INTERACTION BETWEEN THE SODIUM NUCLEI AND THE LATTICE OF SODIUM CHLORIDE

By

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A THESIS

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ABSTRACT

The thesis discusses the interaction between the lattice vibrations and the sodium nuclei of a crystal of sodium chloride. One supposes that the quadrupolar interaction between the sodium nuclear quadrupole moment and the electric field gradient in the crystal provides the mechanism which makes possible an exchange of energy between the crystalline lattice and the nuclear spin system.

If the sodium chloride crystal is in a constant external magnetic field, the Zeeman levels of the sodium nuclei are split; and the nuclear-magnetic-resonance frequency for the sodium nuclei is in the radiofrequency region. At room temperature, the intensity of such frequencies in the spectrum of the lattice vibrations is negligible. Using ultrasonic energy, one can, however, excite the low-frequency vibrational modes of the lattice. If ν' is the frequency of the ultrasonic radiation, then one chooses ν' in such a way that $(E_m - E_{m+2}) = h\nu'$, where m is the magnetic quantum number for the sodium nuclei. Consequently, the ultrasonic energy, by means of the quadrupolar coupling between the lattice and nuclear spin system, produces $\Delta m = \pm 2$ transitions of the sodium nuclei.

Experimentally, one subjects the sodium chloride crystal to a pulse of ultrasonic energy. Several hundred milliseconds later, one applies a radiofrequency pulse of frequency ν, with $\nu = \frac{\nu'}{2}$. Consequently, the radiofrequency energy produces $\Delta m = \pm 1$ transitions of the sodium nuclei. The amplitude of the nuclear induction signal which follows the radiofrequency pulse is a measure of the difference between the populations of adjacent Zeeman levels; hence, the amplitude of the induction signal permits one to study how effectively the ultrasonic energy produces nuclear transitions. This means one can check the hypothesis that the nuclear spin system and crystalline lattice are coupled through the quadrupolar interaction.

One assumes a simplified model for the sodium chloride lattice: the six nearest neighbors of a sodium nucleus are replaced by six equal point charges of magnitude γe, where γ is a parameter, and e is the electronic charge. The experimental data enables one to compute a numerical value for γ, and the result is $\gamma = 0.68$. Measurement of the spin-lattice relaxation time, T_1 for the sodium nuclei in sodium chloride is also part of the experimental work. A value of $T_1 = 7.15$ sec. is the result of the measurement.

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CHAPTER I

INTRODUCTION

Waller[1] gave the first theoretical treatment of electronic paramagnetic relaxation in crystals. The theory assumed that the time variation of the crystalline magnetic field at the site of an electronic spin is responsible for the coupling between the lattice and the spin system. A simple modification made the theory applicable to nuclear paramagnetism; however, the theoretical relaxation times were much longer than the experimental values. In order to account for the nuclear spin-lattic relaxation times which were observed experimentally, Bloembergen[2] and Hatton and Rollin[3] proposed that electronic paramagnetic impurities were responsible for the spin-lattice coupling. Indeed the presence of paramagnetic impurities explained the relatively short spin-lattice relaxation times; however, nuclear magnetic resonance in solids had been confined largely to either protons or nuclei with spin $I = \frac{1}{2}$ Since the nuclear quadrupole moment of nuclei with spin $I < 1$ is zero, no quadrupole effects were observed.

Pound[4] presented the first discussion of nuclear electric quadrupole interactions in crystals and their effects on the nuclear resonance of atomic nuclei in solids. Pound's investigations showed that the interaction of a nuclear quadrupole moment with the electric field gradient produced by neighboring charges broadened and split the nuclear resonance absorption line. Of more importance for our discussion, however, is the fact that the quadrupolar interaction could account for the spin-lattice relaxation times. The experimental evidence indicated that the nuclear quadrupolar interaction was important in crystals with cubic symmetry. After Pound's experimental work J. van Kranendonk[5] wrote a theory for the effect of the nuclear quadrupolar interaction on the spin-lattice relaxation time.

Two processes account for the spin-lattice relaxation of electrons or nuclei in solids: direct and indirect processes. The indirect process is a Raman scattering of phonons, and the direct process requires the annihilation or creation of a phonon accompanied by a transition of an electronic or nuclear spin between magnetic energy levels. Van Kranendonk is concerned with the indirect process. He assumes that a phonon of initial energy $h\nu$ is scattered into a final state with the energy $h\nu'$. The absolute value of the difference between $h\nu$ and $h\nu'$ is the energy of the nuclear spin transition. The nuclear quadrupolar interaction is the only mechanism which van Kranendonk considers responsible for the phonon scattering. If one assumes a Debye distribution for the lattice oscillators, then the theory predicts that the probability of a nuclear transition as a result of a thermal Raman process is proportional to T^7, where "T" is the absolute temperature of the lattice, at temperatures below 0.02Θ (Θ is the Debye temperature). At higher temperatures the transition probability is proportional to $T^2(a - b/T^2)$, where "a" and "b" are constants.

Van Kranendonk applies his theory to a model in which a lattice of the sodium chloride type is replaced by a central nucleus surrounded octahedrally by six equal point charges. The magnitude of the point charges is a variable parameter of the model. In order to obtain spin-lattice relaxation times which agree with experimental values, van Kranendonk finds the point charges must be from 100 to 1000 times the electronic charge. It is difficult to make a comparison between theoretical and experimental results. One knows very little about the quadrupolar interaction.

As Sternheimer[6] and others[7] have shown, the nuclear quadrupole moment induces a quadrupole moment in the electronic shells associated with the nucleus. The induced moment can reduce or enhance (shielding and antishielding effect) the quadrupole moment of a bare nucleus. The actual electric field gradient which a nucleus in a crystalline lattice experiences is also difficult to estimate. Watkins,[8] for example, found that strains in an ionic crystal can produce an electric field gradient. Apparently, the strains cause a mixing of p- and d-type orbitals to the original s-type electronic wave functions of the ions.

Two articles by C. A. Altshuler[9, 10] treat the absorption of ultrasonic energy by spin systems. One generally supposes that the interaction of the electronic magnetic moments with the lattice vibrations of a solid provides a means for the relaxation of the electronic spins after their excitation by resonance absorption of electromagnetic energy. Altshuler considers the possibility of splitting the electronic magnetic energy levels by placing a paramagnetic salt in a constant magnetic field and then producing transitions between the energy levels by means of ultrasonic energy at the resonance frequency. (According to Altshuler, the effect was also considered by Zavoisky.) Lattice vibrations modulate the crystalline electric field. Variation of the crystalline electric field affects the orbital motion of the electron, and the lattice vibrations are coupled to the electron spin through the spin-orbit interaction. In the second paper Altshuler discusses the modulation of internal crystalline magnetic fields as a second mechanism for the transfer of ultrasonic energy from the lattice to electrons or nuclei.

Our discussion has mentioned the direct and indirect processes which account for the spin-lattice relaxation time of electrons and nuclei. Since transitions of electronic or nuclear spins correspond to frequencies which lie in the radiofrequency region, the direct process is negligible until one reaches liquid helium temperature. One must keep in mind, however, that the ultrasonic excitation of an electronic or nuclear magnetic moment to a higher energy state represents a direct process; hence, the frequency of ultrasonic energy will equal the transition frequency.

Altshuler's order-of-magnitude estimates indicate that the resonance absorption of ultrasound by nuclei in solids would be very small. He considers both dipole-dipole and quadrupole coupling of the nuclei to the lattice of the crystal. In liquids, according to Altshuler, conditions are quite favorable for the absorption of ultrasonic energy by nuclei; and he states that one should observe ultrasonic saturation of the nuclear spin system. Now the possibility of indirectly observing the absorption of ultrasound arises. For example, suppose one observes nuclear magnetic resonance absorption of electromagnetic energy. Then the application of an ultrasonic field of the correct frequency and the subsequent saturation of the nuclear spins should destroy the resonance absorption of electromagnetic energy. At the present time absorption of ultrasound by nuclear spins has been observed only by means of this indirect method.

Proctor and Tanttila[11] made the first observation of the influence of ultrasonic energy on the nuclear spin-lattice relaxation time. Ultrasonic vibrations whose frequency equaled the frequency for a nuclear magnetic dipole transition between the pure quadrupolar energy levels of chlorine nuclei in sodium chlorate saturated the energy levels. By applying pulsed radiofrequency energy of the same frequency as the ultrasonic energy and observing the induction signal, the experimenters were able to detect the degree of saturation of the energy levels. (The appearance of an induction signal as a result of the precession of a nuclear quadrupole moment in a non-uniform electric field is discussed in detail by Bloom, Hahn, and Herzog.[12]) The experimental results are compared with a theory proposed by Chang.[13] Chang's theory specifically treats the pure quadrupole resonance of chlorine in sodium chlorate. Proctor and Tanttila find good agreement between experiment and theory for the temperature dependence of the indirect process; however, there is poor agreement between experiment and theory for the dependence of the direct-process relaxation time on the energy density of the ultrasound.

In a later experiment Proctor and Robinson[14] studied the effect of ultrasound on the relaxation time of sodium nuclei in sodium chloride. The experimenters made use of the amplitude of the induction signal, which was produced by the precessing nuclear magnetic moments in a steady magnetic field, to sample the population difference between the magnetic energy levels of a sodium nucleus. The ultrasonic vibrations produced nuclear spin transitions which corresponded to $\Delta m = \pm 2$ where "m" is the magnetic quantum number of the nuclear spin. At the same time, the radiofrequency field produced transitions which corresponded to $\Delta m = \pm 1$. On the basis of a classical model, Robinson computes the electric field gradient which a sodium nucleus experiences. (The ultrasonic waves remove the cubic symmetry of the crystalline electric field.) He compares the calculated gradient with the value obtained from his experimental data. Agreement between the two values is good, and Robinson suggests that van Kranendonk's theory is unnecessary. The data do not tell whether the dipolar or quadrupolar interaction is the more important in determining the spin-lattice relaxation time, but it suggests that the quadrupolar interaction is more important.

This thesis reports the results of an experiment which is a modification of Proctor and Robinson's experiment. Proctor and Robinson used a roughened sodium chloride crystal for a sample and assumed that the ultrasonic phonons were scattered isotropically by the irregularities in the end of the sample. The experiment reported by this thesis concerns unidirectional standing ultrasonic waves in the sodium chloride crystal.

CHAPTER II

EQUIPMENT

A block diagram of the apparatus appears in Fig. 1, and a discussion of the individual components of the apparatus follows.

The magnet

An electromagnet supplied a constant magnetic field. Storage batteries served as a source of current for the magnet, and three batteries in series (96 volts) provided the most stable operating conditions. In order to obtain the sodium resonance with a radiofrequency field of five megacycles/sec., the magnet windings required a current of 6.8 amperes. Three rheostats made possible variation of the current through the windings. A "fine" adjustment of the field was obtained by a rheostat which consisted of flat nichrome wire wound on a ceramic cylinder. A screw of the proper pitch allowed an electrical contact to move along the nichrome wire as one rotated the screw. The magnet windings and the rheostats were water-cooled.

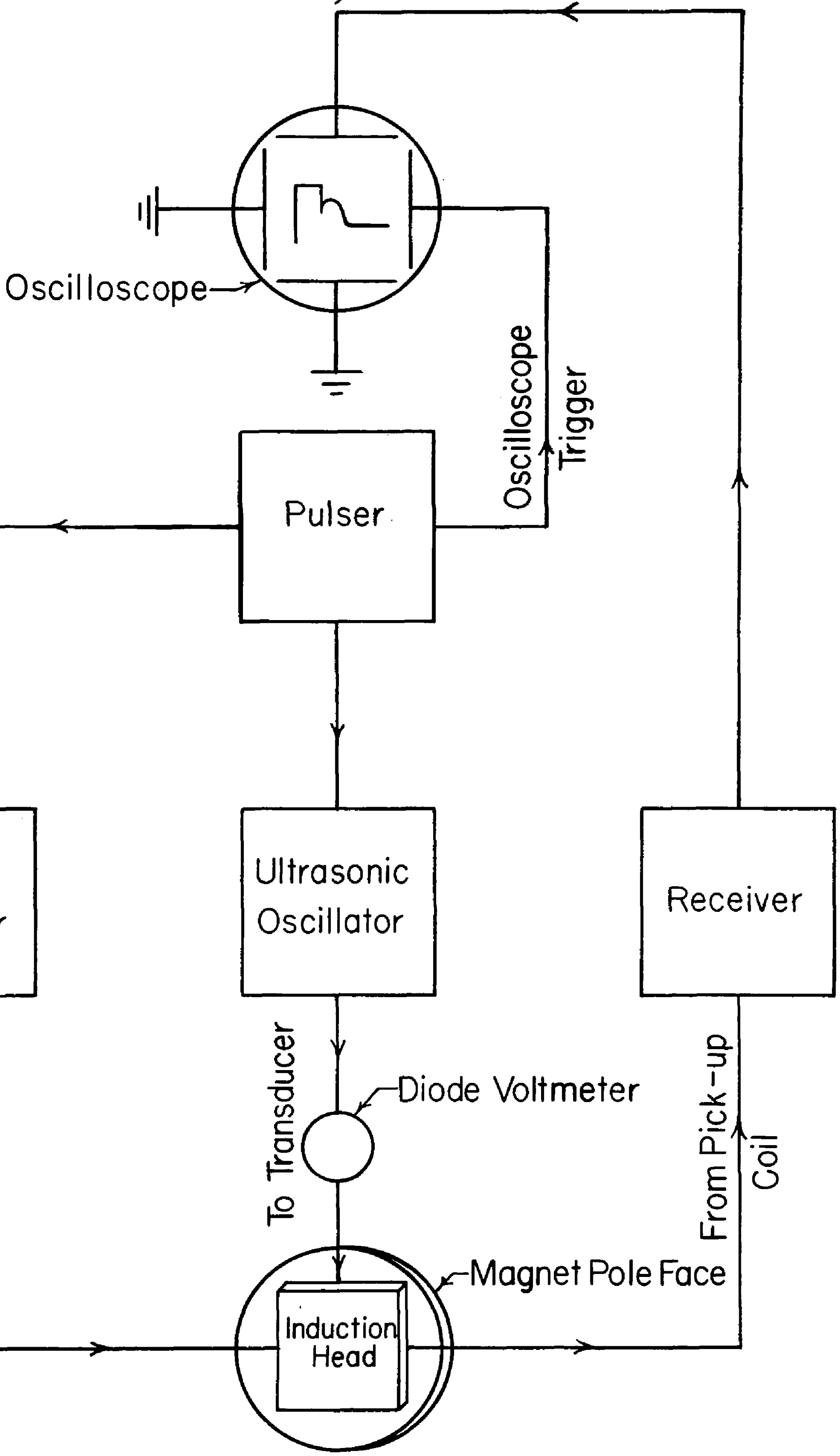


Fig. 1 Block Diagram of Apparatus

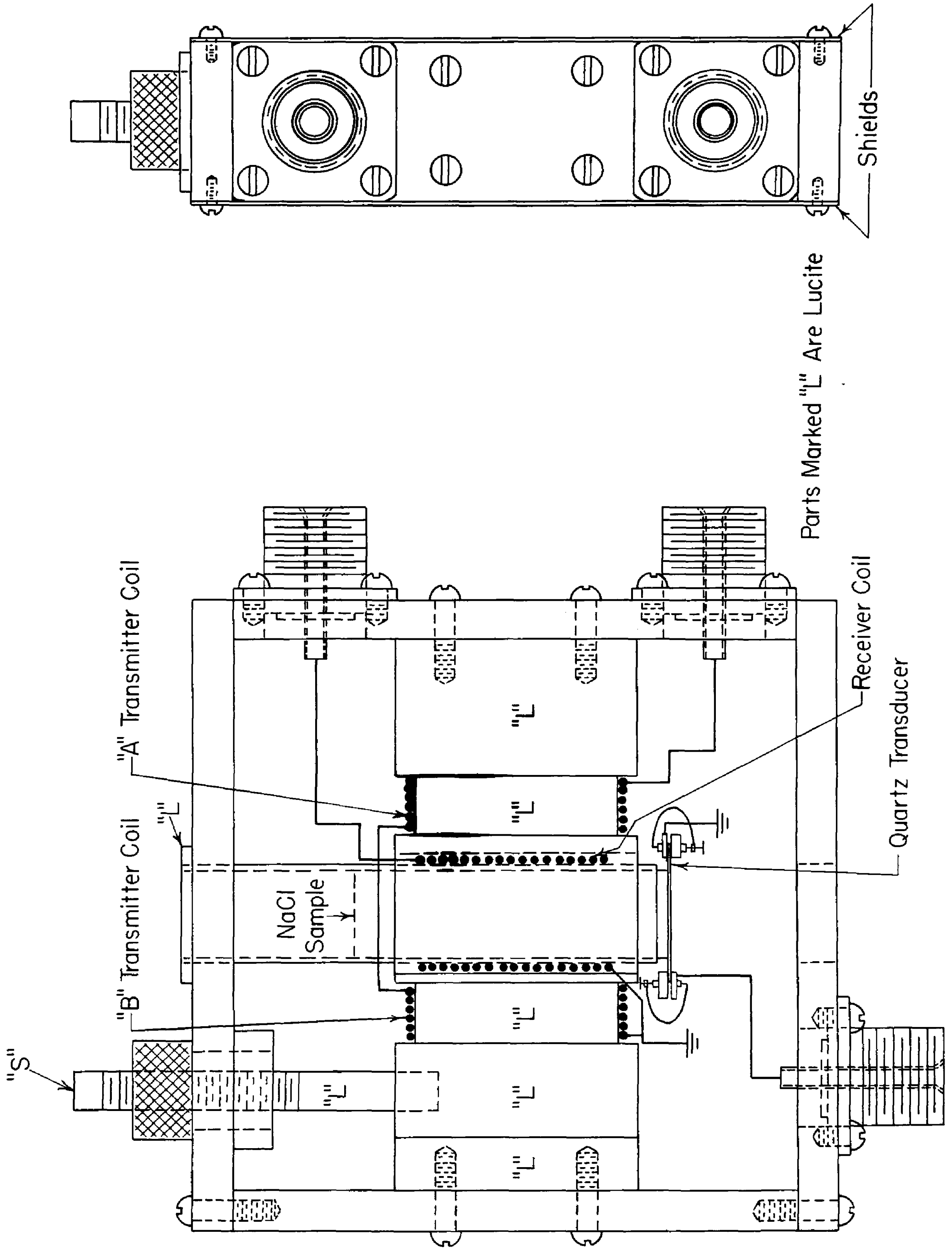
The pole pieces of the magnet were eight inches in diameter and unpolished. The experiments were performed with the pole pieces separated 1-1/8 inches. No attempt was made to measure either the magnitude of the magnetic field in the gap or the homogeneity of the field.

Unfortunately, the magnetic field did not remain constant for a period of time longer than one minute, usually less; hence, the drift of the magnetic field was a constant source of trouble. Although the storage batteries had a capacity of 400 ampere-hours, the provision of a steady magnetic field by current from them was inadequate for the experiment.

