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<tr>
<td>April 21, 1935</td>
<td>Born - Cincinnati, Ohio</td>
</tr>
<tr>
<td>1957</td>
<td>B.A., Miami University, Oxford, Ohio</td>
</tr>
<tr>
<td>1957-1959</td>
<td>Graduate Assistant, Department of Physics, Miami University, Oxford, Ohio</td>
</tr>
<tr>
<td>1959</td>
<td>M.A., Miami University, Oxford, Ohio</td>
</tr>
<tr>
<td>1959-1966</td>
<td>Research Assistant, Department of Physics, The Ohio State University, Columbus, Ohio</td>
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## PUBLICATIONS


FIELDS OF STUDY

Major Field: Physics


Electromagnetism. Professors A. Prebus and G. Arfken

Quantum Mechanics. Professor M. Sessler

Classical Mechanics. Professor J. Korringa

Thermodynamics. Professor J. W. Snider

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CHAPTER I

INTRODUCTION

The solidified inert gases have been extremely useful for fundamental studies of solids because of their relative simplicity. The inert gases form a tightly bound closed electronic shell which means that up to ordinary temperatures the electronic system introduces no particular complication and, as far as the nuclear motion is concerned, can be taken as being in the ground state. Also, since the electronic wave functions lead to a spherically symmetric charge density, the interatomic potential field can be taken as spherical. In most cases the two parameter spherical symmetric Lennard-Jones potential is assumed for the interatomic potential between two atoms. Many aspects of the heavier inert solid systems (Ne, A, Kr, Xe) have been successfully analyzed using classical ideas to describe the basic dynamics with quantum theory being introduced to describe deviations from classical behavior. A good case in point is the Debye specific heat calculations for solid argon. E. R. Dobbs et al. (1) point out the good agreement between experimental Debye temperature measurements and the theoretical Debye curve derived from Leighton's (2) frequency spectrum for the cubic close-packed lattice. On the other hand, the lighter inert solids (He³, He⁴) have presented a difficult analytic problem due to the importance of quantum effects such as a large zero point energy which
makes the fundamental hypothesis of the classical lattice dynamical theories untenable, and this indeed points out one of the interesting aspects of studying the solidified inert gases for here are substances with similar interatomic potentials but with a dynamics varying from near classical to quantum mechanical.

A theory of solid helium based on first principles must grapple with the immensely difficult quantum mechanical many-bodied problem. These difficulties have limited the theoretical discussion (3–8) of solid helium to a consideration of its properties at absolute zero.

There has been much experimental interest in solid helium despite the many practical difficulties associated with using high pressure and low temperatures. A great deal of work has been done on measuring the melting curve of He\(^4\). Domb and Dugdale (9) give a table listing eleven contributors before 1957 to the measurements of the melting curve. The more recent work by Swenson (10-12), and Grilly and Mills (13-15) are the most accurate. The melting curve of He\(^3\) has also received intensive study (13, 16-20).

Until 1953 the only known phase of solid He\(^4\) was the hexagonal close-packed (hcp) which was determined through X-ray analysis (21). Then Dugdale and Simon (22) found a transition in solid helium in the region between 15 and 17°K while doing specific heat measurements. The new phase was determined to have a cubic close-packed structure (ccp). A third phase of solid He\(^4\) was found by Vignos and Fairbank (23) in 1961 during measurements of the velocity
of longitudinal sound waves. This third structure was determined by X-ray analysis (24) to be body-centered cubic (bcc).

Grilly and Mills (15) measured the melting curve and the transition curve of bcc He$^4$. It was found that the bcc region is only about 0.04°K wide at constant pressure and not much wider at constant density, while the total variation of density across the phase is only about 1%. The upper triple point, $T_2$, is very close to the lambda curve of the liquid. Solid He$^3$ also has the same three solid phases (14,25). A diagram of the melting curve and the solid phase boundaries for He$^3$ and He$^4$ is presented in Figure 1.

The equation of state of a solid system can be determined by several different methods. The most direct method used is the piston displacement technique. Other methods used have been the X-ray method, the ultrasonic method, and the calorimetric method. These different methods are discussed by Bernardes and Swenson (26) and Swenson (27). Because solid helium is so compressible, measurements over a relatively small pressure range will provide data over a wide range of volumes. This aspect of solid helium permits the use of the calorimetric method of determining the equation of state. Furthermore, the specific heat at constant volume, together with one PVT relationship which covers the whole range of temperature and volume such as the melting curve data, is sufficient to determine the thermodynamic functions of the solid in the experimental range.

In view of the present interest in the specific heat measurements in the study of solid helium, a review of previous experiments will now be given.
Figure 1

Melting curve of solid He$^3$ and He$^4$ and the transition lines of the three allotropic phases of each isotope.
Specific Heat Experiments on Solid Helium

In 1934 a short article appeared in Nature by Kaischew and Simon (28) on the specific heat of He$^4$ in the temperature range 2.7°K to 3.7°K and at a density of 0.23. They found that $C_V$ agrees with a Debye $\theta$ of 32.5 deg K.

In 1936 Keesom and Keesom (29) measured the specific heat of solid helium at constant volume at seven different molar volumes ranging from 18.3 to 20.0 cm$^3$/mole over the temperature range from 1.2°K to 3°K. The temperature scale used was apparently the 1932 vapor pressure scale which puts the $\lambda$ point at 2.1900°K whereas the present 1958 scale (30) puts the $\lambda$ point at 2.1720°K. Due to the very large sample volume of the calorimeter, the heat capacity of the empty calorimeter could be neglected. After each experiment the helium in the calorimeter was allowed to enter a cylinder of known volume where the pressure and temperature were measured in order to calculate the density of the sample. Keesom and Keesom suggested the possibility that the pressure was not the same throughout the sample because a plot of $C_V$ vs density was not as regular as might be expected. From the specific heat data the density and entropy of melting and solidifying helium was determined. A plot of $\theta$ vs T gave approximately straight lines with $\theta$ rising with falling temperature.

Webb, Wilkinson, and Wilks (31), 1952, measured the specific heat of solid helium for three volumes, 20.6, 19.5, and 18.7 cm$^3$/mole, over the temperature range 0.6 to 1.4°K. The helium sample was solidified in the calorimeter at constant density using the blocked capillary technique; that is,
the calorimeter was filled with liquid to the desired density and the temperature of the calorimeter was adjusted to about 0.05°K above the freezing temperature. After thermal equilibrium had been established, the temperature of the cryostat was lowered rapidly, freezing solid the liquid helium in the calorimeter filling tube which ran through the cryostat. With the filling tube blocked, the bulk of the helium in the calorimeter solidified at constant volume. The density of the liquid just above the freezing point was determined from the pressure and Swenson's (10) melting curve data. Since the density of the liquid in the calorimeter before solidification was equal to that of the solid after solidification, due to the blocking of the filling tube, the density of the solid sample was also known which is the principal advantage of this method of freezing the sample. The authors found that the Debye temperature of their samples of helium increased with falling temperature down to about 0.8°K. Below 0.8°K they reported a slight decrease in θ.

Dugdale and Simon (22), 1953, measured the specific heat at constant volume of He⁴ for twelve different molar volumes ranging from about 200 to 3000 atmospheres and in a temperature range from 4 to 26°K. The high pressure helium sample was produced by permitting helium at about 100 atmos to enter one side of a steel U tube partially filled with mercury. A high pressure oil pump connected to the other side of the U tube then generated the necessary pressure which was communicated to the helium gas by the mercury. The quantity of helium contained in the calorimeter was determined after each experiment by letting the helium sample into a known volume.
Dugdale and Simon found that their specific heat results could be expressed in a universal reduced form as \( C_v = f(T/\varphi) \) where \( \varphi \) is a function of molar volume. From the specific heat measurements and the melting curve data the thermodynamic functions for solid helium were computed over the experimental range. A plot of \( \vartheta \) vs \( T \) revealed that the Debye temperature rises very slowly with falling temperature and for \( T/\vartheta < 0.10 \), \( \vartheta \) was almost independent of temperature.

Heltemes and Swenson (32), 1962, reported measurements on the specific heat of \( \text{He}^4 \) at constant volume for twelve molar volumes ranging from 21.04 to 11.93 cm\(^3\) over a temperature range 0.3 to 2°K. They also made measurements on \( \text{He}^3 \). A modified ADL magnetic refrigerator was used to obtain temperatures down to 0.3°K. The refrigerator employed a superconducting thermal switch for making thermal contact between the calorimeter and the cold reservoir. Unfortunately a heat leak through this thermal valve was believed to cause an error in the specific heat measurements above 1°K; nevertheless a correction was applied to the specific heat data to compensate in part for the leakage. The molar volume of the helium sample was determined from the melting and freezing temperatures which were observed as sharp breaks in the cooling curve. Heltemes and Swenson fitted their specific heat measurements to the equation \( C_v = AT + D(T/\vartheta) \) where \( D \) is the Debye function and \( A \) and \( \vartheta \) are functions of molar volume. This equation implies that the Debye temperature decreases with falling temperature. However, the authors
indicated that their measurements were of an exploratory nature and suggested an error of 5%.

