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THE LINESHAPE TRANSITION IN DILUTE ORTHOHYDROGEN AT LOW TEMPERATURES

The Ohio State University

University Microfilms International 300 N. Zeeb Road, Ann Arbor, MI 48106
THE LINESHAPE TRANSITION IN DILUTE ORTHOHYDROGEN

AT LOW TEMPERATURES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Anujit Mukherjee, B.Sc., M.A.

The Ohio State University

1984

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ACKNOWLEDGMENTS

It is with great pleasure, that I acknowledge my advisor, Dr. James R. Gaines, for his guidance and support. Besides his patient encouragement and helpful suggestions, he has instilled in me, the art of scientific creativity— and for that I am very grateful. I would also like to thank him for help in the production of the manuscript.

My colleagues, Mr. Cheol Lee and Mr. Shinil Cho have been of great help in running the experiments. I would like to thank Mr. Robert R. Merritt for the continued supply of liquid nitrogen and liquid helium, when work was in progress.

I am grateful to my parents, who have always provided me with the inspiration to excel in my academic endeavors. Their love and advice has been invaluable in reaching my goals. I would also like to mention my grandmother, who has had a great influence in my life.

I am indebted to my wife, Mita, for all the moral support I needed to complete this work. Without her continued encouragement, understanding, and endless help, all this would not have been possible. To my newborn, Rahul, acknowledgements know no bounds.
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CHAPTER I

INTRODUCTION

The work described in this thesis, involved the use of NMR techniques to probe the occurrence of a possible phase transition in low concentration solid hydrogen. A lineshape transition has been previously observed below 0.3 K and interpreted in terms of an order–disorder transition. This ordering is one related to the rotational states of a hydrogen molecule. This work is the result of a more complete and systematic study of solid hydrogen, along similar lines. Three independently measured parameters showed minima at the lineshape transition temperature. It would seem, that in order to study phase transitions, more conventional probes like X-Ray scattering and specific heat measurements, be more appropriate. The low atomic number of hydrogen (scattering cross-section is proportional to square of the atomic number) and the low concentration of the orthohydrogen molecules (the specific heat is proportional to the number density of the molecules) make these measurements difficult in our sample. It is for this reason that NMR has been chosen as a probe to investigate the possibility of a phase transition.
Hydrogen, being one of the simplest elements to study, has been historically used not only to formulate many basic theories, but also to experimentally test the strength of many of these theories. In the solid state, work on hydrogen yields a multitude of results, which indicate to experimentalists and theorists alike, the basic interactions that are at play.

Hydrogen is a homonuclear diatomic molecule, which exists in the molecular state under normal pressures. The spin on each proton is \( I = 1/2 \). Symmetry considerations of the total wavefunction of hydrogen results in two types of hydrogen molecules. The complete wavefunction is a product of vibrational, rotational and nuclear wavefunctions. If we assign \( J \) as the rotational quantum number, the \((-1)^J\) parity consideration leads to symmetric space wavefunctions for even values of \( J \) and antisymmetric space wavefunctions for odd \( J \). The antisymmetric space state is paired with a symmetric spin function to give rise to a triplet with \( I = 1 \) so that the \( z \) projection has values \( I_Z = -1, 0, +1 \) and the symmetric space state is paired with an antisymmetric spin function to give rise to a singlet with \( I = 0 \). This is the basis on which hydrogen molecules are differentiated: i.e. those in the highest nuclear spin state are called orthohydrogen and those in the lower spin state are called parahydrogen. Thus we can see why it is that orthohydrogen is observed in magnetic resonance studies (the parahydrogen has no net magnetic moment). Since the \( B/k \) of hydrogen is about 90 K (where the rotational energy levels of the molecules are given by \( BJ(J+1) \)), at low temperatures (less than 4 K),
the hydrogen molecules are practically in their respective ground states i.e. in only the J=1 and J=0 states. Note that the conversion rate for J=1 to J=0 is very small during the time span of experiments presented in this work.

Nuclear magnetic resonance, which was independently developed by two groups headed by F. Bloch and E.M. Purcell, uses the absorption of electromagnetic energy by a spin system, from a radio-frequency source. The first NMR experiments were continuous wave experiments, where one observes the frequency domain directly. Experiments presented in this work are the result of pulsed NMR techniques, where an intense radio–frequency pulse is applied to the sample. Here the time domain is observed. Further details of this technique is given in Chapter II. The first resonance work on hydrogen in the solid state was undertaken by Hatton and Rollin. A more detailed investigation of solid hydrogen was then completed by Reif and Purcell. At this time, there are active groups at Harvard, MIT, Brown, Duke, U. of Florida, and Washington University doing NMR experiments on solid H₂.

The experiments presented in this work, used samples of orthohydrogen with a concentration of 0.2%. The temperature range studied was from 4K to 50 millikelvin. Extensive use of pulse NMR techniques was made in performing these experiments.

Reif and Purcell extensively studied hydrogen (nH₂, 75% oH₂) using NMR techniques. They made detailed studies of the lineshape below the λ-point, in order to examine the splitting of the rotational
states, They showed that the splitting was identical with that obtained by Pake for proton pairs at non-equivalent sites. The splitting was not observed above the \( \lambda \) transition as there was total degeneracy among the rotational substates. Thus, rapid transitions occur between these states and the effect of the intramolecular interaction is averaged out. Below the \( \lambda \)-point, the rotational motion is quenched and the line is split. Hill and Ricketson performed specific heat experiments with hydrogen and an anomaly at this same temperature. Thus, in this case, the lineshape transition was accompanied by a phase transition. There also was a change in the crystal structure - from the hcp lattice structure to the fcc lattice structure. Grenier and White performed similar experiments with Deuterium and observed a similar change in the crystal structure. Gaines, DeCastro and White did NMR studies on \( \mathrm{D}_2 \) and at the same temperature, as the specific heat anomaly, observed a lineshape transition. Thermodynamic variables like \( (\partial p/\partial T)_V \) were also measured with hydrogen samples by Jarvis et.al. Their results showed that the orientational ordering in hydrogen was responsible for a sharp decrease in the change in pressure at constant volume. Here we again see that NMR data do correspond well with measurements of thermodynamic variables.

Having seen a lineshape transition in low concentration \( \mathrm{D}_2 \), Gaines, Mukherjee and Shi claimed that they had seen an order-disorder transition. Considerable theoretical work has been done by several authors. V.B.Kokshenev has recently put forth a series of calculations concerning this transition. In one paper,
Kokshenev\textsuperscript{14}, discusses the possibility of the development of long range order in low concentration hydrogen. This, he claims, arises from the coupling of the orthomolecule rotations with the lattice vibrations. In another work, Kokshenev\textsuperscript{15} presents the effects of a heavy substitutional impurity in solid hydrogen. He says that this impurity can trap an orthomolecule, causing a cluster formation. This heavy impurity will also influence other thermal properties of solid hydrogen at low temperatures. He claims that this would also produce sharp changes in the relaxation times of doped samples. Anomalies would also appear in other thermodynamic properties of the sample (like thermal conductivity) from resonance scattering of phonons by the rotational system. The present work is based on this background.

This work presents data and analysis to show that a lineshape transition does occur. At the temperature at which the lineshape transition occurs, we also have minima in the relaxation times $T_1$ and $T_2$. Thus, an orientational ordering does take place at this transition temperature. Comparing these results with that of Reif and Purcell\textsuperscript{14}, there is every indication of this being characterised also as a phase transition. In that case, there is great deal of importance in choosing the right order parameter. An order parameter which we can use is $1/2 < 2 - 3(J_z)^2 >$. This parameter is 1 below the transition temperature and 0 above the transition. This agrees with the general behaviour of an order parameter in the regime of phase transitions. In this context, we note that NMR techniques have been also extensively applied in the study of liquid crystals. An important parameter determined in this case is the order parameter,
which is a symmetric traceless tensor of rank two. The interpretation of this order parameter comes directly from the NMR spectra of nematics. The dipolar splitting of resonance lines yields a measure of the order parameter. An excellent reference is provided in the review article by Stephen and Straley\(^6\). Conceptually, this dipolar splitting is identical with the order parameter presented earlier on.

Previous work on similar samples had shown that there was possibly some type of a phase transition occurring in the crystal at low temperatures\(^17\). The prime characteristic of this transition was a drastic change in the free induction decay as the sample was cooled beyond the transition temperature — structure developed in the NMR signal. All that was known about this process was that some sort of orientational ordering was taking place. The reasons for this transition were yet to be determined.

It was these results that prompted the present work — to observe the transition (if it occurred) and if possible, to give plausible reasons for the transition. \(T_1\) and \(T_2\) values were measured carefully as a function of temperature and magnet angle. Other relevant parameters e.g. a parameter called normalised signal difference were also carefully measured. The angular dependence of some of these variables gave conclusive evidence about the crystalline nature of the samples — in fact one of them could be clearly characterised as a single crystal. For the first time (in low concentration hydrogen), relaxation times were seen to have minima at the transition temperature. There was some difference between the transition
temperatures during a cooldown and during a warmup. Spin echoes too showed similar differences. All seemed to indicate a hysteresis effect — which generally accompanies a phase transition.

The next set of experiments were directed towards determining the reasons for the transition. It was thought that maybe the HD present in the sample could be the main reason for the transition — the HD is an intrinsic mass defect and could produce a large strain field. This strain field would help in trapping orthohydrogen molecules. A by-product of this trapping process could be what we observe as a phase transition. A control experiment was proposed and completed.

In this experiment two samples were investigated — both were identical, except that one had twice the HD content of the other. The results showed that changing the HD content had almost no effect on the structured part of the signal. The other components of the signal did, however, change. As such, the results did not provide strong support for a trapping process. Another model, based on a 'motional narrowing theory' by Kubo explains the results qualitatively. This model explains the lineshapes both above the transition and below the transition, as limits of a calculated lineshape function. The model will be presented in Chapter II and applied to the data in Chapter V.
Analysis of data taken earlier by Cochran and others was also done. These earlier experiments had HD concentrations in the H2 gas far less than the samples of the present work. Tests of the trapping theory were obtained from the earlier data, too.

Another important feature of the present results was found in the $T_1$ data taken at 4 K. It was found that $T_1$ had no angular dependence at 4 K during the initial cooldown. After the sample had gone through the transition, there did appear a very singular $T_1$ variation with respect to magnet angle at 4 K. The variation seemed to be directly dependent on the crystalline state of the sample. A single crystal would have one peak, two crystals would have two peaks and so on. The $T_1$ analyses for various crystalline shapes has already been theoretically calculated by Fedders. We can draw meaningful comparisons between the present data and the calculation of Fedders - enough to obtain some fairly systematic qualitative agreements.

The thesis has been divided into five chapters. The first chapter gives a simple introduction to the subject while Chapter II presents relevant theory in understanding this work. Chapter III deals with the experimental apparatus used to obtain the data. Chapter IV concerns itself with the results of the experiments. The last and final chapter, Chapter V concludes this work with analysis and discussions of the results.
CHAPTER II

THEORY

2.1 Nuclear Magnetic Resonance: Basic Principles

Nuclear magnetic resonance was developed independently by Bloch\(^1\) and Bloembergen, Purcell, and Pound\(^2\). The method involves the detection of a weak signal whose frequency bandwidth is clustered about a well-defined resonant frequency. Usually, nuclear magnetic resonance refers to the absorption of radiofrequency energy by the spin system - which is the collection of nuclear spins in our sample.

