^2 \gamma_{[a]}^2 D_{[a]}^2 B^2 K^2}{192 \hbar^2 a^6 \; \delta \nu}$$

where e is the electronic charge, Q is the quadrupole moment, B is the amplitude of the ultrasonic wave, K is the propagation constant, a is the lattice constant, $\delta\nu$ is the ultrasonic line width in frequency and $D_{[a]}$ is the contribution to the quadrupolar interaction energy due to the position of the γ e's and is equal to;

$$\frac{1}{(a^\alpha)^5}(X_1 \pm iX_2)\left[-\frac{15}{(a^\alpha)^2}(X_1 \pm iX_2) X_K^\alpha + 6(\delta_{1K} \pm i\delta_{2K})\right] \qquad (1)$$

for a single γ e where the X's are the coordinates of the γ e.

Now $B^2 = 2E/\rho \omega^2$ where E is the ultrasonic energy density, ρ is the density of NaCl, and ω is the ultrasonic angular frequency.

The ultrasonic energy density is given by;

$$E = P T_p / V'$$

where P is the ultrasonic power delivered to the crystal, T_p is the phonon relaxation time and V' is the volume of the sample.

The power is;

$$P \sim V^2/Z$$
$$= k\ V^2/Z$$

where V is the voltage across the quartz, Z is the impedence of the NaCl rod and equal to $\rho\ c_{[a]}S$. S is the area of contact between the quartz and NaCl, and $c_{[a]}$ is the speed of sound in NaCl. Therefore

$$P = k\ V^2 / \rho\ c_{[a]}S$$

Substituting we have

$$(A_o/A)^2 = 1 + \frac{e^4 q^2\ \gamma_{[a]}^2 D_{[a]}^2\ K^2 k\ T_{/[a]}V^2}{35\ \hbar^2 a^6\ \delta_N\ \rho^2 S\ c_{[a]}\ V'\ \omega^2}$$

Experimentally we can plot

$$(A_o/A)^2 = 1 + K_{[a]}\ V^2$$

By comparision

$$K_{[a]} = \frac{e^4 q^2\ \gamma_{[a]}^2 D_{[a]}^2\ K^2 k\ T_{/[a]}}{35\ \hbar^2 a^6\ \delta_N\ \rho^2 S\ c_{[a]}\ V'\ \omega^2}$$
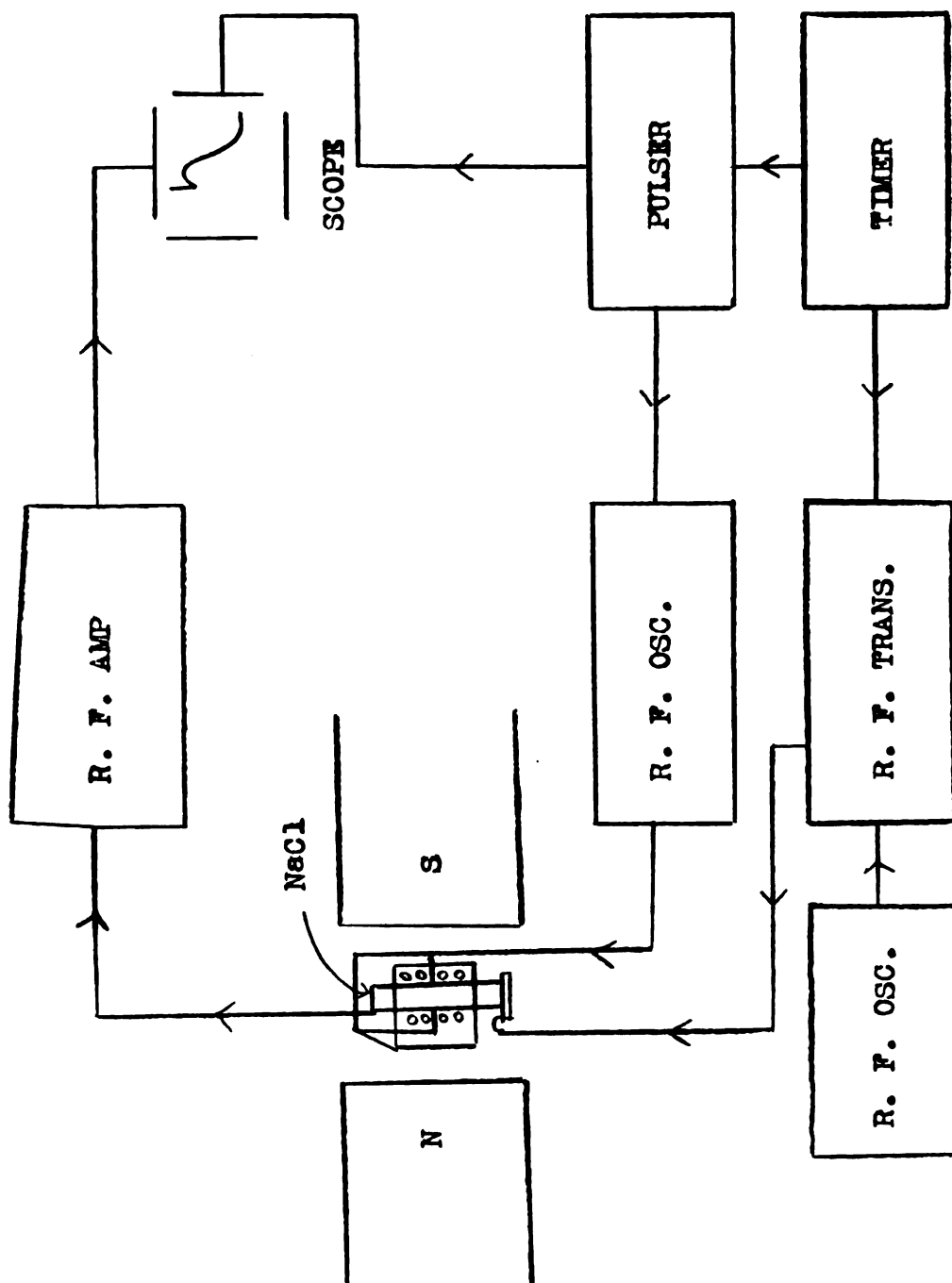
Then