Ahlers (33,34), 1963, 1964, measured the specific heat of solid He⁴ in both the hcp and bcc phases. The measurements in the hcp phase were at low pressures in a molar volume range 21 to 19.8 cm³ and in the temperature range 1.3 to 2.1°K. The molar volumes of the samples were determined from their melting temperatures using the melting data of Grilly and Mills (15). Ahlers found that the Debye temperature of the hcp helium sample increased with falling temperature. Furthermore he reported that at temperatures near the melting line there was an excessive decrease in the Debye temperature which led to Gruneisen γ values as high as 5 and 6, whereas Heltemes and Swenson (32) reported a value of 2.5.

Franck (35), 1964, measured the specific heat at constant volume of five samples of He⁴ for molar volumes from 10.85 to 16.30 cm³ in a temperature range 1.3 to 4°K. The samples were carefully prepared by annealing them up to ten hours at about 0.01°K below the melting point and then cooled to 4°K very slowly taking about eight hours. Franck (35) analyzed his data in the same manner as Heltemes and Swenson by fitting the specific heat data to the equation

\[ C_V = AT + 464.47(T/\Theta)^3 \text{ cal/mole deg} \]

Franck found that the so-called anomalous term, AT, was about 1/3 smaller than that found by Heltemes and Swenson and he attributed this reduction to annealing of the samples.

Theoretically it has been shown by Granato (36) that at low temperatures pinned line dislocations contribute a linear term to the specific heat.
Dugdale and Franck (37), 1964, measured the specific heat of solid He\textsuperscript{4} at constant volume at four different molar volumes, 11.77, 12.22, 14.55, and 16.25 cm\textsuperscript{3} corresponding to a pressure range of about 200 to 2000 atmos. The measurements were made in a temperature range from 3°K up to the melting point and then liquid measurements were made to 29°K. They also made measurements on He\textsuperscript{3} in the high pressure hcp phase. The molar volume of the helium sample was inferred from the melting temperature of the sample by using the melting data of Grilly and Mills (13, 14). After the completion of the heat capacity measurements, the mass of helium in the calorimeter cell was determined by letting the helium into a known volume where the temperature and pressure could be accurately measured. From the PVT data by Keesom (1942) the mass was determined. Due to the bulk of their calorimeter the heat capacity of the helium sample contributed from 30 to 40\% of the total heat capacity near the melting point while it contributed only 5 to 25\% at 3°K. Thus their accuracy below 5°K was greatly reduced. They estimate their error above 5°K to be about 1.5\%.

From the specific heat data which were extrapolated to 0°K and the melting curve data, the entropy, internal energy, and equation of state for the solid were computed for the four molar volumes measured. Dugdale and Franck pointed out that their specific heat measurements could be approximately represented as $C_V = f(v) F(T/\theta)$. A plot of $\theta$ vs $T$ revealed that the Debye temperature rises with falling temperature.
Presented in Table 1 is a summary of information on the specific heat calorimeter used for measurements on solid helium. Presented in Table 2 is a list of the experimental work on the specific heat of hcp solid He⁴ at constant volume, and in Figure 2 a plot of θ vs T represents some of the results of these works.

Despite the fact that there has been a good deal of experimental work on solid hcp He⁴ the results are still not conclusive for there is the question of the linear term in the specific heat at low temperatures, and furthermore Dugdale and Franck and Dugdale and Simon have worked out the thermodynamic functions for hcp He⁴ in the high pressure region for molar volumes 11 to 16 cm³/mole but the specific heat data were not complete enough to determine the thermodynamic functions for the solid in the range 16 to 21 cm³/mole. Thus one of the present interests in solid hcp He⁴ is the specific heat in this latter volume range carried to a low enough temperature so that the thermodynamic functions may be computed and the linear term investigated. The only specific heat measurements on bcc He⁴ are by Ahlers (33, 34), and these results cover only a small part of the bcc region. Furthermore, these results have the very unusual behavior that the Debye theta increases with increasing temperature which Ahlers has interpreted as due to a negative expansion coefficient. A more complete investigation of the bcc phase of He⁴ would be useful.

The only specific heat investigations made on solid He² have been by Heltemes and Swenson (32) in the hcp and bcc regions and by Dugdale and Franck (37) in the high pressure region of the hcp phase. McWilliams (38) also
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<td>8.26</td>
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<td>Liquid He⁴ vapor pressure</td>
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<td>Franck (35)</td>
<td>&lt;3000</td>
<td>Beryllium copper</td>
<td>1.34</td>
<td>-</td>
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<td>-</td>
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<td>Dugdale &amp; Franck (37)</td>
<td>200-2000</td>
<td>Drillrod steel</td>
<td>-</td>
<td>10Ω, 1W carbon resistor</td>
<td>Gas bulb &amp; He⁴ vapor</td>
<td>Liquid H and He⁴ g</td>
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aPressure in units of atmospheres and temperature in degrees K.
bThe old 1932 scale was apparently used.
cThe ferric alum and a diamagnetic filler filled the calorimeter and served both as the cooling pill and the thermometer.
dCopper foil was soldered around the calorimeter to promote heat conduction.
eHas a yield strength of 10 K bars and a lower specific heat than stainless steel.
fContact between the bath and calorimeter was made with a mechanical heat switch.
gThe calorimeter was cooled from 20°K by condensing He⁴ into a small chamber attached to the calorimeter.
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<td>2.7 to 3.7</td>
<td>1</td>
<td>$\theta = 32.5$ deg K</td>
</tr>
<tr>
<td>Keesom &amp; Keesom (29), 1936</td>
<td>18.3 to 20.0</td>
<td>1.2 to 3.0</td>
<td>7</td>
<td>Debye temperature rises with falling temperature</td>
</tr>
<tr>
<td>Webb, Wilkinson &amp; Wilks (31), 1952</td>
<td>18.7 to 20.6</td>
<td>0.6 to 1.5</td>
<td>3</td>
<td>Debye temperature rises with falling temperature, reaches a maximum, and begins to fall</td>
</tr>
<tr>
<td>Dugdale &amp; Simon (22), 1953</td>
<td>10.6 to 17.0</td>
<td>5.0 to 26.0</td>
<td>12</td>
<td>For $T/\theta &lt; 0.10$, $\theta$ almost independent of temperature</td>
</tr>
<tr>
<td>Heltemes &amp; Swenson (32), 1962</td>
<td>11.9 to 21.0</td>
<td>0.3 to 2.0</td>
<td>12</td>
<td>Debye temperature falls with falling temperature</td>
</tr>
<tr>
<td>Ahlers (33, 34), 1963, 1964</td>
<td>19.8 to 21.0</td>
<td>1.3 to 2.1</td>
<td>8</td>
<td>Debye temperature rises with falling temperature</td>
</tr>
<tr>
<td>Franck (35), 1964</td>
<td>10.9 to 16.3</td>
<td>1.3 to 4.0</td>
<td>5</td>
<td>Debye temperature falls with falling temperature</td>
</tr>
<tr>
<td>Dugdale &amp; Franck (37), 1964</td>
<td>11.8 to 16.3</td>
<td>4.0 to 26.0</td>
<td>4</td>
<td>Debye temperature rises with falling temperature</td>
</tr>
</tbody>
</table>
The Debye $\theta$ as a Function of Temperature for hcp He$^4$

The curves are representative of the results of the following experimenters:

Curves $K_1, K_2$ - Keesom & Keesom (29) for the molar volumes 19.91 and 18.36 cm$^3$/mole;

Curves $S_1, S_2, S_3$ - Dugdale & Simon (22) for molar volumes 14.4, 13.0, and 11.7 cm$^3$/mole;

Curves $H_1, H_2$ - Heltemes & Swenson (32) for molar volumes 18.63 and 14.50 cm$^3$/mole;

Curves $A_1, A_2$ - Ahlers (33) for molar volumes 20.80 and 19.87 cm$^3$/mole;

Curves $F_1, F_2$ - Franck (35) for molar volumes 16.30 and 12.14 cm$^3$/mole (the dashed lines represent extrapolations);

Curves $D_1, D_2, D_3, D_4$ - Dugdale & Franck (37) for molar volumes 16.25, 14.55, 12.22, and 11.77 cm$^3$/mole.

