THE RICE INSTITUTE

NUCLEAR MAGNETISM

OF

I^{127} \text{ IN KI}

by

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A THESIS

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INTRODUCTION

Since the first successful experiments in nuclear magnetic resonance were performed in 1946, N.M.R. has developed into a valuable tool for the study of the structure of matter. Using N.M.R., the experimentalist can gain information about solids by using the atomic nucleus as a sensitive probe of local fields. With this in mind, a series of experiments have been conducted at Rice, using N.M.R. at low temperatures to add basic information concerning alkali halides.

The principal quantities of interest in N.M.R. are $T_1$, $T_2$, and $M_0$. $T_1$ is the time parameter which governs the exponential approach to equilibrium of the nuclear spin system and the other degrees of freedom, usually called the "lattice". $T_1$ is also known as the longitudinal relaxation time, as it is the time constant associated with the exponential growth or decay (usually assumed to take place at the same rate) of the magnetization of a sample in the direction of the externally applied field, $H_0$. $T_2$ is called the spin-spin relaxation time or the tranverse relaxation time. $T_2$ is the time parameter associated with the decay of the components of the magnetization perpendicular to the large externally applied field, $H_0$, due to the de-phasing of the individual rotating
magnetic moments. \( M_0 \) is the magnetization proportional to the externally applied large field, \( H_0 \), when the nuclear spin system and the lattice are in thermal equilibrium.

The spin-lattice relaxation time, \( T_1 \), is of interest to the solid state physicist in that it gives a measure of the interaction of the individual nuclei in a solid with the local fields in which the individual nuclei find themselves. By studying \( T_1 \) as a function of the externally applied field, \( H_0 \), the experimentalist can obtain information concerning the distribution in frequency of the lattice oscillators. A study of \( T_1 \) as a function of temperature can yield information concerning the ease at which energy can be transferred from the spin system to the lattice, or from the lattice to the spin system. This then gives an indication of the coupling of the spin system to the lattice as a function of temperature.

Recently, spin-lattice relaxation studies were conducted at Rice on I\(^{127}\) in KI by G. V. Briscoe and C. F. Squire\(^3\), to investigate a theory of quadrupolar relaxation proposed by J. Van Kranendonk.\(^4\) (A brief discussion of this theory is included in Appendix A.) Between 2.17°K and 4.22°K, the measured spin lattice relaxation time, \( T_1 \), did not agree with the predicted values in Van Kranendonk's theory. At low temperatures,
Van Kranendonk's theory predicted a $T^{-7}$ temperature dependence, where the experiments seemed to indicate $T_1$ was temperature independent. However, in the liquid hydrogen range ($14^\circ K$ to $20^\circ K$), the measured values of $T_1$ agreed quite well with the theoretical values. Briscoe investigated a powder specimen and found that in the hydrogen region, $T_1$ was essentially no different from that in the single crystal. The particles in the powder were reduced to such a size that lattice frequencies as high as ten times the Larmor frequency were eliminated. These results supported Van Kranendonk’s theory that the direct interaction of the lattice vibrations with the precessing nuclei was negligible compared to the Raman type process. The Raman process is one in which a lattice wave is scattered by a nucleus, leaving it with an energy $\hbar \nu' \pm \hbar \nu$, where $\nu'$ is the frequency of the lattice wave and $\nu$ is the Larmor precession frequency of the nuclear spin. However, in the helium range, the measured value of $T_1$, for the powder was an order of magnitude shorter than the single crystal $T_1$. No explanation was given for this result. F. Bloch suggested that an impurity relaxation could be the dominant relaxation mechanism in the helium range.

Bloembergen has proposed a paramagnetic impurity relaxation mechanism to account for the relaxation times
observed in supposedly very pure single crystals. He asserted that even in the purest single crystals, about one part in $10^7$ of paramagnetic ions are present. The nuclear spins diffuse through the lattice by means of the spin-spin interaction until they arrive in the vicinity of a paramagnetic ion. In a region surrounding each paramagnetic ion, there is a strong interaction between the nuclear spins and those of the electronically paramagnetic impurities. The spin system of the paramagnetic impurities is in good thermal contact with the lattice and therefore it can readily transfer its acquired energy. This mechanism is a series process in the sense that the slowest process will essentially govern the resultant relaxation time. It has been found that in other alkali halides $T_1$ is temperature independent down to a certain temperature ($\simeq 14^0 K$), then $T_1$ varies as $T^{-2}$.

Because of the discrepancy between theory and experiment in the helium range and the lack of understanding of the type of relaxation mechanism in this temperature range, it was felt that a more thorough investigation should be carried out at low temperatures. It was felt that an investigation of the temperature dependence between room temperature and the hydrogen range would give a better check of Van Kranendonk's theory. In
addition to this, Van Kranendonk's theory predicts an orientation effect of $T_1$, that is, the relaxation time depends on the crystal orientation with respect to the magnetic field. Van Kranendonk assumed that there is no field dependence of $T_1$. This has been investigated. In order to throw more light on the relaxation mechanism in the region where the theory fails, various investigations were carried out. Namely, the field dependence of $T_1$, and the magnetization as a function of field and temperature.

