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the Degree Doctor of Philosophy in the Graduate
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By

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CHAPTER I

INTRODUCTION

The process of heat conduction in a solid at low temperatures, though seemingly simple on a macroscopic scale, is very complicated on a microscopic scale. Theories have been devised for conduction in perfect single crystals as well as for crystals with defects (1, 2). They are by no means complete. Solid hydrogen presents additional problems because of some peculiar properties at low temperatures. Because of these complexities, a brief introduction to thermal conduction and to solid hydrogen will be presented before the thermal conductivity of solid hydrogen is discussed.

1.1 Summary of Thermal Conductivity at Low Temperatures

In a crystal, the atoms vibrate about their equilibrium positions which are arranged in a regular lattice. These atoms are not bound to their equilibrium sites, but are strongly coupled to the neighboring atoms. If the lattice, consisting of N atoms, is perfect, and if the forces between atoms are strictly harmonic, that is, proportional to the relative displacements, a solution to the 3N equations of motion can be found in terms of traveling waves. These waves are the normal modes of vibration of the crystal lattice and are
the mechanism by which energy is transmitted from one end of the crystal to the other. For purely harmonic forces, the conductivity is limited solely by interactions with the crystal boundaries and lattice imperfections. Anharmonic effects couple the modes and cause an additional thermal resistance.

Each normal mode of vibration obeys the classical equation of motion of a harmonic oscillator. In classical theory, the energy is a continuous function. However, the analogous quantum mechanical oscillator has a discrete set of energy values. If the normal modes of a crystal lattice are quantized, we arrive at the concept of phonons. The thermal properties of insulators at low temperatures can be discussed in terms of the interactions between phonons and between phonons and imperfections.

Phonons have particle-like properties and can thus have momentum. Phonon-phonon interactions in which momentum is conserved are referred to as normal processes, or N-processes (3). Because of the periodicity of the lattice, an interaction can occur where some of the phonon momentum is transferred to the lattice as a whole (3). This is called an Umklapp, or U-process. Klemens (1) has shown that N-processes do not contribute to the thermal resistance directly, while U-processes do. At low temperatures, the probability of U-processes will go as the product of the appropriate occupation numbers of the phonon modes,

\[ n_q n_{q'} \approx \exp(-h\nu/kT)\exp(-h\nu'/kT), \]

where \( n_q \) = occupation number of the qth mode, \( h \) = Planck's constant, \( \nu = \) frequency of qth mode, and \( k \) = Boltzmann's constant.
With a Debye model for the solid (3), we need consider only the dominant phonon frequencies, that is, those near the cut-off frequency of the Debye distribution. Thus we can write,

\[ \frac{\hbar}{k} (\nu + \nu') = \beta \Theta, \]

where \( \beta \sim (1/2) \) and \( \Theta \) is the Debye temperature. Then the temperature dependence of the conductivity will be of the form,

\[ K \sim T^n \exp(\beta \Theta / T), \]

where \( n \) is an exponent that depends on the details of the model. Thus, at low temperatures, the conductivity will increase as the temperature decreases. In practice, however, the conductivity will be limited by the size of the specimen.

If we think in terms of a phonon gas, we find that the mean free path of the phonons becomes comparable to the crystal dimensions at temperatures below the \( \nu \)-process region. Using the principles of elementary kinetic theory, the thermal conductivity of a phonon gas is given by

\[ K = \frac{1}{3} C v L, \]  \hspace{1cm} (1) \]

where \( C \) is the lattice specific heat per unit volume, \( v \) is the velocity of sound, and \( L \) is the mean free path. Casimir (4) considered this problem of boundary scattering using a tube filled with electromagnetic radiation and arrived at essentially this result. Klemens (2,5), using a more exact theory of phonon interactions, also obtained this result. Since \( v \) and \( L \) are temperature independent and the specific heat varies as \( T^3 \), the conductivity will be proportional to \( T^3 \).
In summary, at low temperatures the thermal conductivity of a crystal will increase exponentially as the temperature is lowered. It will then decrease as $T^3$ as the phonon mean free path becomes comparable to the crystal dimensions. An example is given in Figure 1 (6).

All of the above considerations are for a perfect crystal. If the crystal has isotopes or imperfections in it, the conductivity will be reduced. Equation 1 can then be generalized to the form:

$$ K = \frac{1}{3} \int S(\omega)\nu L(\omega) d\omega, \quad (2) $$

where $S(\omega)$ is the contribution to the specific heat per unit frequency interval from lattice waves of angular frequency $\omega$, and $L$ is now a function of frequency. Klemens (1) discusses the effects of imperfections on the conductivity. His discussion is summarized in Table 1 which lists the various phonon scattering mechanisms and the way in which they affect the temperature dependence of the corresponding components of the resistivity.

If a form of Matthiessen's Rule (7) can be applied, we should be able to add the resistivities due to the various scattering mechanisms,

$$ W(T) = W_B(T) + W_F(T) + \ldots $$

where $W_B$ is the resistivity due to boundary scattering, $W_F$ the resistivity due to defect scattering, etc. For conductivity measurements this rule usually cannot be rigorously applied, but it has the advantage of physical obviousness. Both Klemens (2) and Ziman (7) discuss the applicability of this rule.
Figure 1

Thermal Conductivity of Sapphire

The plain line indicates a specimen diameter of 3 mm; the open circles - 1.55 mm; the closed circles - 1.02 mm (6).
Thermal conductivity $\text{Watt cm}^{-1}\text{deg}^{-1}$
## TABLE 1

SCATTERING MECHANISMS

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<th>( 1/K(T) )</th>
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<td>External boundaries</td>
<td>( 0 \omega^{0} )</td>
<td>( T^{-3} )</td>
</tr>
<tr>
<td>Grain boundaries</td>
<td>( 0 \omega^{0} )</td>
<td>( T^{-3} )</td>
</tr>
<tr>
<td>Stacking faults</td>
<td>( -2 \omega^{-2} )</td>
<td>( T^{-1} )</td>
</tr>
<tr>
<td>Dislocations (strain field)</td>
<td>( -1 \omega^{-1} )</td>
<td>( T^{-2} )</td>
</tr>
<tr>
<td>Dislocations (core)</td>
<td>( -3 \omega^{-3} )</td>
<td>( T^{0} )</td>
</tr>
<tr>
<td>Long cylinders</td>
<td>( -3 \omega^{-3} )</td>
<td>( T^{0} )</td>
</tr>
<tr>
<td>Point defects</td>
<td>( -4 \omega^{-4} )</td>
<td>( T^{1} )</td>
</tr>
<tr>
<td>Umklapp processes</td>
<td>( -1 \omega^{-1} )</td>
<td>( T^{-3}e^{-\beta \Theta/T} )</td>
</tr>
</tbody>
</table>

Finally, an additional source of thermal resistance could be attributed to molecules that can make transitions between states of different energy. If the molecules can exist in two states separated by an energy \( E \), then transitions could be excited between these states by emission or absorption of phonons of energy \( h\nu = E \). Slack (8) has studied this effect for magnetic impurities and has shown that the conductivity is depressed at temperatures appropriate to the energy of the level spacings. Whether such resonance effects can be observed in hydrogen remains to be determined.
1.2 Properties of Hydrogen

The hydrogen molecule is diatomic with an internuclear separation of 0.75 Å. Because of its small mass, it has a small moment of inertia. Hence, there is a wide separation of the rotational energy levels,

\[ E_J/k = 80°K[J(J + 1)]. \]

At low temperatures the molecular rotation must be treated quantum mechanically. In addition, the Pauli exclusion principle requires that the molecular wave function be antisymmetric under interchange of the two nuclei of spin 1/2. Thus, molecules with total spin quantum number \( I = 1 \) (symmetric in spin) must have antisymmetric rotational wave functions (\( J \) is odd). Molecules with total spin quantum number \( I = 0 \) (antisymmetric in spin) must have symmetric rotational wave functions (\( J \) is even). Because there is only a small probability for a transition from one state to another at normal or low temperatures (9), hydrogen exists as essentially two distinct species—orthohydrogen \( (I = 1, J \text{ odd}) \) and para-hydrogen \( (I = 0, J \text{ even}) \). Equilibrium hydrogen at room temperature consists of 75% ortho-hydrogen and 25% para-hydrogen. However, different ortho-para concentrations can be prepared by using catalysts at low temperatures (9). The concentration of ortho-hydrogen can be determined by measuring the thermal conductivity of the gas (9). An alternate method is to measure the nuclear spin relaxation times of the orthohydrogen molecules in the solid (10). However, this latter method is effective only up to ortho concentrations of about 40%.
Below 14°K hydrogen exists in the solid state. The structure is known to be hexagonal close-packed (hcp) (11), each molecule in the solid having 12 nearest neighbors at a distance $a = 3.75\AA$. [For high ortho-concentrations there is a crystallographic transition at $T \sim 2°K$, but this effect will not be a factor in the temperature and concentration range considered here (11).] With Boltzmann statistics it can be shown that the only rotational states occupied at low temperatures are $J = 0$ and $J = 1$.