Curve $W_1$ - Webb, Wilkinson & Wilks.
made some measurements on bcc He\textsuperscript{3} below 1°K. Heltemes and Swenson fitted their specific heat results to the equation \( C_V = AT + E(T/\varphi) \) where \( A \) is a constant and \( E(T/\varphi) \) is the Einstein specific heat function. Since their results were only exploratory in nature, it would be useful to have more accurate measurements on bcc He\textsuperscript{3} and to perhaps investigate further the rather curious form of the specific heat suggested by Heltemes and Swenson.
CHAPTER II

EXPERIMENTAL METHOD

Experimental Apparatus

The present set of experiments on the specific heat of solid helium was a continuation of the work by Edwards, McWilliams and Daunt (38–41). Few fundamental changes were made in the experimental arrangement. The experimental apparatus consisted of a copper calorimeter employing a magnetic thermometer capable of operation over the temperature range of 0.06°K to 4.0°K in which cooling to the lower temperatures was obtained with liquid He$^4$ in conjunction with magnetic cooling. The following discussion describes the apparatus as used with modifications for the present set of experiments with reference being given where necessary to more complete discussions.

As in previous work the samples of solid helium were contained in a copper calorimeter whose interior was partially filled with a porous sponge of sintered copper to promote thermal contact. The calorimeter was constructed from a cylindrical copper cup which was filled with copper powder of uniform grain size, and then sintered just below the melting point to produce an average pore size in the sintered copper of about ten microns and a surface area about 0.2 m$^2$ (see reference 38 for further details). This sort of construction was primarily intended to give extremely good thermal contact to solid He$^3$ at very
low temperatures (40), and its use may possibly have contributed to the
difficulty of annealing out pressure inhomogeneities in some of the samples.
The volume of the calorimeter was found by filling it with liquid He\(^4\) and then
measuring the amount of gas evolved when it was warmed to room temperature,
making a small correction for the filling tube. On the basis of five
determinations the volume of the calorimeter was found to be \(0.2764 \pm 0.0006\) cm\(^3\). (This is different from the value in references 38-41 because of some
modifications in the construction of the calorimeter.) The filling tube was a
0.010 inch o. d., 0.005 inch i. d., stainless steel tube with 40 inches of 0.003
inch niobium wire slipped into the calorimeter side in order to reduce its dead
volume. A 1000 ohm resistance wire (Evanohm) for introducing heat into the
calorimeter was varnished (G. E. 7031) on the outside of the calorimeter and
connected to niobium leads by spot welding.

The disposition of some important parts of the apparatus is shown in
Figure 3. The cerium magnesium nitrate (CMN) thermometer was enclosed in
a nylon case screwed to the bottom of the calorimeter and contained sixty #32
AWG enamelled wires which were soldered to the calorimeter. Thermal
contact between the CMN crystals and the wires was made by filling the nylon
case with silicone stopcock grease. The two CMN single crystals together
formed a cylinder about 2.7 cm long by 1.1 cm diameter and mass 5.8 gm.
The susceptibility of the crystals was measured by mutual inductance coils
wound on the vacuum jacket and connected to an electronic Hartshorn bridge
(42,43). The output of the bridge was relayed through a tuned amplifier and
Figure 3

Schematic diagram of the specific heat cryostat.

The copper calorimeter is supported by a thin-walled nylon tube from the cooling salt pill of the chromium potassium alum with thermal contact between the cooling salt and the calorimeter being made by a superconducting indium switch. Attached to the bottom of the calorimeter was a nylon pill case containing two single CMN crystals with thermal contact between the calorimeter and the crystals being made by 60 copper wires soldered to the bottom of the calorimeter and enclosing the crystals packed with silicone stopcock grease. Enclosing the calorimeter and cooling salt pills was a vacuum jacket upon which was wound a set of mutual inductance coils used in measuring the magnetic susceptibility of the CMN crystals. Alongside the apparatus diagram is a ruler (in inches) to illustrate the scale.
phase sensitive detector to a chart recorder which gave a continuous measurement of the calorimeter temperature during heat capacity determinations. (The electronic circuits are discussed in Appendices A and B.)

The calorimeter was mechanically supported by a thermally insulating nylon support tube from a hermetically sealed metal case containing 35 gms of chromium potassium alum [made after a design of Barnes, Heer, and Daunt (44)] used as a refrigerant and as an exchange gas getter. The cooling salt container with the calorimeter rigidly attached was suspended by the stainless steel filling tube from a guard or buffer salt pill case containing about 25 gms of manganese ammonium sulphate. This salt pill acted as a thermal sink for the electrical leads and filling tube leading from the He\textsuperscript{4} bath and also aided exchange gas getting. The guard salt in turn was suspended by the stainless steel filling tube from the top of the vacuum jacket which was immersed in the He\textsuperscript{4} bath. The stainless steel filling tube was brought into thermal contact with the bath at the top of the vacuum jacket and then continued to the top of the cryostat in a vacuum jacket. The electrical leads were brought out of the vacuum jacket via kovar-glass seals into a small continuously pumped vacuum chamber (to guard against leaks) and then into the He\textsuperscript{4} bath through another set of seals.

Below 1.2°K thermal contact between the refrigerant salt and the calorimeter was obtained by a superconducting thermal switch of 99.999\% pure indium. The indium wire, of size 0.001" by 0.0005" by 0.75", was placed inside a solenoid of 0.003" niobium wire consisting of about 2000 turns along a
length of 2.5 cm. A current of 0.3 amperes in the solenoid was sufficient to
drive the indium switch normal and thus establish thermal contact between the
cooling salt pill and the calorimeter. The solenoid current was provided by a
power transistor whose base current was controlled by a circuit resembling a
Miller integrator (38). The method used for making such a small indium
thermal switch is described in the caption of Figure 4.

With the calorimeter in the temperature range above 1°K and the
cooling salt pill below 0.1°K, there was a noticeable heat leak between the
calorimeter and the cooling salt pill through the superconducting indium switch
which cooled the calorimeter. This was cancelled when necessary by applying
heat to the calorimeter through an auxiliary heating circuit (Appendix B) which
therefore controlled the temperature drift of the calorimeter.

The very narrow filling tube to the calorimeter was connected outside
the cryostat to a system with a relatively small dead volume, less than 1 cm³,
consisting of a Consolidated Electrodynamics strain-gauge 5000 psi pressure
transducer and a miniature needle valve connected to the gas handling system.
The pressure transducer was chosen in preference to a Bourdon gauge because
of its slightly higher accuracy and because it requires only a very small dead
space. It was calibrated against a free piston gauge and was accurate to better
than ±0.2 atmospheres. Since the equipment was designed for experiments on
solid He³ and solid He³ and He⁴ mixtures, the gas handling system (depicted in
Appendix C) included a small helium cryostat for condensing the specimen gas
as liquid from low pressure storage bottles and vaporizing it at high pressure
Stock indium wire about 1/16" diameter was placed between two polished, clean blocks of tool steel and pressed in a large vise until it was squeezed down to a thickness of about 0.0005". The steel blocks were separated and displaced and then put back together with the indium sheet sticking out past the edge of one of the blocks. A feeler gauge, say 0.020", was set against the side of the displaced block with the 0.020" edge against the indium sheet. A good razor blade was set against the indium sheet to cut it. The feeler gauge was then changed from 0.020" to say 0.019" (depending on the size of the switch desired) and a second cut with the razor blade was made against the indium. This second cut then formed a wire 0.001" wide and 0.0005" thick. The 0.0005" by 0.001" indium wire was much too small and fragile to be soldered; therefore it was installed on the terminals of the apparatus by pressing the 0.0005" by 0.001" indium wire onto larger indium tabs soldered onto the terminals of the calorimeter and cooling salt pill case.
to fill the calorimeter. This technique had the secondary advantage of removing impurities which might otherwise have blocked the narrow calorimeter filling tube.