The induction head

Fig. 2 is a drawing of the induction head. The transmitter coils A and B are orthogonal to the receiver coil R. Each transmitter coil contains three turns of No. 16 copper wire, and the receiver coil contains 16 turns of No. 18 copper wire.

Since a pulse of intense radiofrequency energy is applied to the transmitter coils, one must take measures to prevent saturation of the radiofrequency receiver because of coupling between the receiver coil and the transmitter



Parts Marked "L" Are Lucite

Fig. 2 Induction Head

coils. Two features of the induction head are designed to reduce inductive coupling between the coils. First, the coils are orthogonal and second, screw S permits one to displace transmitter coil A relative to both transmitter coil B and the receiver coil. Capacitive coupling remains, however, and other steps are necessary to reduce receiver saturation.

Easy removal of the bottom plate of the induction head facilitated introduction of samples for study into the receiver coil. The coaxial fitting F provided a means for connecting the ultrasonic oscillator to the induction head. Aluminum plates covered the sides of the head and supplied the necessary shielding.

The radiofrequency oscillator

Except for several minor changes, the circuit for the radiofrequency oscillator is the same as the circuit which Bloom, Hahn, and Herzog[12] used for their studies of free magnetic induction in nuclear quadrupole resonance. A change of the inductance of the tank circuit allowed the oscillator to operate at a frequency in the neighborhood of five megacycles/sec. Values of several capacitors were changed in order to obtain a well-shaped rectangular pulse of radiofrequency energy when the oscillator was gated on. During operation, the optimum value of the plate voltage for the oscillator tube (829-B) was 1175 volts. Addition of a potentiometer to grid circuit of the 6L6 tube allowed one to vary the negative bias of the grid. The maximum amplitude of the radiofrequency envelope at the output terminals of the oscillator was 240 volts.

The pulser

Fig. 3 is a drawing of the pulsing circuit. The pulser contains timing circuits which supply either one pulse of variable duration or two successive pulses of variable duration and spacing. Also the repetition rate of an event (one pulse or two pulses in succession) is variable. The pulser was used to make relaxation time measurements as well as to study the effect of ultrasonic energy on the relaxation time. Each experiment placed different requirements on the pulser; consequently, the timing circuits were modified for the different experiments.

Relaxation time measurements required a single pulse with a variable repetition rate and a pulse width which was variable from a few to several hundred microseconds. By changing the time constants associated with the multi-

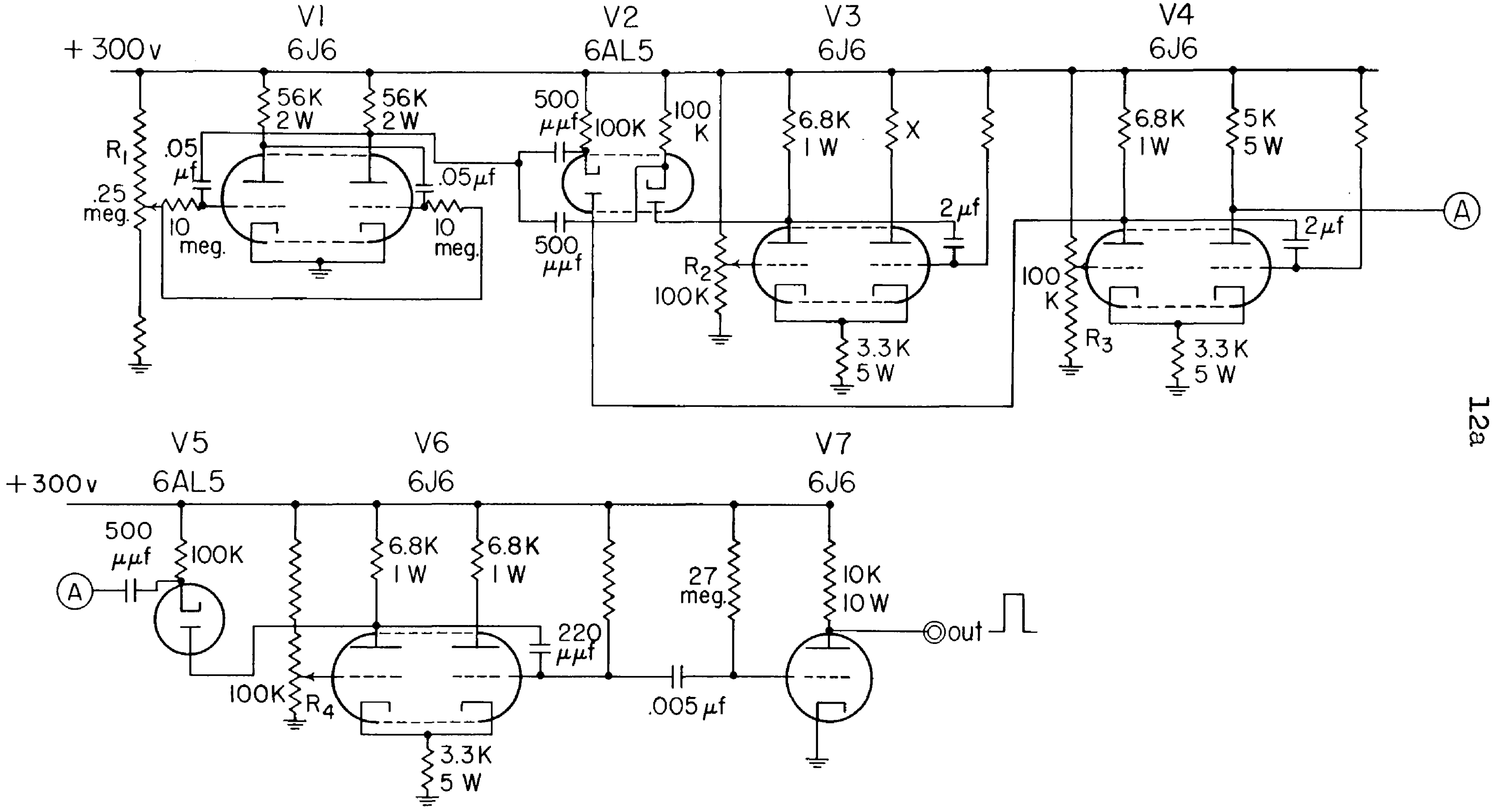

V1
6J6
V2
6AL5
V3
6J6
V4
6J6
+ 300v
56K
2 W
56K
2 W
R1
.25
meg.
.05
μf
.05μf
10
meg.
10
meg.
500
μμf
100K
100
K
500
μμf
6.8K
1 W
X
2μf
R2
100K
3.3K
5 W
6.8K
1W
5K
5 W
2μf
A
100
K
R3
3.3K
5 W
V5
6AL5
V6
6J6
V7
6J6
+300v
500
μμf
A
100K
6.8K
1 W
6.8K
1 W
220
μμf
27
meg.
10K
10 W
out
100K
R4
3.3K
5 W
.005μf

Fig. 3 Pulser

vibrator V1, one changed the repetition rate. A double-pole, double-throw switch made it possible to insert two different combinations of resistance and capacitance; and the potentiometer R1 allowed a continuous variation of the repetition rate over the range determined by the resistance-capacitance combination. The circuit supplied repetition rates from approximately 0.80 pulses/sec. to 0.085 pulses per second.

For the relaxation time measurements the plate of V3 was connected capacitively to the grid of V7. Tube V7 amplified the pulse, and one obtained a positive pulse whose amplitude was approximately 120 volts at the output of the pulser. Application of the positive pulse to the grid of the 6L6 in the radiofrequency oscillator caused the tube, which was normally biased beyond cutoff, to conduct; hence, the pulse gated the oscillator. Potentiometer R2 allowed one to vary the width of the pulse.

The ultrasonic studies required two pulses in succession: first a pulse approximately four seconds long and then approximately 300 milliseconds later a pulse of the order of 60 microseconds long. Both the duration of the pulses and their spacing were variable. The four-second pulse required long time constants in the circuits of V3 and V4. Two microfarad capacitors supplied sufficient capacitance. Variation of potentiometer R2 changed the duration of the first pulse, and variation of R3 changed the spacing between the first and second pulses. Potentiometer R4 determined the width of the second pulse.

By means of a relay the first pulse gated an oscillator whose output drove a quartz transducer. The winding of the relay coil replaced the resistor marked "X" in the plate circuit of V3. One pole of the relay was connected to a source of approximately 400 volts dc; and the other pole of the relay was connected to ground. The moving contact of the relay was connected to the screen grid of the 807 tube in the ultrasonic oscillator (see Fig. 5). Application of the positive voltage to the screen grid gated the oscillator on, and connection of the screen grid to ground turned the oscillator off. In this manner the first pulse controlled the ultrasonic oscillator.

Tube V6 supplied the second pulse. Tube V7 amplified and inverted the output from V6. As a result, one obtained from V7 a positive pulse with an amplitude of approximately 120 volts. The positive pulse gated the radiofrequency oscillator just as it did for the relaxation time measurements. During the ultrasonic experiments, the repetition rate was constant at 0.085 pulses/sec. A regulated power supply provided the plate voltages for the tubes in the pulser circuits.

The receiver

The receiver supplied the most difficult electronic problems. The experiments required the detection of a nuclear induction signal which followed an intense pulse of radiofrequency energy. Since it was impossible to avoid pickup of the radiofrequency pulse by the receiver coil, the possibility of receiver saturation was always present. However, saturation of the receiver for more than several microseconds after the radiofrequency pulse made it impossible to detect nuclear induction in solids. Detection of the sodium induction signal demanded that the receiver have considerable gain with a good signal-to-noise ratio. In general one can say that the experiments required a high-gain receiver with a band pass of several megacycles.

Fig. 4 is a circuit diagram of the receiver. It has four stages and a detector. Each stage is single-tuned by means of a slug-tuned coil. The 6AC7 has large transconductance; and hence, provides a good mean stage gain for a

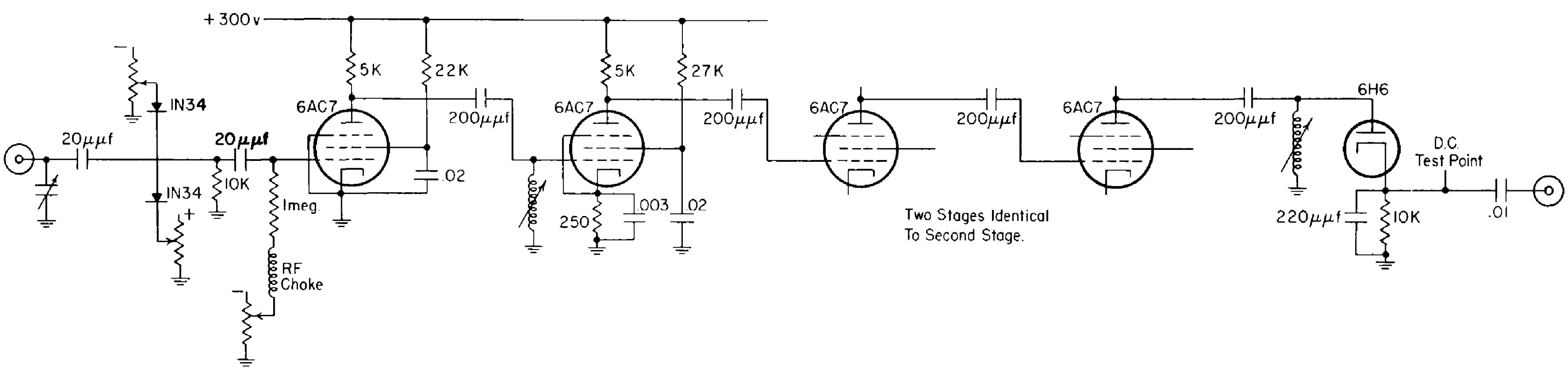


Fig. 4 Receiver

band pass of several megacycles. Adjustment of the receiver for the best response to a nuclear induction signal determined the final tuning. Variable capacitor C1 together with the receiver coil formed a tuned input circuit for the receiver. Only the first stage was gain controlled, and the control was accomplished by varying the negative grid bias of the first stage.

The circuit diagram shows two crystal diodes connected to the grid lead of the first stage; their purpose was to prevent excessive saturation of the receiver. The diodes with proper bias bypassed to ground all positive and negative signals whose amplitudes exceeded seven microvolts. Consequently, the diodes reduced any pick up from the radiofrequency pulse; but they allowed the nuclear induction signal to pass freely.

The receiver was completely shielded, and it was connected to an external ground through a heavy lead. A regulated power supply provided the plate and screen voltages.

The receiver performed satisfactorily and adequately for the experiments. One could obtain an induction signal from protons in glycerine with a signal-to-noise ratio of forty to one; and the signal-to-noise ratio for the induction signal from the sodium nuclei in sodium chloride was approximately 10:1, when the signals were displayed on a Tektronix type 531 oscilloscope.

The ultrasonic oscillator

A Hartley-connected oscillator supplied the driving voltage for the ultrasonic transducer, and Fig. 5 shows a circuit diagram for the ultrasonic oscillator. The resistor in the screen-grid circuit made the oscillator respond sharply to the gating pulse. A description of the gating device and the method of gating appears in the discussion of the pulser.

In order to obtain a large output voltage, the pickup coil was wound concentrically about the inductor in the tank circuit. The output from the oscillator was connected through a coaxial cable to the terminals of the quartz transducer. A variable plate supply voltage for the 807 tube permitted one to change the output voltage of the oscillator. In turn, a Variac connected across the primary of the power transformer for the plate power supply made possible variation of the plate voltage for the oscillator. As a result the peak voltage, measured with a diode voltmeter, across the terminals of the transducer was continuously variable from 10 to 55 volts.

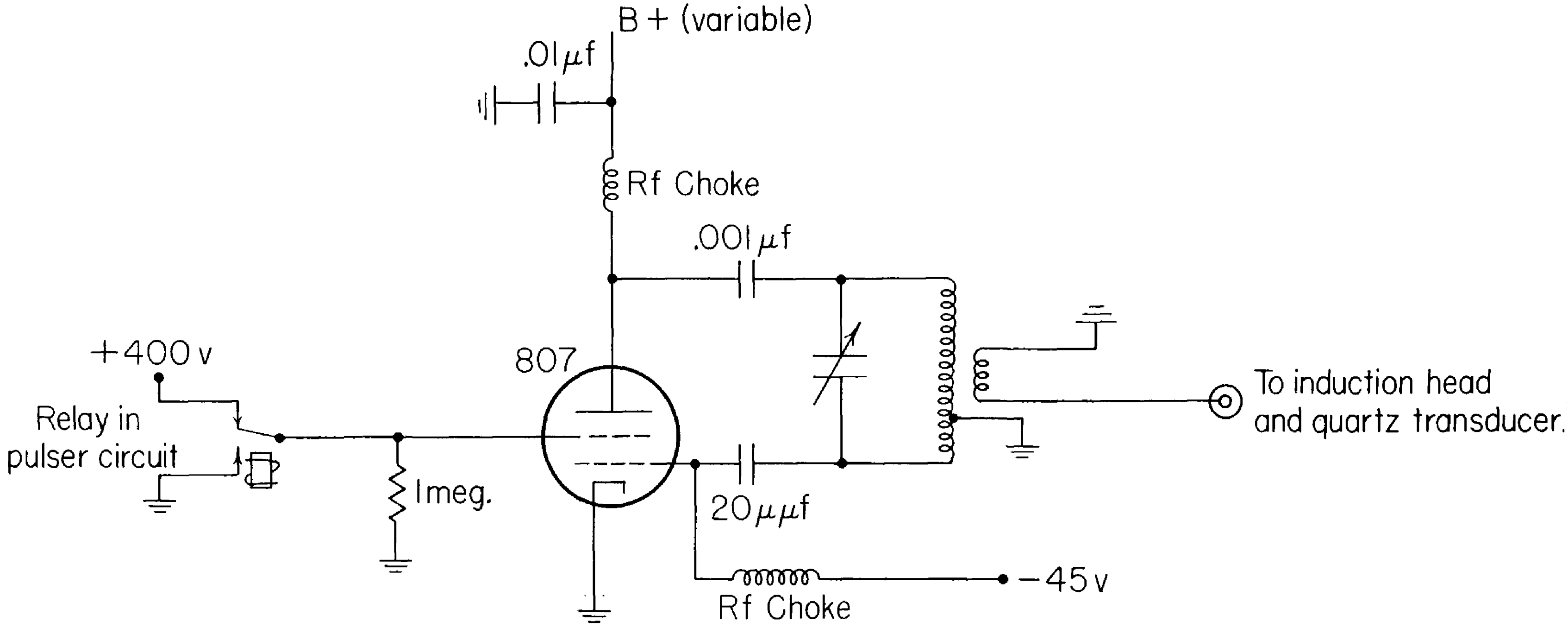


Fig. 5 Ultrasonic Oscillator

The diode voltmeter used to measure the transducer voltages consisted of a 6AL5 diode and a capacitor. A Simpson meter connected across the capacitor indicated peak voltage. The voltmeter was inserted in the coaxial line which led from the oscillator to the transducer by means of a coaxial "T" connector. The "T" was located approximately six inches from the induction head.

CHAPTER III

THEORY

The Ultrasonic Transition Probability

Consider a single crystal of sodium chloride placed in a constant magnetic field, $\vec{H}_0$. We are interested in the interaction of the magnetic moment of a sodium nucleus with $\vec{H}_0$ and the interaction of the sodium nuclear quadrupole moment with an electric field gradient produced by charges surrounding the sodium nucleus. We suppose that the Zeeman interaction is much stronger than the quadrupolar interaction; hence, we treat the quadrupolar interaction as a perturbation of the Zeeman energy. A sound wave in the crystal modulates the quadrupolar interaction, and the quadrupolar interaction supplies a coupling between a sodium nucleus and the crystal lattice. We choose a Cartesian coordinate system which is fixed in the crystal and whose z-axis coincides with the direction of the magnetic field, $\vec{H}_0$. What is the probability per unit time that the sound wave will produce a transition of the sodium nucleus between its Zeeman energy levels?