$$\frac{K_{[a]}}{K_{[b]}} = \frac{\gamma_{[a]}^2 \quad D_{[a]}^2 \quad c_{[b]} \quad T_{,[a]}}{\gamma_{[b]}^2 \quad D_{[b]}^2 \quad c_{[a]} \quad T_{,[b]}} \qquad (2)$$

The ratios that are compared are

$$\frac{K_{[100]}}{K_{[110]}} \; , \quad \frac{K_{[100]}}{K_{[11\bar{1}]}} \quad \text{and} \quad \frac{K_{[11\bar{1}]}}{K_{[110]}}$$

in order to detect the presence of any anisotropy in the $\gamma_{[a]}$.

BLOCK DIAGRAM OF APPARATUS

FIG. 2

EQUIPMENT AND EXPERIMENTAL TECHNIQUES

A block diagram of the equipment is shown in Figure 2 and with the exception of the receiver is the same as used by Kraus and Jendrasiak.

The essential parts of the receiver are, a tuned input consisting of the detector coil and a variable capacitor in parallel followed by three slug tuned stages of R.F. amplification. The signal is then rectified by a diode with the large R.F. pulse cut off by an 1N34 crystal diode as shown in Figure 3.
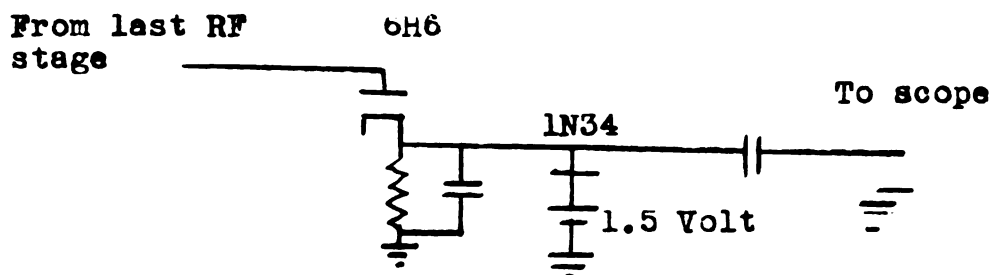

Figure 3

The large magnetic field H_o was made as homogeneous as possible by using proton resonance. The method is as follows: The proton resonance is detected with a marginal oscillator. Then the pole faces are adjusted such that the proton resonance does not change appreciably in frequency over the area of the pole faces.

The sodium chloride crystal was 1 7/8 inches long and

1/2 inches in diameter. The ultrasound in the NaCl crystal was generated by a 10 Mc X-cut quartz crystal coated with silver paint and glued with Duco cement to the end of the NaCl sample. A preliminary experiment showed that if the NaCl sample was used with the ends parallel to each other and perpendicular to its length the ultrasonic impedance would change by a factor of 4 over a range of 20 Kc[7]. When one end was made approximately 3° out of parallel with the other end the ultrasonic impedance was constant.

The R.F. pulse was at a frequency of 5.07 Mc and the frequency of the ultrasound was 10.14 Mc which was well within the tuning range of the quartz.

With the preliminary arrangements taken care of and the equipment adjusted for optimum performance the measurements were taken as follows:

The ultrasound was left on continuously while the measurements were being made. The R.F. field, H_1 was pulsed on for a period of $60\,\mu$ sec. every 3 seconds. The amplitude of the free induction signal was observed for different voltages on the quartz crystal. An A_0 signal, the signal with no ultrasound present, was observed at the beginning and at the end of a series of readings to make sure that the attenuation was caused by the ultrasound.