**Experimental Procedure**

The cryostat was cooled to 77°K by a liquid nitrogen bath and then to 4.2°K by a liquid He⁴ bath with thermal contact between the He⁴ bath, the calorimeter, and cooling salt pills being made by He³ exchange gas. Using the gas handling system, the calorimeter was filled with liquid helium to a pressure slightly greater than the desired freezing pressure. The freezing pressure and freezing temperature, as well as the molar volume of the He⁴ sample, were determined from the melting curve data of Grilly and Mills (14, 15). After allowing a few minutes for equilibrium to be established, the helium bath temperature was rapidly lowered which first solidified the helium in the filling tube because of the good thermal contact at the top of the vacuum jacket, and which second permitted the helium sample in the calorimeter to solidify at constant volume. This technique of solidifying the sample is called the "blocked capillary method" and was used by Webb, Wilkinson and Wilks (31) and also by Edwards, McWilliams and Daunt (38-41). After the helium sample had been solidified, it was found that in order to get a homogeneous sample, the sample should be annealed just below the melting point for an hour more or less depending upon the density. The next step was to calibrate the CMN thermometer against the vapor pressure of the He⁴ bath (the 1958 He⁴ temperature scale (30) was used) in the temperature range 2.2°K to 1.2°K. Upon completion of the
calibration, the He\textsuperscript{4} bath was lowered to its minimum of about 1.2°K and the paramagnetic salts were magnetized in a field of 20 kilogauss for fifteen minutes, and then the He\textsuperscript{3} exchange gas was pumped out for one to one and a half hours until a pressure less than 3 x 10\textsuperscript{-6} mm (measured at room temperature with the pumping line closed off) was read in the vacuum jacket space. After about one-half hour of pumping out the exchange gas, quite often it helped to close off the bath pumping line and allow the bath to warm up to about 1.5°K for brief periods of time; this procedure greatly aided in removing adsorbed gases from the pumping tubes and, if done for a brief period, it did not warm up the salt pills. After removing the exchange gas, the paramagnetic salt pills were demagnetized from the 20 kilogauss over a period of about twenty minutes with most of the demagnetizing time being used to remove the last several thousand gauss. The calorimeter was then cooled to the desired temperature through the indium thermal switch and the specific heat measurements were taken through the solid phase of the sample into the melting region and then into the liquid phase. During the measurements on the bcc solid between 1.4 and 1.8°K, temperature rises of about 0.006°K were made with an accuracy of about 2%. For the hcp solid temperature rises of about 1/20 of the temperature were measured within 1%. The accuracy of the absolute temperature in the region 1 to 2°K (i.e., the region in which the thermometer was calibrated against the He\textsuperscript{4} vapor pressure) was not worse than ± 0.001°K and in the other temperature regions not worse than ± 0.3% of the temperature. The electrical measurements for the heater power were made to about ± 0.2% while the heating
period was measured by a commercial electronic counter to the nearest milli-second. At the end of the experiment the molar volume of the sample was measured to ± 0.3% by expanding the contents of the calorimeter into a known volume connected to a mercury manometer with necessary corrections for the filling tube and dead volume being made. The actual method of measuring the molar volume is described fully in Appendix C.

An analysis of the data was performed with the assistance of a 7094 Scatran computer program which computed the temperature and the specific heat of the calorimeter contents along with its Debye $\theta$. The computer program is described in Appendix E. The specific heat of the empty calorimeter as determined by five experiments which gave a scatter of about 1% is represented in Figure 5.
Figure 5

The heat capacity of the calorimeter, $C_C$, is plotted as the log of $C_C$ versus temperature. The heat capacity of the calorimeter has a minimum near 0.1°K and then begins to rise with falling temperature due to the magnetic heat capacity of the paramagnetic thermometer salt.
 chapte r III

results and discussion o f hcp He\textsuperscript{4}

The heat capacity of the hexagonal phase of He\textsuperscript{4} has been measured at six different molar volumes ranging from 20.93 to 16.90 cm\textsuperscript{3}. The results expressed as Debye thetas are given in Figure 6 where we have also shown the data of Keesom and Keesom (29) (on the 1932 scale of temperature), and Ahlers (33) which are in good agreement with the present work. Smoothed values of $\Theta$ at even temperature intervals are given in Table 3. All of the measured samples were prepared in the way described in the previous section except for the highest density, molar volume 16.90 cm\textsuperscript{3}, which had a melting point and freezing point above 4.2\textdegree K. This sample was obtained by pressurizing the calorimeter to about 3500 psi when the cryostat was at liquid-nitrogen temperature; then liquid helium was slowly transferred into the cryostat in small quantities, taking about half an hour to reach 4.2\textdegree K. The molar volume of the sample was measured at the end of the experiment by expansion into the known volume in the same way as for the less dense samples.

In some samples of hexagonal helium, interesting premelting effects were observed. In one sample, $V = 19.68$ cm\textsuperscript{3}, these appeared when the temperature was still half a degree below the melting point, while in others they did not occur until very close to the melting temperature. The effects were
Figure 6

The heat capacity of hcp He\(^4\) given as the Debye \(\Theta\) for six molar volumes. The short vertical lines give the melting temperature for each volume. The curved, dashed lines about the points at low temperature represent the effect of adding or subtracting 1\% of the calorimeter heat capacity and so give an idea of the approximate accuracy of the data. The solid lines give the results of previous workers: \(K_1\), \(K_2\), \(K_3\), Keesom and Keesom (see reference 29) for \(V = 19.92, 19.34, 18.36\ \text{cm}^3\); \(A_1\), \(A_2\), \(A_3\), \(A_4\), Ahlers (see reference 33) for \(V = 20.921, 20.807, 19.884, 19.816\ \text{cm}^3\), respectively.
TABLE 3. The Debye θ of hcp He\textsuperscript{4}

<table>
<thead>
<tr>
<th>T(°K)</th>
<th>16.90</th>
<th>17.87</th>
<th>V\textsubscript{meas} (cm\textsuperscript{3}/mole)</th>
<th>18.22</th>
<th>19.18</th>
<th>19.68</th>
<th>20.93\textsuperscript{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>(46.0)\textsuperscript{b}</td>
<td>(39.25)</td>
<td>(37)</td>
<td>(33.1)</td>
<td>(30.7)</td>
<td>(26.35)</td>
<td></td>
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<tr>
<td>0.50</td>
<td>...</td>
<td>39.25</td>
<td>...</td>
<td>33.1</td>
<td>30.7</td>
<td>26.3</td>
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<tr>
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<td>26.1</td>
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<tr>
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<td>32.8</td>
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<td>25.4</td>
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<tr>
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<td>32.3</td>
<td>29.7</td>
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<tr>
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<td>45.0</td>
<td>38.5</td>
<td>35.8</td>
<td>31.5</td>
<td>28.8\textsubscript{5}</td>
<td>(23.1)</td>
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<tr>
<td>1.75</td>
<td>44.4</td>
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<td>35.0</td>
<td>30.6</td>
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<tr>
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<td>33.8</td>
<td>28.8</td>
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<td></td>
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</tr>
<tr>
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<td>33.1</td>
<td>27.7\textsubscript{5}</td>
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<tr>
<td>2.75</td>
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<td>T\textsubscript{m}(°K)</td>
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<td>...</td>
<td>3.16</td>
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<td>2.304</td>
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<td>T\textsubscript{f}(°K)</td>
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<td>4.019</td>
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<td>P (atm)</td>
<td>...</td>
<td>160</td>
<td>129</td>
<td>99</td>
<td>78</td>
<td>49</td>
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</tbody>
</table>

\textsuperscript{a} Determined from the pressure and the data of Grilly and Mills.

\textsuperscript{b} Parentheses indicate extrapolated values of θ.

\textsuperscript{c} Beginning of transition to bcc.

observed as an "after heating," that is, in a heat capacity measurement the temperature of the calorimeter continued to rise after the heating current was switched off, and would do so for several minutes until it levelled off in a quasi-exponential manner. However, the apparent heat capacity in such a case, when it was possible to measure it, was the same within the experimental error as that obtained in the absence of premelting effects. It was found that premelting...
could be avoided by annealing the sample for about half an hour or so just below the melting point before cooling it. The premelting was ascribed to parts of the sample having lower densities than the rest, which would melt on heating and then slowly refreeze again at a higher density as the sample became more homogeneous. The proportion of the sample involved was probably very small, less than a few per cent, since the ratio of the heat involved in premelting to the total latent heat of melting was of that order or less.

An important feature of the results shown in Figure 6 is that the Debye $\Theta$ levels off at low temperatures and becomes independent of temperature, allowing one to determine $\Theta_0$, the value at 0°K, within 1 or 2%. We see no evidence in the present work for a contribution to the specific heat, which is linear in the temperature (making the Debye $\Theta$ decrease at low temperatures) comparable to that found by Heltemes and Swenson (32) in both solid He$^4$ and He$^3$. This confirms earlier conclusions in work which included measurements of solid He$^3$ (40). The effect of adding or subtracting 1% of the calorimeter heat capacity to the present data is shown in Figure 6 as the curved, dashed lines about the points at low temperatures. If a linear term in the specific heat exists in the present results, we estimate its order of magnitude to be less than 1% of our calorimeter (background) heat capacity which means that it is less than 5% of the linear term found by Heltemes and Swenson. J. P. Franck (34) has also reported a linear specific heat contribution in solid He$^4$ at high pressure. The largest molar volume investigated in his work was 16.30 cm$^3$, smaller than any in the present experiments. For all annealed samples, Franck
found a coefficient A which was roughly one-third of that found by Heltemes and Swenson at the same density. On the other hand, for an unannealed sample the coefficient A was nearly as large as that found by Heltemes and Swenson, and so Franck has suggested that the linear term is associated with some form of lattice imperfection, which may be partly annealed out at higher temperatures. Again we have no affirmative evidence on this point, but this may be because our specimens were already sufficiently well annealed, or because our experiments do not extend to sufficiently high densities.