The electrostatic potential

Let N be a sodium nucleus and q_α be an external charge. Suppose the sound wave displaces the nucleus, N by $\vec{S}^{(0)}$ and the charge q_α by $\vec{S}^{(\alpha)}$ (see Fig. 6). Here $\rho_m(r)$ is the nuclear charge density at a position $\vec{r}^{(m)}$ from the center of mass of the nucleus. We assume that after a displacement of the nucleus the nuclear charge distribution remains unchanged with respect to the nuclear center of mass. After displacement the electrostatic potential at $\vec{r}_m$ due to the charge q_α is

$$V_\alpha = \frac{q_\alpha}{\eta^{(\alpha)}} . \qquad (1)$$

We expand $\frac{1}{\eta^{(\alpha)}}$ as a function of $r^{(\alpha)}$, $r^{(m)}$, and $\cos\Theta_\alpha$; and the term which arises from the nuclear quadrupole moment is

$$\frac{(r^{(m)})^2}{(r^{(\alpha)})^3} P_2(\cos\Theta_\alpha)$$

, where $P_2(\cos\Theta_\alpha)$ is the Legendre polynomial of order two. Now we have

$$\cos\Theta_\alpha = \frac{\vec{r}^{(\alpha)} \cdot \vec{r}^{(m)}}{(r^{(\alpha)})(r^{(m)})} . \qquad (2)$$

We write the Cartesian components of the vectors in Fig. 6 as follows:

$$\vec{r}^{(m)} = (x^{(m)}, y^{(m)}, z^{(m)}) = (x_i^{(m)}) \qquad (i = 1,2,3)$$

$$\vec{R}^{(\alpha)} = (X^{(\alpha)}, Y^{(\alpha)}, Z^{(\alpha)}) = (X_i^{(\alpha)}) \qquad (i = 1,2,3)$$

$$\vec{S}^{(\alpha)} = (x^{(\alpha)}, y^{(\alpha)}, z^{(\alpha)}) = (x_i^{(\alpha)}) . \qquad (i = 1,2,3)$$

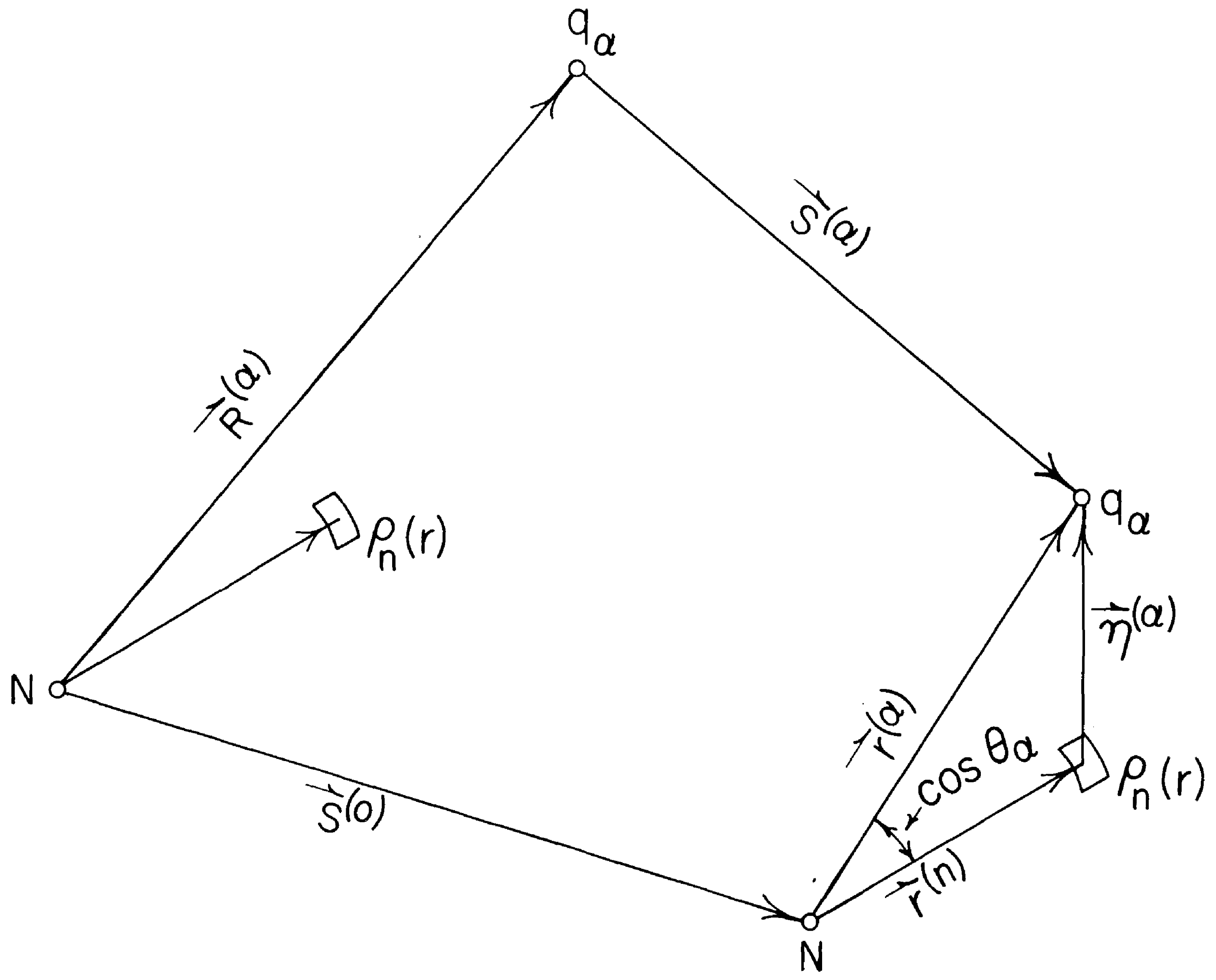


Fig. 6 Positions of Nucleus, N and Charge, q_α Before and After Displacement.

$$\vec{S}^{(0)} = (x^{(0)}, y^{(0)}, z^{(0)}) = (x_i^{(0)}) \qquad (i = 1,2,3)$$

Then $\vec{r}^{(\alpha)} = \vec{R}^{(\alpha)} + \vec{s}^{(\alpha)} - \vec{S}^{(0)}$, (2a)

or $r_i^{(\alpha)} = (X_i^{(\alpha)} + x_i^{(\alpha)} - x_i^{(0)}) = (X^{(\alpha)} + x^{(\alpha)} - x^{(0)})_i$.

The product $\vec{r}^{(\alpha)} \cdot \vec{r}^{(m)}$ becomes

$$\vec{r}^{(\alpha)} \cdot \vec{r}^{(m)} = \sum_{i=1}^{3} (X^{(\alpha)} + x^{(\alpha)} - x^{(0)})_i \cdot x_i^{(m)} . \qquad (3)$$

With the definition $X_i^{(e)} \equiv (X^{(\alpha)} + x^{(\alpha)} - x^{(0)})_i$,

where (e) refers to a charge outside the nucleus, substitution yields

$$\vec{r}^{(\alpha)} \cdot \vec{r}^{(m)} = \sum_{i=1}^{3} X_i^{(e)} x_i^{(m)} = X_i^{(e)} x_j^{(m)} \delta^{ij}$$

(i, j = 1, 2, 3), where summation over the indices i and j is implied.

From eq. (2)

$$\cos^2 \Theta_\alpha = \frac{X_i^{(e)} x_j^{(m)} \delta^{ij} X_l^{(e)} x_m^{(m)} \delta^{lm}}{(r^{(\alpha)})^2 (r^{(m)})^2} .$$

The quadrupolar term of the electrostatic potential is now

$$V_\alpha = \frac{q_\alpha}{2(r^{(\alpha)})^5} \left[3 X_i^{(e)} x_j^{(m)} \delta^{ij} X_l^{(e)} x_m^{(m)} \delta^{lm} - (r^{(m)})^2 (r^{(e)})^2 \right] . \qquad (4)$$

Summation over indices j and m gives

$$V_\alpha = \frac{q_\alpha}{2(r^{(\alpha)})^5} \sum_{i,l=1}^{3} \left[3 X_i^{(e)} X_l^{(e)} x_i^{(m)} x_l^{(m)} - (r^{(m)})^2 (r^{(e)})^2 \right] . \qquad (4a)$$

Next we separate the coordinates $x^{(m)}$ and $X^{(e)}$, i. e., we write the quantity in square brackets as

$$[\quad] = f(X^{(e)}) g(x^{(m)}).$$

We find that
$$f(\chi^{(e)})g(x^{(n)})=\frac{1}{3}\sum_{i,l=1}^{3}\left[3x_i^{(n)}x_l^{(n)}-(r^{(n)})^2\delta^{il}\right]\times$$
$$\times\left[3X_i^{(e)}X_l^{(e)}-(r^{(e)})^2\delta^{il}\right],$$

and
$$V_\alpha=\frac{\gamma_\alpha}{6(r^{(\alpha)})^5}\sum_{i,l=1}^{3}\left[3x_i^{(n)}x_l^{(n)}-(r^{(n)})^2\delta^{il}\right]\times$$
$$\times\left[3X_i^{(e)}X_l^{(e)}-(r^{(\alpha)})^2\delta^{il}\right]. \tag{5}$$

Each of the square brackets may be considered as the components of a tensor. The potential V_α becomes
$$V_\alpha=\frac{\gamma_\alpha}{6(r^{(\alpha)})^5}A:B, \tag{6}$$
where A and B are second-rank tensors. The multiplication indicated by the double dot we define as the product obtained by multiplying the component B_{il} of B by the component A_{il} of A. Let us consider the tensor A:
$$A_{il}=3x_i^{(n)}x_l^{(n)}-(r^{(n)})^2\delta^{il}.$$
The tensor is symmetric; and there are five independent components, since it has zero trace. Each component is a homogeneous quadratic function of x, y, and z. For convenience we shall choose for a new basis the five linearly independent functions $r^2Y_2^m$, where Y_2^m are the unnormalized spherical harmonics of degree two. Then the five independent components, which are sufficient to define the tensor, become in Cartesian coordinates

$$A_0 = \frac{1}{2}(3z^2 - r^2) = r^2 P_2(\cos\theta) = r^2 Y_2^0 \tag{7a}$$

$$A_{\pm1} = 3z(x \pm iy) = r^2 P_2^{\pm1}(\cos\theta)\, e^{\pm i\phi} = r^2 Y_2^{\pm1} \tag{7b}$$

$$A_{\pm2} = 3(x \pm iy)^2 = r^2 P_2^{\pm2}(\cos\theta)\, e^{\pm 2i\phi} = r^2 Y_2^{\pm2}\,. \tag{7c}$$

We drop the subscripts and write the Cartesian coordinates explicitly. We also drop the superscripts and keep in mind that the A's refer to nuclear coordinates. We may treat the tensor B exactly as we have treated A and reduce B to five linearly independent components analogous to the A's of eqs. (7).

We must find the potential V_α in terms of the reduced tensors. We expand the product A:B with A and B in their original forms. Each term of the expansion is a product of a homogeneous quadratic function of the nuclear coordinates and a homogeneous quadratic function of the external charge. The homogeneous quadratic functions of the nuclear coordinates we express as linear combinations of the A_i of eqs. (7), and the homogeneous quadratic functions of the coordinates of external charge we express as linear combinations of the analogous B_i. The explicit expression for V_α is

$$V_\alpha = \frac{8\alpha}{[r^{(\alpha)}]^5}\Big(A_0B_0 + \frac{1}{6}A_{+1}B_{-1} + \frac{1}{6}A_{-1}B_{+1} + \frac{1}{24}A_{+2}B_{-2} + \frac{1}{24}A_{-2}B_{+2}\Big).$$

or

$$V_\alpha = \frac{g_\alpha}{[r^{(\alpha)}]^5} \sum_{i=-2}^{2} C_i A_i B_{-i} , \qquad (8)$$

where the C_i are numerical constants.

The quadrupolar interaction energy

One finds the contribution from the charge g_α to the nuclear quadrupolar interaction energy by multiplying V_α with the nuclear charge density $\rho_n(r)$ and integrating over the region occupied by the central nucleus:

$$H_\alpha = \int V_\alpha \rho_n(r) \, d\tau_n$$

, where H_α is the contribution to the Hamiltonian from the charge g_α . We find

$$H_\alpha = \frac{g_\alpha}{[r^{(\alpha)}]^5} \sum_{i=-2}^{2} C_i B_{-i} \int \rho_n(r) A_i \, d\tau_n . \qquad (9)$$

Next we introduce the components of the nuclear quadrupolar moment which we define as

$$Q_i \equiv \int \rho_n(r) A_i \, d\tau_n , \qquad (i = 0, \pm 1, \pm 2) . \qquad (10)$$

The A_i are functions of the Cartesian coordinates of an element of the nuclear charge. We want to write the A_i as functions of the components of the nuclear spin operator. The theorem which justifies the transformation from Cartesian coordinate operators to spin operators is discussed and proven without the use of group theory by Ramsey[15]. We choose a representation in which both the operator I^2 and the operator I are diagonal. Then in operator form

$$Q_0 = C\left[\tfrac{1}{2}(3I_z^2 - I(I+1))\right] \tag{11a}$$

$$Q_{\pm 1} = \frac{3}{2}C\left[I_z(I_x \pm iI_y) + (I_x \pm iI_y)I_z\right] \tag{11b,c}$$

$$Q_{\pm 2} = 3C\left[I_x \pm iI_y\right]^2. \tag{11d,e}$$

We express the arbitrary constant C in terms of the scalar

$$eQ \equiv \int \rho_m(r)_{m_I = I}(3z^2 - r^2)\,d\tau_m ,$$

or $eQ = (II|3I_z^2 - I(I+1)|II) = 2C(II|Q_0|II)$.

Finally,

$$C = \frac{eQ}{I(2I-1)} \, . \tag{12}$$

The scalar Q is conventionally called, "the nuclear quadrupole moment".

The Hamiltonian H_α is now

$$H_\alpha = \frac{z_\alpha}{[r^{(\alpha)}]^5}\sum_{i=-2}^{2} C_i Q_i B_{-i}^{(\alpha)} \, . \tag{13}$$

The superscript (α) on the B_i indicates that the quantities $B_i^{(\alpha)}$ depend upon the coordinates of the external charge z_α. In particular, the $B_i^{(\alpha)}$ are functions of the relative displacements of the charge z_α with respect to the displacement of the central nucleus. To find the total contribution to the quadrupolar energy from all external charges, we must sum over all charges q_α . Hence, the total quadrupolar interaction energy H' becomes

$$H' = \sum_\alpha H_\alpha = \sum_\alpha \frac{q_\alpha}{[r^{(\alpha)}]^5} \sum_{i=-2}^{2} C_i Q_i B_{-i}^{(\alpha)} \ . \qquad (14)$$

We are interested in the physical situation which exists when a sound wave displaces the nuclei and modulates the quadrupolar interaction energy. We expand the $\frac{B_i^{(\alpha)}}{[r^{(\alpha)}]^5}$ in terms of the relative displacements of the charge q_α with respect to the central nucleus. For convenience we shall make several changes of notation (see Fig. 6 and eq. (2a)). Let

$$\vec{\xi}^{(\alpha)} = \vec{\xi}^{(\alpha)} - \vec{\xi}^{(0)} = (\xi_i^{(\alpha)}), \qquad (i = 1,2,3)$$

and

$$\vec{R}_\alpha = \vec{r}^{(\alpha)} = (X_i^{(\alpha)} + \xi_i^{(\alpha)}).$$

Reference to Fig. 6 shows that $\vec{R}_\alpha = \vec{R}^{(\alpha)}$ when $\vec{\xi} = \vec{0}$.

The general form for the expansion of $\frac{B_i^{(\alpha)}}{R_\alpha^5}$ is

$$\frac{B_i^{(\alpha)}}{R_\alpha^5} = \frac{B_i^{(\alpha)}}{R_\alpha^5}\Bigg|_{\vec{\xi}=\vec{0}} + \sum_{k=1}^{3} \frac{\partial}{\partial \xi_k^{(\alpha)}}\left(\frac{B_i^{(\alpha)}}{R_\alpha^5}\right)\Bigg|_{\vec{\xi}=\vec{0}} +$$

$$+ \sum_{k,l} \frac{1}{2} \frac{\partial^2}{\partial \xi_k^{(\alpha)} \partial \xi_l^{(\alpha)}}\left(\frac{B_i^{(\alpha)}}{R_\alpha^5}\right)\Bigg|_{\vec{\xi}=\vec{0}} \xi_k^{(\alpha)} \xi_l^{(\alpha)} + \cdots \ . \qquad (15)$$

where i = 0, ± 1, ± 2. The explicit expressions for the $B_i^{(\alpha)}$ are:

$$B_0^{(\alpha)} = \frac{1}{2}\left[3\left(X_3^{(\alpha)} + \xi_3^{(\alpha)}\right) - (R_\alpha)^2\right]$$

$$B^{(\alpha)}_{\pm1}=3(X^{(\alpha)}_3+\xi^{(\alpha)}_3)\left[(X^{(\alpha)}_1+\xi^{(\alpha)}_1)\pm i(X^{(\alpha)}_2+\xi^{(\alpha)}_2)\right]$$

$$B^{(\alpha)}_{\pm2}=3\left[(X^{(\alpha)}_1+\xi^{(\alpha)}_1)\pm i(X^{(\alpha)}_2+\xi^{(\alpha)}_2)\right]^2.$$

We consider only processes which produce transitions of the central (the sodium) nucleus between nuclear magnetic energy levels determined by the quantum numbers m and $m\pm2$ (the $\Delta m=\pm2$ transitions). Here the quantum number labels the allowed values of the nuclear spin operator I_z. Experimentally, the angular frequency ω of the sound wave must satisfy the condition $E_m-E_{m\pm2}=\pm\hbar\omega$.