Let us start with a solid consisting of pure para-hydrogen ($J = 0$). If ortho-hydrogen molecules ($J = 1$) are added, we can look for two effects at low concentrations: (1) Isolated ortho molecules will interact with the para-hydrogen lattice, (2) As the concentration increases, there will be an increased probability of having ortho-hydrogen nearest neighbors. The first effect involves the interaction between ortho-hydrogen and para-hydrogen when averaged over the para-hydrogen state $J = 0$. This effect is about zero if the structure of hydrogen is perfectly hcp, but because of the small mass of the hydrogen atoms the large zero-point motion causes the structure to deviate from a perfect hcp lattice. This crystal field interaction with the ortho-hydrogen molecules causes the degeneracy of the $m_J$ levels to be partially removed so that there is a doubly degenerate level ($m_J = \pm 1$) separated from a single level ($m_J = 0$) by an energy $A$. Because of this interaction, the specific heat has a term linear in the ortho-concentration, $x$. Nakamura (12) has used the results of heat capacity measurements to indicate that $A/k$ is of the order of 1°K.
More reliable NMR measurements (13) indicate that $A/k$ is much smaller and about $8.66 \times 10^{-3}\,\text{K}$.

Nakamura (12) has shown that the interaction of a pair of nearest-neighbor ortho-hydrogen molecules is dominated by the quadrupole-quadrupole (QQ) interaction. All other interactions, van der Waals and dispersive forces, contribute less than 10%. The energy level diagram for this interaction is given in Figure 2, where $\Theta/k = 0.82\,\text{K}$ (14). The energy is varying as $r^{-5}$, so that it drops off rapidly for ortho-hydrogen molecules that are more distant. This interaction causes an $x^2$ term to appear in the specific heat (12).

There are now three terms in the specific heat: (a) the crystal field term, (b) the QQ term, (c) the lattice term. The specific heat is of the form,

$$C = \frac{\alpha x + \gamma x^2}{T^2} + \phi T^3,$$

where the coefficients $\alpha$, $\gamma$, and $\phi$ correspond to (a), (b) and (c) above. $\alpha$ and $\gamma$ can be obtained from $A$ and $\Theta$ given above. $\phi$ has been measured by Hill and Lounasmaa (15). Since $\alpha x$ is small compared to $\gamma x^2$ for low concentrations and temperatures above 1°K, we can neglect this term. The relative importance of the remaining terms for a random distribution of ortho-ortho pairs at three different concentrations is shown in Figure 3.

1.3 Thermal Conduction in Solid Hydrogen

Since single ortho-hydrogen molecules and paired ortho-hydrogen molecules possess energy level schemes, the presence of ortho-hydrogen
Figure 2

Energy Levels for QQ Interaction
ENERGY  DEGENERACY

6 \Gamma  \quad 1

\Gamma  \quad 2

0  \quad 4

-4 \Gamma  \quad 2
Figure 3

Specific Heat Terms for Hydrogen
molecules could affect the thermal conductivity. At low ortho-hydrogen concentrations \((x \sim 5\%)\), Meyer has shown that a significant number of paired ortho-hydrogen molecules exist, in addition to the single ortho-molecules present (14). If there is some phonon scattering by these pairs, then it can be expected that as the ortho-concentration increases, there will also be scattering by triangular clusters of ortho-hydrogen molecules, etc. Thus, the conductivity would decrease rapidly as the ortho-hydrogen content is increased. This decrease is represented in the measurements of Hill and Schneidmesser (16), who measured the thermal conductivity of solid hydrogen at various ortho-hydrogen concentrations above 3°K. Their results are shown in Figure 4. Their measurements again exhibit the general features of thermal conductivity at low temperatures: an increase of conductivity as the temperature is lowered followed by a decrease as the boundary scattering region is approached. Unfortunately, the boundary scattering region was not reached and little can be learned about the region below 3°K from their data.
Figure 4

The Thermal Conductivity of Solid Hydrogen

The thermal conductivity of solid hydrogen for various ortho-hydrogen concentrations (○ - 0.5%; ● - 1%; □ - 5%; ○ - 10%;
φ - 29%; ● - 55%; ● - 72%) (Ref. 16).
CHAPTER II

APPARATUS

2.1 Design Considerations

The accuracy of a thermal conductivity measurement at low temperatures can be increased by careful design of the system that is used. Paths of heat conduction that are in parallel with the sample must be known, and eliminated, if possible. In addition, extraneous sources of heat input (radiation, Joule heating, etc.) have to be minimized. A simple geometrical shape for the sample is also desirable.

Since the measurements were to be performed in the temperature range 1.3°K to 6°K, liquid $^4$He was used to maintain these temperatures. This liquid boils at 4.2°K under a pressure of one atmosphere. However, hydrogen liquefies at 20.4°K under a pressure of one atmosphere (17). The triple point is 14.0°K (17). Thus, in order to liquefy and solidify the sample in the cryostat, temperatures that are well above 4.2°K have to be maintained and controlled. This is another factor affecting the design.

The method used here to determine the thermal conductivity differs from the usual procedure. Since this affected the design of the cell, a description of the technique is given in the next section.
2.2 Method of Measurement

The usual method of determining the thermal conductivity of a solid is to put a known amount of heat into one end of a cylindrical sample and to remove that amount of heat from the other end. The temperature gradient along the axis is measured by two thermometers and the conductivity calculated from Eq. 4.

\[
\dot{Q} = KA \frac{dT}{dx},
\]

where \( \dot{Q} \) = heat input,

\( K \) = thermal conductivity,

\( A \) = cross-sectional area of sample,

\( \frac{dT}{dx} \) = temperature gradient along the axis of the sample.

The approach used here is to replace the heater at the end of the sample with a thermometer, while the heaters, instead of the thermometers, are placed along the axis of the rod. A schematic diagram depicting this method is shown in Figure 5. One end of the sample is thermally isolated, while the other end is thermally connected to a large mass whose temperature remains constant. Thus, any heat that is put into the sample will be conducted to this heat sink. A thermometer is located on the isolated end and two identical heaters are attached to the sample a distance \((X_2 - X_1)\) apart. With no power input to the heaters, the temperature of the sample is \( T_0 \), the temperature of the sink. An amount of heat, \( \dot{Q} \), is then supplied to the heater nearest the sink. As the temperature gradient is established between this
Figure 5

Schematic Diagram of the Method Used for

Determination of the Thermal Conductivity
heater and the sink, the temperature of the isolated end rises to \( T_1 \). After equilibrium has been reached and \( T_1 \) measured, the first heater is turned off and the second heater turned on. The heat input, \( Q \), being the same, the temperature of the isolated end rises to \( T_2 \) as the temperature gradient is established between the two heaters. Since the heat current is the same in both instances, the temperature at the first heater is still \( T_1 \). Now

\[
\frac{(T_2 - T_1)}{(X_2 - X_1)} \text{, the cross-sectional area, and } Q \text{ are known, and the conductivity can be calculated from Eq. 4.}
\]

At low temperatures this method has several advantages. If carbon resistors are used as thermometers (see Appendix B), they must be carefully matched in a conventional measurement, and each must be precisely calibrated. Here the heaters should be matched. However, if they are not, the voltage can be adjusted so that the power input is the same. In addition, only one thermometer need be calibrated. If the electrical resistance, \( R \), of a metal or semiconductor is used as a temperature sensor, a knowledge of \( dR/dT \) will determine \( dT/dx \) since

\[
dT/dx = \frac{(T_2 - T_1)}{(X_2 - X_1)} = \frac{(R_2 - R_1)}{(dR/dT)(X_2 - X_1)},
\]

where \( R_1 \) corresponds to \( T_1 \), \( i = 1,2 \). If the temperature is recorded as a function of time after a heater is turned on, the thermal time constants of the system can be obtained. The possibility of obtaining values for the specific heat of hydrogen from these time constants is discussed in Appendix E.
2.3 Cell Design and Construction

During liquefaction and solidification of the hydrogen, it is desirable to be able to observe the process visually so that the growth of the crystal can be carefully controlled. This suggests that a Lucite or glass cell might be used. But this would mean that the cell walls would have to be considerably thicker than if they were made of a low conductivity metal, such as stainless steel. Since the cell acts as a parallel path for the conduction of heat, its walls should be very thin and have a small thermal conductivity at low temperatures. An additional problem arises when transparent windows are placed in the cell, since the joint must be vacuum tight. Since the thermal expansion coefficients of Lucite and glass are very different from those of most metals, it is difficult to make a direct metal-to-glass, or metal-to-Lucite seal that will not break open, and leak, as the temperature is lowered.