The curves of $\theta$ vs $T$ in Figure 6 are all similar in shape and can be represented in a reduced form, as shown in Figure 7, in which we have plotted $\theta/\theta_{0.05}$ versus $T/\theta$, where $\theta_{0.05}$ is the value of $\theta$ when $T/\theta = 0.05$. All the experimental points lie close to the single, continuous curve in the diagram. The deviations from the curve depend very little on molar volume and are probably within experimental error. This diagram allows us to compare our data with the recent measurements of the specific heat by Dugdale and Franck (37) made at higher densities and temperatures. Since their data do not extend down to $T/\theta = 0.05$, we have plotted their measurements as $\theta/\theta_{0.08}$ vs $T/\theta$ and then fitted the resulting curves to ours at $T/\theta = 0.08$. Their lowest density curves, a and b in Figure 7, join ours in a very satisfactory way, but at the higher densities the heat capacity can no longer be expressed in a reduced form, as shown by curves c and d. The measurements of Ahlers (33) at molar volumes between 19 and 20 cm$^3$ have also been plotted in Figure 7 and can be seen to be in excellent agreement with the drawn curve.
Figure 7

The results of Figure 6 plotted in a reduced form. $\theta_{0.05}$ is the value of $\theta$ when $T/\theta = 0.05$. The dashed, lettered curves are the results of other workers: Dugdale and Franck (see reference 37); curve a, molar volume 16.25 cm$^3$; b, 14.55 cm$^3$; c, 12.22 cm$^3$; and d, 11.77 cm$^3$. Ahlers (see reference 24): e, 19.816, and 19.886 cm$^3$. The continuous line through the points is the curve used in calculating the thermodynamic functions.
In Figure 8 we give the values of $\theta_0$ (the extrapolated value of $\theta$ at 0°K) and of $\theta_{0.05}$ used in calculating the reduced plot, Figure 7, as a function of molar volume. Both quantities have been estimated from the data of Figure 6. The graph also shows the very good agreement with the measurements of other authors. (The linear terms found by Franck (34) and Heltemes and Swenson (32) have been subtracted out.) All the data can be represented by the empirical formulas

\[
\begin{align*}
\theta_0 &= (7.12 \times 10^4)V^{-2.60}, \\
\theta_{0.05} &= (6.73 \times 10^4)V^{-2.60}, \\
16.5(\text{cm}^3) &\leq V \leq 21(\text{cm}^3),
\end{align*}
\]

shown as straight lines on the figure. The value of the Gruneisen constant $\gamma = 2.60$ is estimated to be constant within $\pm 0.05$ in this range of molar volume. However, if the data of other workers (22, 32, 35, 37), measured at higher densities, are taken into account, it seems probable that $\gamma$ is in fact a slowly varying function of $V$, varying from about 2.3 in the region of 12 cm$^3$ to 2.6 near 17 cm$^3$.

### Calculation of the Thermodynamic Functions and Equation of State

The specific heat at constant volume as a function of $V$ and $T$, together with the melting curve measurements of Grilly and Mills (14, 15) and one value of the internal energy, is sufficient to determine all the thermodynamic functions of hcp solid helium. Since the specific heat can be expressed in terms of a reduced temperature $\tau = T/\theta_{0.05}$, where $\theta_{0.05}$ is an analytic...
Figure 8

The Debye $\Theta$ at 0°K or $T/\Theta = 0$ (open symbols) and at $T/\Theta = 0.05$ (closed symbols) plotted as a function of molar volume. The circles are the results of the present work, the inverted triangles from Ahlers (see Reference 33), the upright triangles from Heltemes and Swenson (see Reference 32), and the square from Franck (see Reference 35). The values from the last two references have been calculated after subtracting a linear contribution from the heat capacity. The two straight lines have slope $-2.60$ and represent Eq. 1 in the text.
function of $V$ (Eq. 1), the calculations are like those first done by Dugdale and Simon (22). From the solid curve in Figure 7, which gives smooth values of $\theta/\theta_{0.05}$ as a function of $T/\theta$, the specific heat has been expressed as a function of $\tau = T/\theta_{0.05}$, $C_V(\tau)$. The results have been integrated numerically to give the entropy, $S/R = \int_0^\tau (C_V/R\tau')d\tau'$, and the temperature-dependent part of the internal energy, $(U - U_0)/RT = (1/\tau)\int_0^\tau (C_V/R)d\tau'$, as functions of the reduced temperature $\tau$. $U_0$ is the energy at 0°K and depends only on $V$. The results of these calculations are given in Table 4. This table and Eq. 1, to give $\theta_{0.05}(V)$, can be used to determine $S/R$ (shown in Figure 9) or $(U - U_0)/RT$ for any values

<table>
<thead>
<tr>
<th>$T/\theta_{0.05}$</th>
<th>$10^3C_V/R$</th>
<th>$10^3S/R$</th>
<th>$10^3(U - U_0)/RT$</th>
<th>$(K_0^{-1} - K^{-1})V/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.020</td>
<td>1.57</td>
<td>0.52</td>
<td>0.39</td>
<td>0.007</td>
</tr>
<tr>
<td>0.025</td>
<td>3.10</td>
<td>1.03</td>
<td>0.77</td>
<td>0.014</td>
</tr>
<tr>
<td>0.030</td>
<td>5.36</td>
<td>1.77</td>
<td>1.33</td>
<td>0.024</td>
</tr>
<tr>
<td>0.035</td>
<td>8.83</td>
<td>2.84</td>
<td>2.13</td>
<td>0.040</td>
</tr>
<tr>
<td>0.040</td>
<td>13.6</td>
<td>4.31</td>
<td>3.24</td>
<td>0.062</td>
</tr>
<tr>
<td>0.045</td>
<td>20.3</td>
<td>6.27</td>
<td>4.74</td>
<td>0.093</td>
</tr>
<tr>
<td>0.050</td>
<td>29.3</td>
<td>8.83</td>
<td>6.69</td>
<td>0.135</td>
</tr>
<tr>
<td>0.055</td>
<td>41.3</td>
<td>12.2</td>
<td>9.25</td>
<td>0.193</td>
</tr>
<tr>
<td>0.060</td>
<td>56.5</td>
<td>16.3</td>
<td>12.5</td>
<td>0.265</td>
</tr>
<tr>
<td>0.065</td>
<td>75.5</td>
<td>21.5</td>
<td>16.6</td>
<td>0.355</td>
</tr>
<tr>
<td>0.070</td>
<td>98.7</td>
<td>28.1</td>
<td>21.6</td>
<td>0.464</td>
</tr>
<tr>
<td>0.075</td>
<td>126</td>
<td>35.6</td>
<td>27.6</td>
<td>0.596</td>
</tr>
<tr>
<td>0.080</td>
<td>160</td>
<td>44.8</td>
<td>34.8</td>
<td>0.755</td>
</tr>
<tr>
<td>0.085</td>
<td>198</td>
<td>55.7</td>
<td>43.3</td>
<td>0.934</td>
</tr>
<tr>
<td>0.090</td>
<td>239</td>
<td>68.2</td>
<td>53.1</td>
<td>1.12</td>
</tr>
<tr>
<td>0.095</td>
<td>285</td>
<td>82.4</td>
<td>64.1</td>
<td>1.33</td>
</tr>
<tr>
<td>0.100</td>
<td>333</td>
<td>98.2</td>
<td>76.3</td>
<td>1.54</td>
</tr>
</tbody>
</table>
The entropy diagram. The entropy of the hcp phase is given at melting, at the bcc-hcp transition line (dashed), and at constant molar volumes. The lower portion of the melting entropy curve is uncertain because of uncertainty in the molar volume at melting. $T_1$ and $T_2$ are the hcp-bcc liquid triple point temperatures. The entropy of the liquid at melting, and of the bcc phase along the transition line (to be discussed in a later chapter) is shown for reference.
LIQUID