In equilibrium, the populations of the magnetic energy levels follow a Boltzmann distribution of the form \(\exp(-E_m/kT)\). Due to this distribution function, absorption of energy is greater than the induced emission, leading to net energy absorption by the spins. This energy exchange that takes place is one of the essential features of the energy detection. It is by spin-lattice relaxation that the spins can communicate with the lattice and attain a final state of thermal
equilibrium. This relaxation time, characterized by a time constant $T_1$, is called the spin lattice relaxation time.

The sample, is placed in a steady magnetic field $H_0$. A macroscopic nuclear magnetic moment $M$, develops in the sample:

$$M = \frac{\gamma N^2 h^2 I(I+1)}{3kT} H_0$$

$$= x_0 H_0$$

where $I$ is the nuclear spin and $\gamma$ the gyromagnetic ratio. This equation for $M$ is generally valid for systems which obey Curie's law.

The Larmor theorem, states that a magnetic moment $M$ in an external magnetic field $H_0$ obeys the equation:

$$\frac{dM}{dt} = M \times \gamma H_0$$

In pulse nuclear magnetic resonance experiments (which are the experiments described here) an intense radiofrequency pulse with an amplitude $H_1$, is applied to the sample. If such an $H_1$ field is turned on at resonance for a time $t$, the magnetization vector gets rotated by an angle:
When $\theta = \pi/2$ we have a 90° pulse. Immediately following the pulse, the magnetization lies along the y axis. This magnetization decays in time as the system comes back to equilibrium. The spins return to equilibrium by two mechanisms. The magnetization dephases in the x-y plane due to field inhomogeneity — some nuclei will process faster than others. At the same time, the magnetization tends to go back to the z-direction to establish thermal equilibrium. After the 90° pulse, the magnetization induces a decaying sinusoidal voltage in a pickup coil in the x-y plane. The decay of the amplitude takes place according to $\exp(-t/T_2)$. Here $T_2$ is the spin-spin relaxation time. In contrast to $T_1$, which is the spin lattice relaxation time, $T_2$ is the means by which spins interact with each other. The equations lead to the definitions of $T_1$ and $T_2$ are:

$$
\frac{dM_x}{dt} = -\frac{(M_z - M_0)}{T_1} \\
\frac{dM_x}{dt} = -\frac{M_x}{T_2} \\
\frac{dM_y}{dt} = -\frac{M_y}{T_2}
$$

As a result we have,

$$
\frac{dM}{dt} = \gamma(M \times H_0) - \frac{[M_x x' + M_y y']}{T_2} - \frac{M_z - M_0}{T_1} x'
$$

This is Bloch's phenomenological equation that incorporates the
relaxation terms and the free motion terms. The axes \( x', y', z' \), are unit vectors in the laboratory reference frame.

As the magnetization processes in the transverse plane, voltage is induced in the pickup coil. This voltage, given by Faraday's law is:

\[
V = -\frac{N \eta \frac{d\phi}{dt}}{c}
\]

where \( N \) = number of turns
\( c \) = speed of light
\( \phi \) = flux linkage with the coil
\( \eta \) = filling factor.

This gives the voltage as

\[
V(t) = \frac{4\pi N\eta A_0}{c} M(t)
\]

where \( A \) is the cross sectional area of the coil.

The decay of the induced voltage \( V(t) \) follows

\[
V(t) = V_0 \exp(-t/T_2)
\]

This signal is termed the free-induction decay.

An ingenious method, in which the effect of applied field inhomogeneity can be removed, is that of spin echoes. Spin echoes are formed as a result of the successive application of two or more pulses. As an example of spin echoes, let us now physically interpret the \( 90^\circ - 180^\circ \) echo. The sample is first irradiated with a \( 90^\circ \) pulse. The magnetization vector rotates \( 90^\circ \) and is now in the
direction of the y-axis. Immediately following the application of the pulse, the spins start dephasing in the x-y plane. After a time \( \tau \), after the application of the 90° pulse let us apply a 180° pulse along the x-axis. The part of the magnetization still remaining in the x-y plane, suffers a rotation about the x-axis by 180°. Hence, those spins that had dephased more are now behind those that had dephased less. Therefore, following the 180° pulse, the spins begin to rephase to form a net magnetization. As a result, the magnetization refocuses back along the -y axis at time \( 2\tau \). This enables the formation of an inverted spin echo. If the 180° had been applied along the y-axis, rather than the x-axis, the same logic can be seen to apply - except that the echo will have the same sign as the free induction decay.

In the experiments described here, extensive data, relating to \( T_1 \) and \( T_2 \) measurements, were taken. We will describe here the methodology of such measurements. In the 180°-90° sequence, the first pulse prepares the spins in some non-equilibrium configuration and the second pulse measures the magnetization after a certain waiting period. During the waiting period the spins are allowed to relax. This method is called the inversion recovery method of measuring \( T_1 \). The preparation pulse, being a 180° pulse inverts the spins and hence the magnetization from \( M_0 \) to \(-M_0\). The recovery process is one in which the magnetization goes from \(-M_0\) to \(+M_0\). The magnetization after a waiting time of \( \tau \) is

\[
M_x(\tau) = M_0[1 - 2\exp(-\tau/T_1)]
\]
$M_z(t)$ can be obtained for various $\tau$'s and a plot of $M_z$ versus $\tau$ yields $T_1$.

$T_2$, the spin-spin relaxation time or the transverse relaxation time can be obtained by the application of two 90° pulses separated by a waiting time $\tau$. If both the pulses are in phase, they produce an inverted spin echo and if the second is out of phase with respect to the first they produce an upright echo (same sign as the Free induction decay). Varying $\tau$, produces echoes of proportionate heights—greater the value of $\tau$, the more damped the echo will be. These echo heights follow a relationship of the form $e^{-\tau/T_2}$. A plot of echo heights versus $\tau$ yields the value of $T_2$ directly.

In the experiments described in this work NMR has been used as a probe to detect phase transitions. The free induction decay, the spin-lattice relaxation times ($T_1$) and the spin-spin relaxation times ($T_2$), were the main parameters used in performing this study. $T_1$ probes the spectrum at $\omega_0$, while $T_2$ probes the spectrum at $\omega_D$. Thus, these two parameters cover a frequency range spanning three orders of magnitude. Minima occurring in these variables at the same temperature argue strongly in favor of a phase transition.

More details of such measurements and the theories behind them are in the classic references of nuclear magnetism by Agragem22 and Slichter23.
2.2 The Free Induction Decay:

In this section we calculate the form of the Free induction decay, as will be used in analysing the data. The calculation has been extensively dealt with, by Gaines, Mukherjee and Shi\textsuperscript{10}. Some of the salient features, together with the results are presented here.

In the experiments described here, the concentration of the orthohydrogen molecules was very small. Hence the orthohydrogen molecules constitute a noninteracting magnetic ensemble. Thus we can neglect intermolecular interactions and conclude that the NMR spectrum reflects only the intramolecular interaction between the protons. The secular terms in the spin Hamiltonian, in the rotating frame can be written as:

\begin{equation}
H = -u\gamma I_z J_c + \frac{d}{4}(3\gamma^2 - 1)(3I_z^2 - 2)(3J_c^2 - 2)
\end{equation}

where

\begin{align*}
u &= c \cos \theta \\
\theta &= \text{the angle between the magnetic field and the symmetry axis of the crystal} \\
c &= \text{the spin-rotation coupling constant} \\
&= 113.9 \text{ KHz for H}_2 \\
d &= \text{the intramolecular dipole-dipole interaction coupling constant} \\
&= 57.7 \text{ KHz for a free H}_2 \text{ molecule} \\
I_z &= \text{projection of the nuclear spin of the molecule on the} \\
&\text{symmetry axis}
\end{align*}
applied field

\[ J_0 = \text{projection of the orbital angular momentum on the crystal symmetry axis, the c axis}. \]

We note that this is in the rotating frame—that removes the Zeeman part of the interaction. We are thus left with only that part which commutes with the Zeeman interaction.

A model, has been incorporated from the work of Kubo18 to explain transitions between the rotational substates of the orthohydrogen molecule. At the same time the concept of Markovian motion is also introduced. This model allows one to calculate the free induction decay lineshape in two limits—the fast transition limit and the slow transition limit.

In the Fast transition limit, the transitions occurring between the \( m_j \) states are rapid compared to the time required to take the Free induction decay. In the slow transition limit, the transitions occur in a time comparable to that required for obtaining the decay shape.

The key in correctly performing these limits is in assuming that the transition from one frequency to another in the spectrum of discrete lines is a stationary Markov process. As a result all functions of the form \( e^{i\omega t} \) have to be replaced by \( \exp(i_0 \int_0^t f(\tau) \, d\tau) \).
After correctly performing the calculations for the evolution of the signal one obtains:

**Fast Transition Limit**

\[ S(t) = S_0 \exp\left(-\frac{\gamma^2}{3}t\right) \]  

**Slow Transition Limit**

\[ S(t) = 2 \cos \delta t \exp(-\Omega t) + \cos 2\delta t \exp(-2\Omega t) \]

where \( \delta = \frac{3d}{4}(3u^2 - 1) \)

\( \Omega = \text{transition probability per unit time} \)

Thus, in the Fast Transition limit, which is the correct limit for temperatures above \( T_C \), \( T_C \) is the transition temperature of the sample) the shape of the Free induction decay is a pure exponential without any structure. In contrast to the above mentioned limit, the Slow Transition limit is a valid representation of the Free induction Decay for temperatures below \( T_C \). Here the equation for the lineshape predicts a structure, unlike the structureless pure exponential form above \( T_C \).
2.3 The Echo-Response:

Using the aforesaid model, the echo response to a $90^\circ - \tau - 90^\circ$ pulse sequence is determined.

Let us consider a $90^\circ$ pulse which has been applied to the spin system, at a time $t=0$. Let this be a rotation about the $y$-axis.