The measurement of T_1 for each crystal was made with the pulsed nuclear induction apparatus. To make this measurement a 90°-pulse was used. This is an R.F. pulse of

the shortest length such that when repeated in a time t such that $t \ll T_1$ the free nuclear induction signal, A, is O. A 90°-pulse for the sodium nucleus is 140 μ sec. long with 328 peak volts of R.F. with the transmitter coil used. We note that

$$A = A_0(1 - \exp -t/T_1)$$

$$\ln (A_0 - A/A_0) = - t/T_1$$

where t is the time between pulses. Then from a plot of $\ln (A_0 - A/A_0)$ against t on semi-log paper one can obtain T_1 from the slope of the line.

The ultrasonic line widths were measured for each crystal direction to insure that they were invarient. These measurements were made by observing the amplitude of the signal A as a function of the ultrasonic frequency at constant ultrasonic voltage. The characteristic line width was then determined from a graphic plot of A vs. frequency.

EXPERIMENTAL RESULTS

The measurement of T_1 for the three sodium chloride crystals were found to be;

$$T_{1[100]} = 8.1 \pm .5 \text{ seconds}$$
$$T_{1[110]} = 9.7 \pm .5 \text{ "}$$
$$T_{1[111]} = 11.0 \pm .5 \text{ "}$$

Figures 4, 5, and 6 are examples of the type of curve from which T_1 was obtained. It was noted that not only did T_1 change as one changed the direction of the crystal but also it changed slightly as one rotated the crystal about its axis. Since the latter effect had only slight variations the average of the T_1 measurements for each crystal was taken.

Measurement of the ultrasonic line width for the three crystals showed invarience with respect to the crystal direction and a value of $5.30 \pm .30$ Kc was obtained for the three directions.

The speed of sound for the three directions of NaCl was obtained from Kittel[8]. They are
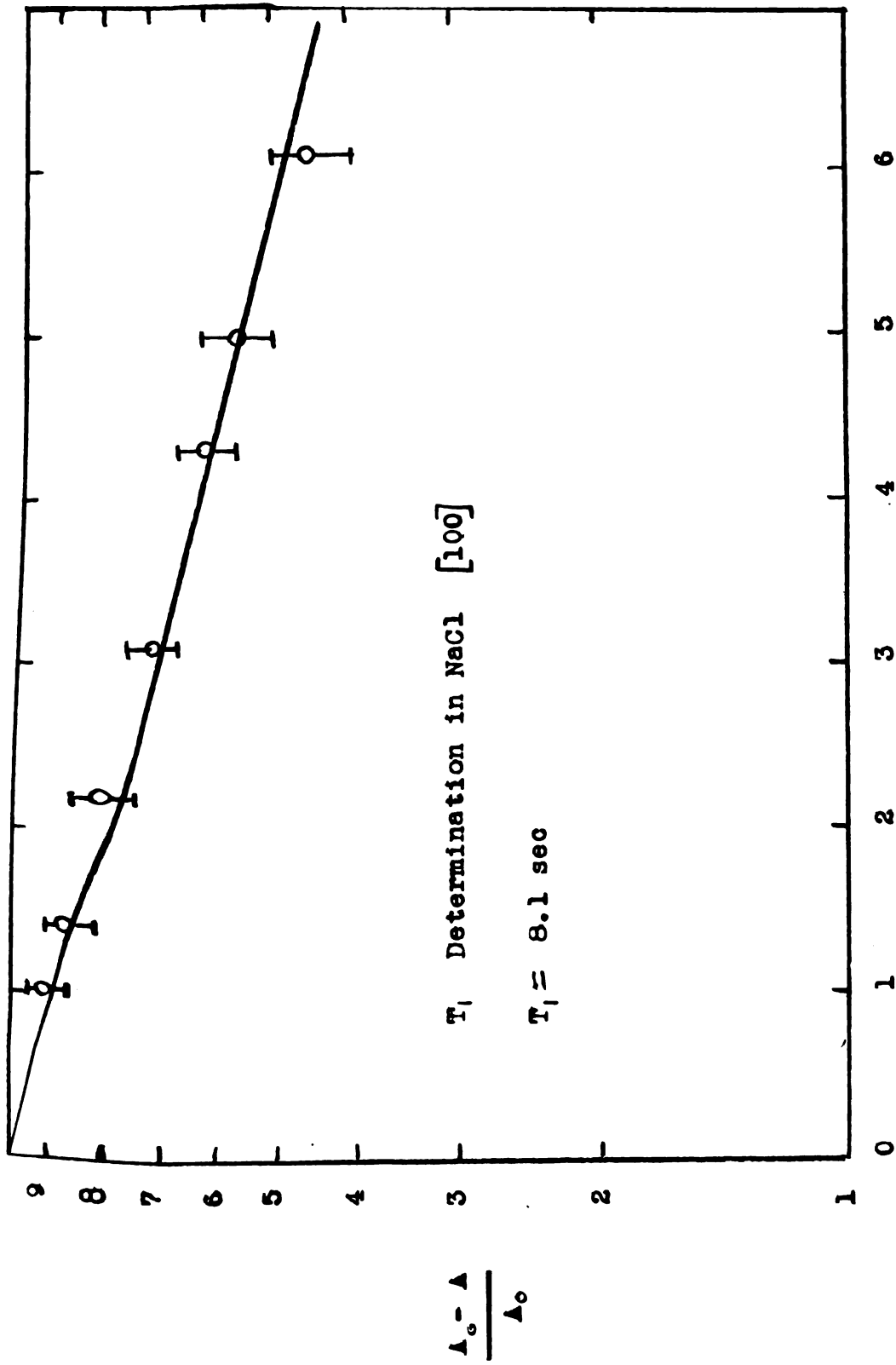
$$c_{[100]} = 4.72 \times 10^5 \text{ cm/sec}$$
$$c_{[110]} = 4.65 \times 10^5 \text{ "}$$
$$c_{[111]} = 4.37 \times 10^5 \text{ "}$$