SOLID + LIQUID

MELTING CURVE

bcc

hcp

\[ V = 17.00 \]

\[ V = 17.50 \]

\[ V = 18.00 \]

\[ V = 18.50 \]

\[ V = 19.00 \]

\[ V = 19.50 \]

\[ V = 20.00 \]

\[ V = 20.50 \]
of $V$ and $T$ below the melting temperature and between $V = 16.5$ cm$^3$ and $V = 21$ cm$^3$. In addition, the change in pressure with temperature, $(p - p_0)$, can be determined from the equation:

$$p - p_0 = \gamma (U - U_0)/V$$

with $\gamma = 2.60 \pm 0.05$. This equation follows from the fact that $C_V$ is only a function of $T$. To complete the calculations the results of the melting curve measurements of Grilly and Mills (14,15) have been used. Grilly and Mills give $p$, $V$, and $T$ at melting from which, using Eq. 2 and Table 4, we have obtained $p_0$, the pressure at 0°K as a function of $V$. Numerical integration of $p_0$ gives the variation of energy with volume at 0°K:

$$U_0(V) - U_{0s}(V) = - \int_{V_s}^{V} p_0 dV'.$$

The resulting values of $U_0/R$ and $p_0$ are given in Table 5; the energy diagram for solid helium is given in Figure 10. For the reference value of the internal energy $U_{0s}$ we have used a value for melting helium, $U_{0s}/R = -5.96°K$ at $V_s = 21.08$ cm$^3$, which is based on the earlier calculations of Swenson (10) who found the melting internal energy to be $-5.99°K$, believing that the melting point was at 25 atmospheres and $V = 21.18$ cm$^3$. The measurements of Grilly and Mills suggest that the melting and freezing volumes used by Swenson are too small by about 0.1 cm$^3$; therefore, a small correction to his value of $U_{0s}/R$ has been made. The correction is of the same order as the probable error in the data used by Swenson.

In addition to the properties of the solid at 0°K, Table 5 gives values of the entropy of the solid at melting $S_m$, the expansion coefficient of the solid at
<table>
<thead>
<tr>
<th>V (cm³/mole)</th>
<th>Tm (°K)</th>
<th>P₀ (atm)</th>
<th>Pm - P₀ (atm)</th>
<th>U₀/R (deg)</th>
<th>(Um - U₀)/R (deg)</th>
<th>Sₘ/R</th>
<th>x₀ x 10² atm⁻¹</th>
<th>xₘ x 10² atm⁻¹</th>
<th>αₘ x 10² deg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.00</td>
<td>4.27</td>
<td>140.7</td>
<td>4.07</td>
<td>-2.56</td>
<td>0.324</td>
<td>0.0997</td>
<td>0.108</td>
<td>0.112</td>
<td>0.47</td>
</tr>
<tr>
<td>17.50</td>
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<td>116.2</td>
<td>3.11</td>
<td>-3.32</td>
<td>0.255</td>
<td>0.0865</td>
<td>0.121</td>
<td>0.125</td>
<td>0.45</td>
</tr>
<tr>
<td>18.00</td>
<td>3.37</td>
<td>95.2</td>
<td>2.29</td>
<td>-3.98</td>
<td>0.193</td>
<td>0.0736</td>
<td>0.140</td>
<td>0.144</td>
<td>0.44</td>
</tr>
<tr>
<td>18.50</td>
<td>3.00</td>
<td>77.4</td>
<td>1.67</td>
<td>-4.50</td>
<td>0.145</td>
<td>0.0627</td>
<td>0.168</td>
<td>0.173</td>
<td>0.45</td>
</tr>
<tr>
<td>19.00</td>
<td>2.69</td>
<td>63.3</td>
<td>1.28</td>
<td>-4.93</td>
<td>0.114</td>
<td>0.0547</td>
<td>0.199</td>
<td>0.204</td>
<td>0.45</td>
</tr>
<tr>
<td>19.50</td>
<td>2.41</td>
<td>51.8</td>
<td>0.95</td>
<td>-5.28</td>
<td>0.0872</td>
<td>0.0468</td>
<td>0.236</td>
<td>0.241</td>
<td>0.43</td>
</tr>
<tr>
<td>20.00</td>
<td>1.86</td>
<td>31.8</td>
<td>0.44</td>
<td>-5.78</td>
<td>0.0427</td>
<td>0.0298</td>
<td>0.326</td>
<td>0.330</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Figure 10

The internal energy of hcp helium at constant molar volumes and at melting.

The portion of the melting curve below 1.6°C is approximate.
melting, \( \alpha_m \), and the isothermal compressibility of the solid at melting, \( \chi_m \).

The expansion coefficient and compressibility can be obtained by applying Eqs. 4 and 5 to the melting curve data:

\[
\frac{dV}{dT} = \left( \frac{\partial V}{\partial p} \right)_T \frac{dp}{dT} + \left( \frac{\partial V}{\partial T} \right)_p = V(\alpha - \chi \frac{dp}{dT})
\]

(4)

\[
\alpha = \gamma \chi C_V / V.
\]

(5)

The Gruneisen Eq. 5 can be derived from Eq. 2 by differentiation. Values of \( dp/dT \) are tabulated by Grilly and Mills and \( dV/dT \) at melting was obtained by numerical and graphical differentiation of their data. Knowing the value of \( \chi_m(V) \), it is possible to find the value of \( \chi(V) \) at any other temperature by applying the small correction given by the expression \( (\chi^{-1} - \chi_0^{-1})V/RT \) in Table 4. This quantity has been obtained by integrating the relation

\[
\left[ \frac{\partial}{\partial T} \left( \frac{\partial V}{\partial T} \right)_T \right]_V = \left[ \frac{\partial}{\partial V} \left( \frac{\gamma C_V}{V} \right) \right]_T
\]

(6)

which yields

\[
[\chi^{-1}(V, T) - \chi_0^{-1}(V)] = (\gamma/V)[(\gamma + 1)(U - U_0) - \gamma TC_V]
\]

(7)

so that \( (\chi_0^{-1} - \chi^{-1})V/RT \) is a function of \( \tau \) only. In this way the values of the compressibility at 0\(^\circ\)K, \( \chi_0(V) \), were obtained from the \( \chi_m(V) \) computed from Eqs. 4 and 5 and both are tabulated in Table 5. It can be seen that the temperature dependence of \( \chi \) is so small as to be negligible for most practical purposes, such as in the calculation of \( \alpha \) from Eq. 5.

Tables 4 and 5 combined with Eq. 1 give sufficient information to calculate any thermodynamic property, including the Gibbs and Helmholtz free
energies, for molar volumes $V \geq 17 \text{ cm}^3$. Dugdale and Franck (37) have given similar data for four volumes in the range $V \leq 16.25 \text{ cm}^3$. Although the two regions of measurement do not overlap, our values of $\theta_0, \theta_0$ and $\theta_0$ can be extrapolated by means of Eq. 1 into the range covered by Dugdale and Franck, and the thermodynamic functions calculated by means of Table 4. When this is done for $V = 16.25 \text{ cm}^3$, one of the molar volumes measured by Dugdale and Franck, it is found that at $3^\circ\text{K}$ their specific heat is about 2% lower than the projection of the present data, their entropy is about 2.5% higher than ours, while their internal energy at $0^\circ\text{K}$ and $17 \text{ cm}^3$ agrees within 1/2% with ours. The difference becomes greater at higher temperatures, for at $5^\circ\text{K}$ their specific heat is about 6% lower than the projection of our data. Dugdale and Franck estimate their error in $C_V$ above $5^\circ\text{K}$ to be about 1.5% and greater at lower temperatures. Considering the error in the present results to be of the same order of magnitude, the difference between the two results does not appear to be too significant in view of the fact that the present results were projected outside the experimental range.

The Melting Properties of hcp Helium

Whenever possible, the present heat-capacity measurements, which, it must be remembered, are at constant volume, were made through the melting point (at which melting begins), then the freezing point (at which melting is completed as the temperature is raised), and in the liquid phase. This is illustrated in Figure 11 for the molar volume 19.18 cm$^3$. The melting and freezing temperatures can be calculated from the data using a lever rule
Figure 11

The heat capacity of solid $\text{He}^4$ as a function of temperature for a sample which passed through the bcc phase and melted and a sample which passed through the hcp phase and melted.
and they are shown in Table 3 which gives $T_m$, $T_F$, and the initial or approximate freezing pressure for various molar volumes. These data are in good agreement with those of Grilly and Mills (14). The molar volumes calculated from the melting and freezing temperatures agree with the measured molar volumes to within a root-mean-square deviation of 0.03 cm$^3$, which is within the experimental accuracy. The volumes which one would expect from the initial pressure do not agree quite so well, but are within an rms deviation of 0.09 cm$^3$. The measurements of $C_v$ in the liquid agree with those of Lounasmaa (47) within 2-3%.