We must calculate the matrix elements

$$(I\,m|H'|I\,m\pm2). \tag{16}$$

The only components of the nuclear quadrupole moment whose matrix elements connect the nuclear states m and $m\pm2$ are the $Q_{\pm2}$; hence, from eqs. (14) and (16)

$$(Im|H'|I\,m+2)=(Im|Q_{-2}|I\,m+2)\sum_\alpha\frac{g_\alpha}{R^5_\alpha}C_2B^{(\alpha)}_{+2}, \tag{17a}$$

and

$$(Im|H'|I\,m-2)=(Im|Q_{+2}|I\,m-2)\sum_\alpha\frac{g_\alpha}{R^5_\alpha}C_2B^{(\alpha)}_{-2}. \tag{17b}$$

Now

$$(I\,m|Q_{+2}|Im-2)=\frac{3eQ}{I(2I-1)}(I\,m|(I_x+iI_y)^2|I\,m-2)$$

$$=\frac{3eQ}{I(2I-1)}\sqrt{(I-m+2)(I+m-1)}\sqrt{(I-m+1)(I+m)}\,, \tag{18a}$$

and $$(Im|Q_{-2}|Im+2) = \frac{3eQ}{I(2I-1)}\sqrt{(I+m+2)(I-m-1)}\times$$

$$\times\sqrt{(I+m+1)(I-m)}\,. \tag{18b}$$

Next we need the expansion of $\frac{B_{+2}^{(\alpha)}}{R_\alpha^5}$ and $\frac{B_{-2}^{(\alpha)}}{R_\alpha^5}$ in terms of the relative displacements of the charge q_α. Since the direct process interests us, we need examine only the linear terms of the expansion (see van Kranendonk[5]). The coefficient of $\xi_k^{(\alpha)}$ is $\frac{\partial}{\partial \xi_k^{(\alpha)}}\left(\frac{B_{\pm 2}^{(\alpha)}}{R_\alpha^5}\right) =$

$$= -\frac{5}{R_\alpha^7}(X_k^{(\alpha)}+\xi_k^{(\alpha)})B_{\pm 2}^{(\alpha)} + \frac{6}{R_\alpha^5}\left[(X_1^{(\alpha)}+\xi_1^{(\alpha)}) \pm i(X_2^{(\alpha)}+\xi_2^{(\alpha)})\right](\delta_{\mu k} \pm i\delta_{2k}),$$

and $$\frac{\partial}{\partial \xi_k^{(\alpha)}}\left(\frac{B_{\pm 2}^{(\alpha)}}{R_\alpha^5}\right)\Bigg|_{\vec{\xi}=\vec{0}} = \frac{1}{(R^{(\alpha)})^5}(X_1^{(\alpha)} \pm iX_2^{(\alpha)})\times$$

$$\times\left[\frac{-15}{(R^{(\alpha)})^5}(X_1^{(\alpha)} \pm iX_2^{(\alpha)})X_k^{(\alpha)} + 6(\delta_{1k} \pm i\delta_{2k})\right]. \tag{19}$$

We shall use van Kranendonk's model of a sodium chloride lattice and suppose that a sodium nucleus is surrounded by six equal point charges. We also assume that the axes of the Cartesian coordinate system coincide with the cubic axes of the crystal. Then the coordinates of the six charges (the sodium nucleus is at the origin) are:

$$\begin{array}{ll} \alpha = 1 & \alpha = -1 \\ (X_1^{(1)}, X_2^{(1)}, X_3^{(1)}) = (a,0,0) & (X_1^{(-1)}, X_2^{(-1)}, X_3^{(-1)}) = (-a,0,0) \\ \alpha = 2 & \alpha = -2 \\ (X_1^{(2)}, X_2^{(2)}, X_3^{(2)}) = (0,a,0) & (X_1^{(-2)}, X_2^{(-2)}, X_3^{(-2)}) = (0,-a,0) \\ \alpha = 3 & \alpha = -3 \\ (X_1^{(3)}, X_2^{(3)}, X_3^{(3)}) = (0,0,a) & (X_1^{(-3)}, X_2^{(-3)}, X_3^{(-3)}) = (0,0,-a) \end{array} \qquad (20)$$

Here "a" is the equilibrium lattice constant. Then for $\alpha = 1$, substitution of eq. (20) into eq. (19) gives

$$\frac{\partial}{\partial \xi_k}\left(\frac{B_{+2}^{(1)}}{R_1^5}\right)\Bigg|_{\vec{\xi}=\vec{0}} = \frac{1}{a^4}\left[-\frac{15}{a} X_k^{(1)} + 6(\delta_{1k} + i\delta_{2k})\right]. \qquad (21)$$

We multiply eq. (21) by $\xi_k^{(1)}$, the k-component of the relative displacement, and sum over the index k:

$$\sum_{k=1}^{3} \frac{\partial}{\partial \xi_k}\left(\frac{B_{+2}^{(1)}}{R_1^5}\right)\Bigg|_{\vec{\xi}=\vec{0}} = \sum_k \frac{1}{a^4}\left[-\frac{15}{a} X_k^{(1)} + 6(\delta_{1k} + i\delta_{2k})\right]\xi_k^{(1)}$$

$$= -\frac{9}{a^4}\xi_1^{(1)} + \frac{6}{a^4}(i)\xi_2^{(1)}.$$

If we retain only linear terms, we find

$$\frac{B_{+2}^{(1)}}{R_1^5} \sim -\frac{9}{a^4}\xi_1^{(1)} + i\frac{6}{a^4}\xi_2^{(1)}.$$

Similarly, we find the linear terms for all the $\dfrac{B_{\pm 2}^{(\alpha)}}{R_\alpha^5}$

The results are:

$$\frac{B_{+2}^{(1)}}{R_1^5} \sim -\frac{9}{a^4}\xi_1^{(1)} + \frac{6i}{4}\xi_2^{(1)} \; ; \quad \frac{B_2^{(-1)}}{R_{-1}^5} \sim \frac{9}{a^4}\xi_1^{(-1)} - \frac{6i}{a^4}\xi_2^{(-1)}. \qquad (23a)$$

$$\frac{B_{+2}^{(2)}}{R_2^5} \sim \frac{9}{a^4}\xi_2^{(2)} + \frac{6i}{a^4}\xi_2^{(2)} \quad ; \quad \frac{B_{+2}^{(-2)}}{R_{-2}^5} \sim -\frac{9}{a^4}\xi_2^{(-2)} - \frac{6i}{a^4}\xi_1^{(-2)} \tag{23b}$$

$$\frac{B_{+2}^{(3)}}{R_3^5} \sim 0 \quad ; \quad \frac{B_{+2}^{(-3)}}{R_{-3}^5} \sim 0 . \tag{23c}$$

The complex conjugate of any of eqs. (23a, b, c) equals the linear terms for the expansion of the corresponding $\frac{B_{-2}^{(\alpha)}}{R_\alpha^5}$.

The presence of a sound wave

Consider a unidirectional standing sound wave propagated in the direction of the x-axis. The displacement of a lattice point is

$$S = A\cos(kx-\delta)\cos\omega t \qquad , \text{ where } k = \frac{2\pi}{\lambda},$$

A is the amplitude of the sound wave, and δ is an arbitrary phase factor. For the central nucleus we find

$$S_1^{(0)} = A\cos\delta\cos\omega t \tag{24}$$

while for the charge q_1

$$S_1^{(1)} = A\cos(ka-\delta)\cos\omega t . \tag{25}$$

Since the product ka is small for a direct process, we make the approximation

$$\cos(ka-\delta) = \cos\delta + ka\sin\delta . \tag{26}$$

Combining eqs. (24), (25), and (26), we have

$$\xi_1^{(1)} = Aka\sin\delta\cos\omega t . \tag{27}$$

Also $$\xi_2^{(1)} = \xi_3^{(1)} = 0 . \tag{28}$$

Computation of the relative displacements of the five other charges shows that:

$$\begin{aligned}
&\xi_1^{(2)} = \xi_2^{(2)} = \xi_3^{(2)} = 0 \\
&\xi_1^{(3)} = \xi_2^{(3)} = \xi_3^{(3)} = 0 \\
&\xi_1^{(-1)} = -Aka \sin\delta \cos\omega t \\
&\xi_2^{(-1)} = \xi_3^{(-1)} = 0 \\
&\xi_1^{(-2)} = \xi_2^{(-2)} = \xi_3^{(-2)} = 0 \\
&\xi_1^{(-3)} = \xi_2^{(-3)} = \xi_3^{(-3)} = 0 .
\end{aligned} \qquad (29)$$

Substitution of the relative displacements in eqs. (23a, b, c) yields

$$\frac{B_{+2}^{(1)}}{R_1^5} \sim -\frac{q}{a^4} Aka \sin\delta \cos\omega t \qquad (30a)$$

$$\frac{B_{+2}^{(-1)}}{R_{-1}^5} \sim \frac{q}{a^4} Aka \sin\delta \cos\omega t \qquad (30b)$$

$$\frac{B_{+2}^{(2)}}{R_2^5} = \frac{B_{+2}^{(-2)}}{R_{-2}^5} = \frac{B_{+2}^{(3)}}{R_3^5} = \frac{B_{+2}^{(-3)}}{R_{-3}^5} . \qquad (30c)$$

Next we expand eq. (17a):

$$(Im|Q_{-2}|Im+2) \sum_{\alpha} \frac{g_\alpha}{R_\alpha^5} C_2 B_{+2}^{(\alpha)} =$$

$$= \frac{3eQ}{I(2I-1)} \sqrt{(I+m+2)(I-m-1)} \sqrt{(I+m+1)(I-m)}\, C_2 \left\{ g_1 \frac{B_{+2}^{(1)}}{R_1^5} + \right.$$

$$\left. + g_2 \frac{B_{+2}^{(2)}}{R_2^5} + g_3 \frac{B_{+2}^{(3)}}{R_3^5} + g_{-1} \frac{B_{+2}^{(-1)}}{R_{-1}^5} + g_{-2} \frac{B_{+2}^{(-2)}}{R_{-2}^5} + g_{-3} \frac{B_{+2}^{(-3)}}{R_{-3}^5} \right\} .$$

Let $g_\alpha = \gamma e$ for all α, where γ is a constant and e is the electronic charge. Substitution of eqs. (30a, b, c) in the expanded form of eq. (17a) determines the matrix element $(Im|H'|Im+2)$:

$$(Im|H'|I\,m+2) = -\frac{e^2Q\gamma}{8I(2I-1)}\sqrt{(I+m+2)(I-m-1)}\times$$
$$\times\sqrt{(I+m+1)(I-m)}\left(\frac{18}{a^3}Ak\sin\delta\cos\omega t\right). \qquad (31)$$

If we recall that $B_{-2}^{(\alpha)} = B_{-2}^{*(\alpha)}$, then from eq. (17b) we find the matrix element

$$(Im|H'|I\,m-2) = -\frac{e^2Q\gamma}{8I(2I-1)}\sqrt{(I-m+2)(I+m-1)}\times$$
$$\times\sqrt{(I-m+1)(I+m)}\left(\frac{18}{a^3}Ak\sin\delta\cos\omega t\right). \qquad (32)$$

With I $= \frac{3}{2}$, eqs. (31) and (32) become

$$(Im|H'|I\,m+2) = (Im|H'|I\,m-2) =$$
$$= -\frac{3e^2Q\gamma}{4}(2\sqrt{3})\left(\frac{Ak}{a^3}\sin\delta\cos\omega t\right). \qquad (33)$$

Transition probability per unit time

Since the matrix elements of the perturbation H' are time dependent, we must use time-dependent perturbation theory to compute the probability per unit time of a $\Delta m = \pm 2$ transition. We expand the state ψ of the perturbed system in terms of the eigenstates ψ_k of the unperturbed system. Let $a_k(t)$ be the coefficient of the eigenstate ψ_k in the expansion. Then first-order perturbation theory shows that (see Schiff, Quantum Mechanics, p. 195).

$$a_k(t) = -\frac{H'^{0}_{km}}{2\hbar}\left[\frac{e^{i(\omega_{km}+\omega)t}-1}{\omega_{km}+\omega} - \frac{e^{i(\omega_{km}-\omega)t}-1}{\omega_{km}-\omega}\right], \qquad (34)$$

where H'^{0}_{km} is time independent and $E_k - E_m = \hbar\omega_{km}$.

If $\omega_{km} - \omega \simeq 0$, the first term of eq. (34) is negligible compared with the second; and

$$a_k(t) = \frac{H'^{0}_{km}}{2\hbar}\,\frac{e^{i(\omega_{km}-\omega)t}-1}{\omega_{km}-\omega}.$$

If the system is initially in the state m and the perturbation is turned on at time $t=0$, the probability of finding the system in the state k, after a time t is

$$|a_k(t)|^2 = \frac{|H'^{0}_{km}|^2}{\hbar^2}\,\frac{\sin^2\frac{1}{2}(\omega_{km}-\omega)t}{(\omega_{km}-\omega)^2}. \qquad (35)$$

Since the nuclear resonance line has a finite width, we express the probability that a nucleus has a Larmor precessional frequency between ω and $\omega + d\omega$ by the normalized line-shape function $g(\omega)$. Then the probability that the system makes a transition in the time t from the state m to one of the states k is

$$W_{km} = \frac{1}{\hbar^2}\int_{-\infty}^{+\infty} |H'^{0}_{km}|^2\,\frac{\sin^2\frac{1}{2}(\omega_{km}-\omega)t}{(\omega_{km}-\omega)^2}\,g(\omega)\,d\omega. \qquad (36)$$

The function $\dfrac{\sin^2\frac{1}{2}(\omega_{km}-\omega)t}{(\omega_{km}-\omega)^2}$ is approximately a δ-function, and $g(\omega)$ is zero outside a definite frequency interval; hence, we write eq. (36) as

$$W_{km}=\frac{|H'^{0}_{km}|^2}{\hbar^2}g(\omega)\int_{-\infty}^{+\infty}\frac{\sin^2\frac{1}{2}(\omega_{km}-\omega)t}{(\omega_{km}-\omega)^2}d\omega$$
$$=\frac{|H'^{0}_{km}|^2}{\hbar^2}g(\omega)\frac{\pi}{2}t$$

The transition probability per unit time is

$$\frac{W_{km}}{t}=\frac{\pi|H'^{0}_{km}|^2}{2\hbar^2}g(\omega).$$

We average over the frequency spread $\delta\omega$ of the resonance line and find the average transition probability per unit time

$$W=\left(\frac{W_{km}}{t}\right)_{av}=\frac{|H'^{0}_{km}|^2}{4\hbar^2\delta\nu}, \qquad (37)$$

where $\delta\nu$ is the line width in frequency.

We have considered the case for $(\omega_{km}-\omega)\simeq 0$. This means that the perturbed system absorbs energy from the radiation field. When $(\omega_{km}+\omega)\simeq 0$, we have emission of energy by the perturbed system. In this case the second term of eq. (34) is negligible in comparison with the first term. Calculation of W_{km} yields the same result as eq. (37).

If we substitute the value of the matrix element from eq. (33) into eq. (37), we find the probability per unit time for a $\Delta m=\pm 2$ transition induced by ultrasonic energy. The result is

$$W = \frac{1}{4\hbar^2 \delta\nu}\left(\frac{27 e^4 \varphi^2 \gamma^2}{4}\right)\left(\frac{A^2 \underline{k}^2}{a^6}\right)\overline{\sin^2 \delta}.$$

Finally, when we average $\sin^2 \delta$ over all values of the arbitrary phase factor δ , we find

$$W = \frac{27}{32}\,\frac{e^4 \varphi^2 \gamma^2 A^2 \underline{k}^2}{\hbar^2 a^6 \delta\nu}. \qquad (38)$$

The Nuclear Magnetization

We shall compute the magnitude of the macroscopic magnetization of the sodium nuclear spin system and find the effect of ultrasonic energy on the magnetization. We consider the spin system in a steady magnetic field and in the presence of ultrasonic energy; however, there is no radiofrequency field present. First, we write the differential equations which determine the populations of the nuclear spin states as a function of time. Solution of the equations for steady state conditions yield the number of sodium nuclei in each spin state, and the macroscopic nuclear magnetization follows immediately.

The differential equations

In order to write the differential equations we must take account of all processes whereby a sodium nucleus can make a transition from one spin level to another. Since ultrasonic energy is present, all $\Delta m = \pm 2$, where m is the magnetic quantum number, transitions are allowed. The probability "W" of such a transition has been found in a previous section, and eq. (38) is the expression for "W".

The spin system of the sodium nuclei is in thermal contact with the sodium chloride lattice. Transitions of the sodium nuclei between spin states strive to bring the spin system and the crystalline lattice into thermal equilibrium. For the thermal processes both $\Delta m = \pm 1$ and $\Delta m = \pm 2$ transitions are allowed. If we let "W_1" and "W_2" be the probability of a $\Delta m = -1$ and $\Delta m = -2$ transition, respectively, the probabilities for the corresponding downward transitions $\Delta m = +1$ and $\Delta m = +2$ are $W_1 \exp\left(\frac{E_m - E_{m+1}}{KT}\right)$ and $W_2 \exp\left(\frac{E_m - E_{m+2}}{KT}\right)$. As an approximation we expand the exponentials and write

$W_1\left(1 + \frac{h\nu}{KT}\right)$ for $\Delta m = +1$ transitions

and $W_2\left(1 + 2\frac{h\nu}{KT}\right)$ for $\Delta m = +2$ transitions,

where

$$(E_m - E_{m+1}) = h\nu.$$

The expansion of the exponentials is valid, since $h\nu \ll KT$ except at very low temperatures.

There is a third process which is responsible for rearranging nuclear spins among the spin states. Mutual spin-spin flipping of the sodium nuclei is the third process, and its effect on the populations of the spin states was suggested by Abragam and Proctor[16]. Each sodium nucleus experiences a local magnetic field because of neighboring sodium nuclei. We may suppose that the local magnetic field consists of two components. The first, a static component, arises from the dipolar interaction of the sodium nuclear moments. The second component is an oscillating field. Since the magnetic moment of each sodium nucleus is precessing in the constant external magnetic field, a neighboring sodium nucleus experiences an oscillatory field whose frequency is the Larmor precessional frequency of a sodium nucleus in the external magnetic field. As a result, the oscillating field from nucleus "a" can flip the spin of nucleus "b". While the spins flip there is an exchange of energy between nuclei "a" and "b". The process requires conservation of the energy of the spin system, and for mutual spin-spin flipping no energy leaks from the nuclear spin system to the crystalline lattice. Spin-spin flipping takes place only between identical nuclear species.

Fig. 7 illustrates spin-flipping for the magnetic energy levels of a sodium nucleus. Only $\Delta m = \pm 1$ transitions are allowed, and the probabilities P_1 and P_2 for mutual spin-flipping are explained in the diagram.