The rotation operator $R$ is given by,

$$R = \exp(-iI_y\theta)$$

where in this case the angle $\theta = \gamma H_1 t$ with $H_1$ being the amplitude of the rotating magnetic field at the resonant frequency of the spins. This field is created by applying a large (about 2 kvolts) radiofrequency voltage pulse of short duration (about 2 μs) to the sample coil. Under the influence of this large pulse, the density matrix $\rho$ evolves in time according to

$$\rho = R\rho(0)R^{-1}$$

In the high temperature approximation,

$$\rho(0) = \exp\left(\frac{\gamma H_0 I_z}{kT}\right) \sim 1 + \left(\frac{\gamma H_0}{kT}\right) I_z$$

$$\rho(t_p) = 1 + \frac{\gamma H_0}{kT}[\exp(-iI_y\theta)I_z\exp(iI_y\theta)]$$

$$= 1 + \frac{\gamma H_0}{kT}[I_z \cos \theta + I_x \sin \theta]$$

for a $90^\circ$ pulse, the pulse length, $t_p$, and the magnetic field amplitude are adjusted so that $\theta = \gamma H_1 t_p = \pi/2$. Thus

$$\rho(t_p) = 1 + \frac{\gamma H_0}{kT}(I_z)$$
This represents the value of the density operator after the first 90° pulse has been applied. The time evolution of $\rho$ after the rf field has been removed is governed by the local magnetic field seen by the molecules. The secular part of the intramolecular Hamiltonian

\begin{equation}
H = - c u I_z J_c + \frac{d}{4}(3J_c^2 - 2)(3\cos^2 \theta - 1)(3I_z^2 - 2)
\end{equation}

may be written as

\begin{equation}
H = - \Delta \omega I_z + a I_z^2 + \text{constant}
\end{equation}

For our purposes, the constant term may be omitted leaving

\begin{equation}
H = - \Delta \omega I_z + a I_z^2
\end{equation}

where $\Delta \omega = cuT_c$

and $a = \frac{3d}{4}(3J_c^2 - 2)(3\cos^2 \theta - 1) = 6(3J_c^2 - 2)$

The free induction decay is $S(t)$ and is given by

\begin{equation}
S(t) = \Re \{ \text{Tr} \{ e^{-i(\Delta \omega I_z + a I_z^2)t} \rho(t_p) \} e^{i(\Delta \omega I_z + a I_z^2)t} I_+ \} / 2
\end{equation}

Since $\text{Tr} I_+ = 0$,

\begin{equation}
S(t) = (1/2) \text{Tr} \{ e^{-iHtI_x} e^{iHtI_+} \}
= (\cos \Delta \omega t)(\cos at)
\end{equation}

The above represents the FID for time $t \geq 0$, which is what evolves after the application of the first pulse.

Now, let us apply a second pulse. Let this pulse be phase shifted with respect to the first by $\gamma$ and produce a rotation of $\beta$. We simulate a phase shift by rotation of the coordinate system about the $z$ axis by an angle $\gamma$. This is given by

\begin{equation}
R = e^{-iI_z \gamma}
\end{equation}
The second 90° pulse, causes a rotation of the spins about the y-axis by $\pi/2$. At the end of the application of the second pulse, the density matrix evolves as

$$
(24) \quad \rho(t > t_p) = e^{-iI_y(t/2)}e^{-iI_z\gamma}(t_{p1})e^{iI_z\gamma}e^{iI_y(t/2)}
$$

where

$$
\rho(t_{p1}) = e^{-iH\tau I_x}e^{iH\tau}
$$

Finally, the signal is observed as the above density matrix evolves due to $H$ and $S(t)$ is given by

$$
(25) \quad S(t) = Tr[e^{-iH(t-\tau)}\rho(t_{p2})e^{iH(t-\tau)}I_+]/2
$$

The explicit calculation yields

$$
(26) \quad S(t) = e^{-i\gamma \cos \gamma} e^{-i\Delta \omega (t-2\tau)} - \sin^2(\pi/2) \cos \alpha(t-2\tau)
+ 2 \cos(\pi/2) \sin^2(\pi/4) \cos \alpha t
+ e^{-i\Delta \omega \tau} \cos(\pi/2) \cos^2(\pi/4)(2) \cos \alpha t
+ \sin^2(\pi/2) \cos \alpha(t-2\tau)
- ie^{-i\gamma \sin \gamma} e^{-i\Delta \omega (t-2\tau)}
- \sin^2(\pi/2) \cos \alpha(t-2\tau)
+ 2 \cos(\pi/2) \sin^2(\pi/4) \cos \alpha t
- e^{-i\Delta \omega \tau} \cos(\pi/2) \cos^2(\pi/4)(2) \cos \alpha t
+ \sin^2(\pi/2) \cos \alpha(t-2\tau)
$$

Let us consider two limiting cases: Phase shift $\gamma = 0$. This is the
90°−τ−90° echo with the sign of the echo opposite to that of the Free induction decay.

(27) \[ S(90°−90°) = (1/2)[(e^{-i(\Delta \omega + a)\tau} - i(-\Delta \omega + a)(-t+\tau))
+ ei(-\Delta \omega + a)\tau e i(\Delta \omega + a)(-t+\tau)]
- {ei(\Delta \omega - a)\tau e i(\Delta \omega - a)(-t+\tau)}
+ ei(-\Delta \omega + a)\tau e i(\Delta \omega - a)(-t+\tau)]\]
\[ = \frac{1}{2}[A - B].\]

The next case is for a phase shifted 90° echo, which has the same sign as the free induction decay.

(28) \[ S(90°−90°90°) = (1/2)[(e^{-i(\Delta \omega + a)\tau} - i(-\Delta \omega + a)(-t+\tau))
+ ei(-\Delta \omega + a)\tau e i(\Delta \omega + a)(-t+\tau)]
+ [ei(\Delta \omega - a)\tau e i(\Delta \omega - a)(-t+\tau)]
+ ei(-\Delta \omega + a)\tau e i(\Delta \omega - a)(-t+\tau)]\]
\[ = \frac{1}{2}[A + B].\]

The difference between the above two echoes

(29) \[ A = A
= (e^{+i(\Delta \omega - a)\tau} - i(-\Delta \omega + a)(-t+\tau)) + ei(\Delta \omega + a)\tau e i(\Delta \omega + a)(-t+\tau)\]

To correctly calculate the difference, we insert the time dependence first, by time averaging in the Kubo sense, and then combining the exponentials. We have the lineshape function \( \Phi \) as
(30) \[ \Phi = \mathcal{W} e^{i(M + i\Omega)t} \] (following Abragam)

where \[ \mathcal{W} = \mathcal{P}_1, \mathcal{P}_2, \mathcal{P}_3 \]

and represents the apriori probabilities associated with the states.

\[
\mathbf{1} = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}
\]

In first order perturbation theory, we have the diagonal term in \( M + i\Omega \) (for exponentials of the type(\( \Delta \omega + \alpha \)),

\[
(31) \quad (M + i\Omega)D = \begin{vmatrix} \xi + \delta + i\Omega_{11} & 0 & 0 \\ 0 & -2\delta + i\Omega_{22} & 0 \\ 0 & 0 & -\xi + \delta + i\Omega_{11} \end{vmatrix}
\]

Doing the same calculations for the \( (\Delta \omega - \alpha) \) terms we get,

\[
(32) \quad (M + i\Omega)D = \begin{vmatrix} \xi - \delta + i\Omega_{11} & 0 & 0 \\ 0 & +2\delta + i\Omega_{22} & 0 \\ 0 & 0 & -\xi - \delta + i\Omega_{11} \end{vmatrix}
\]

Finally going through the dot product calculation carefully, we get

\[
(33) \quad \Delta = (1-p_0)^2 e^{-\Omega_{11}t} \left[ \cos \xi t + \cos \xi(t-2\tau) \right] \cos \delta(t-2\tau)
+ 2p_0^2 e^{-\Omega_{22}t} \cos 2\delta(t-2\tau)
+ 2p_0(1-p_0) \left[ \cos \xi t \cos 2\delta(t-\tau/2) e^{-\Omega_{11}t-\Omega_{22}(t-\tau)} \right.
+ \cos \xi(t-\tau) \cos \delta(t+\tau) e^{-\Omega_{22}t-\Omega_{11}(t-\tau)} \right].
\]
The first two terms contribute to the formation of the echo, while the last term is essentially a damping factor.

2.4 Theory-of-the-Spin-Lattice-Relaxation-Time:

For solids at low temperatures, $T_1$, the spin lattice relaxation time, is defined as the time for the nuclear spins to acquire a spin temperature equal to the lattice temperature. In purely insulating solids the value of $T_1$ is too large for NMR measurements to be made. In order to make NMR measurements feasible the sample must be doped with paramagnetic impurities. In solid hydrogen, the $J=1$ impurities can suffer nearly free rotation. It is this that allows the observed $T_1$ to be short. This rotational energy reservoir acts as an effective medium in coupling the nuclear spin energy to the lattice modes. The observed $T_1$ thus depends on two separate processes: 1) the relaxation of nuclear spins to the rotational degrees of freedom, and 2) the relaxation of the rotational degrees of freedom to the lattice.

Most theories that calculate the spin lattice relaxation time, really calculate the time constant characteristic of the spin-rotation relaxation. The relaxation rate between the rotations and the lattice has been calculated by Walker and Van Kranendonk using both direct relaxation and Raman processes. This relaxation time, calculated, can be written as,
No relaxation data in solid hydrogen suggests that the rotation lattice relaxation is slow enough to provide a bottle neck for the spin-rotation relaxation. It is for this reason that we assume that the spin-rotation relaxation time is identical with the observed relaxation time.

Taking into consideration the analogy between rotational angular momenta and electron spins expressions from Abragam can be modified to give for $T_1$,

\[
\frac{1}{T_1} = \frac{2A^2S(S+1)}{3} \frac{\tau}{1 + (\omega_I - \omega_S)^2 \tau^2}
\]

where the coupling between the nuclear spin I and electron spin S is $A I \cdot S$. Taking both the spin-rotation interaction and the intramolecular dipolar coupling, we have for $(\omega_I - \omega_S)\tau \ll 1$,

\[
\frac{1}{T_1} = \frac{H_I}{h} 2\tau
\]

where $H_I$ is the total Hamiltonian for both interactions.

$\tau$ is determined purely by the correlations between the internal rotational degrees of freedom such as $\langle J_+(t)J_-(0) \rangle$. 
Pursuing the analogy between the electron spin-nuclear spin relaxation and the rotational spin-nuclear spin relaxation, $\tau$ is interpreted as the rotational spin relaxation time. The correlation functions, on which $\tau$ depends, will be a function of the sites which are occupied by rotational spins $J$. Thus $\tau$ is a function of the concentration through the lattice sums leading to a concentration dependence of $T_1$.

Fedders 20 has also calculated the spin lattice relaxation time for solid hydrogen. The Hamiltonian he uses is of the form

$$H = \hbar \omega_d \sum B_{2,m} A^{+2,m} - \frac{2}{3} \hbar \omega_c \sum B_{1,m} A^{+1,m}$$

The spin rotation interaction characterized by $\omega_c$ has the value $7.15 \times 10^5$ sec$^{-1}$ and the dipole-dipole interaction characterized by $\omega_d$ has the value $3.62 \times 10^5$ sec$^{-1}$. The calculation assumes that the relaxation times are dependent 'crucially on the crystal fields experienced by the hydrogen molecules'. For a crystal with axial symmetry his results give

$$T_1(0)^{-1} = \frac{3}{2} \omega_d^2 \left[ 3(1-u^2) F_2(2 \omega_0) + \frac{1}{2}(u+1) F_2(2 \omega_0 - 2 \omega_j u) + \frac{1}{2}(u-1) F_2(2 \omega_0 + 2 \omega_j u) + 3u^2(1-u^2) F_2(\omega_0) + \frac{1}{2}(1-u^2)(1+u^2) F_2(\omega_0 - 2 \omega_j u) + \frac{1}{2}(1-u^2)(1-u) F_2(\omega_0 + 2 \omega_j u) + \frac{2}{3} \omega_0^2(1-u^2) F_1(\omega_0) \right]$$
where \( u = \cos \theta \), \( \theta \) being the angle between \( H_0 \) and the crystal axis

and

\[
F_1(\omega) = \frac{-\Gamma_1}{\omega^2 + \Gamma_1^2}
\]

\( \Gamma_1 \) is the decay rate appropriate for the dipole \((1=1)\) correlation function \( F_{1,m}(\omega) \) and \( \Gamma_2 \) is that for the quadrupole \((1=2)\) correlation function \( F_{2,m}(\omega) \). His calculations show \( T_1 \) variation with respect to magnet orientation: we shall discuss this further in Chapter V.