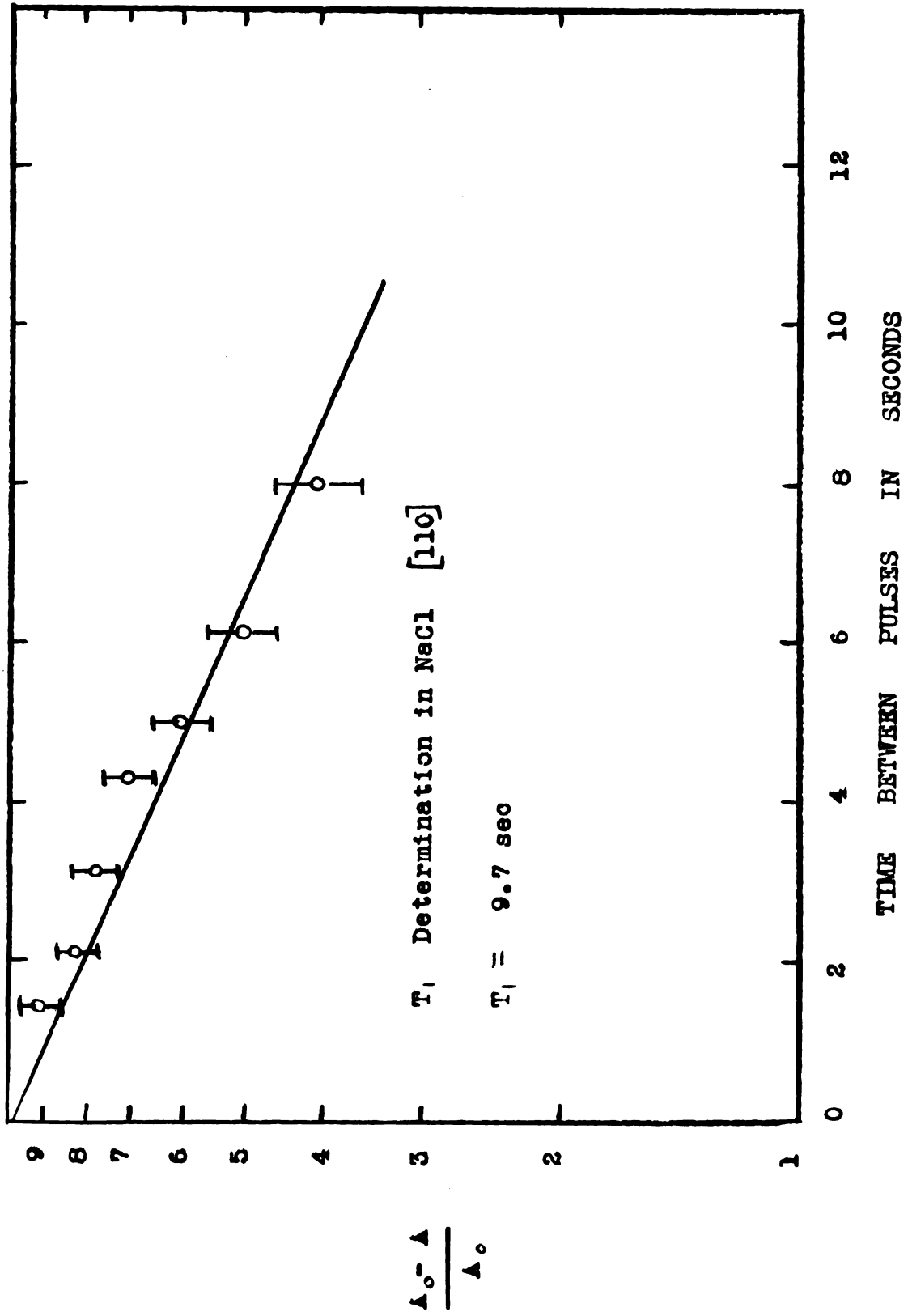Calculation of the $D_{[a]}$'s from equation (1) gives;