If we let N_m be the instantaneous number of sodium nuclei in the energy state specified by the magnetic quantum number m, then the differential equations which describe the populations of energy levels as a function of time are:

$$\frac{dN_{3/2}}{dt} = \left[-N_{3/2}P_1\frac{N_{-1/2}}{N} - N_{3/2}P_2\frac{N_{-3/2}}{N} + N_{1/2}P_1\frac{N_{1/2}}{N} + N_{1/2}P_2\frac{N_{-1/2}}{N}\right] - N_{3/2}W + N_{-1/2}W -$$
$$-N_{3/2}W_1 + N_{1/2}(1+\Delta)W_1 - N_{3/2}W_2 + N_{-1/2}(1+2\Delta)W_2 .$$

$$\frac{dN_{1/2}}{dt} = \left[-2N_{1/2}P_1\frac{N_{1/2}}{N} - N_{1/2}P_2\frac{N_{-1/2}}{N} - N_{1/2}P_1\frac{N_{-3/2}}{N} + 2N_{3/2}P_1\frac{N_{-1/2}}{N} + N_{3/2}P_2\frac{N_{-3/2}}{N} +\right.$$
$$\left. + N_{-1/2}P_1\frac{N_{-1/2}}{N}\right] - N_{1/2}W + N_{-3/2}W - N_{1/2}(1+\Delta)W_1 - N_{1/2}W_2 +$$
$$+ N_{-3/2}(1+2\Delta)W_2 + N_{3/2}W_1 .$$

$$\frac{dN_{-1/2}}{dt} = \left[-2N_{-1/2}P_1\frac{N_{-1/2}}{N} - N_{-1/2}P_2\frac{N_{1/2}}{N} - N_{-1/2}P_1\frac{N_{3/2}}{N} + 2N_{-3/2}P_1\frac{N_{1/2}}{N} +\right.$$
$$\left. + N_{-3/2}P_2\frac{N_{3/2}}{N} + N_{1/2}P_1\frac{N_{1/2}}{N}\right] - N_{-1/2}W + N_{3/2}W - N_{-1/2}W_1 -$$
$$- N_{-1/2}W_2(1+2\Delta) + N_{-3/2}W_1(1+\Delta) + N_{3/2}W_2 .$$

$$\frac{dN_{-3/2}}{dt} = \left[-N_{-3/2}P_1\frac{N_{1/2}}{N} - N_{-3/2}P_2\frac{N_{3/2}}{N} + N_{-1/2}P_1\frac{N_{-1/2}}{N} + N_{-1/2}P_2\frac{N_{1/2}}{N}\right] -$$
$$-2N_{-3/2}W_1 - N_{-3/2}(3\Delta W_1) - N_{-3/2}W + N_{-1/2}W_1 +$$
$$+ N_{1/2}W + N_{1/2}W_2 .$$

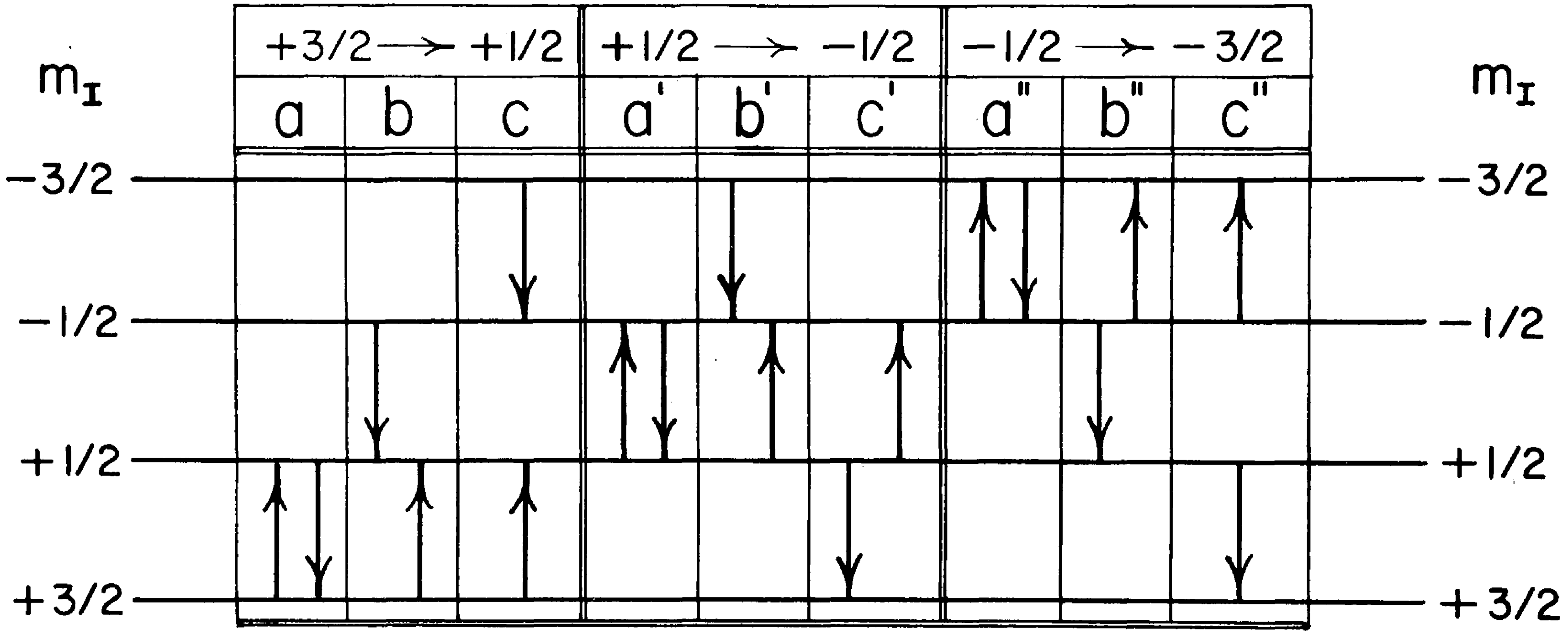


Fig. 7. Mutual Spin Flipping for $I = 3/2$.

Transition Probabilities:

$$W_b = W_{b'} = W_{b''} = W_{c''} \equiv P_1$$
$$W_c = W_{c'} \equiv P_2$$

In these equations we have let $\Delta = \frac{\hbar\omega}{kT}$. The terms in the square brackets express the spin-flipping processes, and they require a word of explanation. Consider the situation whereby a nuclear spin makes a transition from the state $m = +\frac{1}{2}$ to $m = -\frac{1}{2}$ through mutual spin-flipping. Then from Fig. 7 we see that the spin-flipping involves processes b′ and c′ . (We can ignore processes a, a′, and a″ , since they do not change the spin populations.) We shall restrict ourselves to process b′, and compute the change per unit time in the population number $N_{\frac{1}{2}}$. The change due to process b′ is proportional to P_1 , the probability per unit time of the mutual spin flip $(m_{\frac{1}{2}} \rightarrow m_{-\frac{1}{2}})(m_{-\frac{3}{2}} \rightarrow m_{-\frac{1}{2}})$; it is proportional to the number of spins in the level $N_{\frac{1}{2}}$; and finally the process b′ cannot occur if the state $m = -\frac{3}{2}$ is not occupied. Consequently, we write $\left.\frac{dN_{\frac{1}{2}}}{dt}\right)_{b'} = -N_{\frac{1}{2}} P_1 \frac{N_{-\frac{3}{2}}}{N}$, where N is the total number of spins in the spin system. The factor $\frac{N_{-\frac{3}{2}}}{N}$ represents the probability that the level $m = -\frac{3}{2}$ is occupied.

Steady state equations

For steady state conditions we equate the derivatives to zero, and we find the following equations:

$$\begin{aligned}&\left[-N_{\frac{3}{2}}P_1\frac{N_{-\frac{1}{2}}}{N}-N_{\frac{3}{2}}P_2\frac{N_{-\frac{3}{2}}}{N}+N_{\frac{1}{2}}P_1\frac{N_{\frac{1}{2}}}{N}+N_{\frac{1}{2}}P_2\frac{N_{-\frac{1}{2}}}{N}\right]-N_{\frac{3}{2}}(W+2W_1)+\\&+N_{\frac{1}{2}}(W_1+\Delta W_1)+N_{-\frac{1}{2}}(W+W_1+2\Delta W_1)=0\end{aligned}\tag{39a}$$

$$\begin{aligned}&\left[-2N_{\frac{1}{2}}P_1\frac{N_{\frac{1}{2}}}{N}-N_{\frac{1}{2}}P_2\frac{N_{-\frac{1}{2}}}{N}-N_{\frac{1}{2}}P_1\frac{N_{-\frac{3}{2}}}{N}+2N_{\frac{3}{2}}P_1\frac{N_{-\frac{1}{2}}}{N}+N_{\frac{3}{2}}P_2\frac{N_{-\frac{3}{2}}}{N}+\right.\\&\left.+N_{-\frac{1}{2}}P_1\frac{N_{-\frac{1}{2}}}{N}\right]-N_{\frac{1}{2}}(W+2W_1+\Delta W_1)+N_{\frac{3}{2}}W_1+\\&+N_{-\frac{3}{2}}(W+W_1+2\Delta W_1)=0.\end{aligned}\tag{39b}$$

$$\begin{aligned}&\left[-2N_{-\frac{1}{2}}P_1\frac{N_{-\frac{1}{2}}}{N}-N_{\frac{1}{2}}P_2\frac{N_{\frac{1}{2}}}{N}-N_{-\frac{1}{2}}P_1\frac{N_{\frac{3}{2}}}{N}+2N_{-\frac{3}{2}}P_1\frac{N_{\frac{1}{2}}}{N}+N_{-\frac{3}{2}}P_2\frac{N_{\frac{3}{2}}}{N}+\right.\\&\left.+N_{\frac{1}{2}}P_1\frac{N_{\frac{1}{2}}}{N}\right]+N_{\frac{3}{2}}(W+W_1)-N_{-\frac{1}{2}}(W+2W_1+2\Delta W_1)+\\&+N_{-\frac{3}{2}}(W_1+\Delta W_1)=0\end{aligned}\tag{39c}$$

$$\begin{aligned}&\left[-N_{-\frac{3}{2}}P_1\frac{N_{\frac{1}{2}}}{N}-N_{-\frac{3}{2}}P_2\frac{N_{\frac{3}{2}}}{N}+N_{-\frac{1}{2}}P_1\frac{N_{-\frac{1}{2}}}{N}+N_{-\frac{1}{2}}P_2\frac{N_{\frac{1}{2}}}{N}\right]+N_{\frac{1}{2}}(W+W_1)+\\&+N_{-\frac{1}{2}}W_1-N_{-\frac{3}{2}}(2W_1+3\Delta W_1+W)=0\end{aligned}\tag{39d}$$

In these four equations we have assumed that[4] $W_1=W_2$. That is, the probabilities of a transition $\Delta m=-1$ and $\Delta m=-2$ because of thermal relaxation are equal. We add a fifth equation which expresses the fact that the total number of spins must be constant:

$$N_{\frac{3}{2}}+N_{\frac{1}{2}}+N_{-\frac{1}{2}}+N_{-\frac{3}{2}}=N.\tag{39e}$$

Simultaneous solution of any four of the five equations will yield the population numbers N_m.

The linear approximation

We notice that the population numbers N_m appear quadratically in eqs. (39a, b, c, d). To find a solution we shall approximate the quadratic equations by linear equations.

Consider, for example, the product $(N_{\frac{3}{2}} N_{-\frac{1}{2}}) \frac{1}{N}$. According to Abragam and Proctor's suggestion, the mutual spin flips distribute the nuclear spins among the energy levels in such a way that the population numbers N_m are determined by a Boltzmann distribution for a spin temperature T_s . Therefore we write

$$\begin{aligned}\frac{1}{N}(N_{\frac{3}{2}} N_{-\frac{1}{2}}) &= \frac{1}{N}\left[\frac{N}{4}\exp\left(-\frac{E_{\frac{3}{2}}}{kT_s}\right)\frac{N}{4}\exp\left(-\frac{E_{-\frac{1}{2}}}{kT_s}\right)\right] \\ &\simeq \frac{1}{4}\frac{N}{4}\left(1-\frac{E_{\frac{3}{2}}}{kT_s}\right)\left(1-\frac{E_{-\frac{1}{2}}}{kT_s}\right) \\ &\simeq \frac{1}{4}\left[\frac{N}{4}\left(1-\frac{E_{-\frac{1}{2}}}{kT_s}\right)+\frac{N}{4}\left(1-\frac{E_{\frac{3}{2}}}{kT_s}\right)-\frac{N}{4}\right] \\ &\simeq \frac{1}{4}\left(N_{-\frac{1}{2}}+N_{\frac{3}{2}}-\frac{N}{4}\right).\end{aligned}$$

We may treat all terms of the form $N_p N_\gamma$ similarly and find in general

$$\frac{1}{N}(N_p N_\gamma) \simeq \frac{1}{4}(N_p + N_\gamma) - \frac{N}{16} \,. \qquad (40)$$

Using eq. (2), we find for eq. (1a)

$$\begin{aligned}&-\frac{1}{4}(N_{-\frac{1}{2}}+N_{\frac{3}{2}})P_1 + \frac{N}{16}P_1 - \frac{1}{4}(N_{-\frac{3}{2}}+N_{\frac{3}{2}})P_2 + \frac{N}{16}P_2 + \frac{1}{4}(2N_{\frac{1}{2}})P_1 - \frac{N}{16}P_1 + \\ &+ \frac{1}{4}(N_{\frac{1}{2}}+N_{-\frac{1}{2}})P_2 - \frac{N}{16}P_2 - N_{\frac{3}{2}}(W+2W_1) + N_{\frac{1}{2}}(W_1+\Delta W_1) + \\ &\qquad + N_{-\frac{1}{2}}(W+W_1+2\Delta W_1) = 0 \,.\end{aligned}$$

We find similar expressions for eqs. (39a, b, c, d), and the linear approximation consists of the following equations:

$$-N_{\frac{3}{2}}(P_1+P_2+4w+8w_1)+N_{\frac{1}{2}}(2P_1+P_2+4w_1+4\Delta w_1)+$$
$$+N_{-\frac{1}{2}}(P_2-P_1+4w+4w_1+8\Delta w_1)-N_{-\frac{3}{2}}P_2=0 \qquad (41a)$$

$$N_{\frac{3}{2}}(2P_1+P_2+4w_1)-N_{\frac{1}{2}}(5P_1+P_2+4w+8w_1+4\Delta w_1)+$$
$$+N_{-\frac{1}{2}}(4P_1-P_2)+N_{-\frac{3}{2}}(P_2-P_1+4w+4w_1+8\Delta w_1)=0 \qquad (41b)$$

$$N_{\frac{3}{2}}(P_2-P_1+4w+4w_1)+N_{\frac{1}{2}}(4P_1-P_2)- \qquad (41c)$$
$$-N_{-\frac{1}{2}}(5P_1+P_2+4w+8w_1+8\Delta w_1)+N_{-\frac{3}{2}}(2P_1+P_2+4w_1+4\Delta w_1)=0.$$

$$-N_{\frac{3}{2}}P_2+N_{\frac{1}{2}}(P_2-P_1+4w+4w_1)+N_{-\frac{1}{2}}(2P_1+P_2+4w_1)-$$
$$-N_{-\frac{3}{2}}(P_1+P_2+8w_1+12\Delta w_1+4w)=0 \qquad (41d)$$

$$N_{\frac{3}{2}}+N_{\frac{1}{2}}+N_{-\frac{1}{2}}+N_{-\frac{3}{2}}=N \qquad (41e)$$

We shall solve the system of equations formed by eqs. (41a, b, d, e).

Solution of the linear approximation

The determinant of the coefficients of the system of equations can be expanded to yield the following equation:

$$\text{Det.}=2\left[2(P_1+2P_2)+(16w_1+8w+12\Delta w_1)\right]\times$$
$$\times\left[-8P_1(4)(w+w_1+\Delta w_1)-P_1(8w_1+4\Delta w_1)-\right.$$
$$\left.-4(w+w_1+\Delta w_1)(8w_1+4\Delta w_1)\right]. \qquad (42)$$

As an approximation, we drop all terms which contain $\Delta=\frac{\hbar\omega}{KT}$ as a factor and retain only terms which involve the probabilities P_1 and P_2 quadratically. Our neglecting terms which contain P_1 or P_2 linearly is justified, since the spin flips take place in a time which is very short compared with the time required for a thermal relaxation process, and $w, w_1 << P_1, P_2$. The approximations reduce the determinant to

$$\text{Det.} \simeq -2(4)\left[16P_1(P_1+2P_2)(w+w_1)+4P_1(P_1+2P_2)w_1\right]. \qquad (43)$$

Using eq. (43) and the system of equations, eqs. (41a, b, d, e), we compute the population differences $(N_{\frac{3}{2}}-N_{\frac{1}{2}}),(N_{\frac{1}{2}}-N_{-\frac{1}{2}})$, and $(N_{\frac{1}{2}}-N_{-\frac{3}{2}})$. To find the population differences, we neglect terms which involve $(\Delta)^2$ but retain terms which contain Δ linearly. For example,

$$(N_{\frac{3}{2}}-N_{\frac{1}{2}}) \simeq \frac{-N(4\Delta w_1)(10P_1+8w+8w_1+16\Delta w_1)(P_1+2P_2+8w_1+12\Delta w_1+4w)}{\text{Det.}}$$

We also retain only terms which contain P_1 or P_2 quadratically. Then

$$(N_{\frac{3}{2}}-N_{\frac{1}{2}}) \simeq \frac{N\Delta w_1(5P_1)(P_1+2P_2)}{16P_1(P_1+2P_2)(w+w_1)+4P_1(P_1+2P_2)w_1},$$

$$= \frac{N\Delta}{4}\,\frac{1}{1+\frac{4w}{5w_1}}\,. \qquad (44)$$

Since $2T_1 = \frac{1}{w_1}$, we may express eq. (44) in terms of the spin-lattic relaxation time :

$$(N_{\frac{3}{2}}-N_{\frac{1}{2}}) \simeq \frac{N\Delta}{4}\,\frac{1}{1+\frac{8}{5}wT_1}\,. \qquad (45)$$

Similarly, we find the same result, eq. (45), for the population differences $(N_{\frac{1}{2}} - N_{-\frac{1}{2}})$ and $(N_{-\frac{1}{2}} - N_{-\frac{3}{2}})$; consequently, we have

$$(N_{\frac{3}{2}} - N_{\frac{1}{2}}) = (N_{\frac{1}{2}} - N_{-\frac{1}{2}}) = (N_{-\frac{1}{2}} - N_{-\frac{3}{2}}) \simeq \frac{N\Delta}{4} \frac{1}{1 + \frac{8}{5} W T_1} . \qquad (46)$$

The result, eq. (46), of the linear approximation predicts that in general the temperature of the spin system is higher than the lattice temperature. If the ultrasonic transition probability W is zero, the population differences equal $\frac{N\Delta}{4}$; but $\frac{N\Delta}{4}$ is the population difference for the spin system and the crystalline lattice in thermal equilibrium.

The macroscopic magnetization

The macroscopic magnetization of the nuclear spins is

$$M = \frac{3}{2} N_{\frac{3}{2}} + \frac{1}{2} N_{\frac{1}{2}} - \frac{1}{2} N_{-\frac{1}{2}} - \frac{3}{2} N_{-\frac{3}{2}} = \frac{3}{2}(N_{\frac{3}{2}} - N_{-\frac{3}{2}}) + \frac{1}{2}(N_{\frac{1}{2}} - N_{-\frac{1}{2}}) .$$

In the absence of ultrasonic radiation, $W = 0$; and we find the nuclear magnetization

$$M_0 = \frac{3}{2}(3)\frac{N\Delta}{4} + \frac{1}{2}\frac{N\Delta}{4} = 5\frac{N\Delta}{4} . \qquad (47)$$

With the ultrasonic transition probability not zero, we have

$$M_W = \frac{3}{2}(3)\frac{N\Delta}{4}\frac{1}{1 + \frac{8}{5}WT_1} + \frac{1}{2}\frac{N\Delta}{4}\frac{1}{1 + \frac{8}{5}WT_1}$$

$$= 5\frac{N\Delta}{4}\frac{1}{1 + \frac{8}{5}WT_1} . \qquad (48)$$

The ratio of eq. (47) and eq. (48) yields

$$\frac{M_W}{M_0} = \frac{1}{1 + \frac{8}{5} W T_1} \; . \qquad (49)$$

Eq. (49) predicts that for sufficiently large values of the ultrasonic transition probability W, we can reduce the nuclear magnetization to a small fraction of its equilibrium value M_0.

CHAPTER IV

THE EXPERIMENTAL METHOD

Measurement of the spin-lattice relaxation time, T_1

The spin-lattice relaxation time, sometimes called the longitudinal relaxation time, was introduced phenomenologically by Block[17]. Consider a system of nuclear spins, for example, a crystal, in a vanishingly small magnetic field. The nuclear Zeeman levels are degenerate. If we thrust the spin system into a strong magnetic field, the degeneracy of the Zeeman levels is removed, but the nuclear spins are nearly equally distributed among the Zeeman levels. After sufficient time, the Boltzmann law determines the distribution of the nuclear spins among the magnetic energy levels as the spin system and lattice approach thermal equilibrium. We may say that the initial temperature of the spin system in the magnetic field was greater than the lattice temperature, and its final temperature is the lattice temperature. The spin lattice relaxation time T_1, is a measure of the time required for the spin system to cool from a high temperature to the lattice temperature. In the Introduction we mentioned several proposed mechanisms which bring the spin system and the crystalline lattice into thermal contact.