With the above in mind, the system shown in Figure 6 was designed and constructed. The entire system is immersed in a liquid $^4\text{He}$ bath that is maintained at 4.2°K. The evacuated Pyrex glass tube, or vacuum jacket, surrounds the copper shield and cell and effectively insulates it from the main bath. This glass vacuum jacket is sealed to a copper flange (not shown) by an indium O-ring as described in Appendix A. A small container of liquid $^4\text{He}$ ($^4\text{He}$ sub-pot) is used to determine the temperature of the shield and cell assembly. Its temperature can be varied between 4.2°K and 1.2°K by reducing the vapor pressure above the liquid. A copper shield is soldered to the sub-pot and serves two purposes: it acts as a radiation shield for the sample, and
Figure 6

Hydrogen Cell and Shield Assembly
PYREX GLASS

$^4$He SUBPOT

FILL TUBE

HEAT EXCHANGERS

COPPER SHIELDS

$^4$He VACUUM

ELECTRICAL TERMINALS

COPPER RESISTOR

STAINLESS STEEL

LUCITE

H$_U$

H$_M$

H$_L$

SHIELD HEATER

FILL TUBE

RESISTOR

1 CM.
conducts heat from the sample to the sub-pot. Two slits were machined in this shield for sample observation. Soldered to the sub-pot and shield is a 0.036" i.d. copper tube that is used for transferring the hydrogen to the cell. This fill line, which runs down the center of an evacuated tube from the top of the cryostat, is thermally anchored to the sub-pot before reaching the cell. The heaters on the fill line and shield are used for temperature control during liquefaction and solidification of the hydrogen sample.

The fill line terminates in a piece of oxygen-free, high conductivity (OFHC) copper that serves as the bottom of the cell as well as the heat sink for the sample. This piece is bolted to the bottom of the shield by brass screws, and Apiezon N grease is applied to all areas of contact to increase the thermal conductance of the joint. A germanium resistor, $R_s$, is placed on the bottom plate. By measuring the resistance of $R_s$, the temperature can be determined from a resistivity-temperature calibration.

Lucite cylinders were machined to the shape shown, and sealed to copper flanges at the top and bottom of the cell by indium O-rings. This is discussed in Appendix A. The lower "window" has a small capillary from the hole in the copper base to the larger hole that forms part of the cell proper.

We hope to have produced single crystal specimens by nucleating the growth at the junction of the capillary and copper plate. Indeed, as solid began to form, a phase boundary could be observed moving up the tube from this point.

The main portion of the cell consists of a stainless steel tube with wall thickness 0.010". Three small slits were made in the walls of the tube at
right angles to the axis and 0.005" thick copper tabs soldered in place a
distance 1.1 cm apart. The heaters were of 0.001" Evanohm wire wound onto
copper forms and fastened to the tabs with GE 7031 varnish. The resistance of
each heater was 4800 ± 200 ohms. Three heaters were used so that two values
could be obtained for the conductivity. One value would serve as a check on the
other.

The thick flange on the upper portion of the cell served as a place to
mount the upper thermometer. Another germanium resistor, $R_c$, served as
this temperature sensor and was placed in a copper cylinder that was soldered
to the flange. Apiezon N grease provided thermal contact. The thermometer
leads were thermally anchored at the isolated end by winding them about the
flange before they were taken to the terminals on the shield. All leads from
the heaters and resistors were of 0.005" manganin wire and were thermally
anchored at this terminal.

The upper Lucite window was used to determine when the cell was full
of liquid. Solid could also be observed at this window when the crystal was
formed.

After assembly, the total volume of the cell was 2.2 cc.

2.4 Vacuum Lines and Hydrogen System

The vacuum lines and hydrogen system are shown in Figure 7.

As discussed in the previous section, the $^4$He sub-pot is used to cool
the cell and shield assembly. This sub-pot, in the lower portion of the cryostat,
Figure 7

Vacuum Lines and Hydrogen System
is connected to the 5/8" copper vacuum line at the top of the cryostat by a 1/2"
stainless steel tube. By adjusting the valve in the 5/8" line that goes to the
mechanical pump, the vapor pressure of the \(^4\)He, and hence the temperature,
can be controlled. Temperatures between 1.2°K and 4.2°K can be attained.
Note that the manometers can indicate the vapor pressure in either the \(^4\)He
bath or in the sub-pot. A mercury manometer is used for high pressures,
while an oil manometer is used for low pressures.

The line that is used to pump the vacuum jacket is a 1/2" thin-walled
stainless steel tube that is joined to a 1" copper line at the top of the cryostat.
This system can be pumped by an oil vapor diffusion pump that is backed by a
mechanical pump. The liquid nitrogen trap in the line prevents oil vapors
from back-streaming to the cryostat. The trap also freezes out any condensable
vapors that might be present in the system. The discharge gauge (as well as
the ion gauge in the hydrogen line) is capable of reading pressures between
10\(^{-3}\) and 10\(^{-7}\) torr.

The 1/16" fill line for the hydrogen cell is thermally connected to the
sub-pot before it becomes concentric with the vacuum jacket pumping line.
Thus it is thermally isolated from the main \(^4\)He bath. To prevent premature
blockage of the fill line during condensation of hydrogen, a 200 ohm manganin
wire heater is varnished onto the tube. The line is encased in Teflon tubing for
further insulation. The fill line joins a 1/4" copper vacuum line at the top of
the cryostat. The pumping system for the hydrogen fill line is then quite
similar to that used for the vacuum jacket.
The copper electrical leads (0.003") are thermally connected to the shield and the upper flange of the vacuum jacket. Thus, any heat that is conducted down the leads will be transferred to the main $^4$He bath, rather than to the cell. The leads are brought to the top of the cryostat through a 1/4" stainless steel tube that is open to the vacuum jacket, but sealed at the top of the cryostat.

2.5 Thermometer and Heater Circuits

Figure 8 is a block diagram of the electrical equipment that was used for conductivity measurements. Except for the germanium resistor on the heat sink, all of the shielded resistor leads pass directly through a switch box. This box switches the Malaker bridge to either of the germanium resistors, or to any of the carbon resistors that were used as secondary temperature monitors. These carbon resistors were placed on the cell to indicate the temperature at points on the isolated end and near the lower window. After observing them in the early experiments, it was found that the carbon resistors were unnecessary since the germanium resistors gave excellent indications of the temperatures that were necessary for a conductivity determination.

The Malaker bridge, which is essentially an AC Wheatstone bridge, was used to determine the resistance of the temperature monitors. A three-wire connection was used for the germanium resistors. This method insured that compensation has been made for lead resistance. For more precision, the AC output of the bridge was fed into a Model HR-8 lock-in amplifier from
Figure 8

Thermometer and Heater Circuit Block Diagram
Princeton Applied Research. This amplified the signal and increased the signal-to-noise ratio. With this arrangement a change of 1 ohm in 40,000 could easily be seen. This corresponds to a temperature change of about 0.2 millidegrees. The DC output from the bridge was fed into a chart recorder for the purpose of measuring the thermal time constants of the system.

The shield resistor leads were fed into a switch box. This allowed us either to measure the actual resistance of the shield resistor with the bridge, or to read the voltage drop across the resistor with the digital voltmeter when a small DC current passed through it. With this arrangement, the germanium resistor on the cell, $R_c$, and the resistor on the shield, $R_s$, could be monitored simultaneously. Thus, any temperature changes at the heat sink could be detected during a measurement.

The leads to the heaters on the cell passed through a switch box so that each heater could be switched to the power supply. The decade box in series with the heaters allowed us to change the voltage drop across the heaters which was monitored by the digital voltmeter. Since this voltage drop was constant to 0.1% once the decade box was set, the voltmeter could quickly be switched back to the shield resistor once a voltage was recorded. Knowing the voltage across a heater, $V$, the power input, $\dot{Q}$, could be determined from

$$\dot{Q} = \frac{V^2}{R_i},$$

(5)

where $R_i$ is the resistance of the $i^{th}$ heater.
2.6 **Resistor and Heater Connections**

The detailed circuit for the resistors and heaters is shown in Figure 9. As explained above, the resistor on the isolated end of the cell, $R_c$, can be monitored at the same time as the resistor on the shield, $R_s$. (Actually the voltage, $V_s$, across $R_s$ is monitored. If $V_s$ remains the same at a given current, then $R_s$ is constant, indicating the temperature is constant.) This is indicated by the positions of the switches $S_1$, $S_2$ and $S_3$ in the figure. Over most of the temperature range 1.2°K to 4.2°K, $V_s$ can be read to 0.01 mv out of about 30 mv. The 1 Megohm resistor in series with $R_s$ insures that the current drain on the battery is very small. Because the resistance of $R_s$ is of the order of $10^4$ ohms at low temperatures (compared to $10^6$ ohms), the battery is almost a constant current source. In addition, since the current is so small, we do not have to worry about Joule heating in $R_s$. By throwing switches $S_1$ and $S_2$, the resistance of $R_s$ could be read directly. During any given run this was not often done, since the resistance-temperature characteristic of $R_s$ was known to be similar to $R_c$ and we were interested in keeping $R_s$ at a constant value rather than knowing $R_s$ absolutely. Any change in temperature at the heat sink could be detected by observing the corresponding change in $V_s$. This is discussed further in Section 3.3.