Interesting observations have been made on relaxation times of the decay of the magnetization with time, as opposed to the time dependence of its growth. These observations indicate that the relaxation times are different for the two methods by a factor of two or three.
EXPERIMENTAL APPARATUS

Nuclear Magnetic Resonance Spectrometer

Figure 1 is a block diagram of the components of the nuclear magnetic resonance spectrometer. The magnetic field is supplied by a six inch water cooled electromagnet constructed by Varian Associates. The power supply for the magnet was also constructed by Varian Associates. The oscillator, r.f. amplifier, and detector are part of a commercial unit obtained from Nuclear Magnetics Corporation, and based on a design of Watkins.

The radio frequency coil wound around the sample in the magnetic field, $H_0$, supplies an oscillating field, $H_1$, at right angles to $H_0$. If this coil is made part of a tank circuit in a marginal oscillator, then any small change in its driving impedance due to the absorption of r.f. energy by the nuclear spin system results in a modulation of the r.f. voltage across the coil. If this voltage is amplified and detected, it can be displayed on an oscilloscope, or recording galvanometer. The amplitude of this modulation is proportional to $H_1 \chi''$, where $\chi''$ is the imaginary part of the Bloch susceptibility.
In the temperature ranges where $T_1$ is relatively short, a high frequency recording galvanometer manufactured by Minneapolis Honeywell was used to record data, otherwise, observations were made directly from an oscilloscope. To provide the modulation field, several hundred turns of copper wire were wound around the pole faces of the magnet. The audio voltage was provided by an audio oscillator and amplified by a Dynakit Power Amplifier.

**Cryogenics**

In order to obtain the various low temperatures used in the experiment, the sample was held in a sample holder at the end of a rigid coaxial line inside the inner dewar of a two dewar assembly. The outer dewar contained liquid nitrogen and the inner dewar contained liquid nitrogen, hydrogen, or helium, depending on the temperature range of interest. When lower temperatures than the normal boiling point of the bath were required, they were obtained by pumping on the bath with a mechanical pump. By measuring the vapor pressure above the bath with a manometer, it was possible to determine the temperature of the bath. Since these techniques are conventional in low temperature research, no further
However, since much of the success of some of the measurements can be attributed to the coaxial line, it would be well to give a brief discussion of its construction. When designing a coaxial line of this type, several things should be kept in mind. Namely, the line must have a relatively low loss factor, and it must be a poor thermal conductor. The capacity should be low, and the line should be relatively rigid to minimize variations in capacity due to vibration.

Because of these considerations, the line was constructed in the following manner. (See Figure 2) A 1/2 inch Monel tube, A, was used as the outer conductor and the inner conductor was a 1/32 inch stainless steel capillary, B, with several thousandths of copper plated on the outside. The center conductor was held in place by 1/2 inch long polyethylene spacers, C, approximately three inches apart on the line. The capillary was brought out of the top end of the line through a Kovar seal, D, and soft soldered to a standard coaxial connector, E. Because Monel is slightly magnetic, a brass cylinder, F, four inches in length, was used for the lower part of the line. A lucite sample holder, G, fit into the end of the brass tube. The inner conductor went through a hole in the sample holder and was soft
COAXIAL LINE AND PROBE

FIGURE 2
soldered to the coil lead, H. The coil, I, was wound around the sample holder and enclosed in a one inch diameter copper cylinder, J, which was soft soldered to the outer conductor of the coaxial line. The copper cylinder was necessary to shield the coil from stray radiation. A small cap, K, fit over the end of the sample holder, which could be removed in order to remove the sample between runs. This feature also made it possible to use water in the sample holder when making preliminary measurements at room temperature, as the I$^{127}$ signal was difficult to observe at this temperature. The coil used in the helium and nitrogen range was composed of 27 turns of #24 enameled copper wire, while in the hydrogen range the coil had 30 turns of #26 enameled wire. In both cases a Q in excess of 100 was obtained. The coaxial line came through an "0" ring stuffing box, L, at the top plate, M, which permitted the rotation of the sample for orientation studies.

At no time during the course of the experiment were microphonics serious. Because of the low heat leak, a dewar of helium (2 liters) lasted from 19 to 23 hours, depending on how well the nitrogen was maintained in the outer dewar.
Specimen

The KI crystal used in the experiment was obtained from the Harshaw Chemical Company, and was of high purity. The sample was fashioned into a cylinder \( \frac{3}{4} \) inches long and \( \frac{1}{2} \) inch in diameter, with a crystal axis along the axis of the cylinder.
PROCEDURE

The components of the nuclear magnetic susceptibility are

\[
\chi' = \frac{1}{2} \gamma_0 \omega_0 T_2 \left[ \frac{(\omega_0 - \omega) T_2}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right]
\]

\[
\chi'' = \frac{1}{2} \gamma_0 \omega_0 T_2 \left[ \frac{1}{1 + (\omega_0 - \omega)^2 T_2^2 + \gamma^2 H_1^2 T_1 T_2} \right]
\]

where

\( \chi' \) - static susceptibility

\( T_2 \) - spin-spin relaxation time

\( T_1 \) - spin-lattice relaxation time

\( \omega_0 \) - Larmor frequency

\( \gamma \) - gyromagnetic ratio

\( H_1 \) - r.f. magnetic field

The spectrometer employed in this series of experiments detects only changes in \( H, \chi'' \), and when data is actually being taken, the condition

\[
\gamma^2 H^2 T_1 T_2 \ll 1
\]

is usually employed.