For very low \( J=1 \) concentrations, Harris 26 predicts that \( T_1 \) should be proportional to the orthohydrogen concentration \( x \), if the Suhl-Nakamura or indirect interaction between the \( J=1 \) molecules dominates are the EQQ interaction.
CHAPTER III

EXPERIMENTAL TECHNIQUES

This chapter has been divided into six broad sections. They are:

3.1 The Hydrogen Preparation Apparatus.
3.2 The Dilution Refrigerator and the Gas Handling System.
3.3 Thermometry.
3.4 The Data Acquisition System.
3.5 The Electronics.
3.6 The Magnet.

3.1 The Hydrogen Preparation Apparatus

Normal hydrogen gas is taken from a cylinder and passed through a large nitrogen cold trap and then into the sample cell of a 'cryotip refrigerator' (Air Products). Two smaller traps are present right before the gas encounters the cell. These traps help in considerably reducing the non-hydrogen content of the gas. Before commencing the
trapping and liquefaction process, the complete system is pumped down to a pressure of about $10^{-5}$ to $10^{-6}$ Torr. The bulbs to be used for storing the parahydrogen were also pumped out to the above stated pressure. Before any new bulbs were used they were properly flamed to remove any impurities present. The whole system was pumped out for about two days by means of a diffusion pump before the sample was prepared. All joints were well greased.

The cell contained chrome-alumina catalyst to convert the hydrogen. The temperature was maintained by a continuous flow of liquid helium into the refrigerator. The control was well achieved by a proper maintenance of the cryotip and shield flows. The vapor pressure of the liquid was maintained at about 500 Torr for about 4 to 5 hours or longer depending on the required orthohydrogen concentration. During the time that the conversion was taking place, the bulbs were flushed out at least three times with the parahydrogen and then subsequently evacuated. The temperature measurement in the cryotip was performed by means of a pre-calibrated diode. There also was a heater in thermal contact with the sample cell in order to provide a temperature increase whenever required. After the conversion had been completed, the cryotip flow was very slowly reduced in order to increase the temperature of the hydrogen. The cell was also opened up to the bulbs. Care was taken to see that there was no sudden overheating of the liquid sample. The bulbs were usually filled to about 500 mm of mercury pressure. They were then quickly transferred to the hydrogen gas handling system at the top of the dilution refrigerator. Within half an hour of this transfer, we
were ready to start condensing the parahydrogen into the sample cell.

A diagram of the sample preparation system is given in Fig.1.

3.2 The Dilution Refrigerator and the Helium Gas-Handling System

After the sample has been prepared in the cryotip, the gaseous sample was taken in a glass bulb and placed atop the dilution refrigerator system. The dilution refrigerator, which produces cooling down into the millikelvin range, uses a $^3$He-$^4$He mixture (in the correct proportions) to circulate through the system. The cooling takes place in a part of the fridge called the mixing chamber, onto which is attached the sample cell. Further details of the dilution refrigerator have been discussed extensively by Wheatley27 and by Lounasmaa28. This particular refrigerator without a sample inside was capable of maintaining a temperature of about 45 millikelvin. The heat removing capability of the refrigerator has already been tabulated by Kohl29.

The lowest temperature reached by the refrigerator depends on a number of factors: the size of the sample cell, the means of achieving thermal contact with the mixing chamber (helium or a bundle of wires), and the orthohydrogen concentration.

The sample cell is diagrammatically shown in Fig.2. The cell is made of glass and oxygen-free-high-conductivity copper. Thermal
FIGURE 1

THE SAMPLE PREPARATION SYSTEM
Sample cell

Pressure gauge

Valve

Nitrogen trap

Glass bulb

0-400 mm

H₂ tank

To cryotip dewar space

0-760 mm

Pumps
FIGURE 2

THE SAMPLE CELL
contact of the sample with the mixing chamber was achieved by means of a bunch of Litz wires, properly cleaned and stripped. The NMR coil surrounded only the glass portion of the cell. A controlled amount of 4He exchange gas in the vacuum can (the can directly surrounding the fridge), together with a small amount of liquid helium in the tail end of the dewar, allowed one to condense the hydrogen easily (without getting plugged in the fill line). There was a pressure gauge on each of the fill lines and the equality of these pressures indicated that both the lines were free and the sample well condensed. The sample was then cooled to 4 K. The cooling was done very slowly taking about two hours. The sample was then warmed up to between 10 K and 12 K and then the temperature quenched very quickly (in about fifteen minutes). This provided a form of annealing so as to help in breaking the sample off the walls of the cell, and preventing unnecessary strains in the hydrogen crystal.

The gas handling system has also been described elsewhere. The diagram of the system is given in Fig.3.

3.3 Thermometry

The thermometers used in this experiment were precalibrated against the susceptibility of CMN. Different thermometers were used in different temperature ranges. The range from room temperature to 4.2 K was covered by a silicon diode. The conductivity - temperature
FIGURE 3

THE GAS HANDLING SYSTEM OF THE DILUTION REFRIGERATOR
variation of the diode is given in Fig.4. In the range 4.2 K to about
500 mK, thermometers (called SI and OMIX) with overlapping ranges
were used. The temperature characteristics of these two thermometers
are given in Fig.5 and in Fig.6. The useful range of OMIX, an Allen
Bradley 220 ohm resistor, extended down to below 40 millikelvin.
Every time a measurement was made, care was taken to see that the
temperature was stable. Stability of the temperature was maintained
to within 1 to 2 millikelvin at the lowest temperatures. The fitting
constants for the conductivity versus temperature curves for the
thermometers called SI and OMIX are given by Sokol31.

3.4 The Data Acquisition System

By 'Data Acquisition System' we mean the system used to collect
the pulsed NMR data, from the experiment, which is stored, and hence
subsequently analysed.

The center of this system is the Commodore Pet Minicomputer. The
Pet supports the IEEE interface and can be programmed either in BASIC
or in Machine Language. The general layout of the system is shown in
Fig.7, in block form. An explanation of the various parts follow.

The Biomation 1010 is a type of transient recorder. It is
connected to the Pet through a programmed I/O interface. The
Biomation has a 10 bit resolution (hence its designation as 1010) and
a 4096 word memory. When the data transfer program is called, the
FIGURE 4

THE DIODE CHARACTERISTICS
FIGURE 5
'SI' CHARACTERISTICS
FIGURE 7

LAYOUT of DATA ACQUISITION SYSTEM
data from the Biomation is added to data, already present in a basic array, and then stored there. Thus the Biomation acts as a signal averager in order to improve the signal to noise ratio. The data is handled in quantized units called sectors. A sector consists of 256 words from the Biomation. The data transfer program can transfer from 1 to 8 sectors of the data from the Biomation, depending on the particular application. After a pulse sequence is executed, the data transfer program is repeatedly called, and this is how the averaging is performed.

The oscilloscope, which gives us a real time display of the accumulated signal is connected through a fast D/A (digital to analog converter) to the Pet. The scope display is obtained by a commercial D/A converter interfaced to the memory bus. The scope operates by means of an interrupt routine and generates a display every 1/60 of a second when enabled. It displays data in the memory array or some subset of it. The screen display routine is also set up on a sector basis and the scope can display anywhere from 1 to 8 sectors in the array (usually 4 sectors only were used). This scope, thus allows one to view the data as it keeps coming to the Pet, and the averaging performed. Both the scope and the Biomation have interfaces that operate off the memory expansion connector.

The interfacing of the Pet with the experiment is through a GPIB (General Purpose Interface Box) box. The GPIB is used to send commands to modules that attach onto the GPIB. It contains a microprocessor, which converts the commands sent to it into
appropriate commands for the modules. The Pet connects to a printer, two disk drives (Drive 8 for data storage and Drive 9 for Command files) through the IEEE bus. The pulse sequencer is one of the more important modules that connect to the GPIB through an interface. This module has pulse outputs to trigger pulse generators and phase outputs to set the phases. An A/D (analog to digital converter), attached to the Pet through the GPIB, allows one to read the temperature. The temperature is measured by reading the conductivity of the sensors and then converting that reading into temperature units by using the fitting equation for that particular sensor. A D/A attached to the Pet can also be used to set the gain of the receiver and through its connection to the GPIB allows one access to a plotter.

The data acquisition program works so that different commands can be called by a two character code - the first refers to a specific mode, the second is a function related to that mode.

The general features of the execution of a command are as follows: First, the data acquisition program is loaded onto the Pet (from drive 9). By pressing appropriate keys on the Pet keyboard, the measurement process commences. The commands are sent out through the appropriate modules, all of which use the GPIB for interfacing purposes. The data starts accumulating in the Pet memory until all the averaging is performed (of course, the correct gain and the required Biomation parameters have to be preset and the system prepared for taking data). A diagram of what appears, during a typical run, on the Pet screen is given in Fig.8. Finally the data is
FIGURE 8

PET SCREEN during DATA ACQUISITION
**MODE : MEASURE**
**FUNCTION : MANUAL**
**RB-10-AIS**
**EXECUTING**

**CURSOR :**
**VALUE :**

<table>
<thead>
<tr>
<th>DATA TRANSFER PARAMETERS</th>
<th>AVERAGING PARM.</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
<td>DISPLAY</td>
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<td>DISC</td>
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<td>ERASE</td>
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<tr>
<td>PLOT</td>
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</tr>
</tbody>
</table>

**PULSE SEQUENCE :**
**RB-10-A1**

**BIOMATION**
- DATA MODE : ADD
- INPUT SENS : .2 V
- SWEEP A : .2 U
- SWEEP B : 1.0 U
- SWEEP MODE : SINGLE
- DELAY : 0.00

**SPECTROMETER**
- A LENGTH : 1.1 U
- B LENGTH : 2.2 U
- C LENGTH : 0.7 U
- D LENGTH : 0.0 U
- GAIN : 1.0

**MAGNET**
- FIELD : 7.1 KG
- ANGLE : 135

**THERMOMETRY**
- SENSOR : SI
- RANGE : 200 M
- COND. : 41.32
- SET POINT : 0.0
manually or automatically written on floppy mini diskettes and printed out on the attached printer. A detailed account of the Basic program which is used for the collection of data has been given by Sokol\textsuperscript{31}.

3.5 The Electronics

The electronics used in these experiments were commensurate with those used for pulsed nuclear magnetic resonance work. A block diagram of the entire electronics is given in Fig. 9. A description of the important components follow.