The rest of the circuit is fairly straightforward. The potential drop across the heaters $H_L$, $H_M$, and $H_U$ (Figure 6) can be measured by switching $S_3$ to $V_L$, $V_M$ and $V_U$ respectively. The current to the heaters is controlled
Figure 9

Resistor and Heater Connections
by $S_4$ and the decade box in series with the heaters. This current can be read with the ammeter $A$, if desired.
CHAPTER III

MEASUREMENTS AND ANALYSIS OF DATA

3.1 The Hydrogen Sample

A sample of low ortho-hydrogen content was prepared by allowing liquid hydrogen (ortho content ~ 5%) to be in contact with a chrome alumina catalyst for several hours. The ortho concentration of the resultant sample was determined to within ± 10% by measuring the spin-lattice relaxation times of the solid (10). Immediately after the conversion process, the concentration was about 0.2%. After measuring the thermal conductivity of the solid at this concentration, the hydrogen was stored at room temperature for several days to allow some para-to-ortho conversion to take place, before another conductivity measurement was made. Thus the same sample was used for the majority of the measurements.

3.2 Hydrogen Liquefaction and Solidification

As described in Appendix C, the hydrogen sample was released into the gas handling system before the contents of the vacuum jacket had cooled below 20°K. The pressure of the exchange gas in the vacuum jacket (p ~ 0.3 millitorr) and the power input to the heaters were then adjusted to maintain a
slow cooling rate, as indicated by the shield resistor, $R_s$, and the cell resistor, $R_c$. Usually the power inputs to the fill tube and shield heaters were about 1 and 0.3 watt, respectively. Below 20°K ($R_c \sim 90$ ohms), a liquid meniscus was observed in the lower portion of the cell. Within an hour this liquid level progressed into the upper Lucite block. After the heaters had been turned off, a phase boundary could be observed moving slowly up the tube. Within twenty minutes, the entire sample solidified.

It should be noted that no special care was taken to anneal the sample, since, upon solidification, a uniform cell temperature in the vicinity of 14°K was very difficult to maintain with the present apparatus.

3.3 Measurements

After the cell had reached a constant temperature, as determined by the temperature of the $^4$He in the sub-pot, measurements were begun. All initial resistance and voltage values were recorded before the first cell heater, $H_L$ (see Figure 6, Chapter II), was turned on. Following the procedure outlined in Section 2.2, each power input and resistance was recorded at each step. Special care was taken to maintain a constant power input to the sample. Since the shield resistor was monitoring the temperature of the heat sink, it was necessary to keep its resistance constant during a conductivity determination. This was accomplished by adjusting the temperature of the $^4$He sub-pot, to compensate for any thermal drifts. It should also be noted that the chart recorder plotted the heating curves for the
3.4 Calculation of Conductivities

The conductivities were obtained by rearranging Eq. 4,

\[ K = \frac{Q}{A} \frac{\Delta X}{\Delta T}. \]  

(6)

The values for the cross-sectional area, \( A \), and the distance between heaters, \( \Delta X \), were obtained from the cell geometry. Because the resistances of the cell heaters had previously been measured, the power input, \( \dot{Q} \), could be calculated from the measured voltages across the heaters.

Using the multiple heater method (Section 2.2), two resistances, \( R_{C1} \) and \( R_{C2} \), were measured corresponding to the temperatures \( T_1 \) and \( T_2 \) in Figure 5. The temperature is known as a function of the resistance from the calibration curve (Appendix B). The sample's temperature is taken to be that temperature that corresponds to the mean, \( \bar{R} \), of \( R_{C1} \) and \( R_{C2} \):

\[ T = f(\bar{R}). \]  

(7)

From the calibration curve we also obtain values for

\[ \frac{dT}{dR} = f'(\bar{R}). \]  

(8)

Then, if the change in resistance, \( \Delta R = (R_{C1} - R_{C2}) \), is small, the temperature change at the end of the sample can be calculated:

\[ \Delta T = \Delta R \cdot f'(\bar{R}). \]  

(9)
The above procedure was programmed into a Hewlett-Packard 9100A calculator so that the experimental data could be entered as input data to obtain the conductivities.

3.5 Time Constants for the Heating Curves

Figure 10 shows schematically the chart record of a sample heating curve, translated into a graph of temperature-versus-time by means of the chart recorder calibration (Appendix D) and the resistor calibration (Appendix B).

The curve was assumed to be exponential and of the form,

$$\frac{T_f - T}{T_f - T_0} = \exp(-t/\tau) \tag{9}$$

where $T_f$ = final temperature,

$T_0$ = initial temperature,

$T$ = temperature at time $t$,

$\tau$ = time constant or thermal relaxation time.

The time constant $\tau$ was determined by taking the natural logarithm of the left-hand side of Eq. 9 and plotting it versus time. The appropriate quantities are indicated in Figure 10. Figure 11 is an example of the semi-log plot whose slope is $\tau^{-1}$. Time constants from many heating curves were plotted against the average temperature of each to show how the thermal time constant varied with temperature. These curves for the various concentrations are presented and discussed in Section 4.5. (Note that $T_f - T_0$ is large
Figure 10

Schematic Diagram of a Heating Curve
Figure 11

Time Constant for a Heating Curve
\( \frac{T_f - T}{T_f - T_0} \)

- \( T_0 = 2^\circ K \)
- \( T_f = 2.728^\circ K \)
- \( \bar{T} = 2.36^\circ K \)
- \( \tau = 0.285 \text{ min} \)
indicating that the average temperature may not be very representative. This might cause a large amount of scatter in the data especially if $\tau$ is varying rapidly.)

3.6 Sources of Error and Corrections

The primary problem in a thermal conductivity measurement is that there are undoubtedly means of conducting heat away from the heaters other than the sample itself. These methods of heat transfer will each be considered and discussed.

Some of the heat input could be conducted via a small amount of residual exchange gas in the vacuum jacket. This effect was minimized by pumping on the vacuum jacket continuously during a run. The pressure in the vacuum line at the top of the cryostat was $10^{-5}$ torr or less at all times. For heat transfer between the cell and copper shield, whose temperature was about 0.2°K below that of the cell, the loss is considerably less than 1% of the heat input to the sample. Even if one considered transfer directly between the cell and the main bath at 4.2°K, the loss for a typical heat input of $250 \times 10^{-6}$ watts is only about 1%.

The cell was effectively shielded from room temperature radiation. The copper radiation shield protected that region of the cell where the conductivity measurements were made. In addition, an aluminum foil shield, with slits cut in it for visual observation, was placed over the glass vacuum
jacket. Another foil shield, without slits, was placed over the tail of the nitrogen dewar when not making visual observations.

Heat could have been conducted by the manganin leads of the heaters and resistors, since they were thermally anchored at the shield. Using the thermal conductivity equation, the heat conducted by the leads is of the order of $10^{-5}$ milliwatts. This amounts to only about a 0.1% loss for the lowest power input.

The leads to the heaters could be responsible for an additional heat input, by causing excessive Joule heating. This effect was minimized by making the resistance of the heaters about 500 times greater than the resistance of the leads.

Finally, the stainless steel tube that makes up the middle portion of the cell is thermally in parallel with the hydrogen in a conductivity measurement. The thermal conductivity of the stainless steel was determined in a preliminary run using an empty cell. The results are shown in Figure 12. The cross-sectional area of the hydrogen is about 5.5 times that of the stainless steel. If, for example, the conductivity of the hydrogen is 20 mw cm$^{-1}$ deg$^{-1}$ at $1.5^\circ$K, then the ratio of the heat conducted by the hydrogen to that of the stainless steel is 100:1. For most of the samples the conductivity of the hydrogen is greater than 20 mw cm$^{-1}$ deg$^{-1}$, so that a correction is unnecessary. For low conductivity samples, the correction must be made.

Perhaps the largest source of error in the measurements was the drifting of temperatures at the heat sink. The temperature of the sink was
Figure 12

Thermal Conductivity of Stainless Steel
THERMAL CONDUCTIVITY (mW cm⁻¹ deg⁻¹)

TEMPERATURE (°K)
monitored by a germanium resistor. The voltage of the resistor, $V_s$, was monitored on the digital voltmeter. Since the current through the resistor was almost a constant, a change in $V_s$ reflected a change in the temperature. By keeping $V_s$ constant, the temperature would be almost constant. $V_s$ was nominally 10 millivolts and could be read to the nearest hundredth of a millivolt. A change of 0.01 millivolts corresponds to a drift in temperature of about 1 or 2 millidegrees. Since most of the temperature differences in a conductivity measurement were of the order of 50 to 100 millidegrees, this amounts to perhaps a 4 or 5% error. However, it was sometimes necessary to use very small temperature gradients, so that in some cases the error might be as large as 10%.

In conclusion, it may be stated that the error associated with the conductivity for a given ortho-hydrogen concentration is between 5% and 10%. If the conductivities for different ortho-hydrogen concentrations are compared, then there will be an additional 10% uncertainty connected with the concentration determination (Section 3.1).
CHAPTER IV

DISCUSSION OF RESULTS

4.1 The Thermal Conductivity Data

The thermal conductivity of solid para-hydrogen containing small amounts of ortho-hydrogen was measured between 1.3°K and 6°K. The data for ortho concentrations between 0.2% and 5% are given in Figures 13 and 14. (The data in Figure 13 is for a sample from one batch of hydrogen, while Figure 14 represents data from a similar, but not identical, batch.) In general, the conductivity for a given ortho-hydrogen concentration is consistent with the discussion in Chapter I; i.e., it increases as the temperature is lowered, reaches a maximum, and then decreases.