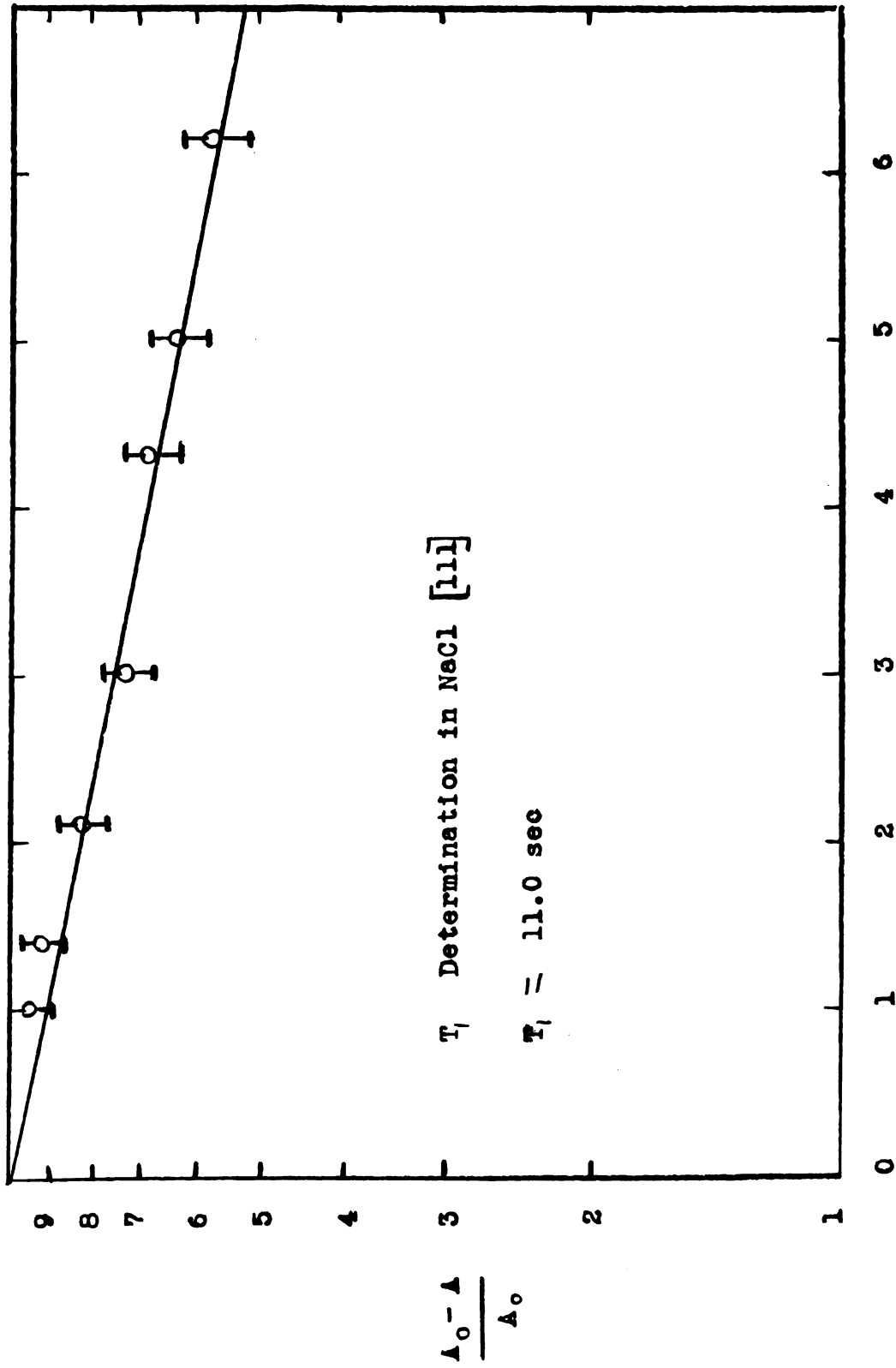$D_{[100]} = 18.00$, $D_{[110]} = 12.70$, and $D_{[111]} = 14.12$. These values were calculated from the nearest and next

T_1 Determination in NaCl [100]

$T_1 = 8.1$ sec

TIME BETWEEN PULSES IN SECONDS

FIG. 4   MEASUREMENT OF T_1[100]

FIG. 5   MEASUREMENT OF $T_1[110]$

T_1 Determination in NaCl [110]

$T_1 = 9.7$ sec

T_1 Determination in NaCl [11]

$T_1 = 11.0$ sec

TIME BETWEEN PULSES IN SECONDS

FIG. 6 MEASUREMENT OF T_1 [11]

nearest ions.