For a collection of nuclear spins each with spin $I = \frac{1}{2}$ one can show that the approach of the spin system to thermal equilibrium with the lattice is described by the equation:

$$(N_0 - N) = (N_0 - N_\alpha)\, e^{-\frac{t}{T_1}} \tag{50}$$

where

$N_0 =$ number of excess nuclei in the lower energy state at thermal equilibrium

$N_\alpha =$ number of excess nuclei in the lower energy state at time $t = 0$.

If the nuclear spin $I > \frac{1}{2}$, it is not always possible to introduce a single spin-lattice relaxation time. Also a single relaxation time may not be valid if more than one process is effective in bringing the spin system to thermal equilibrium with the lattice. Although for sodium $I = \frac{3}{2}$, the quantity which we determine experimentally is a measure of the effectiveness of the relaxation mechanism or mechanisms; and we shall call it the spin-lattice relaxation time, T_1.

Pulse techniques provide a convenient means for measuring T_1. In order to understand the method, we regard the net magnetization of the spin system as a macroscopic magnetic moment. Let M_0 be the magnitude of the macroscopic moment for conditions of thermal equilibrium. Consider a sample of sodium chloride placed in the coil R of Fig. 2. Introduce a coordinate system with its x-axis coincident with the oscillator coils A and B; its y-axis coincident with the receiver coil R; and its positive z-axis coincident with the direction of the steady magnetic field $\vec{H}_0$. When the spin system and crystalline lattice are in thermal equilibrium, $\vec{M}_0$ is parallel to $\vec{H}_0$. We subject the sodium nuclei to a pulse of radiofrequency energy by connecting the coils A and B to a gated oscillator tuned to the proper frequency. If the oscillator is tuned to the Larmor frequency of precession of $\vec{M}_0$ about $\vec{H}_0$, the macroscopic moment $\vec{M}_0$ will precess toward the xy-plane through a polar angle θ:

$$\theta = \omega_1 t_w = \gamma H_1 t_w$$

where

γ = gyromagnetic ratio for sodium
H_1 = intensity of the radiofrequency magnetic field
t_w = duration of the pulse of radiofrequency energy.

It is convenient to choose $\vec{H}_1$ and t_w in a way which will make $\theta = \frac{\pi}{2}$ (a 90^0 -pulse); consequently, immediately after the pulse $\vec{M}_0$ lies in the xy-plane. With the radiofrequency field no longer present, $\vec{M}_0$ precesses in the xy-plane and induces a voltage in the receiver coil R. The magnitude of the induced voltage is proportional to M_0. After amplification one observes on an oscilloscope screen the nuclear induction signal which follows the pulse.

If after application of a 90° -pulse we apply a second 90° -pulse at a time $t < T_1$, the magnitude of the magnetization which precesses into the xy-plane during the second pulse is proportional to the fraction of $\vec{M}_0$ which returned to thermal equilibrium (became realigned with $\vec{H}_0$) in the time between the end of the first pulse and the application of the second pulse. At any given time the magnitude of M_0 in the direction of $\vec{H}_0$ is proportional to the excess number of nuclei in each energy state relative to the next higher energy state. For a 90° -pulse, N_a in eq. (50) is zero, and we may write for eq. (50)

$$\ln (N_0 - N) = \ln N_0 - \frac{t}{T_1} . \qquad (51)$$

The amplitude of the induction signal which follows the second pulse is proportional to N in eq. (51). Experimentally, we can vary the time t of eq. (51) by varying the repetition rate of the radiofrequency pulses. A semi-logarithmic plot of $(N_0 - N)$ as a function of the time interval between pulses yields a straight line whose slope is $(-\frac{1}{T_1})$.

In the experiment, whose results we shall report, for measuring T_1 of sodium nuclei in sodium chloride, the frequency of the radiofrequency field $\vec{H}_1$ was 5.00 megacycles per sec.; and the variable repetition rate allowed the time interval between successive pulses to be varied from 1.25 sec. to 11.8 sec. The sodium chloride crystal was supplied by Harshaw Chemical Co.; and the same crystal was used later for the ultrasonic experiments. The nuclear induction signal was observed visually on the oscilloscope. Signal amplitudes were read directly from the calibrated oscilloscope screen.

Preparation of the sodium chloride crystal for ultrasonic studies

The sodium chloride crystal was a cylinder one-half inch in diameter and two inches long. The axis of the cylinder coincided with the (100)-crystalline axis. The ultrasonic waves were propagated in the direction of the axis of the cylinder; and in order to insure good unidirectional standing waves, the bases of the cylinder were ground and polished to make them parallel. Optical grinding powders provided the grinding medium. For a lubricant during the grinding both acetone and mineral oil were used; however, mineral oil was more satisfactory than acetone. A steel right-angle block was used as a guide to keep the ground bases perpendicular to the axis of the cylinder. As a further precaution during the grinding operation, the sodium chloride cylinder was rotated about its axis. After polishing, a mechanical measurement showed that the bases were parallel to within ± 0.001 in.

A X-cut quartz plate with a fundamental frequency of ten megacycles/sec. was the transducer. The quartz was 3/4 in. square, and opposite faces were plated with aluminum. Spring-loaded brass clips provided a means for connecting opposite faces of the quartz plate to the output terminals of the ultrasonic oscillator. The transducer was cemented to one face of the sodium chloride crystal. A mixture of talc and sodium silicate solution acted as the cementing medium. Determination of the proper consistency of the cement is somewhat of a problem. Cement which is too thin does not provide proper bonding, and cement which is too thick hardens too rapidly. Before the cement sets, one must take care that the face of the quartz transducer is parallel to the face of the sodium chloride crystal. Finally, the sodium chloride and cemented transducer were placed in an electric oven, and the temperature was gradually raised from room temperature to approximately 90° C and then cooled slowly to room temperature. The heating and cooling took place over a period of about 16 hours. Mechanical measurements showed that the transducer and sodium chloride faces were parallel within ± 0.003 in. Fig. 2 shows the transducer-sodium chloride system in its experimental position in the induction head.

The impedance of the quartz was measured on a radiofrequency bridge over a frequency range from 9.800 megacycles/sec. to 11.00 megacycles/sec. After the quartz had been cemented to the sodium chloride, the impedance of the combination was measured over the same frequency range. Frequencies were measured with a type BC 221 frequency meter.

Measurement of ultrasonic effects

With the lattice of the sodium chloride crystal and the spin system of sodium nuclei at thermal equilibrium in the steady magnetic field $\vec{H}_0$, pulsed ultrasonic energy irradiated the crystal for 3.95 sec. Following the ultrasonic pulse and 0.25 sec. later, a pulse of radiofrequency energy sampled the population differences of the sodium nuclear magnetic energy levels. The duration of the radiofrequency pulse was fifty-six microseconds. A nuclear induction signal followed the radiofrequency pulse, and the amplitude of the induction signal served to indicate any ultrasonically induced transitions of the sodium nuclei. The induction signals were observed visually, and their amplitudes were ready directly from the calibrated screen of the Tektronix oscilloscope. The sequence of events, ultrasonic pulse followed by a radiofrequency pulse, was repeated every 9.75 sec. A stop watch timed the duration of the ultrasonic pulse; the calibrated time sweep of the oscilloscope determined the length of the radiofrequency pulse. The interval between the ultrasonic and radiofrequency pulse was measured from the oscilloscope sweep.

The choice of frequency of the ultrasonic energy was determined by selecting a suitable point from the real part of the impedance curve (Fig. 11) of the loaded quartz transducer, and the ultrasonic oscillator (see Fig. 1) was tuned to the chosen frequency. The radiofrequency oscillator (see Fig. 1) was tuned to one-half the ultrasonic frequency. The frequencies were monitored by a Hallicrafters SX-62A receiver and measured with a type BC 221 frequency meter.

When the ultrasonic and radiofrequency oscillators were tuned to their proper frequencies and the apparatus was working satisfactorily, the amplitude of the induction signal following the radiofrequency pulse was observed with no ultrasonic energy present. Next the ultrasonic oscillator was activated; and with a specific voltage across the quartz transducer, the amplitude of the induction signal was observed. The diode voltmeter (see Fig. 1) measured the peak voltage applied to the transducer, and the amplitude of the induction signal was recorded for different transducer voltages.

CHAPTER V

EXPERIMENTAL RESULTS

The spin-lattice relaxation time

Fig. 8 shows a plot of a representative set of experimental data which one uses to determine the spin-lattice relaxation time, T_1 . A discussion of the theory of the measurement appears in Chapter IV, and Fig. 8 is a plot of eq. (51). From the slope of the line, we find

$$\frac{1}{T_1} = \frac{1}{7.10} \; ; \quad T_1 = 7.10 \text{ sec.}$$

Ten determinations of T_1 were made, and the average of the ten values is $T_1 = 7.15 \pm .28$ sec.

The parameter γ

In the theory of Chapter III we replaced the ions of the sodium chloride lattice by point charges of magnitude γe. We shall obtain a numerical value for γ from theobserved ultrasonic attenuation of the nuclear induction signal.

Eq. (38) for the ultrasonic transition probability contains A^2 , the amplitude squared of the displacement of an ion due to the sound wave. If $\mathcal{E}$ is the energy density of

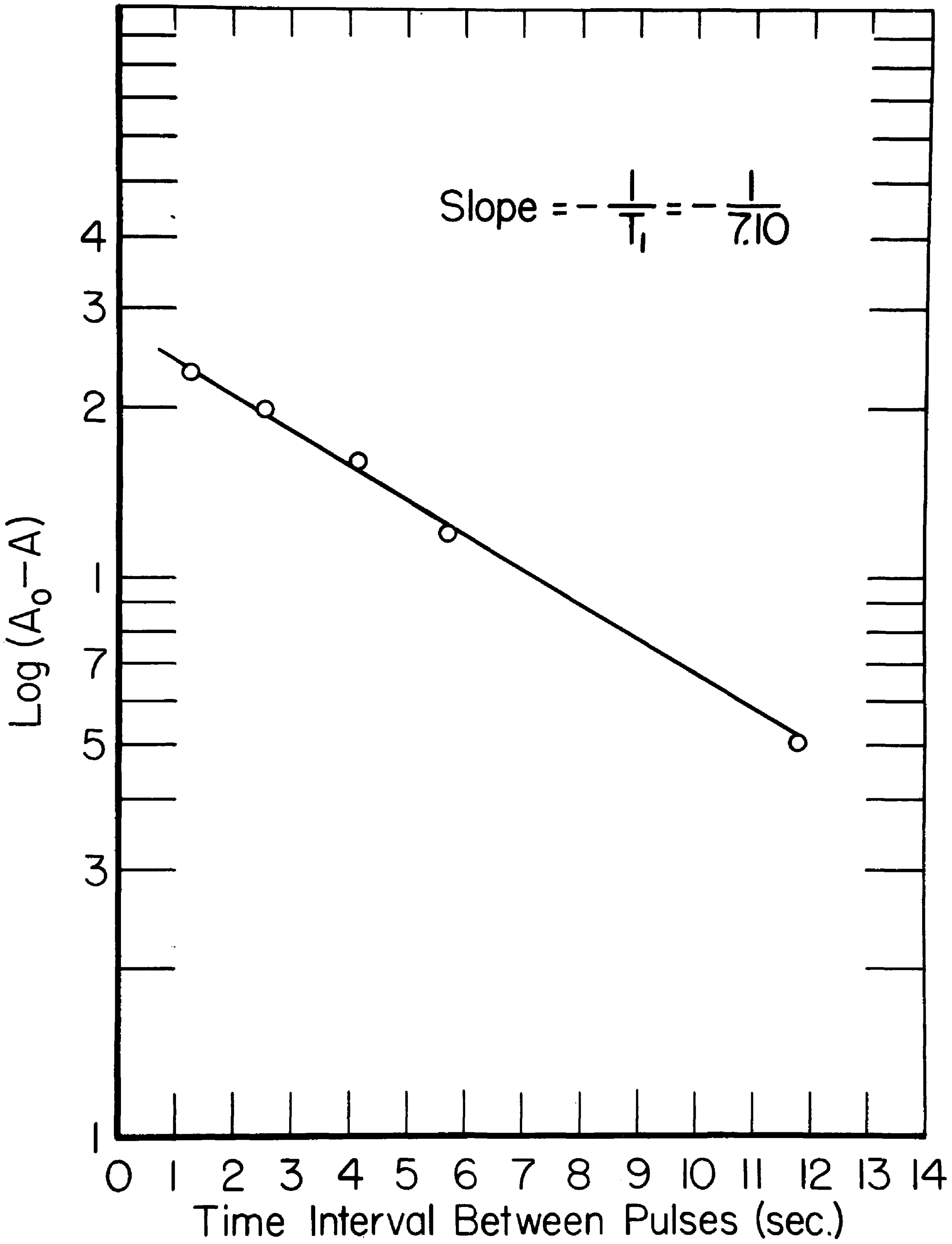


Fig.8 Measurement of Relaxation Time.

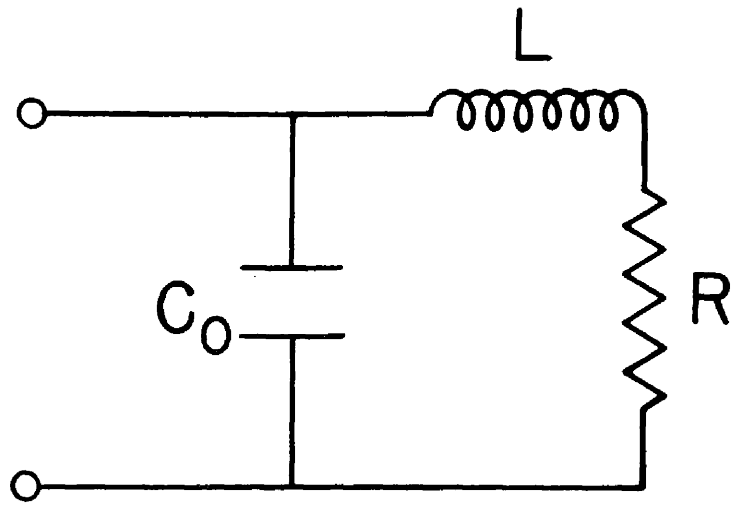
the ultrasound in the sodium chloride, then $A^2 = \frac{2E}{\rho\omega^2}$, (52) where

ρ = density of NaCl
ω = angular frequency of the ultrasound

We compute the energy density E, by finding the power P_s dissipated in the sodium chloride. The quartz transducer and the transducer loaded with the sodium chloride were replaced by equivalent electrical circuits[18, 19]. The equivalent circuit together with the values of the electrical components are shown in Fig. 9.

The capacitance C_o is the capacitance of the X-cut quartz, plated on opposite faces, and treated as a parallel plate capacitor. The frequency for operating the transducer was chosen from Fig. 10 and Fig. 11, and the value chosen was ν = 10.2 mc/sec. From Fig. 10 and the reactive part of the impedance of the quartz one can determine the effective resistance of the unloaded quartz. From Fig. 11 and the reactive part of the impedance of the loaded quartz one can determine the effective resistance of the loaded quartz. The small inductance in series with resistance was necessary to maintain the capacitance C_o constant. It is attributed to the difficulty in reading small changes in the reactive part of an impedance from the radiofrequency bridge.

If V is the rms voltage across the quartz, one sees



Quartz Unloaded	Quartz Loaded
$C_0 = 49 \mu\mu f$	$C_0 = 49 \mu\mu f$
$L = 6.14 \mu h$	$L = 8.81 \mu h$
$R = 350 \Omega$	$R = 2970 \Omega$

Fig. 9 Equivalent Circuit for Loaded and Unloaded Quartz Transducer.