4.2 Temperature Dependence of the Conductivity

The temperature dependence of the conductivity is best illustrated by referring to Figure 15. Here \( (K/T^3) \) is plotted versus \( (1/T) \). At high temperatures (small \( 1/T \)) the conductivity seems to approach \( T^3 \exp (\beta \Theta /T) \), where \( \beta \Theta = 54.5 \). At low temperatures (large \( 1/T \)) the conductivity varies approximately as \( T^3 \). It seems that there are two resistive mechanisms in operation: Umklapp scattering and boundary scattering. If these resistance
Figure 13

Thermal Conductivity of Solid Hydrogen

(0.34% - 5% $\text{o-H}_2$)
Figure 14

Thermal Conductivity of Solid Hydrogen

(0.2% and 0.71% o-H₂)
$K(\text{w cm}^{-1}\text{deg}^{-1})$

$T(\text{oK})$

- $\odot$ : 0.2% o-H$_2$
- $\triangledown$ : 0.71% o-H$_2$
Figure 15

Temperature Dependence of the Conductivity
terms are additive, as suggested by Klemens (1), then it should be possible
to reconstruct the entire conductivity curve from them. When this is tried,
the peak value obtained for the conductivity is noticeably greater (by about
50%) than that found in the data. This is not an unusual occurrence, because
it has often been shown that the peak value of the conductivity is very
sensitive to the presence of small impurity concentrations in a sample. If the
impurities are point defects, the thermal resistivity due to them varies as $T$.
Then, adding resistivities,

$$W(T) = (aT^3)^{-1} + bT + (dT^3 \exp \beta \Theta / T)^{-1}. \quad (10)$$

The curves in Figures 13 and 14 were drawn using this expression for $W(T)$.
These curves were fitted to the data at three different temperatures to
determine $a$, $b$ and $d$ for each concentration. It is not a least-squares fit and
is only an approximation using Eq. 10. Addition of resistivities is not correct,
but it does present an understandable picture of the situation.

The values for the constants in Eq. 10 are given in Table 2. The
magnitudes of $b$ and $d$ should not be taken too seriously, because Eq. 10 is a
first approximation. For instance, the value for $b$ implies an impurity
concentration of $D_2$ of 0.1%. This is about ten times larger than the natural
abundance. Carruthers (18) shows that an overestimate of $b$ is not uncommon.
TABLE 2
CONSTANTS FOR ADDITION OF RESISTIVITIES

<table>
<thead>
<tr>
<th>x(%)</th>
<th>a(mw/cm deg$^4$)</th>
<th>b(mw/cm$^{-1}$)</th>
<th>d(mw/cm deg$^4$)</th>
<th>$\beta$</th>
<th>$\xi$(°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.20</td>
<td>110</td>
<td>$1.4 \times 10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
<tr>
<td>0.34</td>
<td>92</td>
<td>$10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
<tr>
<td>0.52</td>
<td>61.5</td>
<td>$10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
<tr>
<td>0.71</td>
<td>55</td>
<td>$10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
<tr>
<td>1.1</td>
<td>32.9</td>
<td>$10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
<tr>
<td>2.5</td>
<td>15.3</td>
<td>$10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
<tr>
<td>5.0</td>
<td>4.6</td>
<td>$10^{-4}$</td>
<td>$1.2 \times 10^{-4}$</td>
<td>1/2</td>
<td>109</td>
</tr>
</tbody>
</table>

4.3 Ortho-Hydrogen Dependence of the Conductivity

If a $T^3$ dependence is assumed at low temperatures, the constant $a$ in Eq. 10 is seen to be different for different concentrations of ortho-hydrogen. Using Eq. 1 (Chapter I), an apparent phonon mean free path was calculated for each sample. The value for the specific heat was obtained from Hill and Lounasmaa (15) and the velocity of sound was calculated from the known value of the Debye temperature (15) using the Debye model (19). This assumes a constant velocity of sound that is independent of ortho-hydrogen content.

Actually, the velocity of sound is probably a weak function of the
ortho-hydrogen concentration, but no values for it were available in the literature. However, a constant value for this velocity will not be too bad an approximation because the Debye temperatures for different concentrations do not differ to any great extent (17).

The mean free paths are shown in Figure 16 plotted versus $x$, the ortho-hydrogen concentration. The line indicates a slope of minus one on this log-log plot of the data. At low concentrations the mean free path is, thus, proportional to $1/x$. At concentrations greater than about 5%, the mean free path deviates from this relationship. The errors are larger for the low concentration samples because of the combined effects of a poor thermal connection to the heat sink and small temperature drifts of the heat sink. The poor thermal connection is required for proper temperature control in the cell during the crystal growing process. The temperature drifts of the sink ($\sim 0.0005^\circ K$) introduce direct errors into the determination of the temperature difference, $\Delta T$, maintained across the sample. Because of the poor connection to the heat sink, measurements at the lowest temperatures could be made only if $\Delta T$ were kept small ($\sim 0.002^\circ K$).

The mean free paths in Figure 16 are considerably less than the cell diameter (5.8 mm). Despite the uncertainties in the low concentration data, there is evidence for a saturation region below 0.3% ortho-hydrogen, with the mean free path approaching a constant value that is about 1/10 of the cell diameter. It should be noted that the value of 0.2% is an upper limit for the lowest concentration shown in Figure 16. The instrumentation used to measure
Figure 16

Concentration Dependence of the Phonon Mean Free Path
the concentrations was not accurate for concentrations that were 0.2% or lower. Two additional points should be made before continuing the discussion. The phonon mean free paths seem to be determined by two mechanisms in the low temperature region: (1) scattering from the cell walls, (2) some as yet unknown mechanism that causes the mean free path to be about 1/10 of the cell diameter. The mean free path calculated from Eq. 1 is the result of both these effects. The mean free paths in Figure 16 have been corrected for the effect of the cell walls. In addition, the concentration of the 0.52% ortho-hydrogen sample has an uncertainty associated with it. Unfortunately, the concentration of this sample was determined several months after the conductivity had been measured. During that period it was stored at 4.2°K. Knowing the storage time and the approximate conversion rate in the solid (9), the concentration was extrapolated to the date of the experiment.

4.4 Mechanisms for Additional Thermal Resistance

Obviously, simple addition of thermal resistances is a first approximation. However, it does present a simple interpretation of the results. The appearance of the 1/x and T^3 dependence at low temperatures does not depend on this addition of resistances and is not an approximation. Possible explanations for it will now be discussed:

(a) The T^3 dependence would seem to indicate phonon scattering that is independent of frequency, as in boundary scattering. This could occur if large clusters of ortho-hydrogen molecules were present, whose size was larger
than the phonon wavelength. At temperatures much below the Debye temperature, the dominant phonon wavelength in a Debye distribution is \( \lambda = a^3 \Theta^{-1} \), where \( a^3 \) is the molecular volume. For hydrogen \( a \) is about 4 Å. Then at 2°K, \( \lambda \sim 200 \text{ Å} \). Thus, the diameter of the ortho-hydrogen clusters would have to be larger than 200 Å. A cluster this size would contain about \( 10^5 \) ortho-molecules. Although these samples contain enough ortho-hydrogen molecules to provide such a structure, measurements by Harris et al. (14) indicate that there is no tendency for ortho-hydrogen molecules to form large clusters. There is a probability for pair formation at low concentrations, but this is of the same order of magnitude as one would expect by using geometrical arguments.

(b) Callaway (20) calculates the combined conductivity due to boundary scattering, N-processes, impurity scattering, and U-processes. He does not use Klemens' additive resistance approximation but evaluates the proper integrals. The curves 1 to 6 in Figure 17 were computed using Callaway's model, for various concentrations of point defects in LiF (21). Note that the dashed lines seem to converge on the low temperature side. The curves for ortho-hydrogen seem to be parallel on the low temperature side, and thus there appears no chance for convergence. Note the resemblance to \( \alpha \) and \( \beta \).

Curves \( \alpha \) and \( \beta \) in Figure 17 were obtained experimentally by Pohl (21). Curve \( \alpha \) is for a crystal of LiF. Curve \( \beta \) is for the same crystal after color centers (F-centers) were introduced by X-irradiation. Note the non-convergence on the low temperature side. An F-center is identified with an electron bound to
Figure 17

Thermal Conductivity of LiF with F-centers (Ref. 21)
a negative ion vacancy in an ionic crystal (22). Thus it would be a point
defect in the lattice. Callaway's calculation is known to give a reasonable
explanation for isotopic defects, but the F-center data cannot be explained by
his equations. Walton (23) attempts to explain the F-center data by phonon
excitation of virtual transitions of the electron bound to the F-center. His
results seem to give a reasonable, though approximate, explanation of the
data. Thus, phonon interaction with low-lying energy levels might explain
the hydrogen data. Slack and Galgin (8) show that energy levels can produce
resonances in the conductivity. These resonances cause a slight depression of
the conductivity in the vicinity of the temperature corresponding to the
resonant energy. Referring to the CQ energy level scheme for hydrogen in
Chapter I, a resonance might occur at temperatures of 2°K and 3°K if the
dominant phonon energy is taken as 1.6kT (7). Unfortunately, the peak of the
conductivity curve is near 3°K for most samples, and the effect is not obvious.
(Perhaps this effect might be connected with the depression of the peak.)
However, note the slight depression of the conductivity curves (Figure 15)
below 2.5°K. Since this depression is not very pronounced, it would be
difficult to attribute this definitely to resonance. It would be interesting to
look for resonance effects, with better temperature regulation, between 0.5°K
and 3°K.