The theoretical ratios calculated from equation (2) are;

$$\frac{K[100]}{K[110]} = 1.62 \left(\frac{\gamma[100]}{\gamma[110]}\right)^2 \pm .08$$

$$\frac{K[100]}{K[111]} = 1.10 \left(\frac{\gamma[100]}{\gamma[111]}\right)^2 \pm .05$$

$$\frac{K[111]}{K[110]} = 1.50 \left(\frac{\gamma[111]}{\gamma[110]}\right)^2 \pm .08$$

Figures 7, 8, and 9 show a plot of (A_0/A) against the square of the quartz voltage for each crystal direction. The slope of the line, $K_{[a]}$, was found to be;

$$K_{[100]} = 10.3/1000 \pm 20\%$$

$$K_{[110]} = 6.7/1000 \pm 20\%$$

$$K_{[111]} = 10.0/1000 \pm 20\%$$

and the ratios of these K values are;

$$\frac{K[100]}{K[110]} = 1.56 \pm .26$$

$$\frac{K[100]}{K[111]} = 1.03 \pm .20$$
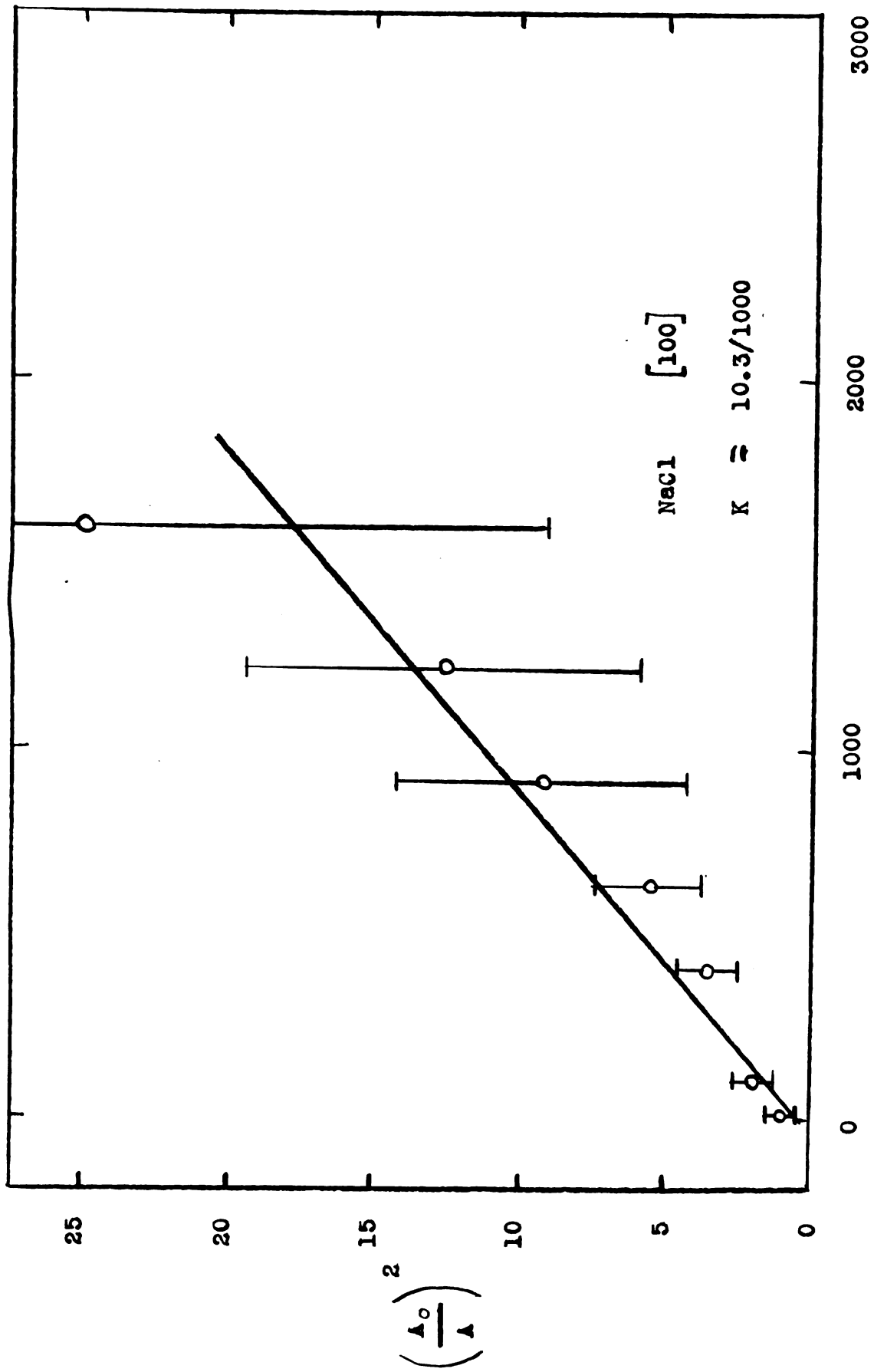
$$\frac{K[111]}{K[110]} = 1.49 \pm .26$$

NaCl [100]