Therefore, one has

\[
H, \chi'' = \frac{1}{2} \frac{\gamma_0 \omega_0 T_2 H_1}{1 + (\Delta \omega)^2 T_2^2}
\]
At resonance, \( \Delta \omega \) is zero and \( H, \chi'' \) is given by the following equation:

\[
H, \chi'' = \frac{1}{2} \gamma_0 \omega_0 T_2 H_1 = \frac{1}{2} \omega_0 T_2 H_1 \frac{M_0}{H_0}
\]  

(2)

From equation (1) and remembering that the signal observed is proportional to \( H, \chi'' \), one can see that for sufficiently small \( H_1 \), the signal increases linearly with \( H_1 \), but with sufficiently large \( H_1 \), the signal goes to zero. This is called complete saturation and means that radio frequency energy is being put into the spin system faster than the spin system can transfer this energy to the lattice, causing an equal population of the spin states and giving rise to zero magnetization. In this manner, one can measure \( T_1 \), the Spin-lattice relaxation time by saturating the spin system, then lowering \( H_1 \), and watching the exponential growth of \( H\chi' \) with time. The characteristic time of this exponential growth is just \( T_1 \). Sometimes when \( T_1 \) is sufficiently long, it is not possible to observe continuously the growth of the signal as the minimum of \( H \) of the spectrometer is too large. There are two possible ways to circumvent this difficulty. If \( T_1 \) is long, one can saturate the signal with a large \( H_1 \), then change \( H_0 \) away from the resonance value and lower \( H_1 \). At a known time later, restore \( H_0 \) to the resonance value and observe the signal amplitude.
Repeating this process for different elapsed times, one can plot out the signal amplitude against time and in this manner determine the relaxation time. If $T_1$ is shorter, one can increase the modulation amplitude and lower the modulation frequency. The effective $H_J$ is reduced because the Larmor condition is satisfied a smaller percentage of the time.

All measurements of relaxation times by the growth process were taken by one of the two methods described above. In the helium range, where $T_1$ is long, the signal was saturated by manually sweeping the field through the resonance field value. The field was then changed away from the resonance value. At known times later, the signal amplitude was measured on the oscilloscope using a wide modulation and low modulation frequency. In this manner, the curve

$$S = S_0 \left(1 - e^{-t/T_1}\right)$$

was determined, from which one can deduce $T_1$ and $S_0$, which is proportional to $M_0$. (See Figure 3)

In the other temperature ranges, the signal was saturated by sweeping through the resonance condition with a small modulation. When the signal was saturated, a wide modulation was turned on at a lower frequency while the small modulation was turned off. The signal
GROWTH OF SIGNAL FOR $^{127}$ IN KI

$T = 2.17^\circ K$, $H_0 = 6.2$ KG

THE SOLID CURVE IS GIVEN BY

$S(T) = S_0 \left(1 - \exp \frac{T}{T_1}\right)$

WHERE $S_0 = 30.7$, $T_1 = 170$ MINUTES

FIGURE 3
was recorded on the Visicorder, which gave a series of signals, the amplitude of which was proportional to the magnetization. From the exponential envelope, one could then determine $T_1$. $T_1$ measurements were made at various different field values ($H_0$) in the helium range by the following method. The signal was saturated at the measuring value of $H_0$, say 6 Kg, then $H_0$ was changed to 3 Kg. The signal was allowed to grow with $H_0 = 3$ Kg, but when a signal amplitude was to be recorded, $H_0$ was changed back to 6 Kg in a time $\tau$ such that $\tau \ll T_1$ and $\tau \gg T_2$. This insured the fact that the populations of the energy levels remained constant during the time $\tau$ so that the growth of the signal with time was indicative of the signal in a 3 Kg field. This process is referred to as an adiabatic process in the Ehrenfest sense.

Measurements of relaxation processes in the reverse direction were also carried out. In making measurements of the growth of the signal after saturation, one can say the spin system has been raised to an infinite temperature while the lattice remains at the temperature of the bath. By letting the signal grow to its maximum value at a certain bath temperature, $T_L$, and magnetic field, the spin system and the lattice came into equilibrium and one can say $T_L = T_2$. Now if the bath temperature is raised in a time short compared to $T_1$, but long compared to $T_2$, then
and a new Boltzmann distribution will obtain. In this manner, relaxation times could be measured where initially $T_\perp > T_\parallel$ as opposed to the case where initially $T_\parallel > T_\perp$. Likewise, $H_0$ was changed after equilibrium was reached between the spin system and the lattice, and the relaxation time was measured.