(c) The interior of the crystal may have large scale defects such as
grain boundaries, dislocations, cracks, etc., that limit the mean free path.
Because it was difficult to anneal a sample, this does seem to be a plausible
argument. The principle difficulty is relating the grain size, etc., to the ortho-hydrogen concentration in a way that gives the proper concentration dependence for the mean free paths. Cottrell (24) has shown that foreign atoms in a host lattice might migrate to dislocations to release the total strain in the crystal. This would increase the thermal conductivity by release of the strain, but the lining up of the defects would decrease it by the introduction of an interior structure.

The presence of a mosaic structure would reduce the mean free path. Here the ortho-hydrogen molecules need not migrate to the mosaic boundaries, but would act as "anchoring points" for this web-like imperfection. This would explain the concentration dependence. However, Klemens (2) has shown that phonon scattering for a mosaic structure is frequency dependent, and the resistivity is proportional to $1/T$. Such a term does not appear in our expression for the conductivity. Now grain boundaries would give the proper temperature dependence ($K \sim T^3$), and the concentration dependence could be explained by assuming that the ortho-hydrogen molecules act as nucleating points for the imperfections. A similar argument could be used to discuss the presence of cracks.

All of the above arguments are based on the premise that an ortho-hydrogen molecule is mechanically very different from its para-hydrogen neighbors. However, for all practical purposes, an ortho-hydrogen molecule has the same size, mass, mechanical force constants, etc., as a para-hydrogen molecule. It is difficult to see why its presence in the para-hydrogen
lattice should introduce effects similar to those produced by, say, a carbon atom in an iron lattice.

(d) The influence of N-processes may not be negligible in the $T^3$ region. Callaway (25) has considered the effect of N-processes in the U-process region and applied the results to Walker and Fairbank's measurement of the thermal conductivity of solid $^4\text{He}$ with $^3\text{He}$ impurity (26). Walker and Fairbank assumed a clustering of $^3\text{He}$ atoms, or a lining up of the $^3\text{He}$ atoms along dislocations as a possible explanation for their data. Callaway showed that by not neglecting the effect of N-processes, a reasonable explanation of the data could be given without assuming clustering or $^3\text{He}$ dislocations. He obtained the proper temperature and concentration dependence $K^{-1} \sim x(1-x)$ for Walker and Fairbank's data.

All of the above arguments present possible explanations for the observed effects, although (a) does not appear very probable. It seems clear that the low temperature conductivity data will not be satisfactorily explained without a considerable extension of the theory of heat conduction in solid hydrogen. In particular, the following three items seem to merit further study:

(i) Phonon interaction with the energy levels.

(ii) Ortho-hydrogen molecules as mechanical impurities in para-hydrogen.

(iii) The role of N-processes in heat transport.
4.5 **Time Constants**

The thermal time constants of the conductance cell (Section 3.5) are plotted as a function of temperature in Figure 18. For the purpose of clarity only four concentrations are depicted in this figure. The time constants for the other concentrations are very close to those for the 0.34% sample. The curves were drawn merely to indicate the general trend of the data. Because of the non-linearity of the chart recorder and the large \((T_f - T_0)\) (Section 3.5), the scatter of the data is too great for satisfactory curve fitting. It must be remembered that these data were not the primary objective of this work.

Using the model in Appendix E, values for the specific heat of the hydrogen with ortho-concentration \(x\), relative to the specific heat of the 0.34% ortho-hydrogen sample, can be obtained. From Eq. 13, the time constant will be roughly proportional to \(C/K\), where \(C\) is the total heat capacity and \(K\) is the thermal conductivity. Thus, from the conductivity data and the expression for the specific heat (Eq. 3), we can see that the time constant should increase as the ortho-hydrogen content increases. Figure 18 illustrates this trend.

Table 3 lists the ratios of the specific heats to that of the 0.34% ortho-hydrogen at three different temperatures for three different concentrations. \(C(x)/C(0.34)\) represents the ratio as calculated from the model in Appendix E; \(C_1(x)/C_1(0.34)\) represents the ratio as calculated from the expression for the specific heat in Eq. 3 (Chapter I). Numerical values for \(\alpha\) and \(\gamma\) can be easily obtained from the partition functions for the energy level schemes due to the
Figure 18

Heating Curve Time Constants
crystal field and the GQ interactions (Figure 2) if it is assumed that the ortho-
hydrogen molecules are randomly distributed throughout the sample.

Comparison of the two ratios for a given temperature and concentration
indicates that the deviation is fairly large. Some error could be caused by the
inaccuracy of the model in Appendix E and the fact that the actual experimental
system is quite complicated. For instance, it is assumed in the model that the
temperature at the heater is equal to the temperature of the isolated end

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>x(%)</th>
<th>( \frac{C_1(x)}{C_1(0.34)} )</th>
<th>( \frac{C(x)}{C(0.34)} )</th>
<th>( \gamma_c ) (joule-deg/mole)</th>
<th>( \gamma_e ) (joule-deg/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.75</td>
<td>1.1</td>
<td>1.7</td>
<td>2.0</td>
<td>133</td>
<td>164</td>
</tr>
<tr>
<td>1.75</td>
<td>2.5</td>
<td>4.9</td>
<td>6.1</td>
<td>133</td>
<td>162</td>
</tr>
<tr>
<td>1.75</td>
<td>5.0</td>
<td>16.7</td>
<td>16.5</td>
<td>133</td>
<td>122</td>
</tr>
<tr>
<td>2.0</td>
<td>1.1</td>
<td>1.4</td>
<td>1.6</td>
<td>151</td>
<td>192</td>
</tr>
<tr>
<td>2.0</td>
<td>2.5</td>
<td>3.3</td>
<td>5.1</td>
<td>151</td>
<td>255</td>
</tr>
<tr>
<td>2.0</td>
<td>5.0</td>
<td>10.5</td>
<td>14.7</td>
<td>151</td>
<td>212</td>
</tr>
<tr>
<td>2.25</td>
<td>1.1</td>
<td>1.3</td>
<td>1.3</td>
<td>164</td>
<td>173</td>
</tr>
<tr>
<td>2.25</td>
<td>2.5</td>
<td>2.4</td>
<td>3.5</td>
<td>164</td>
<td>279</td>
</tr>
<tr>
<td>2.25</td>
<td>5.0</td>
<td>6.8</td>
<td>11.4</td>
<td>164</td>
<td>289</td>
</tr>
</tbody>
</table>
(Figure 23). This is not necessarily true for all concentrations, and it can be expected that there will be a time lag between the heater and thermometer.

Now let us look at the expression for the specific heat (Eq. 3, Chapter I),

\[ C = \frac{\alpha x + \gamma x^2}{T^2} + \varphi T^3. \]  (3)

The term that is linear in \( x \) is a small correction to the anomalous specific heat at the temperatures and concentrations used here, so we shall neglect it. Hill and Lounasmaa (15) have measured the coefficient, \( \varphi \), of the \( T^3 \) term. If one assumes that the specific heat of the 0.34% ortho-hydrogen sample is the same as the lattice specific heat (this amounts to, perhaps, a 10% error), then experimental values, \( \gamma_e \), can be obtained for the coefficient of the \( x^2 \) term in the anomalous specific heat. In the last two columns of Table 3, these are compared to the values, \( \gamma_c \), that have been calculated from the partition function for the QQ energy level scheme in Figure 2, Chapter I [\( \Gamma/k = 0.82^\circ K \) (14)]. Generally, the experimental values are larger than the theoretical values. This could be due to indirect method of measurement of the specific heat. However, \( \gamma_c \) was obtained by assuming a random distribution of ortho-hydrogen molecules, and Meyer et al. (14) have shown that the pairing of the ortho-hydrogen molecules deviates from a random distribution. The pairing is a function of both temperature and concentration. Meyer's data indicate that, for ortho-hydrogen concentrations less than \( \sim 3\% \), the random distribution underestimates the number of pairs formed in the
temperature range 1°K to 2°K. Our measurements of the specific heat tend to confirm his results by showing that \( \frac{\gamma x^2}{T^2} \) is larger than expected.