The Transmitter:

The transmitter was a modified version of the one designed by Lowe and Tarr\textsuperscript{32}. A 30 MHz crystal oscillator was used as the R.F. signal generator. This is the Larmor frequency of the protons. The magnetic field, $H_0$ from the Varian magnet was tuned accordingly. There are two inputs into the transmitter— one from the gate circuit called Gate In and the other from the Phase shifter called RF In. The output of the Transmitter, called RF Out goes through a matching box into the probe. This transmitter provided a very high power radio-frequency pulse. The pulse was about 1000 volts peak-to-peak when connected with the coil and about 650 volts peak-to-peak when attached to a dummy load. The pulse width was about 1.3 microseconds for a 90° pulse. The repetition rate used was a function of the particular sample and of the temperature. Care was taken to see that
FIGURE 9

BLOCK DIAGRAM of ELECTRONICS
no part of the signal was lost by measuring sample height as a function of the repetition rate.

The Probe:

The probe consisted of the correct combination of an inductance and a capacitance matched to give a good signal at 30 MHZ. The coil used was made of copper, properly stripped and potted in sulphur. The capacitance was obtained by similarly potting a number of ceramic capacitors and soldering them to the coil. Sulphur was used, since it had no protons, and it prevented mechanical vibrations of the coil and the capacitors. Also attached to the coil–capacitor system was a matching box consisting of crossed diodes in order to protect the receiver when the pulse was on. The transmitter was also isolated when the pulse was off.

The Receiver:

The receiver was made according to the design of Adduci and Hornung. The recovery time of the receiver was about 3 microseconds. The complete system (receiver plus probe and coil) had a dead time of about 10 microseconds. It was a two stage receiver. It was constructed utilizing two Optimax amplifiers. The amplifier had a linear response and the maximum gain possible was about 1000. There was practically no attenuation. When the coil was properly tuned, the signal to noise ratio was adequate for this work being about 4 to 1 for a single trace at 4.2 K on a 0.2% OH\textsubscript{2} sample of volume 0.1 cc. The gain of the receiver was always calibrated by means of a R.F. signal generator.
The Data Storage System:

The coil-capacitor system is connected through a preamplifier, a phase sensitive detector, and a buffer, to the Biomation 1010. As described earlier, the Biomation 1010 is the transient recorder used to perform the signal averaging. The Biomation is interfaced to the Pet minicomputer, which in turn has attached to it, disk drives for collecting the data. The data was then transferred to the PDP 11/34, where it was analyzed.

3.6 The Magnet

The magnet used in these experiments was a water cooled electromagnet made by Varian. The magnet current was provided by (and controlled by) a Varian Fieldial Mark IV. The stability of the magnet depended on its operating temperature which in turn depended on the water that was being used to cool it. In order to improve the purity of the water (so as not to plug the coils in the magnet), a water softener was used before the water encountered the magnet. Care was also taken to see that when the magnet was turned on, the field was increased very slowly. Tuning the system for resonance also needed adjustments of the field—this too was performed in the slowest possible manner. The magnet was capable of rotation through 180°. The field of the magnet was found to be homogeneous to within 1 part in 10^5 over a volume of about 1 cc. A free precession signal from ^3He
FIGURE 10

HELIUM-3 SIGNAL AT 4K
atoms at 1 K in liquid helium was used to check the homogeneity. This is shown in Fig. 10.
In this chapter the data from the experiments is presented. The chapter has been subdivided into three sections. The sections are:

4.1 NMR Data on low concentration Hydrogen.

4.2 The Lineshape Transition.

4.3 The Control Experiment.

4.1 NMR Data on Low concentration Hydrogen

Here we describe, the typical process of conducting an experiment with low concentration hydrogen. All the samples described were low concentration orthohydrogen prepared from normal hydrogen gas by catalytic conversion at about 20 K. After the samples were made in
the cryotip refrigerator they were evaporated into clean glass storage bulbs and quickly transferred to the dilution refrigerator system. The refrigerator was already precooled to 4 K. The dewar had liquid helium only in the tail end. The vacuum can surrounding the fridge had a controlled amount of helium exchange gas. The fridge, the vacuum can, the sample cell were all leak tested at room and helium temperatures. The gas handling system (the part of the fridge system by means of which the helium mixture circulates) was also carefully leak checked. If leaks were present in the gas handling system, the mixture would stop circulating and one would be forced to abort the experiment. Within half an hour after the hydrogen sample was transferred, the fill line heaters were turned on and the hydrogen started to condense. After the required amount of hydrogen had filled the sample (enough to fill the glass region of the cell), the condensing process was stopped. The sample was then slowly cooled and then annealed. Within about 2 to 3 hours the sample was crystallized and the sample temperature was reduced to 4 K. It is then that the actual NMR measurements started.

At 4 K, $T_1$ and $T_2$ were measured carefully, as a function of magnet angle. It was these values of $T_1$ and $T_2$ which allowed one to make a determination of the orthohydrogen concentration. Gaines and Hardy have already tabulated the values of $T_1$ and $T_2$ as a function of orthohydrogen concentration. These are plotted out in Fig.11 and in Fig.12 respectively. The recovery of the magnetization from saturation does not follow a single exponential form. We note that the $T_1$ used for this determination is the value of $T_1$ found from the
FIGURE 11

$T_1 \text{ VERSUS } \text{OH}_2 \text{ CONCENTRATION}$
FIGURE 12

$T_2$ VERSUS $OH_2$ CONCENTRATION
After data at 4 K had been taken, (which typically lasts a few hours) the subpot of the dilution refrigerator was filled and was pumped on. The mixture was also slowly put into the fridge from the storage tanks. Within 1 to 2 hours the sample temperature was nearly 1 K. At 1 K, the above measurements were repeated. Care was taken every time to see that the repetition rate of the pulse sequence was good enough so that no part of the signal was lost. Also every reading was taken so that there was temperature stability in the sample. As the temperature was slowly lowered, we looked for spin echoes.

Completion of the 1 K data heralded the further cooling of the sample. Subsequent cooling was achieved by allowing the helium mixture to circulate through the fridge. As the cooling took place, the above readings were repeated with the utmost care. Temperature stability (to within 5 mk) was attained by means of a temperature controller attached to the system.

As the temperature decreased, the free induction decay indicated if a lineshape transition had taken place or not. All readings to be quoted were taken during the cooldown except for the double crystal data, where the data was taken during a warmup. Once one obtained echoes, the $T_1$ measurements were made with the following pulse sequence - $90\_x-90\_x-90\_x$. When echoes were not observed, (which was generally above about 600 mk. during the first cooldown) $T_1$ was
measured from a $180_x-90_x$ pulse sequence. $T_2$ measurements were made from both $90_x-90_x$ and the $90_x-90_y$ pulse sequences. These echo sequences were well documented as a function of magnet angle variation as were the free induction decays. The above measurements were repeated very carefully at the lowest temperature, which in these experiments typically was around 60 millikelvin.

After the readings were taken at this minimum temperature, the sample was very slowly warmed up by supplying a small, regulated current to the mixing chamber heater. At each temperature, after visual stability of the Potentiometric Conductance Bridge (the PCB reading which indicated the temperature of the sample in terms of the conductivity of the sensor) was obtained, a free induction decay was periodically taken until two successive traces gave the same value of the amplitude at a particular cursor position. Thus one could be sure that a particular temperature had been reached, and that the sample was thermally stable at that temperature. All the above measurements were repeated at the same temperature while warming up. Care was taken to see that there was no excessive overheating of the sample during the warmup. Finally, at 4 K angular dependence of $T_1$ was very carefully repeated. At a few angles, five readings were made so as to determine the standard deviation present in the measurements.

After the 4 K data was taken, the sample was heated, opened up to the bulbs, the mixture taken back to the tanks, and the experiment completed. Before commencing on the next experiment, the system was generally warmed up to room temperature, the sample cell well pumped
out and flushed with hydrogen, and the whole system purified and leak tested.

4.2 The Lineshape Transition

Here we present experimental data on low concentration hydrogen which indicate the presence of a lineshape transition around 250 millikelvin. We note that during the course of these experiments, thousands of free induction decays and spin echoes were taken. Each and every one of them have not been presented here - but what is shown is indicative and very typical of the results.

In Fig. 13 is shown the typical free induction decay at 4 K, together with the corresponding Fourier transform. There was no change in $T_1$ as a function of magnet angle (to within 10%).

We now present the signal at about 530 millikelvin in Fig. 14. We note that no structure has yet appeared on the signal. At this temperature a spin echo can just be observed, though not very clearly. In Fig. 15 is presented echoes at the same temperature. The upper diagram is one obtained during the first warmup, and the lower is one obtained during the initial cooldown.

As the sample was cooled further, a beat structure starts appearing on the signal. The structure typically appeared at about 250
FIGURE 13

FID and FOURIER TRANSFORM at 4K (Time displaced for clarity)
FIGURE 14

FID at 530 MK. during FIRST COOLDOWN
FIGURE 15

upper - ECHO during FIRST WARMUP
lower - ECHO during FIRST COOLDOWN
millikelvin and it increased as the temperature was lowered. Fig. 16 shows the free induction decay and the transform at 110 millikelvin. In these figures, the HD signal has been removed in order to accentuate the orthohydrogen signal. Note how clearly the structure is visible in the signal. At the lowest temperature, which was about 68 millikelvin, the structure seemed to be a maximum. The free induction decay at this temperature was taken a large number of times until one was satisfied that the spin temperature of the sample and the temperature as indicated by the conductance bridge were one and the same. At this temperature, extensive $T_1$ and $T_2$ measurements were made as a function of angle. In the next figure, Fig. 17 we show the free induction decay and the transform at a magnet position of 135° at a temperature of 68 millikelvin.

Fig. 18 shows the cusp-like behavior in $T_1$ as a function of temperature. The $T_1$ values plotted are all obtained by the 90°-90°-90° pulse sequence. The plot clearly indicates that there is a minimum in $T_1$ at the same temperature at which structure appears in the free induction decay. Fig. 19 shows the variation of $T_2$ with temperature and this too shows a distinct minimum at the temperature of the lineshape transition. $T_2$, the spin-spin relaxation time has been determined by a spin echo method. This spin echo is obtained when a pair of 90° pulses are applied separated by a variable time interval. If the time interval is $\tau$ then the decay of the echoes is an exponential with a time constant of $T_2$. Another variable was seen to have definite temperature dependence — called here the 'absolute signal difference'. The absolute signal difference is obtained in the
FIGURE 16

FID and TRANSFORM at 110 MK. during COOLDOWN
FIGURE 17

FID and TRANSFORM at 68 MK. DURING COOLDOWN AT 135° MAGNET ANGLE
FIGURE 18

$T_1$ VERSUS TEMPERATURE
FIGURE 19

$T_2$ VERSUS TEMPERATURE
following manner: At each temperature, there was a position of the magnet where the structure was a maximum and one, where it was a minimum. At these positions the 90°-90° and the 90°-90° produced echoes of varying amplitudes. Let us denote these by S1 and S2 respectively; (S1 - S2) was a function of magnet angle; the absolute signal difference was the S1 (maximum structure) - S2 (minimum structure) for a particular temperature. This variable seemed to be at a maximum at the lowest temperature and as the sample warmed, decreased until it nearly zeroed itself out after the structure disappeared. This behavior is shown in Fig. 4-20. In this plot the absolute signal difference has been normalised: the normalising factor being the sum (S1 + S2). The following table lists the typical data indicative of the T1 minimum.

\[ \text{TABLE 1} \]

<table>
<thead>
<tr>
<th>TEMPERATURE(K)</th>
<th>T1(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.542</td>
<td>3.09</td>
</tr>
<tr>
<td>0.369</td>
<td>2.35</td>
</tr>
<tr>
<td>0.288</td>
<td>1.7</td>
</tr>
<tr>
<td>0.201</td>
<td>2.3</td>
</tr>
<tr>
<td>0.122</td>
<td>2.8</td>
</tr>
<tr>
<td>0.045</td>
<td>3.1</td>
</tr>
</tbody>
</table>

The next set of data given in Table 2 indicates a typical T2 variation with respect to temperature for these low concentration
FIGURE 20

NORMALISED SIGNAL DIFFERENCE VERSUS TEMPERATURE
samples.