When making measurements in the helium range, it was possible to observe the proton resonance signal from the protons in the sample holder. Therefore it was possible to eliminate errors in signal amplitude measurements due to drift in the electronics, and to obtain reasonably accurate information concerning the validity of the Curie law, $M_0 = \frac{CN_0}{T}$. 
RESULTS

Nitrogen Temperature Range

The experimental values of $T_i$, in the liquid nitrogen temperature range, are shown in Table 1, with the calculated values from Van Kranendonk's theory (See Appendix A and Table 5). Figure 4 shows the theoretical curve of Van Kranendonk for one of the crystal axes in the direction of $H_0$ with the measured values. In this temperature range, the signal to noise ratio was not too favorable, and as a result, the errors in $T_i$ are of the order of 20%. The value at 63.3°K is more reliable than at other temperatures in this range because the $N_i$ bath was quieter, and as a result, lower r.f. levels were used. This probably accounts for the values of $T_i$ departing from theoretical values at higher temperatures. A study of line shapes is discussed in Appendix B.
### TABLE 1

Spin-Lattice Relaxation Times, $T_1$, for $^{127}$I

In Single Crystal KI

For the Temperature Range 63°K to 78°K

with the Magnetic Field $H_0 = 6.3$ Kg

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>Measured $T_1$ (sec)</th>
<th>Aver. Meas. $T_1$ (sec)</th>
<th>Theoretical $T_1$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>63.3</td>
<td>.46</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63.3</td>
<td>.39</td>
<td>.39 $\pm$ .08</td>
<td>.375</td>
</tr>
<tr>
<td>63.3</td>
<td>.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>63.3</td>
<td>.31</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.0</td>
<td>.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>65.0</td>
<td>.34</td>
<td>.32 $\pm$ .07</td>
<td>.351</td>
</tr>
<tr>
<td>65.0</td>
<td>.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.0</td>
<td>.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>67.0</td>
<td>.31</td>
<td>.27 $\pm$ .06</td>
<td>.323</td>
</tr>
<tr>
<td>67.0</td>
<td>.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td>77.5</td>
<td>.17</td>
<td>.17 $\pm$ .07</td>
<td>.230</td>
</tr>
</tbody>
</table>
Figure 4

$T_1$ in $1^{27}$I in K1 between 63.3 $^\circ$K and 77.5 $^\circ$K with $H_o = 6.3$ KG. The solid curve is from Van Kranendonk's theory.
Helium Temperature Range

Two measurements were made of $T$, at each of three different temperatures in the liquid helium range with \( H_0 = 6.2 \) Kg. The growth method for low temperatures described in the Procedure was used to make these measurements. (See Figure 3) In addition to determining $T$, it was possible to determine $S_0 (\sim M,)$ and thereby check the Curie law. These results are shown in Table 2. $T$, was also measured for several different values of $H_0$ at $4.22^\circ$K. These results are included in Table 2. Figure 5 gives a plot of $S_0$ as a function of $H_0$.

Three measurements were made of the relaxation time where initially the lattice temperature and spin temperature were $1.42^\circ$K, and then the bath was raised to $4.22^\circ$K. The relaxation time in this case was found to be several times greater than the $T$, determined by the growth method. In addition to these measurements, the relaxation time of the decay of the magnetization (See Table 3) was measured where both the spin temperature and $H_0$ were lowered by a factor of three. While the temperature of the bath remained at $4.22^\circ$K, the spin temperature dropped to $1.42^\circ$K because the demagnetization was essentially adiabatic. This is true because the Boltzmann
factor remained unchanged.

All relaxation curves were plotted in such a manner that it was possible to determine if the relaxation processes were truly exponential with a single relaxation time. All the curves indicated a true exponential process within the experimental error. Figure 6 is an example of such a curve.
TABLE 2

Spin-Lattice Relaxation Time, $T_1$, and Magnetization, $M_0$, of $^{127}$I in KI as a Function of Field and Temperature

Data Taken by the Growth Method

<table>
<thead>
<tr>
<th>$T^\circ$ K</th>
<th>$H_e$ (Kg)</th>
<th>$S_c \propto M_0$</th>
<th>$T_1$ (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.22</td>
<td>6.2</td>
<td></td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>4.22</td>
<td>6.2</td>
<td></td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>2.17</td>
<td>6.2</td>
<td></td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>2.17</td>
<td>6.2</td>
<td></td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>1.48</td>
<td>6.2</td>
<td></td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>1.48</td>
<td>6.2</td>
<td></td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>4.22</td>
<td>6.9</td>
<td>2.36</td>
<td>205 $\pm$ 15</td>
</tr>
<tr>
<td>4.22</td>
<td>6.2</td>
<td>2.06</td>
<td>170 $\pm$ 10</td>
</tr>
<tr>
<td>4.22</td>
<td>3.0</td>
<td>1.01</td>
<td>120 $\pm$ 15</td>
</tr>
<tr>
<td>4.22</td>
<td>2.6</td>
<td>0.79</td>
<td></td>
</tr>
<tr>
<td>4.22</td>
<td>1.5</td>
<td>0.60</td>
<td></td>
</tr>
</tbody>
</table>
INVESTIGATION OF THE CURIE LAW AT 4.22°K FOR I27 IN

\[ S_0 \propto M_0 \] - ARBITRARY UNITS

\[ H_0 - \text{KG} \]
TABLE 3

Relaxation Time of Decay of the Magnetization

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.42°K</td>
<td>4.22°K</td>
<td>6.2 Kg</td>
<td>6.2 Kg</td>
<td>455 min.</td>
</tr>
<tr>
<td>4.22°K</td>
<td>4.22°K</td>
<td>6.9 Kg</td>
<td>2.3 Kg</td>
<td>495 min.</td>
</tr>
</tbody>
</table>
\[ \ln \frac{S(T) - S_F}{S_I - S_F} \]