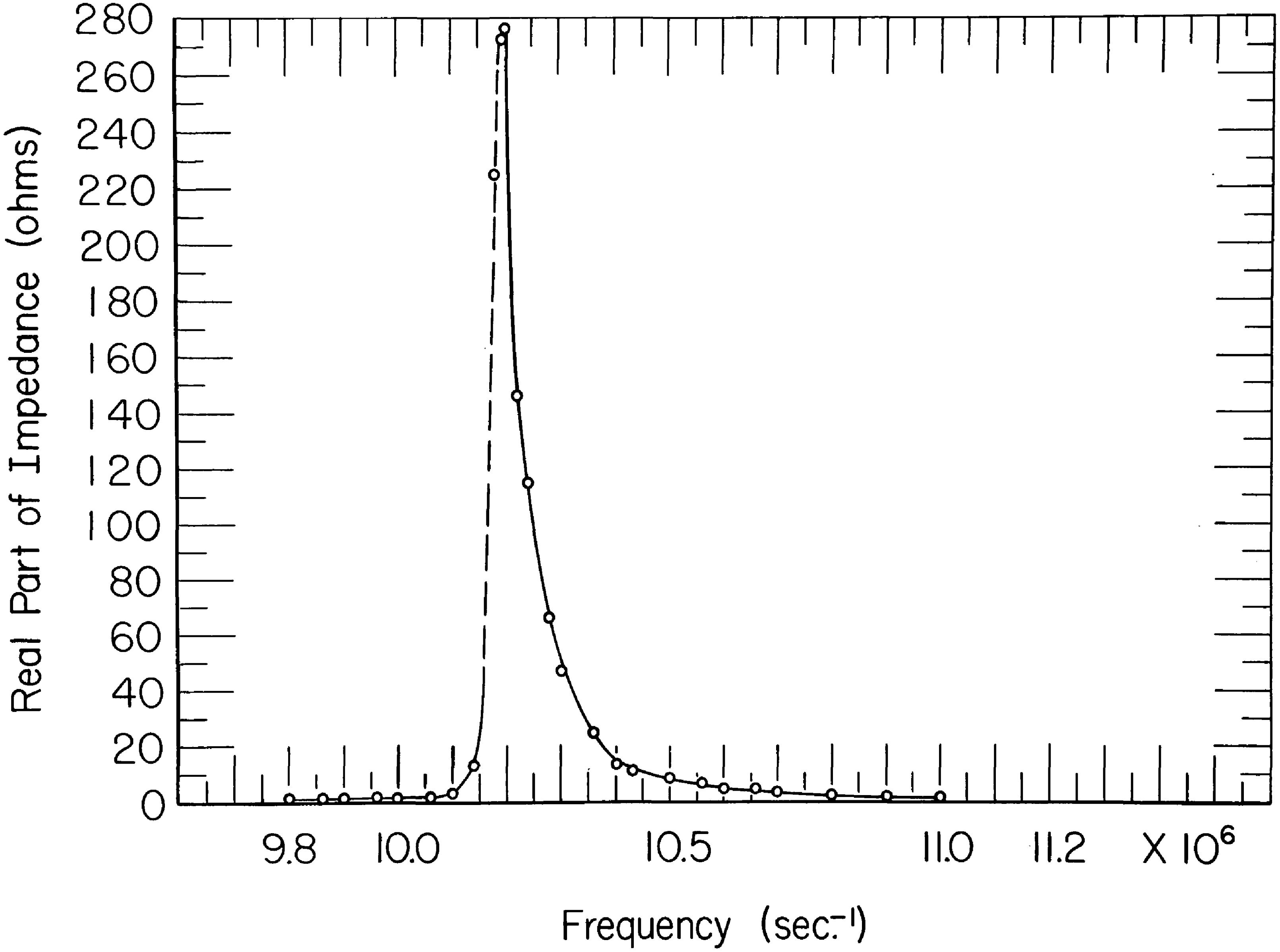


Fig. 10 Real Part of Impedance of Quartz

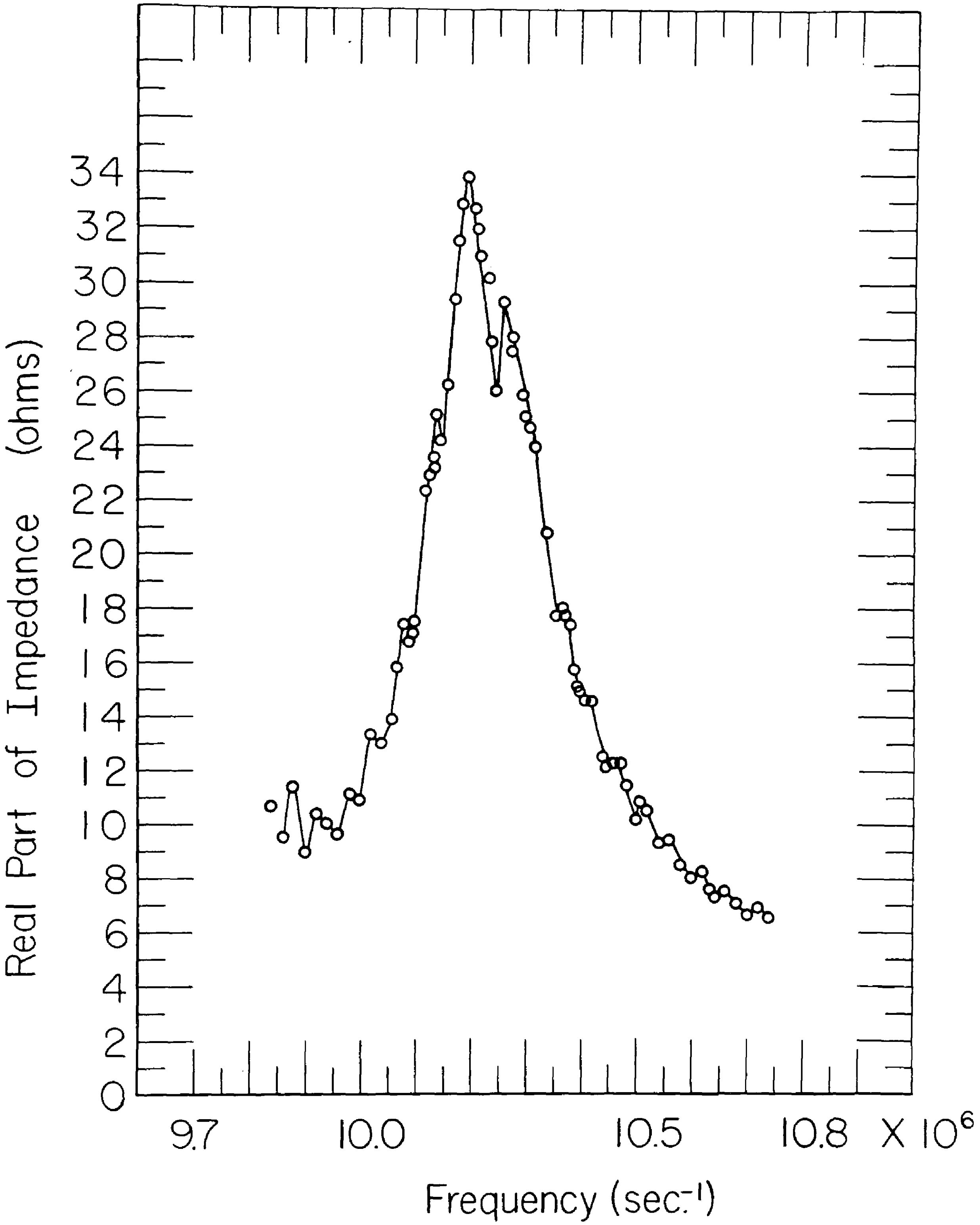


Fig. 11 Real Part of Impedance of Quartz and Sodium Chloride.

from Fig. 9 that the power P_s dissipated in the sodium chloride is

$$P_s = \frac{R_s}{R_T^2} V^2,$$

, where R_s is the effective resistance of the sodium chloride, and R_T is the total effective resistance of the loaded quartz. From Fig. 9,

$$R_s = 2620\,\Omega$$

$$R_T = 2970\,\Omega$$

Hence,

$$P_s = (2.97)(10^{-4})\, V^2 \text{ watts} . \qquad (53)$$

In order to determine the energy density E, we must introduce the phonon relaxation time τ_p. The phonon relaxation time is a measure of the time required for a phonon of frequency ω to be scattered into a phonon of frequency ω'. We shall use the value of τ_p measured by Proctor and Robinson[14]. The value quoted in reference (14) is incorrect, and the corrected value[20] is $\tau_p = 0.78 \times 10^{-3}$. Then with eq. (53), we have

$$E = \frac{P_s \tau_p}{V'} = \frac{(.78)(2.97)(10^{-7})}{V'} V^2 , \qquad (54)$$

where V' is the volume of the sodium chloride crystal. Since

$$V' = 6.44 \text{ cc}, \qquad E = (.36)\, V^2 \text{ ergs/cc} . \qquad (55)$$

The ultrasonic transition probability, eq. (38) is

$$W = \frac{27}{32} \frac{e^4 \varphi^2 \gamma^2 A^2 k^2}{\hbar^2 a^6 \delta\nu} ,$$

and we shall use the following values for the constants which appear in this equation:

$e = 4.80 \times 10^{-10}$ esu,	electron charge
$Q = 0.10 \times 10^{-24}\,\mathrm{cm}^2$,	sodium nuclear electric quadrupole moment
$\lambda = 4.62 \times 10^{-2}$ cm,	wave length of the ultrasonic waves in sodium chloride
$k = \frac{2\pi}{\lambda} = 136\,\mathrm{cm}^{-1}$	
$a = 2.82 \times 10^{-8}$ cm,	equilibrium lattice spacing for sodium chloride

From eq. (52) and eq. (53), we find

$$A^2 = (8.1)(10^{-17})\,V^2, \qquad (56)$$

where the density of the sodium chloride is $\rho = 2.16$ gm/cc. The width of the nuclear resonance line is given by $\delta\nu = \frac{1}{\pi T_2}$, where T_2 is the spin-spin relaxation time. We estimate T_2 from the length of decay of the nuclear induction signal. Experimentally, we estimate $T_2 = 100\,\mu$sec.. Hence,

$$\delta\nu = 3.18 \times 10^{3}\,\mathrm{sec}^{-1}. \qquad (57)$$

Substitution of the numerical values for the constants, eq. (56), and eq. (57) into eq. (38) yields

$$W = (3.8)(10^{-4})\,V^2\gamma^2\,\mathrm{sec}^{-1}. \qquad (58)$$

Fig. 12 is an experimental plot of the ratio A/A_0 as a function of the square of the rms voltage across the transducer. Here A is the amplitude of the induction signal with ultrasonic attenuation, and A_0 is the signal amplitude in the absence of ultrasonic attenuation. Eq. (49) is the theoretical expression for A/A_0:

$$\frac{A}{A_0} = \frac{1}{1 + \frac{8}{5} wT_1} \quad . \tag{49}$$

If we arbitrarily set $wT_1 = 1$, then from eq. (49) we find $A/A_0 = 0.384$. Fig. 12 shows that when $A/A_0 = 0.384$, the voltage $V^2 =$ 800 volts. Hence, if we write $wT_1 = k V^2$, where k is a proportionality factor, we find $k = \frac{1}{800} = 1.25 \times 10^{-3}$. With $k = 1.25 \times 10^{-3}$, eq. (49) becomes

$$\frac{A}{A_0} = \frac{1}{1 + \frac{8}{5}(1.25)(10^{-3})V^2} \quad . \tag{59}$$

Fig. 13 is a plot of the theoretical curve, eq. (59).

Since $wT_1 = 1$ and $V^2 =$ 800 volts, we can use the experimental value of T_1 = 7.15 sec. and eq. (58) to determine the parameter γ . We find $\gamma = 0.68$.

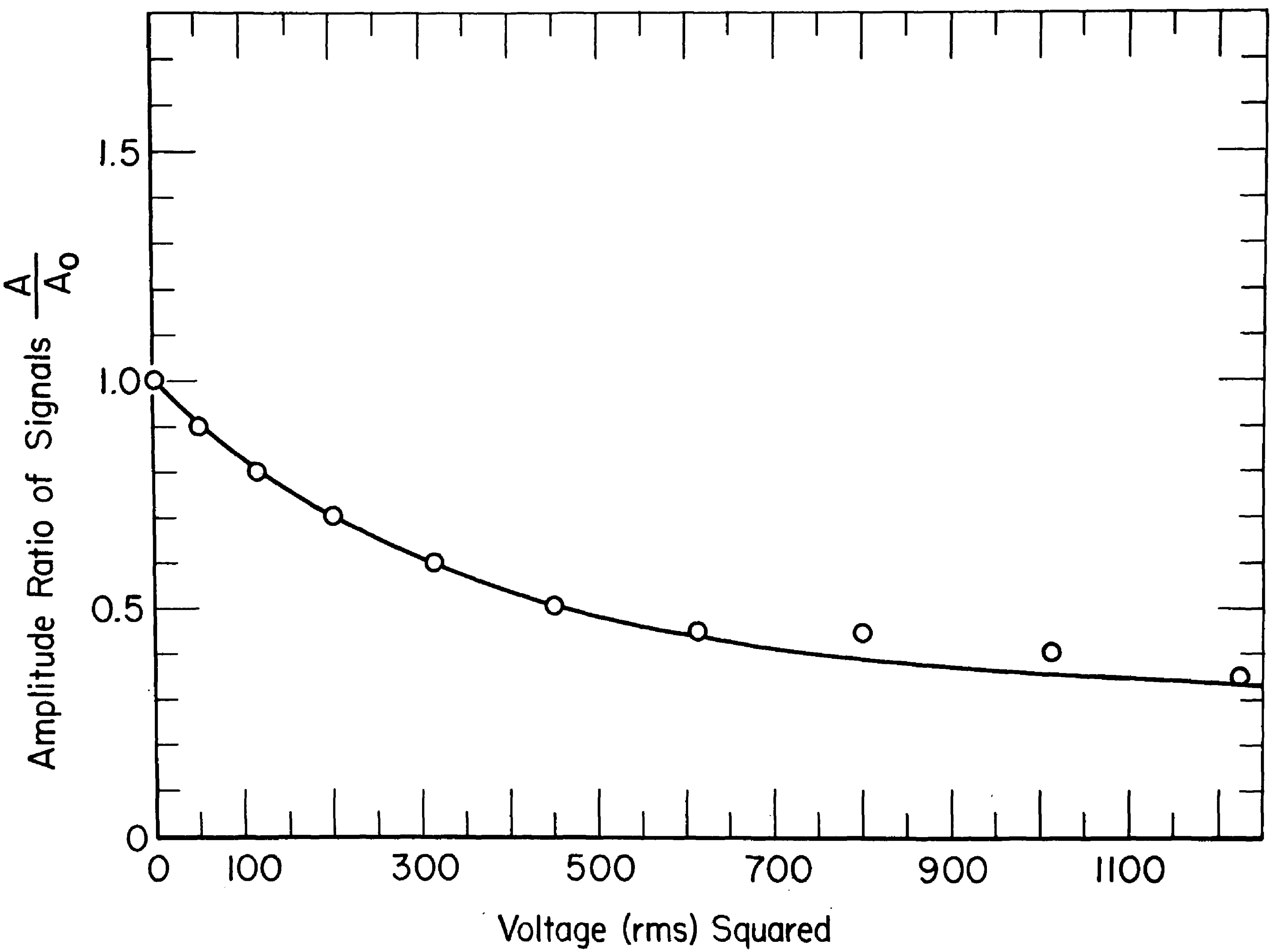


Fig. 12 Experimental Ultrasonic Attenuation of Induction Signal

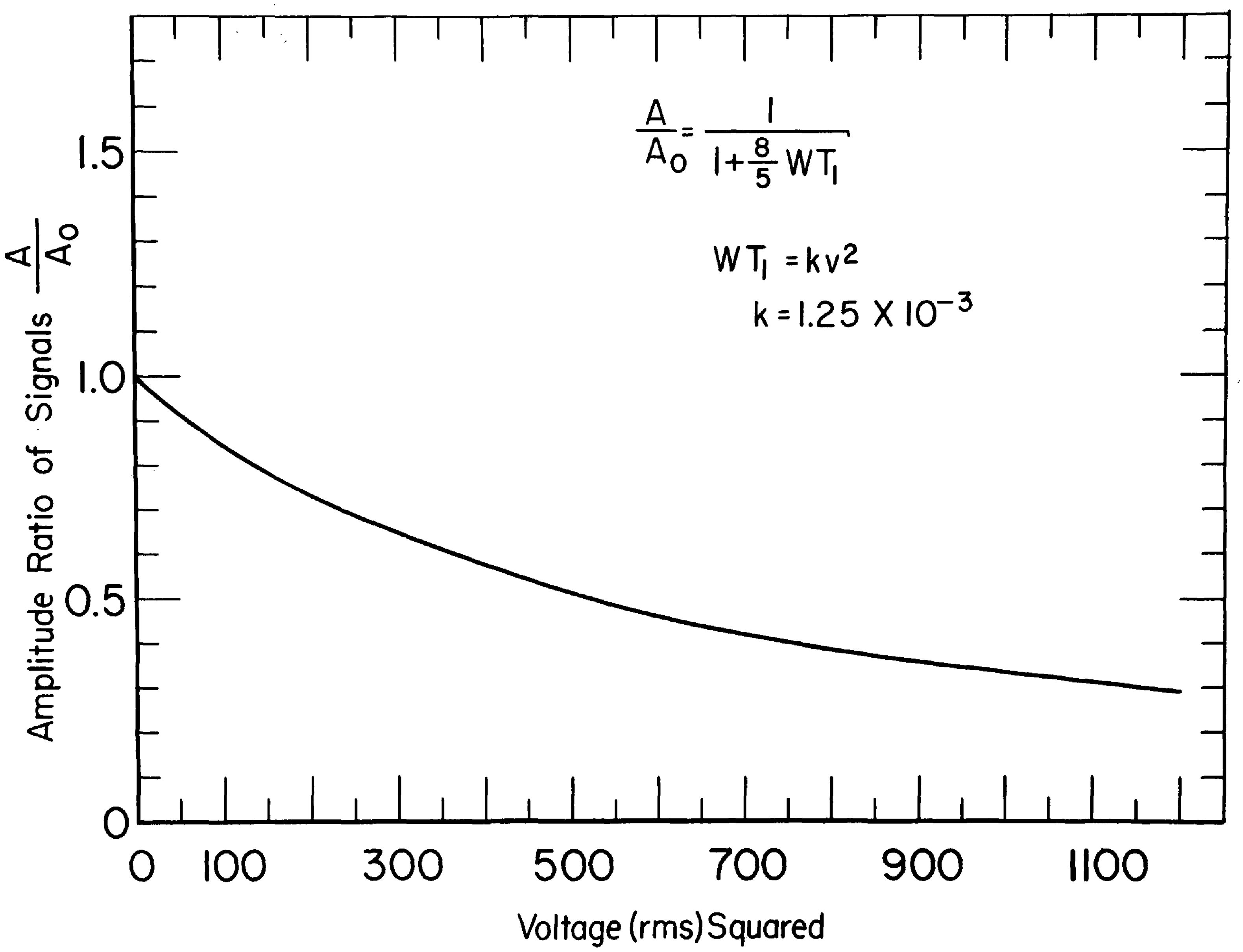


Fig. 13 Theoretical Attenuation of Induction Signal

CHAPTER VI

DISCUSSION

The spin-lattice relaxation time

The experimental value $T_1 = 7.15 \pm .28$ agrees with the value $T_1 = 7.5$ found by Proctor and Robinson[14]. The writer is unaware of other determinations of T_1 for sodium nuclei in sodium chloride.

The parameter γ

The magnitude of $\gamma = 0.68$ calculated in this thesis is one-half the value found by Proctor and Robinson[14]. The value stated in reference (14) is incorrect, and in a private communication to the writer Proctor and Robinson find $\gamma = 1.36$. On the basis of the six point-charge model, a γ of 0.68 indicates that a sodium nucleus sees an effective charge slightly less or, within the limits of accuracy of the experiment, equal to the charge of a single electron on each of its six nearest neighbors. One should not expect to find a $\gamma \sim 1000$ as suggested by van Kranendonk[5], since his calculation treats only indirect processes; but the treatment in this thesis is concerned with direct processes. Comparison of Fig.12 and Fig.13 shows that the experimental results and theory agree quite well; however, the experimental curve does not show sufficient attenuation for large voltages. The effect is due to inhomogeneities in the external magnetic field.

It is difficult to determine the amplitude of the displacement of an ion in the presence of a sound wave. Both this experiment and Proctor and Robinson[14] use the phonon relaxation time and the ultrasonic energy density in the sodium chloride to find the displacement of an ion. The computation of γ used the value of the phonon relaxation time measured by Proctor and Robinson for their experimental conditions. It is possible that a different experimental condition would yield a different phonon relaxation time. The bridge measurements indicated that energy losses in the quartz were small; hence, energy input to the composite oscillator (quartz and sodium chloride combination) was quite effective in producing nuclear transitions ultrasonically. One may question the validity of the use of the radiofrequency bridge for measuring the losses in the sodium chloride. The sodium chloride crystal does not cover the entire face of the transducer; hence, the quartz is also radiating into the air. Therefore, all of the energy losses indicated by the bridge were not dissipated in the sodium chloride. The equivalent circuit which was used neglected losses in the sodium silicate-talc cement; however, these losses should be small. In general the use of a phonon relaxation time and equivalent circuit to compute the displacement of an ion in the sodium chloride is unsatisfactory. It would be desirable to measure the ionic displacements directly, since the weakest point in this experiment was the computation of the displacement.

The values of γ found by different experimenters do not agree. In his most recent experiment Proctor[21] has found $\gamma = 8.1$. Proctor's experiment employed a Q-meter measurement and the phonon relaxation time to determine the amplitude of the sound wave in the sodium chloride. Until experimental methods are refined and one can make reliable calculations of γ it is without point to speculate about the significance of the parameter γ and the correctness of the six point-charge model of the sodium chloride lattice.

APPENDIX

Theory of Pulsed Nuclear Induction

We consider a system of nuclear spins placed in a constant magnetic field $\vec{H}_0$. At time $t = 0$ we apply a pulsed radiofrequency field of magnitude $2H_1$ and frequency ω. The time duration of the field $\vec{H}_1$ is t_w, and its direction is at right angles to the steady field $\vec{H}_0$.