It should be noted that no attempt has been made to estimate \( \alpha \), the coefficient of the \( x \) term in the specific heat, although a knowledge of \( \alpha \) would enable one to determine the magnitude of the crystal field splitting, \( A \), of the \( m_f \) levels (Section 1.2). Previous estimates (12) from specific heat measurements give \( A/k \sim 1°K \). This can be compared with the value obtained from NMR measurements, \( A/k \sim 8.7 \times 10^{-3}°K \) (13). In the light of Meyer's work, it is easy to understand the discrepancy. Estimates for \( A \) from the specific heat were obtained by assuming that the term \( \gamma x^2/T^2 \) could be calculated from a knowledge of \( \Gamma (\sim 1°K) \) and the number of ortho-hydrogen pairs (random distribution). These assumptions for \( \Gamma \) and the number of pairs are now known to be incorrect, and unless the exact number of ortho-hydrogen pairs is known, it will be very difficult to obtain a reliable estimate for \( A \) from specific heat measurements.

In conclusion, although the method of measurement is indirect, reasonable values for the anomalous specific heat of hydrogen are obtained. Further investigation of the ortho-hydrogen energy level schemes in para-hydrogen by direct specific heat measurements is certainly needed.

4.6 Direction of Future Research

The techniques of liquefaction and solidification could certainly be improved in future research. Better temperature control in the vicinity of
14°K is needed so that annealed samples could be studied. Optical techniques might be used to insure the presence of strain-free and defect-free single crystals. It would also be interesting to grow the crystal under pressure and to maintain an external pressure during the conductivity measurement. This might provide information about the intermolecular forces and the phonon spectrum.

Future research could include the study of deuterium, D$_2$; hydrogen deuteride, HD; and additional samples of hydrogen. The conductivities of hydrogen samples containing larger concentrations of ortho-hydrogen molecules would be more difficult to analyze, but the investigation might provide further insight into the nature of ortho-para alloys. The deuterium could be studied and compared to the results obtained from the hydrogen investigations. Now HD would be expected to be analogous to para-hydrogen in a conductivity measurement, so that pure HD could be compared to pure para-hydrogen. Additional avenues of research include: H$_2$ in D$_2$, H$_2$ in HD, D$_2$ in HD, etc.

When crystals of the hydrogen alloys are grown, the possibility of concentration gradients in the crystal exists. This should be investigated, and eliminated, if possible.

The need for experiments at lower temperatures was discussed in Section 4.4.

The basic technique used to measure the conductivity is satisfactory. However, some sort of temperature regulator should be used to control the
temperature of the heat sink. This regulator should be able to hold the temperature of the sink to ±10 microdegrees for several minutes.
APPENDIX A

LOW TEMPERATURE VACUUM SEALS

A.1 Copper-Indium-Lucite Seal

A copper-indium-Lucite seal was used on the hydrogen cell so that visual observations could be made of the liquefaction and solidification.

A piece of 3/4" Lucite rod was machined to the shape shown in the lower portion of Figure 19. All surfaces were then polished. A mating piece was machined from oxygen-free, high conductivity copper (OFHC) and is shown in the upper portion of the figure. A 0.032" indium O-ring was placed between the two pieces, which were then bolted together using brass screws. As the screws are tightened, the indium is compressed and flows between the dissimilar materials forming a vacuum seal.

This seal was thoroughly tested for leaks at room temperature, nitrogen temperatures, and helium temperatures, and was found to perform satisfactorily. After several thermal cycles, it does tend to open up, but can be made to reseal by tightening the screws.
Figure 19

Copper-Indium-Lucite Vacuum Seal
COPPER

TAPPED HOLES

INDIUM O-RING

LUCITE

1 CM.
A. 2 Copper-Indium-Glass Seal

A copper-indium-glass seal was used as a vacuum seal on the vacuum jacket and was found to be free of leaks down to 1°K. Like the Lucite seal above, the copper-indium-glass seal may leak slightly after several thermal cycles, but can be resealed by tightening the screws.

This type of seal is shown in Figure 20. The upper flange is machined from OFHC copper and the mating surface is cleaned and polished. The glass portion is a piece of Pyrex glass tube that has been flared at the end, and then ground to a flat surface. A thin coating of Apiezon N grease is placed on the flat surface. An indium O-ring is made from 0.062" indium wire and placed in the shallow locating groove in the copper. A copper collar is placed around the glass and attached to the upper flange with brass screws. As the screws are tightened, the indium flows, forming a vacuum seal. A felt cushion, placed between the collar and the glass, prevents the glass and copper from being directly in contact.
Figure 20

Copper-Indium-Glass Vacuum Seal
GROUND PYREX GLASS FLANGE

COPPER TAPPED HOLES

INDIUM O-RING

FELT CUSHION

COPPER

1 CM
APPENDIX B

GERMANIUM RESISTOR CALIBRATION

The problems encountered when making accurate measurements of low temperatures are well known. The primary standard is usually the vapor pressure of a liquefied gas and secondary standards, such as the electrical resistance of a metal, are in common use. Because of their high resistivity, carbon resistors have received wide application as resistance thermometers at helium temperatures. However, they unfortunately have the disadvantage that they must be recalibrated each time after being cycled to room temperature. The need for recalibration can be eliminated by resorting to the use of carefully prepared semiconducting materials as temperature sensors. Suitably prepared germanium crystals are available commercially from Cryo-Cal, Inc. The manufacturer states that these crystals can be thermally cycled with a calibration change of about one part in $10^5$.

The resistivity of doped germanium can be approximated by an expression of the form

$$\frac{1}{\rho} = \sum_{i=1}^{n} C_i e^{-\varepsilon_i/kT},$$

where $n$ may be equal to 2 or 3 at low temperatures (27). However, it has been found that there may be small-scale deviations from this equation which...
could be important when using the resistance of germanium as an indication of the temperature (28). Therefore, three conditions were set for the calibration:

1. Accurate temperatures must be obtained.
2. \( \frac{dR}{dT} \) must be continuous for the purposes of obtaining small temperature differences from the known resistance differences.
3. The curve must be capable of being extrapolated beyond 4.2°K to about 6°K.

Ten calibration points were obtained between 1.2°K and 4.2°K using the vapor pressure of liquid \(^4\)He as a primary standard. Pressures were read to 0.01 mm of Hg and converted to temperatures using the 1958 NBS \(^4\)He vapor pressure table (29). Thus, at 2°K, for instance, the temperature uncertainty should be about \(10^{-4}\)°K.

Since the resistance of the thermometer might depart from a smooth curve, a least squares fit to the calibration points might not be the best approach. Accordingly, five of the calibration points were chosen, and a smooth curve was made to pass through these points. The general expression used for the calibration curve was

\[
Ax^2 + Bxy + Cy^2 + Dx + Ey + F = 0, \tag{11}
\]

where \(x = 1/T\) and \(y = \ln R\). The deviations of the other five points from the curve were then tabulated. The calibration curve was taken to be that curve which minimized the fluctuations in the deviations of the remaining five points.
The relative importance of each term in the calibration equation is given in Table 4 at three different temperatures. Table 5 lists resistances; temperatures, $T_c$, calculated from these resistances; measured temperatures, $T$; and temperature deviations, $(T - T_c)$. The deviation curve, $(T - T_c)$ versus $T_c$, is shown in Figure 21. Knowing a resistance $R$, we can now calculate a temperature $T_c$ from

$$x = \frac{1}{T_c} = -\frac{(By + D) \pm \sqrt{(By + D)^2 - 4(Cy^2 + Ey + F)}}{2}$$

and then apply a correction, if necessary, to obtain $T$.

**TABLE 4**

<table>
<thead>
<tr>
<th>$T_c$</th>
<th>$x^2$</th>
<th>1.1xy</th>
<th>$-6y^2$</th>
<th>14.9x</th>
<th>7.6y</th>
<th>-25.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.413</td>
<td>0.50</td>
<td>8.6</td>
<td>-78.5</td>
<td>10.6</td>
<td>84.1</td>
<td>-25.3</td>
</tr>
<tr>
<td>2.648</td>
<td>0.14</td>
<td>3.8</td>
<td>-54.28</td>
<td>5.64</td>
<td>70.0</td>
<td>-25.3</td>
</tr>
<tr>
<td>4.218</td>
<td>0.1</td>
<td>2.1</td>
<td>-41.9</td>
<td>3.5</td>
<td>61.5</td>
<td>-25.3</td>
</tr>
</tbody>
</table>

With the above information, we can now obtain an expression for $(dR/dT)$. Let

$$f(x,y) = x^2 + Bxy + Cy^2 + Dx + Ey + F = 0.$$  \hspace{1cm} (12)

Then,

$$\frac{dy}{dx} = -\frac{(\partial f/\partial x)}{(\partial f/\partial y)}.$$
<table>
<thead>
<tr>
<th>R (ohms)</th>
<th>$T_c$ (°K)</th>
<th>$T$ (°K)</th>
<th>$[T - T_c]$ (°K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1200</td>
<td>6.244</td>
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<td>110030</td>
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<td>1.190</td>
<td>0</td>
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</tbody>
</table>
Figure 21

Deviation Curve for Resistor Calibration
Substituting $x = 1/T_c$ and $y = \ln R$ into Eq. 12, we obtain,

$$\frac{dR}{dT_c} = \frac{R}{T_c^2} \left[ \frac{2/(1/T_c^2) + B \ln R + D}{2C \ln R + B(1/T_c^2) + E} \right].$$

But $T$ and $T_c$ are not necessarily the same, so

$$\frac{dR}{dT} = \frac{dR}{dT_c} \left( \frac{dT_c}{dT} \right)$$

where $(dT_c/dT)$ can be obtained from the deviations curve of Figure 21. (Note the exaggerated vertical scale.) This correction factor is shown as a function of $T_c$ in Figure 22. Finally for small $\Delta R$ and $\Delta T$,

$$\Delta T = \frac{-\Delta R}{(dT_c/dT)} \left[ \left( \frac{2/(1/T_c^2) + B \ln R + D}{2C \ln R + B(1/T_c^2) + E} \right) \right]^{-1}.$$

It should be noted that $R$ in the above is an average value for the two resistances (corresponding to temperatures $T_1$ and $T_2$ in Figure 5) that were obtained in a conductivity measurement. The negative sign is inserted because an increase in $T$ corresponds to a decrease in $R$.