**DECAY OF MAGNETIZATION OF \(^{127}\)I IN KI FROM \(S_I \alpha M_o\) AT 6.9 KG AND 4.22°K TO \(S_F \alpha M_o\) AT 2.3 KG AND 4.22°K

\[ S(T) = S_F + (S_I - S_F) \exp \frac{T}{T_1} \]

\(T_1 = 495\) MINUTES

**FIGURE 6**
Hydrogen Temperature Range

$T_1$ was measured for several different crystal orientations at 20.4°K. The results are shown in Table 4. In Figure 7, the measurements are compared to the theory. The $T_1$ values are averages. Several measurements were made of signal amplitude for a particular elapsed time from saturation, and these values were averaged. This process was repeated for several elapsed times, and the growth curve was then plotted. $T_1$ was measured at 16.6°K using the same method. This result is also shown in Table 4. The theoretical values for $T_1$, shown in Table 4 are based on Tanttila and Jennings’ value of $T_1 = 0.14$ sec. at 293°K.
TABLE 4

Spin-Lattice Relaxation Time $T_1$ of $^{127}$I in KI
as a Function of Temperature and Orientation
($\theta$ - angle between 001 axis and magnetic field)

<table>
<thead>
<tr>
<th>$T^\circ K$</th>
<th>$H_0$ (Kg)</th>
<th>$\theta$</th>
<th>Theoretical</th>
<th>Measured $T_1$ (sec)</th>
<th>Measured $T_1$ (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.4</td>
<td>3.5</td>
<td>0°</td>
<td>17.2</td>
<td>16.9 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>20.4</td>
<td>3.5</td>
<td>10°</td>
<td>16.9</td>
<td>17.2 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>20.4</td>
<td>3.5</td>
<td>20°</td>
<td>16.0</td>
<td>17.0 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>20.4</td>
<td>3.5</td>
<td>30°</td>
<td>15.2</td>
<td>15.0 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>20.4</td>
<td>3.5</td>
<td>45°</td>
<td>14.6</td>
<td>14.3 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>16.6</td>
<td>3.5</td>
<td>0°</td>
<td>43.5</td>
<td>38.0 ± 4.0</td>
<td></td>
</tr>
</tbody>
</table>
SOLID CURVE IS FROM VAN KRAENENDONK'S THEORY

\[ H_{\parallel} \text{ vs. } \theta \text{ DEGREES} \]

\[ T_1\text{-SEC.} \]

ORIENTATION EFFECT OF $T_1$ AT 20.4 K

FIGURE 7
DISCUSSION OF RESULTS

In the nitrogen and hydrogen temperature ranges, the measured values of $T_1$ agree very well with Van Kranendonk's theory. The one adjustable parameter in the theory was eliminated by using Tanttila and Jennings' value of $T_1$, measured at room temperature, as discussed in the Appendix A. In the hydrogen range, the temperature dependence of $T_1$ agrees favorably with that measured by Briscoe, using a different crystal. It appears then that $T_1$ is independent of paramagnetic impurity content in KI in this temperature region. This is not found to be true in other alkali halides where the quadrupolar relaxation mechanism is not the dominant mechanism. In the hydrogen range, the orientation dependence of $T_1$ from the theory fits the observed orientation dependence of $T_1$ within the experimental error. The agreement of $T_1$ measurements at 3 Kg and 20.4°K and those made by Briscoe at 6 Kg and 20.4°K support Van Kranendonk's assumption that $T_1$ is independent of $H_0$. However, in the liquid helium range, the measured values of $T_1$ are temperature independent. The predicted temperature dependence of $T_1$ due to the quadrupolar relaxation mechanism is $T^{-7}$ in the helium range. It was also observed that $T_1$ is dependent on the Magnitude of $H_0$ at 4.22°K, which also contradicts Van Kranendonk's theory.
No orientation dependence was observed below 4.22°K. Therefore, it is evident that the dominant relaxation mechanism is not electric quadrupolar at temperatures of 4.22°K and lower. In other words, another relaxation process has taken over.

The Curie law \( M = M_0 \frac{C H_0}{T} \) was found to be valid at all temperatures and magnetic fields investigated. This permitted the measurement of the relaxation time of decay of the magnetization. To determine the final value of \( S = S_0 \) within 5% by the growth method, it is necessary to wait a time equal to 3 \( T_1 \)'s after saturation. Therefore, in the liquid helium range with \( H_0 = 6 \) Kg where \( T_1 \) is 170 minutes, it takes 8 1/2 hours to get the magnetization grown up to 5% of its maximum or equilibrium value. Then, when the field or temperature was changed, it was sufficient to observe the decay for an interval of one \( T_1 \), or about 8 hours. The final value of the magnetization could then be predicted by the Curie law. This final value is necessary in order to determine \( T_1 \). (See Figure 3)

By having the magnetization at its maximum value, the temperature of the spin system is in equilibrium with the lattice temperature. Then by quickly lowering the magnetic field (at constant bath temperature), the spin temperature is reduced by the ratio of the reduction of \( H_0 \) and therefore a nuclear cooling has been effected.
This is true because the Boltzmann factor remained constant. However, it would not be practical to use this effect for cooling some other system, as the relaxation time appears to be very long. There is a practical limit on just how low we may take the nuclear spin temperature and this seems to be about 0.1°K, based on an initial field at 9 Kilogauss and a bath temperature at 0.9°K. At high initial fields, it would be necessary to wait a very long time for the magnetization to grow up to its maximum value (say, 40 hours at 15 Kilogauss).