During the time $0 < t \leq t_w$, the Hamiltonian for the system of nuclear spins is

$$\mathcal{H} = -\vec{\mu}\cdot\vec{H}_0 - \vec{\mu}\cdot 2\vec{H}_1 . \qquad (1)$$

Let the steady magnetic field $\vec{H}_0$ be directed along the z-axis of a Cartesian coordinate system and the field $\vec{H}_1$ directed along the x-axis. Then eq.(1) becomes

$$\mathcal{H} = -\gamma\hbar I_z H_0 - \gamma\hbar I_x (2H_1 \cos\omega t), \qquad (2)$$

where γ is the gyromagnetic ratio of the nuclear species which we are considering, I_z and I_x are the operators for the z- and x- components, respectively, of the nuclear spin. For the total wave function ψ we must solve the Schrödinger equation

$$\mathcal{H}\psi = i\hbar \frac{\partial\psi}{\partial t} . \qquad (3)$$

Let the nuclei have a spin $I = \frac{3}{2}$. We expand the wave function ψ :

$$\psi = \sum_{m=-\frac{3}{2}}^{\frac{3}{2}} C_m(t)\phi_m e^{-i\omega_m t}, \qquad (4)$$

where

$$-\gamma\hbar I_z H_0 \phi_m e^{-i\omega_m t} = E_m \phi_m e^{-i\omega_m t}.$$

Substitution of eqs.(2) and (4) into eq.(3) yields

$$-2\gamma\hbar H_1 \cos\omega t \sum_m C_m(t) e^{-i\omega_m t} I_x \phi_m =$$

$$= i\hbar \sum_m \dot{C}_m(t)\phi_m e^{-i\omega_m t}. \qquad (5)$$

If we use the relationship $I_x = \frac{1}{2}(I_+ + I_-)$,

where $I_+ = (I_x + iI_y)$ and $I_- = (I_x - iI_y)$,

we may write eq.(5) as

$$i\hbar \sum_m \dot{C}_m(t)\phi_m e^{-i\omega_m t} =$$

$$= -\gamma\hbar H_1 \cos\omega t \sum_m C_m(t) e^{-i\omega_m t} I_+ \phi_m -$$

$$-\gamma\hbar H_1 \cos\omega t \sum_m C_m(t) e^{-i\omega_m t} I_- \phi_m. \qquad (6)$$

The non-zero matrix elements of the operators I_+ and I_- are

$$(m|I_-|m+1) = \sqrt{(I-m)(I+m+1)}$$

$$(m|I_+|m-1) = \sqrt{(I+m)(I-m+1)}.$$

Using these matrix elements and the orthonormality of the wave functions ϕ_m, we find from eq.(6)

$$\dot{C}_m = i\omega_1 \cos\omega t \Big[(m|I_+|m-1)C_{m-1}(t) e^{-i(\omega_{m-1}-\omega_m)t} +$$

$$+ (m|I_-|m+1)C_{m+1}(t) e^{-i(\omega_{m+1}-\omega_m)t}\Big], \qquad (7)$$

where $\omega_1 = \gamma H_1$. If we let $\Delta\omega = (\omega_{m-1} - \omega_m) = (\omega_{m+1} - \omega_m)$ and require that the spin system absorbs energy from the radiofrequency field, then we have $(\omega - \Delta\omega) = 0$; and eq.(7) yields the following differential equations for the coefficients $C_m(t)$:

$$\dot{C}_{\frac{3}{2}} = i\omega_1 \frac{\sqrt{3}}{2} C_{\frac{1}{2}} \tag{8a}$$

$$\dot{C}_{\frac{1}{2}} = i\omega_1 C_{-\frac{1}{2}} + i\omega_1 \frac{\sqrt{3}}{2} C_{\frac{3}{2}} \tag{8b}$$

$$\dot{C}_{-\frac{1}{2}} = i\omega_1 \frac{\sqrt{3}}{2} C_{-\frac{3}{2}} + i\omega_1 C_{\frac{1}{2}} \tag{8c}$$

$$\dot{C}_{-\frac{3}{2}} = i\omega_1 \frac{\sqrt{3}}{2} C_{-\frac{1}{2}} \tag{8d}$$

In eq.(8) we replace $\frac{d}{dt}$ by the operator D, and we have a set of four linear homogeneous equations for the C_m. If the equations have a non-trivial solution, the determinant formed from the coefficients of the C_m must vanish:

$$\begin{vmatrix} D & -i\omega_1\frac{\sqrt{3}}{2} & 0 & 0 \\ -i\omega_1\frac{\sqrt{3}}{2} & D & -i\omega_1 & 0 \\ 0 & -i\omega_1 & D & -i\omega_1\frac{\sqrt{3}}{2} \\ 0 & 0 & -i\omega_1\frac{\sqrt{3}}{2} & D \end{vmatrix} \tag{9}$$

Expansion of eq.(9) yields

$$D^4 + \frac{5}{2}\omega_1^2 D^2 + \frac{9}{16}\omega_1^4 = 0$$

with the roots

$$D = \pm \frac{i}{2}\omega_1 \tag{10a}$$

$$D = \pm \frac{3i}{2}\omega_1 \tag{10b}$$

For $D = \frac{i}{2}\omega_1$ we find from eq.(8) that

$$C_{\frac{1}{2}} = \frac{1}{\sqrt{3}} C_{\frac{3}{2}}\,;\; C_{-\frac{1}{2}} = -\frac{1}{\sqrt{3}} C_{\frac{3}{2}}\,;\; C_{-\frac{3}{2}} = -C_{\frac{3}{2}}. \tag{11}$$

Since we may write

$$C_{\frac{3}{2}} = A_+ e^{\frac{i}{2}\omega_1 t},$$

where A_+ is an arbitrary constant, eq.(11) determines the C_m in terms of the constant A_+. We treat eq.(8) similarly for each root of eq.(10). The complete solution of eq.(8) will express each C_m as a linear combination of four terms: one term for each root of eq.(10). We find, therefore,

$$C_{\frac{3}{2}} = A_+ e^{i\frac{\omega_1}{2}t} + A_- e^{-i\frac{\omega_1}{2}t} + B_+ e^{i\frac{3\omega_1}{2}t} + B_- e^{-i\frac{3\omega_1}{2}t} \tag{12a}$$

$$C_{\frac{1}{2}} = \frac{A_+}{\sqrt{3}} e^{i\frac{\omega_1}{2}t} - \frac{A_-}{\sqrt{3}} e^{-i\frac{\omega_1}{2}t} + \sqrt{3}\, B_+ e^{i\frac{3\omega_1}{2}t} - \sqrt{3}\, B_- e^{-i\frac{3\omega_1}{2}t} \tag{12b}$$

$$C_{-\frac{1}{2}} = -\frac{A_+}{\sqrt{3}} e^{i\frac{\omega_1}{2}t} - \frac{A_-}{\sqrt{3}} e^{-i\frac{\omega_1}{2}t} + \sqrt{3}\, B_+ e^{i\frac{3\omega_1}{2}t} + \sqrt{3}\, B_- e^{-i\frac{3\omega_1}{2}t} \tag{12c}$$

$$C_{-\frac{3}{2}} = -A_+ e^{i\frac{\omega_1}{2}t} + A_- e^{-i\frac{\omega_1}{2}t} + B_+ e^{i\frac{3\omega_1}{2}t} - B_- e^{-i\frac{3\omega_1}{2}t}. \tag{12d}$$

We must determine the four arbitrary constants A_+, A_-, B_-, B_+ in eq.(12) from the condition of the spin system at time $t = 0$. Suppose the system has been in the steady magnetic field $\vec{H}_0$ prior to application of the pulse long enough for the spins to reach thermal equilibrium. We are interested in the number of excess spins in each energy level relative to the level $m = -\frac{3}{2}$. The energies of the magnetic energy levels are

$$E_{-\frac{3}{2}} = \frac{3}{2}\gamma\hbar H_0;\ E_{-\frac{1}{2}} = \frac{1}{2}\gamma\hbar H_0;\ E_{\frac{1}{2}} = -\frac{1}{2}\gamma\hbar H_0;\ E_{\frac{3}{2}} = -\frac{3}{2}\gamma\hbar H_0.$$

At thermal equilibrium we assume a Boltzmann distribution of the spins among the energy levels. Then the excess spins in each level are

$$(N_{-\frac{1}{2}} - N_{-\frac{3}{2}}) = \frac{N}{4}\frac{\gamma\hbar H_0}{KT} \tag{13a}$$

$$(N_{\frac{1}{2}}-N_{-\frac{3}{2}})=\frac{N}{4}\,\frac{2\gamma\hbar H_0}{KT} \tag{13b}$$

$$(N_{\frac{3}{2}}-N_{-\frac{3}{2}})=\frac{N}{4}\,\frac{3\gamma\hbar H_0}{KT}\,. \tag{13c}$$

From eq.(13) we find that the probabilities for excess spins in the four levels are:

$$P_{-\frac{3}{2}}=0\,;\; P_{-\frac{1}{2}}=\frac{1}{6}\,;\; P_{\frac{1}{2}}=\frac{1}{3}\,;\; P_{\frac{3}{2}}=\frac{1}{2}\,. \tag{14}$$

Consequently, at time $t=0$ the coefficients C_m must satisfy the conditions

$$|C_{-\frac{3}{2}}(0)|^2=0 \qquad |C_{\frac{1}{2}}(0)|^2=\frac{1}{3}$$
$$|C_{-\frac{1}{2}}(0)|^2=\frac{1}{6} \qquad |C_{\frac{3}{2}}(0)|^2=\frac{1}{2}\,. \tag{15}$$

A solution of eq.(15) is

$$C_{-\frac{3}{2}}(0)=0 \qquad C_{\frac{1}{2}}(0)=\frac{1}{\sqrt{3}}e^{i\alpha}$$
$$C_{-\frac{1}{2}}(0)=\frac{1}{\sqrt{6}}e^{i\beta} \qquad C_{\frac{3}{2}}(0)=\frac{1}{\sqrt{2}}e^{i\delta}, \tag{16}$$

where α, β, and δ are arbitrary phase factors. Using eq.(12) and eq.(16), we obtain

$$\mathrm{Re}\,(A_+ + A_- + B_+ + B_-)=\frac{1}{\sqrt{2}}\cos\delta \tag{17a}$$
$$\mathrm{Im}\,(A_+ + A_- + B_+ + B_-)=\frac{1}{\sqrt{2}}\sin\delta$$

$$\mathrm{Re}\,\left(\frac{A_+}{\sqrt{3}}-\frac{A_-}{\sqrt{3}}+\sqrt{3}B_+-\sqrt{3}B_-\right)=\frac{1}{\sqrt{3}}\cos\alpha$$
$$\mathrm{Im}\,\left(\frac{A_+}{\sqrt{3}}-\frac{A_-}{\sqrt{3}}+\sqrt{3}B_+-\sqrt{3}B_-\right)=\frac{1}{\sqrt{3}}\sin\alpha \tag{17b}$$

$$\mathrm{Re}\,\left(-\frac{A_+}{\sqrt{3}}-\frac{A_-}{\sqrt{3}}+\sqrt{3}B_++\sqrt{3}B_-\right)=\frac{1}{\sqrt{6}}\cos\beta \tag{17c}$$
$$\mathrm{Im}\,\left(-\frac{A_+}{\sqrt{3}}-\frac{A_-}{\sqrt{3}}+\sqrt{3}B_++\sqrt{3}B_-\right)=\frac{1}{\sqrt{6}}\sin\beta$$

$$\mathrm{Re}\,(-A_+ + A_- + B_+ - B_-)=0 \tag{17d}$$
$$\mathrm{Im}\,(-A_+ + A_- + B_+ - B_-)=0$$

Let $\mathrm{Re}\,A_+ = x$; $\mathrm{Re}\,A_- = y$; $\mathrm{Re}\,B_+ = u$; $\mathrm{Re}\,B_- = v$. (18)

Substitution of eq.(18) into eq.(17) yields the system of equations:

$$\begin{aligned} x + y + u + v &= \frac{1}{\sqrt{2}} \cos\delta \\ \frac{x}{\sqrt{3}} - \frac{y}{\sqrt{3}} + \sqrt{3}\,u - \sqrt{3}\,v &= \frac{1}{\sqrt{3}} \cos\alpha \\ -\frac{x}{\sqrt{3}} - \frac{y}{\sqrt{3}} + \sqrt{3}\,u + \sqrt{3}\,v &= \frac{1}{\sqrt{6}} \cos\beta \\ -x + y + u - v &= 0. \end{aligned} \tag{19}$$

The solution of eq.(19) is

$$\begin{aligned} x &= \frac{1}{8} \cos\alpha - \frac{1}{8\sqrt{2}} \cos\beta + \frac{3}{8\sqrt{2}} \cos\delta \\ y &= \frac{-1}{8} \cos\alpha - \frac{1}{8\sqrt{2}} \cos\beta + \frac{3}{8\sqrt{2}} \cos\delta \\ u &= \frac{1}{8} \cos\alpha + \frac{1}{8\sqrt{2}} \cos\beta + \frac{1}{8\sqrt{2}} \cos\delta \\ v &= -\frac{1}{8} \cos\alpha + \frac{1}{8\sqrt{2}} \cos\beta + \frac{1}{8\sqrt{2}} \cos\delta \end{aligned} \tag{20}$$

The imaginary parts of A_+, A_-, B_+, B_- follow from eq.(20) if we replace "cosine" by "sine". Our solution for the arbitrary constants A_+, A_-, B_+, and B_- is:

$$A_+ = \frac{1}{8}\left(e^{i\alpha} - \frac{1}{\sqrt{2}} e^{i\beta} + \frac{3}{\sqrt{2}} e^{i\delta}\right) \tag{21a}$$

$$A_- = \frac{1}{8}\left(-e^{i\alpha} - \frac{1}{\sqrt{2}} e^{i\beta} + \frac{3}{\sqrt{2}} e^{i\delta}\right) \tag{21b}$$

$$B_+ = \frac{1}{8}\left(e^{i\alpha} + \frac{1}{\sqrt{2}} e^{i\beta} + \frac{1}{\sqrt{2}} e^{i\delta}\right) \tag{21c}$$

$$B_- = \frac{1}{8}\left(-e^{i\alpha} + \frac{1}{\sqrt{2}} e^{i\beta} + \frac{1}{\sqrt{2}} e^{i\delta}\right) \tag{21d}$$

For time $t > t_w$, the solution of the Schrödinger equation is $\psi = \sum_m a_m \phi_m e^{-i\omega_m t}$.

At time $t = t_w$, we require of the coefficients a_m:

$|a_m|^2 = |C_m(t_w)|^2$ or $a_m = C_m(t_w) e^{i\omega_m t_w}$.

The phase $\omega_m t_w$ is the angle through which a spin in the state m precesses in the time t_w. Finally, the wave function for time $t \geq t_w$ becomes

$$\psi = \sum_m C_m(t_w) \phi_m e^{-i\omega_m (t - t_w)}. \qquad (22)$$

The magnitude at any time $t > t_w$ of the nuclear signal induced in a coil with its axis parallel to the x-axis is proportional to the x-component μ_x, of the resultant nuclear magnetic moment. Since $\mu_x = \gamma \hbar I_x$, we must compute the expectation value of the nuclear spin operator I_x. We have

$$\langle I_x \rangle = (\psi^* | I_x | \psi) = \tfrac{1}{2} (\psi^* | I_+ + I_- | \psi). \qquad (23)$$

Using the wave functions of eq.(22), we find that

$$\begin{aligned}(\psi^* | I_+ | \psi) &= \sqrt{3}\, C^*_{-\frac{1}{2}} C_{-\frac{3}{2}} \exp. i(\omega_{-\frac{1}{2}} - \omega_{-\frac{3}{2}})(t - t_w) + \\ &\quad + 2 C^*_{\frac{1}{2}} C_{-\frac{1}{2}} \exp. i(\omega_{\frac{1}{2}} - \omega_{-\frac{1}{2}})(t - t_w) + \\ &\quad + \sqrt{3}\, C^*_{\frac{3}{2}} C_{\frac{1}{2}} \exp. i(\omega_{\frac{3}{2}} - \omega_{\frac{1}{2}})(t - t_w). \\ &= \exp. [-i\Delta\omega(t - t_w)] [\sqrt{3}\, C^*_{-\frac{1}{2}} C_{-\frac{3}{2}} + \\ &\quad + 2 C^*_{\frac{1}{2}} C_{-\frac{1}{2}} + \sqrt{3}\, C^*_{\frac{3}{2}} C_{\frac{1}{2}}], \end{aligned} \qquad (24)$$

where $(\omega_{-\frac{1}{2}} - \omega_{-\frac{3}{2}}) = (\omega_{\frac{1}{2}} - \omega_{-\frac{1}{2}}) = (\omega_{\frac{3}{2}} - \omega_{\frac{1}{2}}) = -\Delta\omega$.

Also

$$(\psi^{*}|I_{-}|\psi)=\exp.\,i\Delta\omega(t-t_{\omega})[\sqrt{3}\,C^{*}_{-\frac{3}{2}}C_{-\frac{1}{2}}+2C^{*}_{-\frac{1}{2}}C_{\frac{1}{2}}+\sqrt{3}\,C^{*}_{\frac{1}{2}}C_{\frac{3}{2}}]. \qquad (25)$$

We can compute the quantities in the square brackets of eq.(24) and eq.(25) by using eq.(21) and eq.(12). (In eq.(12) we must set $t=t_{\omega}$.) Computation shows that any term in the expansion of eq.(24) or eq.(25) which contains a function of the phase factors α, β, and δ as a factor vanishes when one averages the functions over all possible values of the phase factors. Consequently, one finds that

$$(\psi^{*}|I_{+}|\psi)=\exp.[-i\Delta\omega(t-t_{\omega})]\,(-\tfrac{5}{12}e^{-i\omega_{1}t_{\omega}}+ \\ +\tfrac{5}{12}e^{i\omega_{1}t_{\omega}}), \qquad (26a)$$

$$(\psi^{*}|I_{-}|\psi)=\exp.[i\Delta\omega(t-t_{\omega})]\,(-\tfrac{5}{12}e^{i\omega_{1}t_{\omega}}+ \\ +\tfrac{5}{12}e^{-i\omega_{1}t_{\omega}}). \qquad (26b)$$

Then

$$2<I_{x}>=-\tfrac{5}{12}(e^{i\omega_{1}t_{\omega}}-e^{-i\omega_{1}t_{\omega}})(e^{i\Delta\omega(t-t_{\omega})}- \\ -e^{-i\Delta\omega(t-t_{\omega})}),$$

and

$$<\mu_{x}>=\frac{5\gamma\hbar}{6}\sin\omega_{1}t_{\omega}\sin\Delta\omega(t-t_{\omega}). \qquad (27)$$

It follows from eq.(26a) and eq.(26b) that

$$<\mu_{y}>=\frac{5\gamma\hbar}{6}\sin\omega_{1}t_{\omega}\cos\Delta\omega(t-t_{\omega}). \qquad (28)$$

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