K = 10.3/1000

QUARTZ VOLTAGE SQUARED

FIG. 7 MEASUREMENT OF K [100]

FIG. 8 MEASUREMENT OF K[110]
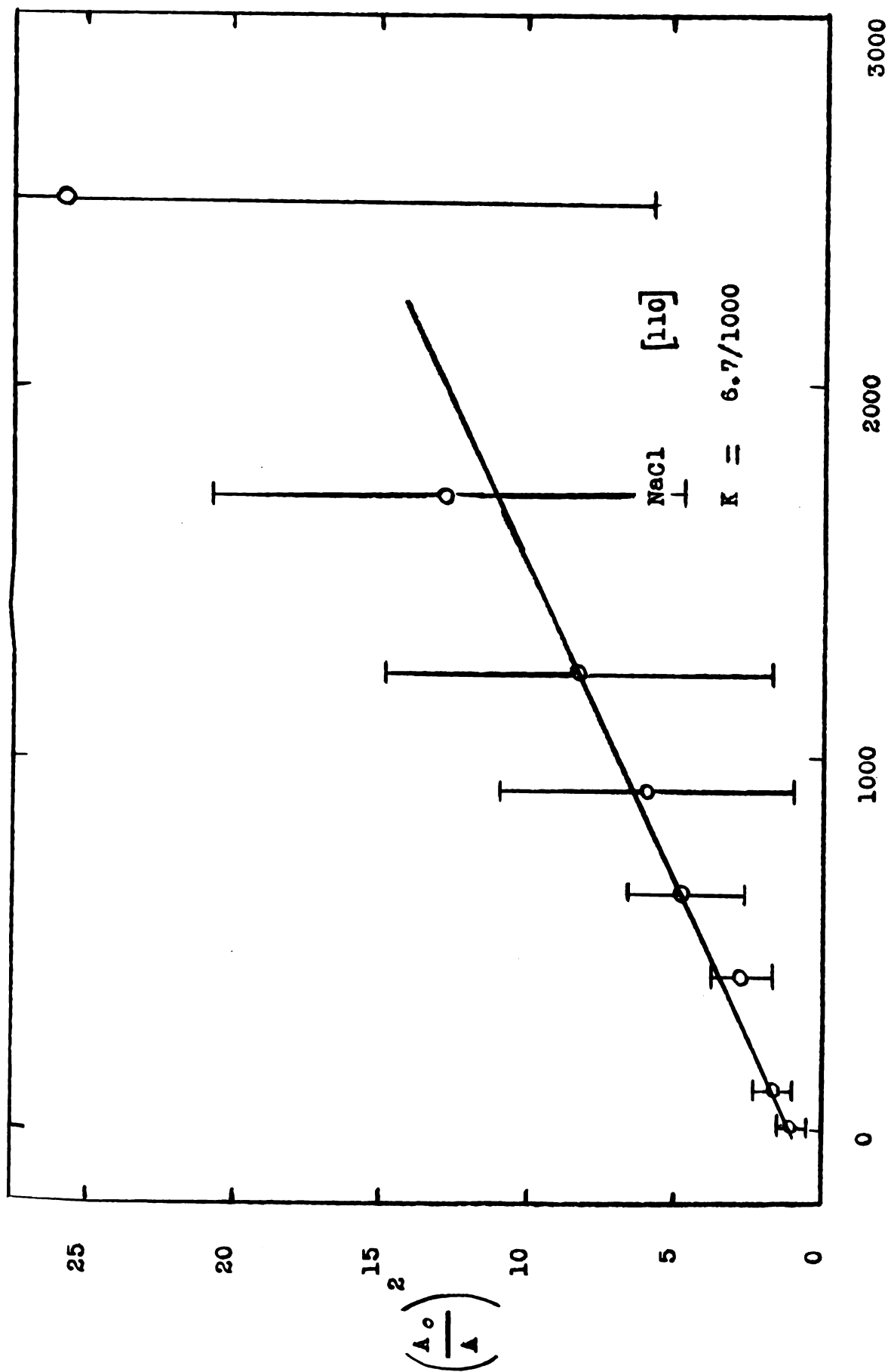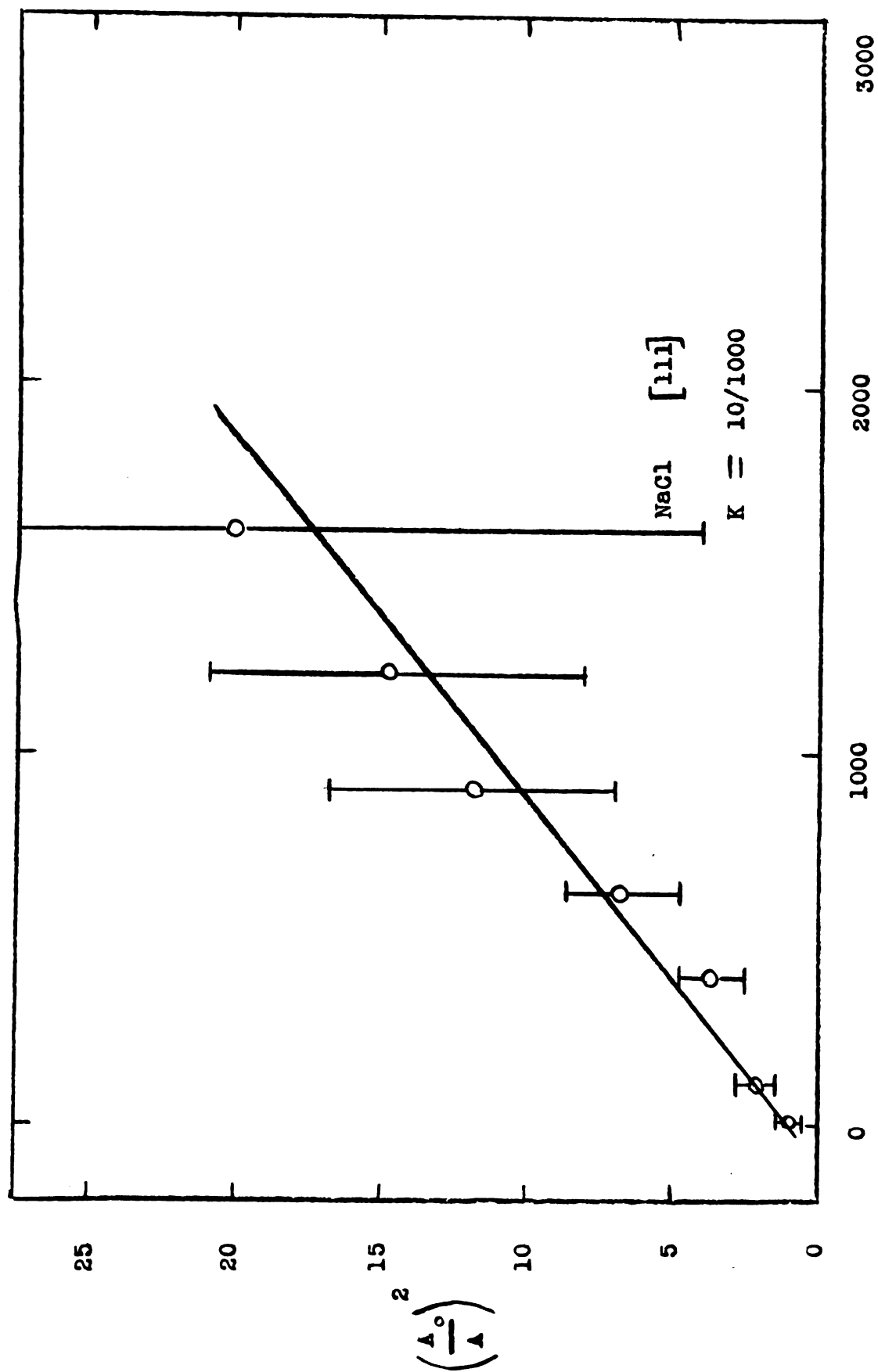
QUARTZ VOLTAGE SQUARED