The fact that the relaxation time is longer for decay of the magnetization as opposed to its growth can be explained by the following argument. At sufficiently low temperatures, the lattice oscillators are mostly in the lowest energy levels, and they must ultimately constitute the source or sink of heat. If the spin temperature is raised above that of the lattice, then for equilibrium to obtain, energy must transfer from the spin system to excite the lattice. However, when the spin system is at lower temperature than the lattice, energy must transfer from the lattice to the spin system. But if the lattice oscillators are mostly in the lowest energy levels, they cannot easily transfer energy to the spin system and therefore the relaxation time will be longer. We would speculate that it may be possible to
obtain information concerning the lattice frequency spectrum by measuring $T_1$, for decay of the magnetization at low temperatures and in a wide range of magnetic fields.

A discussion of line shape studies is included in the Appendix B.
CONCLUSIONS

In agreement with the findings of Briscoe and Squire, the quadrupolar relaxation mechanism as proposed by J. Van Kranendonk successfully explains the spin-lattice relaxation time $T_1$ between room temperature and the liquid hydrogen temperature range. $T_1$ is orientation dependent, but is independent of $H_0$ in this range, which also agrees with Van Kranendonk's theory. However, in the liquid helium range, at least down to 1.4 K, $T_1$ is temperature independent. In this region, $T_1$ is field dependent and orientation independent. Also in this low temperature region, the relaxation time is several times longer for decay of the magnetization as compared to its growth.

The Curie law was found to be valid at all temperatures and fields investigated. In the liquid helium range, nuclear cooling was done. However, it had little practical application, because of the extremely long relaxation times.

The line shape is orientation dependent and indicates an asymmetry in the absorption signal. $T_2$ is also orientation dependent in the hydrogen and nitrogen regions, in such a manner that the area under the absorption curve tends to remain constant.
APPENDIX A

Theory of Quadrupolar Nuclear Spin-Lattice Relaxation

The following is a brief qualitative discussion of a paper by J. Van Kranendonk, in which general theoretical expressions are derived for the nuclear spin lattice relaxation time, $T_1$, in crystalline solids from the interaction of the nuclear electric quadrupole moment with the crystalline electric field.

The following assumptions are made:

1. The dependence of the crystalline field at a nucleus on the displacements of the nuclei composing the solid from their equilibrium positions is restricted to this nucleus and its nearest neighbors.
2. The frequencies of the normal lattice vibrations are assumed to be independent of the direction of the wave vector $\mathbf{k}$ and of the polarization.
3. The nuclei involved in the spin lattice relaxation are located at equivalent lattice sites, so that they are subjected to similar crystalline fields.
4. We shall further neglect the influence on the quadrupolar relaxation of the coupling between the nuclear spins, which results from the interaction between the magnetic moments of the nuclei and from other possible
effects.

The relaxation can then be expressed in terms of the transition probabilities indicating the rate at which thermal fluctuations in the crystalline field induce transitions between the various spin states of a particular nucleus.

The next step is to write a general expression for the interaction energy involved when a system of nuclear spins, with the nuclei possessing quadrupolar moments, is placed in an external field, $H_0$. The Hamiltonian for this system can be written in the following form:

$$ H = H_L + H_Z + H' $$

where $H_L$ is the energy of the lattice vibrations of the crystal, and $H_Z$ is the Zeeman energy of the magnetic moment of the crystal nucleus in the external field $\vec{H}$:

$$ H_Z = -\gamma h \cdot \vec{H} \cdot \vec{I} $$

$\vec{I}$ is the nuclear spin operator expressed in units $h$, and $\gamma$ is the nuclear gyromagnetic ratio. Finally, $H'$ is that part of the total energy that is due to the presence of the nuclear electric quadrupolar moment.

The part of the Hamiltonian which is a result of
the interaction between the nuclear quadrupole moment and the lattice electric field can be written as follows:

\[ H' = \alpha \int \rho(\vec{r}) \nabla^2 \phi(\vec{r}) \ d\vec{r} \]

where \( \rho(\vec{r}) \) is the charge density of the nucleus and \( \nabla^2 \phi(\vec{r}) \) is the potential of the crystalline field in the neighborhood of the central nucleus in the absence of a nuclear quadrupole moment. The constant, \( \alpha \), is a result of the quadrupole moment not being equal to zero and expresses the reinforcement of the crystalline field at the nucleus due to the polarization of its own electron cloud charge by its quadrupole moment. In calculating \( \nabla^2 \phi(\vec{r}) \) there are other multiplication factors which arise. One is a result of the polarization of the cloud charge of the central nucleus by the surrounding ions. This is the shielding effect. There is also a co-valent effect which is usually much more important than the shielding effect. This is due to the deformation of the cloud charge of the ion by the lattice vibrations and results in an electric field gradient at the central nucleus which can interact strongly with the quadrupole moment. It is assumed that all these effects can be lumped into one constant, \( \gamma \), which is of the order of \( 10^3 \) for KI in order to give agreement between experiment and theory.
We now develop the quantity \( \propto V(\mathbf{r}) \) in powers of the distance \( \mathbf{r} \) from the equilibrium position of the central nucleus. The term independent of \( \mathbf{r} \) gives rise to a force on the nucleus, which has already been included in \( H_{\perp} \). Since the nucleus has only a quadrupole moment, we need further retain only the terms that are quadratic in \( \mathbf{r} = x, y, z \). These may be written in the form

\[
\propto V^0(\mathbf{r}) = \sum_{\mu=2}^{+2} \mathcal{W}_\mu \, Y_\mu(\mathbf{r})
\]

in which

\[
\gamma_0 = 3z^2 - r^2, \quad \gamma_{\pm 1} = z(x \pm iy), \quad \gamma_{\pm 2} = (x \pm iy)^2
\]