We have also obtained the discontinuities in the specific heat, $\Delta C_v$, on melting and freezing. These are given in Figure 12 with previous values taken from Keesom and Keesom (29) and Lounasmaa (48). It has been shown by Lounasmaa (48) and Goldstein (49) that, on passing from a single phase to a mixture of two phases at constant volume, the discontinuity in the heat capacity is given by:

$$\Delta C_v = T(dV/dT)^2/V_x$$

(8)

where $V$ and $x$ are the volume and isothermal compressibility of the single phase.

The Compressibility and Expansion Coefficient

Equation 8 with the smoothed values of $\Delta C_v$ at melting and the values of $dV/dT$ derived from Grilly and Mills' data gives a set of values for the compressibility of melting hcp helium in addition to those obtained from Eq. 4.
Figure 12

The discontinuity in the heat capacity at constant volume on melting (full curve, closed symbols) and on freezing (dashed curve, open symbols).

Present work, ◦, ●; Keesom and Keesom (see Reference 29), ▼; Ahlers (see Reference 33), ■; Lounasmaa (see Reference 48), Δ. $T_2$ is the upper hcp-bcc liquid triple-point temperature.
and tabulated in Table 5. Furthermore, a third set can be derived from the equation:

$$\chi = \frac{V \Delta C_v}{[\gamma C_v - V(d\rho/dT)]^2 T}$$

(9)

which is obtained by eliminating $(dV/dT)$ from Eqs. 4 and 8. All three sets of compressibilities, which depend on Grilly and Mills' and the present data in different ways, are in agreement within about ±7%, as is shown in Figure 13. No values of $\chi$ are shown for $V > 20.5$ cm$^3$ since the value of $(dV/dT)$ is very small and unreliable in this region and there are no values of $\Delta C_v$ available either. Figure 13 also shows the melting compressibility obtained by Stewart (50) at 4°K (triangle). Some preliminary, unpublished data of E. R. Grilly in the region of $V = 20$ to 21 cm$^3$ are in good agreement with the present data, although the value ($3.9 \pm 0.2$) x 10$^{-3}$ atm$^{-1}$ obtained by J. N. Kidder at $V = 20.5$ cm$^3$ is about 15% higher (51). The compressibility of the freezing liquid was calculated with Eq. 8. The liquid has a compressibility which is considerably less than that of the solid at the same density but slightly larger than the solid which is in equilibrium with it, as shown in Figure 13.

The thermal expansion coefficient of the melting solid can be derived from the available experimental data in four different ways depending on which of the quantities, $\Delta p/dT$, $dV/dT$, $\Delta C_v$, $C_v$, are dropped from the equations. Three of these simply use the Gruneisen Eq. 5 together with the three values of the compressibility discussed above. Since the three different ways of obtaining the compressibility are in substantial agreement with each other, they lead to
Figure 13

The compressibility $\chi$ of hcp He\textsuperscript{4} at melting and at 0°K, and of liquid He\textsuperscript{4} at freezing. The full lines for the solid have been calculated from the melting curve data of Grilly and Mills and the specific heat using Eqs. 4, 5, and 7. The line for the liquid at freezing was calculated from $\Delta C_V$ and the melting curve data with Eq. 8. The dashed lines link the compressibilities for the liquid and solid in equilibrium at 2, 3, and 4°K. Other values for the compressibility of the melting solid are from $\Delta C_V$ and Eq. 8 ($\Delta$), and from Eq. 9 ($\Box$). The circles represent values of the compressibility of the solid at 0°K calculated from the velocity of sound. The full circles, $\bullet$, are from the velocity of sound with Eq. 12 and the open circles, $\bigcirc$, from the velocity of sound and the Debye theta at 0°K, $\theta_0$, with the help of Eq. 11. The inverted triangle, $\nabla$, represents a direct measurement of the compressibility of the solid at 4°K by Stewart (see reference 50).
MELTING

$^\circ \text{K}$

LIQUID

$T=0$

$V(\text{cm}^3/\text{mole})$

$K \times 10^3 (\text{atmos}^{-1})$

$2^\circ \text{K}$

$3^\circ \text{K}$

$4^\circ \text{K}$

LIQUID

$T=0$

$V(\text{cm}^3/\text{mole})$
substantially the same values of the expansion coefficient as those given in Table 5, which are shown as the full line in Figure 14.

A fourth equation for \( \alpha \) is obtained by substituting \( \chi \) from Eq. 8 into

\[
\alpha = \frac{1}{V} \frac{dV}{dT} + \frac{T}{V \Delta C_V} \left( \frac{dV}{dT} \right)^2 \frac{d\rho}{dT}
\]  

(10)

The results from this equation, shown as open squares in Figure 14, are not reliable because they are given by the sum of two large terms of opposite sign. The expansion coefficient of the freezing liquid has also been calculated with Eq. 10 (open circles); however, the same difficulty applies and the results should only be regarded as semiquantitative.

The Elastic Properties of hcp Helium

A hexagonal crystal has five elastic constants. At present, at any given density we know only three quantities relating to the low-temperature elastic properties of hcp helium. They are the isothermal compressibility, the velocity of sound, measured by Vignos and Fairbank (52), and the Debye \( \theta \) at 0°K. To proceed further additional assumptions must be made: one that has been made frequently is that the crystal is, at least approximately, isotropic. The number of independent elastic coefficients is then reduced to two, for instance, the bulk modulus, \( \chi^{-1} \), and the rigidity modulus. The validity of this assumption is easily tested by calculating one of the three known quantities mentioned above from the other two. For an isotropic solid,
The expansion coefficient, \( \alpha \), of solid He\(^4\) at melting and of liquid He\(^4\) at freezing. The full line was obtained from the Gruneisen Eq. 5 and the compressibility at melting as given by the full line of Figure 13. The squares and the circles represent values for the hcp phase and the liquid calculated with Eq. 10; as explained in the text, these values are not very reliable.
The figure depicts a graph with the Y-axis labeled as $\alpha \times 10^3$ (deg$^{-1}$) and the X-axis labeled as $T(\degree K)$. The graph shows two curves: one labeled "LIQUID" and another labeled "SOLID". Additionally, there is a curve labeled "hcp".
where \( v^t \) and \( v^L \) are the velocities of transverse and longitudinal sound at 0\(^\circ\)K. Vignos and Fairbank found that the velocity of sound in their experiments did not depend on temperature, so we have assumed that their data apply at 0\(^\circ\)K and have used their measurements for \( v^L \) and the present measurements of \( \theta_0 \) to calculate \( v^t \) from Eq. 11. It is found that the transverse velocity is approximately one-half of \( v^L \) at the same density and that the low temperature heat capacity is dominated by the transverse modes. From \( v^L \) and \( v^t \) the compressibility \( \chi \) of the supposedly isotropic solid can be found. The values of \( \chi \) calculated in this way are shown as the open circles in Figure 13. They should be compared to the other experimental values, bearing in mind the difference between the melting and 0\(^\circ\)K compressibilities shown in the figure. On the average the points calculated from the velocity of sound and the Debye \( \theta \) are in agreement with the values from the specific heats and PVT data. This indicates that the velocity of longitudinal sound and the present data are consistent with an assertion that hcp He\(^4\) is isotropic. Vignos and Fairbank (52) pointed out that if the average velocity of sound in their experiments was used in the equation

\[
\theta_0 = \frac{\hbar}{k} \left( \frac{6\pi^2 N_0}{V} \right)^{1/3} \left( \frac{2}{3v^3_t} + \frac{1}{3v^3_L} \right)^{-1/3}
\]

(11)

to calculate the compressibility \( \chi \), the results were in fair agreement with the values available from other methods. A comparison with the present values of
x is made in Figure 13, where compressibilities from Eq. 12 are shown as closed circles; as can be seen, the differences are for the most part just outside experimental error. Equation 12 is appropriate for the velocity of longitudinal waves in an isotropic crystal whose elastic constants satisfy the Cauchy relations; that is, $C_{15} = C_{44}$, $C_{11} = 3C_{12}$ for a hexagonal crystal.

However, just recently Lipschultz and Lee (63) have measured the transverse velocity of sound in hcp He$^4$ at 25.6 atmospheres and have found the sound velocities to be different for each crystal grown, varying from 230 to 315 m/sec. The lower velocity, 230 m/sec, when compared with the Debye $\theta$, the longitudinal velocity, and the compressibility, is completely consistent with the assertion that hcp He$^4$ is isotropic. But if one is to accept the results of Lipschultz and Lee that for some hcp crystals the transverse velocity can be 315 m/sec, then one must conclude that it is only a coincidence that the isotopic model is consistent with the other experimental results and that hcp He$^4$ is highly anisotropic. A recent theory by Nosanow and Werthamer (64) has also stated that hcp He$^4$ is very anisotropic.