**TABLE 2**

<table>
<thead>
<tr>
<th>TEMPERATURE (K)</th>
<th>T2 (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.051</td>
<td>50.1</td>
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<tr>
<td>0.123</td>
<td>48.2</td>
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<td>0.152</td>
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<tr>
<td>0.256</td>
<td>35.0</td>
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<tr>
<td>0.282</td>
<td>33.1</td>
</tr>
<tr>
<td>0.320</td>
<td>159.1</td>
</tr>
<tr>
<td>0.380</td>
<td>266.0</td>
</tr>
<tr>
<td>0.420</td>
<td>0.480</td>
</tr>
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</table>

The following table Table 3 lists the values of the normalised signal difference, as defined in the text, as a function of temperature.

**TABLE 3**

<table>
<thead>
<tr>
<th>TEMPERATURE (K)</th>
<th>NORM. SIG. DIFF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.057</td>
<td>0.80</td>
</tr>
<tr>
<td>0.163</td>
<td>0.20</td>
</tr>
<tr>
<td>0.221</td>
<td>0.003</td>
</tr>
<tr>
<td>0.310</td>
<td>0.001</td>
</tr>
</tbody>
</table>
To further emphasize that $T_0$ does refer to an important temperature, Fig. 21 has all three variables plotted on the same graph. They all show definite changes in behavior at $T=T_c$.

Next data points are presented to substantiate the angular dependence of the free induction decay at 68 millikelvin for the single crystal sample. Fig. 22 shows the free induction decays for the magnet positions 155° and 65°. The upper diagram shows a definite beat structure while the lower does not. Fig. 23 indicates the same type of behavior for in phase spin echoes ($90_x-90_x$)–the upper has a structure, while the lower has no structure. We note that there is a 55° difference between the maximum structure position and the zero structure position, suggestive of a magic angle situation. This was a major indication of the single crystal nature of this sample.

Let us go back to Fig. 15. The figure indicates that hysteresis is present here, as it should be in any type of phase transition. In the upper diagram, an out of phase echo is clearly present during the first warmup of the sample. In the lower figure, the same echo is barely visible during the first cooldown. All scales, temperature, receiver gains, number of traces and other relevant parameters are identical for these two signals.
FIGURE 21

$T_1, T_2$, SIGNAL DIFFERENCE VERSUS TEMPERATURE
FIGURE 22

FID at 68 MK. upper - 155 ° POSITION, lower - 65 ° POSITION
FIGURE 23

ECHO at 68 MK. upper - 155 °, lower - 65 °
In the next figure, the result of a $T_1$ study, with respect to angle, after the sample has gone through the lineshape transition (this is at 4 K) is shown. The FID has returned to its original form—with no beat structure. Clearly we observe an angular variation of $T_1$, which was absent during the initial cooldown of the 'virgin' sample. Also to be noted is the presence of only one peak over a 90 degree sweep. This is shown in Fig. 24.

In an attempt to understand this complicated behavior, we will try to deconvolute the signal. Fig. 25 indicates the total signal obtained at the minimum temperature, which we decompose later on. In the next three digrams is shown the breakdown of the total signal into its components—in Figures 26, 27 and in 28. The signal at low temperatures could be decomposed into three parts—the long tail generally attributed to the HD (Fig. 26), the structured part belonging to the orthohydrogen (Fig. 28), and an unstructured part (Fig. 27) also due to the orthohydrogen.

In Fig. 29 is shown the comparison between the actual signal and the reconstructed (i.e. theoretical, assuming the Kubo model in the slow transition limit). The fit between experiment and theory seems to be fairly good.

The next figure (Fig. 30), Fourier transforms of the signal, indicate the change in the lineshape as the temperature changed. The lineshapes shown are at 4.2 K, 1.1 K, 460 mk., 84 mk., respectively. All are drawn on the same scale and hence comparable among themselves.
FIGURE 24

$T_1$ VERSUS ANGLE at 4K
FIGURE 25

TOTAL SIGNAL at LOWEST TEMPERATURE
Total Signal

Amp. (A.U.)

$T \ (\mu s)$
FIGURE 26

HD COMPONENT (S₁)
FIGURE 27

OH$_2$ ( NO STRUCTURE ) COMPONENT
FIGURE 28

OH$_2$ (STRUCTURE) COMPONENT
FIGURE 29

COMPARISON OF ACTUAL FID and THEORETICAL FIT
FIGURE 30

FOURIER TRANSFORMS at 4K, 1K, .46K, .084K
1. 4.2 K
2. 1.1 K
3. 0.46 K
4. 0.084 K
In Fig. 31 a typical low temperature echo is shown. Also shown, is an indication that the free induction decay resembles not the corresponding spin echo but it is nearly equivalent to the difference of the out of phase and the in phase echoes. The lower diagram in the figure is a comparison of the transforms of the free induction decay and that of the echo difference. This has been discussed in more detail in Chapters II and V.

The next few figures refer to a sample felt to be a double crystal sample. The data from this sample as regards the lineshape transition were very similar to the single crystal data so that only the major differences will be mentioned. Fig. 32 is the low temperature free induction decay at 75°. The beats beyond 50 microseconds were the only variable parts of the structure as the magnet was rotated. It was found that unlike the single crystal results where we had only one structureless position, here we had two such positions (at 75 and at 105 degrees). The next diagram, Fig. 33, indicates the angular variation of $T_1$ at 4 K after the sample had been cycled through the lineshape transition. We note the presence of two peaks unlike the single crystal case where we only had one. Fig. 34 and Fig. 35 indicate good Gaussian and exponential fits to echo decay data at low temperatures (we have used echo decay times in order to calculate $T_2$). Figures 36, 37, 38 indicate the variation of $T_1$, $T_2$ and the absolute signal difference with respect to temperature. All these indicate a definite change at the temperature of the lineshape transition, just as we found in the single crystal.
FIGURE 31

upper - TYPICAL LOW TEMPERATURE ECHO (out of Ph)
lower - TRANSFORM of FID and of ECHO DIFFERENCE
The image contains two graphs. The top graph shows the amplitude (A.U.) as a function of time (T, in μs) with values ranging from 0 to 200 μs. The bottom graph illustrates the frequency (kHz) on the x-axis and the F.T. (A.U.) on the y-axis, ranging from 0 to 192 kHz.
FIGURE 32

FID at 55 MK. at 75° POSITION for DOUBLE CRYSTAL
FIGURE 33

$T_1$ VERSUS ANGLE for DOUBLE CRYSTAL SAMPLE
FIGURE 34

TYPICAL GAUSSIAN DECAY IN $T_2$ MEASUREMENTS
FIGURE 35

TYPICAL EXPONENTIAL DECAY IN $T_2$ MEASUREMENTS
FIGURE 36

$T_1$ VERSUS TEMPERATURE for DOUBLE CRYSTAL
FIGURE 37

$T_2$ VERSUS TEMPERATURE for DOUBLE CRYSTAL
FIGURE 38
NORMALISED SIGNAL DIFFERENCE VERSUS TEMPERATURE
All the above data thus present a strong case in favor of an ordered phase in low concentration orthohydrogen below 250 millikelvin. An explanation for this will be offered later on in Chapter V.

4-3 The Control Experiment

In order to probe the role of the HD impurities in these samples, the following experiments were done: Low concentration hydrogen was made in the cryotip and put in two bulbs. One bulb was immediately connected with a precleaned glass wand and inserted in a liquid helium dewar for storage so that the conversion would be nearly absent. The sample in the other bulb was crystallised, cooled by dilution refrigeration, and experimented on. The HD content of the first sample used was determined from the signal breakup—it was about 1000 ppm (parts per million). The amplitude of the structured component was also determined. After completing the first experiment, an amount of HD equal to 1000 ppm was added to the stored sample and the same experiments performed. It was hoped that the two samples would be identical except for their HD content. From the data there appeared to be a correlation between the amount of the HD present and the amplitude of the structured and unstructured components. The signals from the samples at 1 K are presented in Fig. 39—the upper one is for the sample with the extra HD (referred to as sample B) and the lower one is the signal for the original sample (called sample A, now
FIGURE 39

FID at 1K. upper - SAMPLE A (800 PPM. HD), lower - SAMPLE B (1600 PPM. HD)
onwards). Note the change in the $T_2$ for the long tail as well as the amplitude. Fig. 40 is a typical free induction decay at 220 millikelvin right before the structure set in. In Fig. 41 is shown the $T_1$ versus temperature for sample A. Fig. 42 is the $T_2$ variation for the same sample. These two had about the same concentration of orthohydrogen as planned — about .18 % as determined from $T_1$ and $T_2$ at 4K. Fig. 43 and Fig. 44 are the $T_1$ and $T_2$ variations for sample B.

The breakup of the signal was done in a manner which was exactly the same as before so that the components obeyed Curie law. The amplitudes of the signal components are as follows:

**SAMPLE A**: 0.2 % OH$_2$ and 866 ppm of HD

\[ S_{HD} = 1310 \]
\[ S_{OH2 \text{ no str.}} = 1889 \]
\[ S_{OH2 \text{ str.}} = 6173 \]

**SAMPLE B**: 0.2 % OH$_2$ and 1600 ppm of HD

\[ S_{HD} = 2418 \]
\[ S_{OH2 \text{ no str.}} = 817 \]
\[ S_{OH2 \text{ str.}} = 7240 \]
FIGURE 40

FID at 220 MK.
FIGURE 41

$T_1$ VARIATION for SAMPLE A
FIGURE 42

$T_2$ VARIATION for SAMPLE A
FIGURE 43

$T_1$ VARIATION for SAMPLE B
FIGURE 44

\( T_2 \) VARIATION for SAMPLE B

137
The graph shows a plot of $T_2$ (μs) against $T$ (K). The data points suggest a trend where $T_2$ increases with increasing temperature $T$. The x-axis represents temperature in Kelvin (K), ranging from 0 to 500 K, while the y-axis represents $T_2$ in microseconds (μs), ranging from 0 to 1000 μs.
These results will be discussed in more detail in Chapter V. Analysis of other relevant data will also be presented in that section.
In this chapter, analysis of the data is presented, in terms of various models to help understand the experimental results presented in Chapter III. The most important finding of these experiments is that all parameters measured by NMR support the contention that a cooperative transition in low concentration solid hydrogen does take place. Three independently measured variables show drastic changes at a specific temperature $T_C$. Further experiments were performed in an attempt to understand this apparent transition. The HD molecules, present in the sample as an impurity, were thought to be a possible cause. Finally, a motional narrowing model, first used by Kubo\textsuperscript{18} was used to interpret the experimental results related to the transition in fairly simple terms. Spin lattice relaxation times were measured at 4K before and after the sample had gone through the temperature region characteristic of the transition. These data seemed to agree well with theoretical calculations made by Fedders\textsuperscript{20}. The free induction decay lineshape had been earlier thought to be identical with the trailing edge of a spin echo. The lineshape deduced from an
echo depends on the specific pulse sequence used. It has been observed that the FID lineshape closely resembles the signal from the difference between the in phase and out of phase echoes. Comparisons with theory are also made along these lines.