Then the expression for the interaction energy becomes

\[
H' = \sum_\mu \mathcal{W}_\mu \int f(\mathbf{r}) \, Y_\mu(\mathbf{r}) \, d\mathbf{r} = \sum_\mu \mathcal{Q}_\mu \, \mathcal{W}_\mu
\]

The \( \mathcal{Q}_\mu \) are the components of the nuclear quadrupole moment, the equivalent-operators of which, \( I = \text{constant}, \) are given by:

\[
\mathcal{Q}_0 = B \left[ 3I_z^2 - I(I+1) \right]
\]

\[
\mathcal{Q}_{\pm 1} = \mp \frac{B}{2} \left[ I_z I_\pm + I_\pm I_z \right]
\]

\[
\mathcal{Q}_{\pm 2} = B (I_\pm)^2
\]
\[ B = \frac{e Q}{I(2I-1)} \quad \text{and} \quad \phi = \langle II|Q_{\mu}|II\rangle, I_{z} = I_{x} + i I_{y} \]

c being the elementary charge, and \(|II\rangle\) the \(m = I\) state of the nucleus. The only non-vanishing matrix elements of \(Q_{\mu}\) are \(\langle m+\mu/|Q_{\mu}/m\rangle\).

The coefficients \(W_{\mu}\) are functions of the displacements \(\vec{\tau}_{i} = \vec{s}_{i} - \vec{s}_{o}\) of the nuclei relative to the displacement, \(\vec{s}_{o}\) of the central nucleus, and we can therefore develop \(W_{\mu}\) in powers of the \(\vec{\tau}_{i}\).

Doing this, we can get an expression for the interaction energy \(H'\) in powers of the \(\vec{\tau}_{i}\).

\[ H' = H_{o}' + H_{1}' + H_{2}' + \cdots \]

The constant term \(H_{o}'\) gives rise to the static quadrupolar interaction which perturbs the originally equally spaced Zeeman levels of the nucleus in the external magnetic field. We shall assume that \(H_{o}'\) is small compared to the Zeeman energy, so that the states of the nuclear spin can be characterized by the magnetic quantum number \(m\).

The higher-order terms \(H_{1}'\), \(H_{2}'\), \(\ldots\) gives rise to the relaxation processes. For all practical purposes, only the first order effect of the quadratic term \(H_{2}'\) need be considered. The linear term \(H_{1}'\) gives rise in first order to the so called direct processes in
which the nuclear spin makes a downward (upward) transition and one of the lattice oscillators is excited (de-excited). The probability of this process is proportional to the number of lattice oscillators, the frequency of which is equal to the resonance frequency, and since this frequency is $\approx 10^7$ cps, the contribution of the direct processes is negligible. The first order effect of the quadratic term $H_2'$ gives rise to the so called Raman processes in which the nuclear transition is accompanied by the excitation of one and the de-excitation of another lattice oscillator. These Raman processes prove to be the relevant relaxation processes.

The probability that a nucleus makes a transition from a state $m$ to a state $m+\mu$ as a result of this Raman process can be written as follows, if the lattice oscillators are in equilibrium at a temperature $T$:

$$P(m, m+\mu) = \frac{V^2}{8\pi^3 \hbar^2 v^3} \int_0^{\omega_m} k' f(\omega_k)^2 \left\{ |H_2'(\lambda, \lambda')|^2 \right\} d\omega_k$$

$V$ is the volume of the crystal and $v$ is the velocity of sound in the crystal. $H_2'(\lambda, \lambda')$ is the matrix element of $H_2'$ corresponding to the process in which a nuclear spin makes the transition $m \rightarrow m+\mu$, a lattice oscillator $\lambda$ is excited and a lattice oscillator $\lambda'$ is de-excited. The difference in frequency $\omega_k - \omega_k'$ is small compared to most of the lattice frequencies present, so
that we may say $\omega_k = \omega_k'$. The curly brackets indicate an average over all values of $k$ and $k'$. This average occurs because we have assumed $\omega_k$ independent of the direction of $k$, so that the first Brillouin zone may be replaced by a sphere. $\omega_m$ is the maximum lattice frequency allowed. The function $f(\omega)$ is defined so that the number of oscillators $\lambda$ with $\omega$ in $d\omega$ is given by

$$f(\omega) d\omega = \frac{V}{(2\pi^2)^n} f(\omega) k^2 d\omega$$

In order to calculate $P(\omega, \omega + \mu)$, it is necessary to evaluate $H_i' (\lambda, \lambda')$ and to assume a frequency distribution, $f(\omega)$, and a cutoff frequency $\omega_m$. $H_2' (\lambda, \lambda')$ can be evaluated by expressing $H_2'$ in terms of the normal coordinates of the lattice vibrations.