The calibration curve has been extrapolated beyond 4.2°K to about 6°K with the belief that $T = T_c$ in this region for the following reasons:

1. The equation was fitted such that the curvature at 4.2°K was weighted against the other points, so that $dR/dT_c$ should be close to $dR/dT$ in this region.

2. During the course of obtaining conductivity data, approximate calibration points were obtained at 19°K and 14°K. If a smooth
Figure 22

Correction Factor for dR/dT
curve is drawn between these points and 4.2°K, the calibration curve and the drawn curve practically coincide.
APPENDIX C

PRELIMINARY STEPS IN MAKING A RUN

Preparations for making a run were made several days in advance. All vacuum and gas-handling systems were first checked for leaks. The vacuum jacket and the hydrogen handling system were then pumped with oil vapor diffusion pumps for two days to remove any residual gases or vapors that might be present. (Liquid nitrogen traps were used to prevent any back-streaming of oil vapor.) The space between the double walls of the helium dewar was flushed with air and then evacuated to remove any helium gas that might have diffused through the glass during the previous run.

Preparatory to putting liquid nitrogen in the nitrogen dewar, the liquid $^4\text{He}$ space was evacuated to a pressure of about 50 millitorr. The $^4\text{He}$ sub-pot and the hydrogen handling system were both evacuated. A small amount ($P \sim 40$ millitorr) of $^4\text{He}$ exchange gas was placed in the vacuum jacket to insure some thermal contact with the liquid $^4\text{He}$ space. Liquid nitrogen was then placed in the nitrogen dewar. Under normal conditions the system would cool to 77$^\circ$K in about four hours. For convenience, the nitrogen was often placed in the nitrogen dewar the night before a run, and the system was allowed to pre-cool overnight.
The morning of the run the electronics were turned on to allow the components to reach thermal equilibrium. The gas pressures in all systems were then checked for any abnormalities. The hydrogen fill tube was closed off and the hydrogen sample bottle placed into position. The tube connecting the bottle to the hydrogen handling system was evacuated and checked for leaks. After closing off the pump, the hydrogen was released into the cryostat. The heaters on the fill tube and shield were turned on to prevent blockage of the fill tube during cool down. One atmosphere of helium gas was placed in the helium dewar and liquid helium transferred.
APPENDIX D

CALIBRATION OF THE CHART RECORDER

The chart recorder was used to provide a record of the heating curve for the cell after the first heater was turned on. Because the output of the Malaker bridge was nonlinear, it was necessary to calibrate the recorder in terms of resistance. This was achieved in the following way:

1. The bridge was switched to a decade box whose resistance could easily be read.

2. After balancing the bridge, an off-balance signal was sent to the recorder by purposely changing the bridge resistance from its null value. For instance, if the decade box was set at 3000 ohms, the bridge resistance would be changed from 3000 to 1000 ohms.

3. The position of the chart recorder pen was noted.

4. The resistance of the decade box would then be decreased in convenient steps, noting the pen position at each step. Thus, each position on the chart corresponded to a known resistance.

5. The bridge was then switched back to the cell resistor.
APPENDIX E

MODEL FOR THE SPECIFIC HEATS

The thermal time constants of the system were measured for the purpose of obtaining values for the specific heat of hydrogen. Since the actual cell assembly is rather complicated, a simple model was devised. This model is shown in Figure 23. The heat sink at temperature $T_4$ corresponds to the $^4$He sub-pot. The copper portion of length $Z_2$ represents the shield surrounding the cell. The hydrogen is assumed to be a good conductor compared to the unknown thermal resistance at junction 2-3.

With a heat input $\dot{Q}$ to the heater at $(Z_1 + Z_2)$, the temperature $T_1$ rises. Let us assume that the temperature at the heater is equal to $T_1$. We then have

$$\dot{Q} = \frac{K_H A_H (T_1 - T_2)}{Z_1} = \frac{T_2 - T_3}{W_{23}} = \frac{K_c A_c (T_3 - T_4)}{Z_2}$$

where the subscripts H refer to the hydrogen and c refers to the copper. The symbols $K$ and $A$ represent the thermal conductivity and cross-sectional area, respectively. $W$ represents a thermal resistance. Thus $W_{23}$ is the thermal resistance at junction 2-3, and

98
Figure 23

Model for the Specific Heats
Using an electrical analogy, there is a "heat current", \( \dot{Q} \), and a thermal "potential difference", \( T_1 - T_4 \). The total resistance is given by

\[
W_T = \frac{Z_1}{K_H A_H} + W_{23} + \frac{Z_2}{K_c A_c}.
\]

Then,

\[
\dot{Q} = \frac{T_4 - T_1}{(Z_1/K_H A_H) + W_{23} + (Z_2/K_c A_c)}.
\]

When the system is heated,

\[\frac{dQ}{dT} = C dT,\]

where \( C \) is the total heat capacity. Then,

\[
\frac{dQ}{dT} \cdot \frac{dT}{dt} = C \frac{dT}{dt}
\]

\[\dot{Q} = CT.\]

Equating the two expressions for \( \dot{Q} \),

\[CT = \frac{T_4 - T_1}{W_T}.
\]

Now, actually,

\[T_1 = T(t)\]

and \( T_4 \) is a constant. Solving the differential equation,
where $T_0$ is some initial temperature. Thus, we have a time constant, $\tau$, given by

$$\tau = W_T C. \quad (13)$$

Now $C$ is the sum of the heat capacities for the copper, $C_c$; hydrogen, $C_H$; Lucite, $C_L$ (cell "windows"); and the junction 2-3, $C_{23}$. Let us assume $C_{23} = 0$. In addition, we will only consider the temperature region where the $T^3$ law for the conductivity of the hydrogen is valid. This conductivity will be a function of ortho content (Chapter IV). For a given temperature, $T$, and two ortho concentrations, $i$ and $j$,

$$\tau_i = (C_c + C_{Hi} + C_L)W_{Ti} = C_i W_{Ti}$$

$$\tau_j = (C_c + C_{Hj} + C_L)W_{Tj} = C_j W_{Tj}$$

Subtracting,

$$\frac{\tau_i}{C_i} - \frac{\tau_j}{C_j} = \left[ \frac{1}{K_{Hi}} - \frac{1}{K_{Hj}} \right]$$

Since (below $2^\circ$K),

$$K_{Hi} = K_0 T^3$$

$$\frac{\tau_i}{C_i} - \frac{\tau_j}{C_j} = \frac{Y}{T^3}$$
where
\[ y = \frac{Z}{A_H} \left[ \frac{1}{K_{0i}} - \frac{1}{K_{0j}} \right]. \]

Let \( C_K = C_c + C_L \). Rearranging terms and multiplying by \( C_i C_j \),
\[ C_K(\tau_i - \tau_j) + \tau_i(C_{Hj}) - \tau_j(C_{Hi}) = \frac{y}{T^3} \left[ \frac{C_i^2}{K} + C_c(C_{Hi} + C_{Hj}) + C_{Hi}C_{Hj} \right]. \]

Finally,
\[ C_{Hj} \left[ \tau_i - \frac{YC_K}{T^3} \right] - C_{Hi} \left[ \tau_j + \frac{YC_K}{T^3} \right] - \frac{YC_{Hi}C_{Hj}}{T^3} = \frac{Y}{T^3} C_i^2 + (\tau_j - \tau_i)C_K. \]

All of the above are known except \( C_{Hi} \) and \( C_{Hj} \). Let us define \( C_{Hi} \) as equal to one for \( x_i = 0.34\% \). Then,
\[ C_{Hj} = \frac{(YC_K^2)/T^3 + \tau_2 + (YC_K)/T^3 + (\tau_j - \tau_i)C_K}{\tau_i - (YC_K/T^5) - Y/T^3} \quad (14) \]

In the vicinity of \( 2^\circ K \) the heat capacity of copper is essentially linear in \( T \) (30). The heat capacity of Lucite is varying as \( T^3 \) (31). Since the amounts of copper and Lucite present are known, a value for \( C_{Hj} \) can be obtained relative to the value of \( C_{Hi} \) when \( x_i = 0.34\% \), if \( \tau_i \) and \( \tau_j \) are known.
REFERENCES