FIG. 9 MEASUREMENT OF K [11]

DISCUSSION

The experimental results show that γ is isotropic within 20% since the ratios,

$$\frac{\gamma_{[100]}}{\gamma_{[110]}} = \frac{\gamma_{[100]}}{\gamma_{[111]}} = \frac{\gamma_{[111]}}{\gamma_{[110]}} = 1$$

This would indicate that γ is a scalar within the experimental accuracy.

One possible source of error which was not taken into account was the phonon relaxation time, T_ρ, which was assumed the same in all directions. That the phonon relaxation time is the same in all directions is not at all obvious. However, phonon relaxation times are not easy to measure and no attempt was made to measure them.

A small error enters in when one pulses the R.F. at a rate (3 sec.) faster than T_1. The A_o is not the true A_o reading but since one is dealing in ratios, A_o/A, the error is small and compensating.

The results of this experiment support rather well the theory of the interaction of the sodium nuclei and the lattice of sodium chloride given by Kraus.

REFERENCES

1. W. A. Proctor and W. G. Robinson, Phys. Rev. $\underline{104}$, 1344 (1956)

2. O. Kraus, Thesis, (M.S.U.)

3. G. L. Jendrasiak, Thesis, (M.S.U.)

4. J. Van Kranendonk, Physica $\underline{20}$, 781 (1954)

5. M. Bloom, E. L. Hahn and B. Herzog, Phys. Rev. $\underline{97}$, 1699 (1955)

6. O. Kraus and W. H. Tanttila, Phys. Rev. $\underline{109}$, (1958)

7. D. A. Jennings and W. H. Tanttila, Acoust. Sec. Am $\underline{30}$, (1958)

8. C. Kittel, (John Wiley & Sons, Inc., New York, 1953)

9. W. H. Tanttila, Private communication