At first, we describe the method used to analyse the free induction decays. One of the more important parts of the signal lies in the first few time channels of the data. Due to the electronics, there is present a blocking time, during which there is no data output — and this unfortunately is in the initial part of the free induction decay. In order to do a correct analysis of the data one has to reconstruct the FID, supplying an extrapolation from finite time to time $t = 0$, so that we can have a complete picture of the signal from zero time onwards. The FID is the Fourier transform of the cw lineshape. The value of the FID at $t = 0$ is proportional to the total magnetization. Although, in these experiments, we have tried to remove this difficulty by having the smallest possible delay after the intense r.f. pulse has been applied, there are always some inherent difficulties with this problem. They are: (i) the origin of time for the FID actually is in the middle of the pulse (Barnaal and Lowe), (ii) there may be a significant deadtime after the pulse due to ringing in the probe and saturation of the receiver, (iii) the signal-to-noise ratio may be poor especially for samples with a short $T_2$ so that the magnitude of the signal may be significantly reduced before one can observe it. Problem (iii) has been dealt with by taking a large number of traces. The signal to noise ratio is proportional to $(N)^{1/2}$ where $N$ is the total number of traces taken. Problems (i) and (ii)
have been effectively taken care of, by doing the reconstruction of the signal to zero time. The concept of 'proper reconstruction' lies essentially in the validity of Curie law for these samples. As an example, consider an ensemble of spin-1/2 nuclei in a static magnetic field $H$. The nuclei have two energy states separated by $\Delta E=2\mu H$ where $\mu$ is the magnetic moment of the nucleus. The nuclei would distribute themselves between the two states according to the Boltzmann relation, so that the ratio of the spins in the upper energy state to those in the lower energy state is $\exp(-\Delta E/kT)$. There is thus a population difference in the energy domain (more populated in the lower energy state). This gives rise to a net magnetisation $M_0$ where $M_0$ is given by

$$M_0 = \frac{N\gamma^2h^2I(I+1)H}{3kT} = \frac{C}{T}$$

where $C$ is a constant for constant values of $I, N, H$. Thus as the temperature $T$ is decreased, the magnetisation increases in the same proportion. It is this relationship that has been made use of, in determining $M_0$ at time $t=0$. The product of the initial signal height and the absolute temperature is predicted to be constant. An extrapolation of the FID that yields a spin temperature equal to the lattice temperature is consistent with Curie law behavior.

The FID from 4K to the transition temperature was a fairly smooth curve of the exponential type without oscillations. As the sample was cooled below the transition temperature, the FID developed an oscillatory beat structure. In addition there was a long tail present
(long, as the decay time was particularly long — of the order of hundreds of microseconds). It was these two features that first suggested the attempt to break up the signal into three major components — a long tail, a structured component with beats present, and an unstructured part with a decay constant, $T_2$, of about 60 µs. Both the part associated with the HD($S_1$) and the part associated with the oH$_2$($S_2+S_3$) was individually made to follow Curie law in order to obtain their respective amplitudes at zero time. Hence, the total signal also abided by Curie law. At all temperatures, care was taken to see that good temperature stability was present, or else the validity of Curie law itself would be questionable.

Let us now discuss the breakup of the signal in some more detail. The HD molecule, unlike the orthohydrogen molecule, at low temperatures, has $J=0$. The HD molecules thus can only relax by means of a cross-relaxation technique via the orthohydrogen molecules. This has been extensively treated by Agragam$^{22}$ in his historic treatise. Due to this cross-relaxation and the lack of a direct process such as that of oH$_2$ molecules, it takes much longer for the HD molecules to relax. This provides one with means of identifying the long tail part of the FID with HD. The part of the lineshape attributable to the HD has been fitted by using the relationship:

$S_1 = S_1(0) \exp \left(-t^2/T_2^2\right)$

where $S_1(0)$ is the amplitude of the HD signal. The fit has been seen to be particularly good, as the tail completely disappears from the signal after the subtraction has been done. The rest of the signal i.e. $S(t) - S_1(t)$ can thus be attributed purely to orthohydrogen
molecules. This component of the signal, due to the orthohydrogen molecules, can be further broken up into two parts. One is the component which has no structure at all denoted by $S_2(t)$ and the other is the structured part denoted by $S_3(t)$. As indicated earlier, the signals from each of these components were extrapolated to time $t=0$, consistent with Curie law. The results of experiments done on three samples are given completely in Chapter IV. $S_1$, $S_2$, and $S_3$ have been obtained for typical FID lineshapes at low temperatures. The component $S_3$ develops as the temperature is lowered. Hence we can directly relate the transition to the structured component we call $S_3$. We shall return to the analysis of these components later on.

We will now discuss the FID lineshape observed in the experiments performed. The first one of these experiments concerned a low concentration sample that showed all indications of being a single crystal. From $T_1$ and $T_2$ measurements at 4K, the orthohydrogen concentration was determined (using a precalibrated chart of these relaxation times as a function of concentration). As the sample was cooled below 280 mK, a beat structure appeared on the FID. At the lowest temperature, the structure was the most pronounced. At this lowest temperature (which was 68 mK), the magnet was rotated. At one specific angle, the beat structure on the FID completely disappeared. At another specific angle, the structured signal had its maximum value. The angular interval between these two extreme positions was 55°. As we shall show later, it was this complete disappearance of structure at a certain angle that indicated the single crystal nature of the sample. In fact the angle value of 55° also indicated that the
c-axis of the crystal was in the horizontal plane. In order to understand the reasons for the appearance of structure, another experiment was performed where the concentration of the HD molecules was doubled, although the orthohydrogen concentration was nearly the same (about 0.2%). It was surmised that the HD impurities could have some direct link to the transition. In that case, the structured component $S_3$ would then definitely increase. As shown in Table III of Chapter IV there does not seem to be any correlation between $S_3$ and the HD concentration. Fig. 45 also indicates this feature. The basic thought in performing such an NMR experiment lay in the following reasoning. The HD molecules, present in the hydrogen sample, are intrinsic mass defects in the system. As a result of these mass defects, a strain field could be created in the sample. This strain field would help in trapping orthohydrogen molecules by attracting neighboring $^2$H$_2$ molecules into their vicinity. This trapping process, taking place over the whole sample, would result in a clustering phenomenon. Then, the structured component would be a direct measure of this clustering process of the hydrogen molecules getting trapped by the HD molecules. A great deal of motivation for the trapping theory came from trying to explain the angular dependence in $T_1$ at 4K after going through the lineshape transition. It seemed as if there was present a hysteresis involved in this transition. The event characterising this hysteresis could be the strain field introduced by the mass defects due to the HD impurities. We use the relationship,

$$\frac{S_3}{S_1} = \frac{N_0I_0(I_0+1)}{N_{HD}I_{HD}(I_{HD}+1)}$$

(41)

to calculate the number of orthohydrogen molecules trapped by each HD molecule. Here, $S_1, S_2, S_3,$ represent the signal components, $I_0$ is the
FIGURE 45

$S_2$ VERSUS HD CONCENTRATION
spin of the orthohydrogen molecule, and \( I_{\text{HD}} \) is the spin on the HD molecule. \( N_0 \) and \( N_{\text{HD}} \) are the concentrations of the hydrogen and HD molecules, respectively. Consulting the data in Chapter IV, we obtain,

\[
\frac{s_3}{s_1} = \frac{6173}{1310} = \frac{8}{3} \frac{N_0}{N_{\text{HD}}}
\]

This gives us a value of \( N_0 / N_{\text{HD}} \) as 2. This implies that two hydrogen molecules are getting trapped by one HD molecule. This calculation is for the first set of experiments, where the HD concentration was determined from the \( \text{OH}_2 \) concentration and the observed ratio of the signals (though, we note that the HD concentration was much higher than the natural abundance value of 300 ppm.) The second set of experiments was performed with the HD concentration doubled by adding the required amount of HD gas to the stored hydrogen gas. In this latter case, we have obtained,

\[
\frac{N_0}{N_{\text{HD}}} = \frac{3.7240}{8.2418} = 1 \text{ (to the nearest integer)}
\]

Analysis of previous low concentration work by Cochran\(^{19} \) where the HD content was equal to the natural abundance yields a value of 6, for this ratio. The analysis of the Cochran data was performed in exactly the same manner as this has been. The trapping theory thus gives different numbers of orthohydrogen molecules trapped per HD molecule depending on the HD concentration. The number is different for samples having different HD concentrations but nearly same orthohydrogen concentrations. If the HD molecules were, in fact, acting as traps, they would be expected to do so in a fairly consistent manner — the number of molecules trapped by each HD molecule should be the same, and the structured component ought to
change with changing HD concentrations. Thus a strong conclusion, in
favor of the trapping mechanism could not be made. One of the basic
assumptions we have made, is that all these HD molecules can behave as
traps. This, of course, may not be the case - the number of HD
molecules that behave as traps could be a complicated function of the
HD concentration. Another important consideration in this analysis
has been the decomposition of the signal into its three components and
then assigning names to each of these components. This breakup will be
discussed next.

Remembering that $S_2$ and $S_3$ are the signal contributions from the
orthohydrogen molecules, by determining the values of $S_1, S_2, S_3$ we
can calculate the HD concentration. For the first sample, this came
out to 866 ppm. We note that this result is an experimentally
determined quantity - dependent solely on the signals, and the $OH_2$
concentrations, and the model used. In the next experiment, HD was
added to double the HD concentration. From the same equation we
determined the HD content to be 1600 ppm. This is just as one would
expect from the amount of HD added, to the amount that was earlier
present. This clearly indicates that the signal breakup has been
correctly performed in that $S_2$ and $S_3$ scale with $OH_2$ concentration and
$S_1$ scales with HD concentration. Further, when we plot $S_1$ as a
function of HD concentration for four different experiments (with
differing HD concentrations) we obtain a very good straight line fit.
This is shown in Fig. 46. It indicates the excellent correlation
between $S_1$ and the HD concentration. $S_2$, the part that was clean and
structureless was easy to obtain. All one had to do was to remove the
FIGURE 46

$S_1$ VERSUS HD CONCENTRATION
structure from the hydrogen part of the signal. It was seen that as the sample cooled from $T_c$ onwards, $S_3$ also increased. This definitely showed that there was no arbitrariness in the breakup of the hydrogen part of the signal into $S_2$ and $S_3$.