By evaluating $H_2' (\lambda, \lambda')$ and assuming the following for crystals of the NaCl type, Van Kranendonk determined $P(\omega, \omega + \mu)$.

Assume the frequency spectrum is of the Debye form, namely, $f(\omega) = 1$. Also that the cutoff frequency, $\omega_m$, is given by $\omega_m = \frac{k}{\Theta} \Theta_o$, where $k$ is Boltzmann's constant and $\Theta$ is the Debye characteristic temperature at $T = 0^\circ K$. Furthermore, assume the direction of the external field is along one of the crystalline axes. Assume that the spin lattice coupling is due to the
interaction of the nuclear quadrupole moment with the electric field arising from six equal point-charges placed on the six neighboring lattice sites. All other charges are supposed to be removed from the crystal, so that we consider a bare nucleus in the field of six point charges. The magnitude, \( q = \frac{e}{c} \), of these charges is the only adjustable parameter of the model. The dimensionless quantity \( \gamma \) is a measure of the strength of the spin lattice coupling.

Finally, the transition probability is:

\[
P(m, m + \mu) = \gamma^2 \left| Q_\mu m \right|^2 C T^* \quad E_\mu(T^*)
\]

where

\[
C = \frac{27 e^2}{3 \pi \alpha^2 \nu^3 a^6}
\]

d - mass density

\( a \) - lattice spacing

\( v \) - velocity of sound

\( e \) - electron charge

\[
Q_\mu m = \langle m + \mu | Q_\mu | m \rangle \quad T^* = \frac{T}{\Theta_0}
\]

and \( E_\mu(T^*) \) is a calculated function of the temperature.

Finally, the transition probability depends on the orientation of the crystal with respect to the magnetic field and this serves to modify the functions \( E_\mu(T^*) \).

Since there is no unique relaxation time, Van Kranendonk defines \( T_i \) by means of the equation \( T_i = \frac{1}{\beta} \),
where $P$ is averaged over all values of $\mu$ and $\nu$.

Therefore, $T_1$ is given by

$$T_1 = \frac{\gamma^2 \zeta \tau_{\kappa}^2 |Q_{\mu \nu}|^2 E_{\mu}(\infty) E^*(T^*)}{\pi^2 \tau_{\kappa}^2 E^*(T^*)}$$

which can be written as

$$T_1 = \frac{T_0}{\gamma^2 \tau_{\kappa}^2 E^*(T^*)}$$

where $E^*(T^*)$ can be taken from Figure 8 for $T^* \geq 0.1$

and for $T^* \leq 0.02$, $E^*(T^*) = 1.4 \times 10^4 T^5$.

Values for $T_1$ of I$^{127}$ in KI, as a function of temperature according to Van Kranendonk, are given in Table 5. The calculations are based on $T_1 = 0.014$ sec. at $T = 293^0K$ from Tanttila and Jennings.$^{10}$ In Figure 9, the orientation dependence of $T_1$ is shown as calculated from Van Kranendonk's theory, and may be used for all temperature ranges.
TABLE 5

Values for $T_1$ of $^{127}$I in KI as a Function of Temperature

According to the Theory of J. Van Kranendonk

The calculation is based on $T_1 = 0.14$ sec. at $T = 293^\circ$K

from Tanttila and Jennings and $\Theta_0 = 130^\circ$K from Briscoe and Norwood.

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<th>$T^\circ$K</th>
<th>$T^* = T/\Theta_0$</th>
<th>$E^<em>$ (T</em>)</th>
<th>$T_1$ (sec)</th>
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APPENDIX B

Line Shape Observations

In the nitrogen range, attempts were made to observe an orientation dependence of $T_1$, but no orientation dependence was observed. The errors associated with these measurements were large enough to obscure any orientation effect. However, it was observed qualitatively that the line shape had an orientation dependence. The absorption curve was asymmetrical. The degree of asymmetry varied with orientation of the sample and was a maximum every $90^\circ$. Recently, investigations of the effect of strains on the line shape of $^{127}$I in KI were conducted by E. Otsuka. The experiments indicated that when the crystal was strained, the line shape was asymmetrical. The degree of asymmetry depended on the crystal orientation with respect to $H_0$. These results are in agreement with the qualitative observations made in the nitrogen temperature range.

It was also observed that the amplitude of the absorption signal was orientation dependent. (See Figure 10) This was observed in the hydrogen range as well as at nitrogen temperatures. In the hydrogen range, the wings were more pronounced when the 001 direction was
VARIATION OF SIGNAL AMPLITUDE WITH ORIENTATION

T = 63.3°K, \( H_0 = 6 \) KG  SINGLE CRYSTAL \( ^{127}\text{I} \) IN KI

ROTATION ABOUT 100 AXIS

\( \theta \) - DEGREES
45° to $H_0$. The amplitude of the signal was a minimum at 45° and a maximum at 0°. This would tend to keep the area under the absorption curve constant and independent of orientation. In view of these observations, it appears that $T_2$ is orientation dependent and is a maximum when $T_1$ is a maximum.
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