Let us consider the trapping theory in the light of the NMR frequency spectrum. If there are orthohydrogen molecules trapped, whose number ranges from one to six for each HD molecule, the NMR frequency spectrum should be quite complicated being composed of contributions from pairs, triples and higher order clusters. Very few pronounced peaks were observed. The only large discernable peak was the one near 42 KHz. This is one of the three frequencies seen by Meyer in his pair spectrum of hydrogen. We may try to explain the possible absence of the peaks by arguing, as Harris has done that these clusters of three or molecules simply give a broad structureless line. The frequency spectrum, by itself, cannot be used to completely rule out the trapping theory.

We shall now analyse the experimental results by resorting to a theory first given by Anderson and Kubo. This theory has been previously incorporated in some earlier low concentration experiments and has been discussed in great detail by Gaines, Mukherjee and Shil. In these earlier experiments the most important feature had been the observation of the structure on the FID at low temperatures. No other independent variables had been measured. In our experiments three different variables, $T_1$, $T_2$, and the echo signal difference (explained earlier) showed minima around the transition temperature. We have
thus tried to combine these results in order to give a coherent explanation to the complete set of experiments. The theory will be discussed in brief and then consider its implications with respect to the data in this thesis. The model based on the work of Kubo incorporates the effect of Markovian motion on the lines of the frequency spectrum. The problem has been solved in two limits - the fast transition limit and the slow transition limit. At temperatures below $T_c$ (the transition temperature) we have what we call the slow transition limit. In this limit, the transitions occur slowly enough to be observed, giving rise to structures, and hence to discrete lines in frequency space. Above $T_c$, the transitions occur so fast, that the discrete lines are not observed in the time span of a FID sweep. Hence, in this case, we observe a clean unstructured signal. In the fast transition limit we can calculate the lineshape function (obtained earlier in Chapter II) to be

$$ S(t) = S_0 \exp\left[ -\frac{2\delta^2}{3\Omega} t \right] $$

Above $T_c$, we thus have a pure exponential for that part of the signal corresponding to the orthohydrogen molecules. In the slow transition limit, we obtain for the lineshape function,

$$ S(t) = S_0[\cos(\delta t)\exp(-\Omega t) + \cos(2\delta t)\exp(-2\Omega t)] $$

where, $\delta = (3u^2-1)3d/4$ with $u = \cosine$ (angle between crystal axis and the magnetic field)

$$ d = \text{intramolecular coupling constant} = 57.7 \text{ KHz.} $$

In this limit the pure exponential is modulated by a cosine function, giving rise to the structure that is generally observed below $T_c$. When $\delta = 0$, we find,
This is the case where there is no structure on the signal, even at low temperatures. This case can be obtained for a single crystal if the magnetic field direction is suitably chosen. At this magnet orientation,

\[(3u^2-1)(3d/4) = 0\]

\[u = (1/3)^{1/2}\]

\[\theta = 55^\circ\]

Thus the angle between the position of maximum structure and that of no structure at the lowest temperature is 55°. This position at which the structure completely disappears is called the magic-angle. The angle of 55°is thus only possible if the crystal axis lays exactly in the horizontal plane. Any other orientation would not have given this value, because then we would have to take into account the projection of the axis in the horizontal plane. It is this behavior that has allowed us to conclude that the sample is a single crystal.

In the second sample, we obtained two such positions in a 60 degree range. This suggested that the sample consisted of two crystals. In both samples T1 measurements were made at 4K before and after the sample had gone through the lineshape transition as a function of magnet angle. In both cases, there were no T1 variations with respect to angle for the ‘virgin’ sample. In the first sample (i.e. the single crystal) after warmup, a plot of T1 versus magnet angle showed a single peak. The second sample, gave two peaks in the plot of T1 versus magnet angle. These data have already been presented in Chapter IV. Fedders20, in his theory of spin-lattice
relaxation times for very low concentration \( \text{OH}_2 \), calculates \( T_1 \) for various symmetries. Since our data seems characteristic of a single hop crystal with axial symmetry, we have compared our data with Fedders' calculation for axial symmetry. Referring to his complex calculation, we make the approximation that,

\[ \left[ \right] \gg \omega. \]

The \( T_1 \), then simplifies to,

\[
\frac{1}{T_1} = \frac{\omega^2[A + Bn^2]}{\gamma_1}
\]

where \( \alpha \) is the cosine of the angle between the \( c \) axis of the crystal and the magnetic field and

\[ A = 15.08 \]

\[ B = 4.91 \]

Fitting the maximum and minimum values of \( T_1 \) to this expression gives us an excellent fit, as is shown in Fig 47. Though the Fedders theory may not be exactly applicable in our case, (as the concentration range he considers is much lower than ours) there seems to be good agreement between the two results. Extending the Fedders' theory to a sample consisting of two single crystals, we would expect two peaks in \( T_1 \). This is just what we observe in the second sample. Thus there does seem to be a one-to-one correlation between the number of crystals and the number of peaks in a plot of \( T_1 \) versus magnet angle at 4K.
FIGURE 47

$T_1$ FIT using PEDDER THEORY
Let us now consider some other details of Fedders' calculation in the light of our experiments. Fedders' calculation holds for single crystal orthohydrogen samples where the crystal field is very large. In the initial stage of the experiment (at high temperatures) we have a sample with a small crystal field. As the sample is cycled through the lineshape transition, the crystal field must increase enormously, as we find $T_1$ to be angle dependent at 4K. The parity between our $T_1$ results at 4K and Fedders' calculation questions the source of this crystal field. Clearly if any sort of comparison has to be made, our data should also reflect the presence of such a large crystal field. The strain field, produced by the HD molecules acting as mass defects, would be a very plausible source of a large crystal field. It was the nurturing of this idea that led to the trapping theory and a test of this theory lay in the Control experiment. Even though the ratio of the number of $OH_2$ molecules trapped by each HD molecule did not come out to be consistent for different HD concentrations, the trapping theory cannot be ruled out. Conclusive evidence in favor of the trapping theory was not obtained. The problem could very easily lie in some of the basic assumptions made in analysing the data in the light of this theory. As an example, no theoretical basis exist for predicting quantities like the number of traps - which is one of the more important points in the theory. The signal breakup, which was another important basis gave expected values of orthohydrogen and HD concentrations. Hence, as far as the hydrogen ($S_2 + S_3$) and HD ($S_1$) components are concerned, the breakup was performed correctly. The Cochran data seemed to also show that the total signal could be broken up into three different components. Curie law was used to determine
the components. This further supported the breakup. Fedders’ calculations seem to corroborate the single crystal model as has also been predicted by the ‘motional’ model. This has been a novel way of predicting and verifying the crystalline state of a solid hydrogen sample.

In the past, by all groups, it has been assumed that the trailing edge of an echo is identical to the FID. In experiments described here, echo measurements show that the FID is not simply related to any specific echo but is really most similar to the signal obtained from the difference in the $90_y - 90_x$ echo and the $90_y - 90_y$ echo. The calculation (using the Kubo model to incorporate motion) has been performed in Chapter II. The first two terms in this echo difference are those that contribute in the refocussing of spins. The last term is a pure damping term. The calculation does not explicitly show that the FID is identical with the signal from the echo difference. But experimental results clearly indicate that the FID is most similar to the difference of these echoes. Fig. 48 is the FID at a certain angle at the lowest temperature of 55 mk. Fig. 49 is the signal formed from the echo difference. Note the almost exact position of the beats and their identical heights. Fig 50 shows the 90-90 echo. Similarly, in Fig. 51 through 53 we give diagrams showing the above for a different pulse interval. These figures go to demonstrate clearly that the FID does not resemble the 90-90 echoes. Rather, they are nearest in form to the difference of the in phase and out of phase echoes.
FIGURE 48

FID at 68 mk.
FIGURE 49

ECHO DIFFERENCE at 68 mk.
Signal (A.U.)

Time (μs)
FIGURE 50

OUT of PHASE ECHO at 68 mk.
FIGURE 51

FID at 80 mk.
FIGURE 52

ECHO DIFFERENCE at 80 mk.
FIGURE 53

ECHO at 80 mk.
The lineshape transition is accompanied by minima in the relaxation times. This minimum in the relaxation time can be physically interpreted as a collapse in the fluctuation spectrum for the orientations. The correlation times associated with this spectrum increase smoothly and rapidly until it reaches a maximum value at \( T_c \). The normalised signal difference, another variable, that shows a change as we approach \( T_c \), can be calculated, using the Kubo method. The result, finally obtained is far too complicated to analyse. We also have determined a variable called \( \Omega/d \) (as is defined in the paper by Gaines et al.). The change in this variable over temperature seems to follow closely with their results.

In Chapter I, brief mention has been made about NMR experiments on \( \text{O}_2\) samples (greater than 50%) where not only a singularity in the specific heat was observed, but also a NMR lineshape change was present. It is now accepted that this was the result of the cooperative ordering of the ortho-molecules. Experimental techniques like X-Ray scattering and neutron diffraction have shown that this transition is accompanied by a change in the crystal structure from the hcp lattice to the fcc lattice. The EQQ (electric quadrupole-quadrupole) interaction caused this ordering to take place by lifting the degeneracy of the \( J=1 \) state. Since, in the experiments presented in this work, there is also a lifting of the rotational degeneracy, it is reasonable to expect an order-disorder type of phase transition. In our case, the transition is not brought about by the EQQ interaction (as the concentration is not the same), but by some other indirect mechanisms. For the first time, the transition has been
well characterised with the help of independently measured variables. The transition has been explained with the help of the Kubo theory. The theory has given an acceptable explanation for the transition and for the signal both above and below the transition temperature. There is also present in these results an indication of hysteresis. We refer back to Fig. 15. In this figure we see no echo while cooling down. But once we have passed through the lineshape transition, there is a definite echo at that same temperature. We note that most phase transitions are almost always accompanied by some form of hysteresis.

In conclusion, our data does indicate a lineshape transition at 280 mk. At the same temperature, we also observe minima in $T_1$, $T_2$ and the normalised signal difference. Experiments on orthohydrogen samples with 50% oH$_2$ also have shown minima in $T_1$, $T_2$ and also a lineshape transition. But changes in crystal structure or in the specific heat were not observed. Below the lineshape transition temperature, it was originally proposed that these samples froze into a 'glass' phase. None of the thermodynamic parameters measured have given any indication of a glass transition, so current thinking is that no phase transition occurred. Thermodynamic parameters are yet to be measured in samples with 0.2% oH$_2$. Once such measurements are performed, the question about a phase transition can be answered more precisely. We also have to bear in mind the experiments that first initiated this train of thought - those with nH$_2$, where a lineshape transition occurred simultaneously with a phase transition. In our case, clearly, there is undoubtedly an ordering of the rotational degrees of freedom, together with a lineshape change and minima in
relaxation times. More work is warranted to determine if the transition really depends on fluctuations in strain parameters of the crystal, or on the crystal growing techniques, or on the type of sample cell used. Once these parameters have been carefully considered, we can well assert the validity of our model to a far greater extent. At this stage, we are forced to keep the answer open, as to whether a phase transition occurred or not.
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