Discussion of the Temperature Dependence of $\theta$

Since the quantum dynamical-lattice problem for helium has not yet been solved, the best one can do in discussing the temperature dependence of $\theta$ is to compare it with the other solidified inert gases and in a semiquantitative manner with classical lattice dynamical theory. Figure 15 presents in reduced form the temperature dependence of the Debye $\theta$ for krypton (54), argon (55),
The temperature dependence of the reduced Debye $\Theta$ of hcp He$^4$ compared with that of solid argon, solid krypton, and the classical lattice model of Leighton for $\gamma/\alpha = 0.0$ and $-0.1$. $\theta_{0.05}$ is the value of the $\Theta$ at $T/\Theta = 0.05$. 
the present results for hcp He\textsuperscript{4}, and Leighton's (56) classical lattice model. Leighton's model is for a face-centered cubic crystal, like solid argon and krypton, and includes next-nearest-neighbor as well as nearest-neighbor interactions. The ratio of the force constants for these interactions, $\gamma/\alpha$, is related in the model to the compressibility and $\theta_0$. If we ignore the fact that we are dealing with a hexagonal crystal and calculate this ratio from the present values of $\kappa$ and $\theta_0$, it varies between -0.10 to -0.15 depending on the density. It is obvious from the figure that the Debye $\Theta$ varies much more strongly with temperature than either the other inert gases or the Leighton model with $\gamma/\alpha \sim -0.1$. A comparison with bcc He\textsuperscript{4} and hcp and bcc He\textsuperscript{3} will be made in a later section, but we remark here that the relative temperature dependence of $\Theta$ in these other forms of solid helium is only slightly different from that in hcp He\textsuperscript{4}. 
CHAPTER IV

RESULTS AND DISCUSSION OF bcc He$_4$

As in our work on hcp He$_4$, the heat capacity measurements were made at constant volume so that samples with densities corresponding to the body-centered cubic region of the phase diagram followed a path like that labeled "a" in the molar volume temperature diagram of Figure 16 and in the P-T diagram of Figure 17. In Figure 18 is presented a summary of the phases and transitions that a sample of helium will pass through when its temperature is raised from absolute zero at constant volume in the volume range $20.90 < V < 22.22$ cm$^3$/mole. For example, from Figure 18 it is seen that a sample of solid He$_4$ with volume $V = 20.92$ cm$^3$ at very low temperature will, in equilibrium, be in the hcp phase. As its temperature is raised one may follow this volume down Figure 18 to see the various phases and transitions this volume would make.

In some experiments specific heat measurements were taken first in the single phase hcp region and then in the two-phase, hcp + liquid region before the lower triple point temperature $T_1$ was reached. At $T_1$ it was invariably observed that some superheating of the hcp liquid mixture occurred: the temperature of the calorimeter could usually be raised about 10 mdeg above $T_1$ before the bcc phase finally appeared. The temperature then suddenly dropped...
Figure 16

Volume-temperature diagram for He$^4$ in the neighborhood of the bcc phase. The open circles show the results of Grilly and Mills (see Reference 15) with temperatures corrected with Eq. 15; the open triangles show the results of Ahlers (see Reference 33) with volumes determined from bcc melting temperatures using Grilly and Mills' corrected bcc-(bcc + liquid) melting line; the closed circles are the present results with volumes determined in the same manner, except for the point at 1.481$^\circ$K where the volume was determined from the (hcp + bcc)-bcc boundary. The hcp-(hcp + bcc) line has been drawn using Grilly and Mills' data for $\Delta V_{fr}$ and Ahlers' and the present results for the (hcp + bcc)-bcc line. The dashed lines a and b represent the constant-volume paths shown in Figure 17.
Figure 17

Pressure-temperature diagram for He$^4$ in the neighborhood of the bcc phase. The phase boundaries have been drawn using the results of Grilly and Mills (see Reference 15) with the temperature corrected by Ahlers (see Eq. 15 and Reference 33). The arrows indicate two possible, constant-volume paths, a and b.
Figure 18

A summary of the phases and transitions which a sample of helium in the volume range 20.93 cm$^3$ to 22.22 cm$^3$ will pass through at constant volume as its temperature is raised from zero. The circles represent single phases; the squares, two phases; and the hexagonal figure represents transitions.
and became more or less constant while the latent heat, \( L_1 \), necessary to convert the sample to an hcp + bcc solid mixture was supplied by the heater. By measuring the "fore-drift" and "after-drift" before and after heating the calorimeter through \( T_1 \), it was possible to measure the latent heat to a few percent. The correction necessary for the heat supplied to raise the temperature of the sample and calorimeter was calculated from the heat capacity measurements made above and below \( T_1 \). The principal difficulty in determining the latent heat like this was the very long time required to attain equilibrium in the two-solid hcp + bcc mixture. This was demonstrated when the heat was turned off above \( T_1 \) at the end of the latent heat determination. The temperature of the calorimeter dropped in a quasi-exponential manner with time until levelling off to a steady rate of drift some ten or fifteen minutes later. This slow approach to equilibrium, also observed by Ahlers (33), always occurred in the two-solid mixture and made it difficult and tedious to get reliable heat capacity measurements in this region. To check our measurements and the consistency of the other data used in determining the latent heat, we also measured a sample (average molar volume \( V = 21.13 \text{ cm}^3 \)) which did not intersect the pure bcc phase, but followed a path like that labeled "b" in Figures 16 and 17. This sample contained liquid helium II both above and below \( T_1 \); consequently, the thermal relaxation time was correspondingly lower, about three minutes. The latent heat, \( L_2 \), occurring at the upper triple point, \( T_2 \), and the heat capacity just below and just above \( T_2 \) were also measured for several samples. The
calorimeter contained liquid helium I both below and above the triple point (see a and b in Figures 16 and 17) and the relaxation times were reasonably short.

It is a remarkable fact that the melting heat capacities measured just below and just above the triple points seem to be the same within experimental error. Figure 19 shows the measurements for three different molar volumes in the neighborhood of the melting λ point, $T_\lambda$, and the upper triple point, $T_2$. The closed symbols represent measurements when the sample was partly bcc and partly liquid; the open symbols are for melting hcp. The closed symbols above $T_2$ are for superheated, melting bcc. As the diagram shows, the results for melting hcp He$_4$ can all be extrapolated to $T_2$ so as to intersect the curves for melting bcc, and the maximum difference in heat capacity at $T_2$ between melting hcp and bcc samples at the same density is less than a few per cent. The same fact is seen in Ahlers' measurements (33) for $V = 20.940$ cm$^3$. At the lower triple point, $T_1$, following the melting curve (path b in Figures 16 and 17, and volume 21.13 in Figure 21), the difference in heat capacity is less than about 5%. At $T_1$, but following the transition line above $T_1$ (path a and volume 20.99 in Figure 21), no definite conclusion could be reached because of the uncertainties introduced by the long relaxation time in the two solid region. Some thermodynamic analysis of this apparent equality of the melting heat capacities at the triple points has been attempted, but without reaching a definite conclusion. It appears likely that the equality is not exact and that it can be justified only approximately.
Figure 19

The heat capacity of (liquid + solid) $\text{He}^4$ at constant volumes in the neighborhood of $T_\lambda$ and the upper triple point, $T_2$. The triangles refer to sample numbers 3 and 4 of Table 7 and the circles to sample number 7. The filled points refer to measurements on (bcc + liquid) mixtures, including some superheated above $T_2$; the open symbols refer to (hcp + liquid) mixtures. The heat capacity of both types of mixture at a given volume is approximately the same at $T_2$. 
Figure 20

The heat capacity of He\(^4\) at constant volume in the neighborhood of the bcc phase for two selected volumes.
$V = 21.03$

$V = 20.99$

$hcp + bcc$

$bcc + liq$

$liq + hcp$
Figure 21

The heat capacity of He at constant volume in the neighborhood of the lower triple point (bcc-hcp-liquid) for three selected volumes.
The measured molar latent heats at the triple points, given in terms of entropies, $L_1/T_1$, $L_2/T_2$, are plotted as a function of the volume per mole of the sample $V$ in Figure 22. They can be understood by means of the following argument: Denote the three phases by the suffices $a$, $b$, $c$, with the convention that phases $a$, $b$, are present below the triple point and $a$, $c$, above. Then the entropy, $S$, of the sample (all extensive quantities are molar) is given by:

$$S = -\frac{dG}{dT} + V \frac{dp}{dT} = S_a + (V - V_a) \frac{dp}{dT}$$  \hspace{1cm} (13)

where $G$ is the Gibbs function and where $V_a$ and $V$ are the volumes per mole of the phase $a$ and of the sample as a whole. The total derivatives with respect to $T$ are along the phase equilibrium line. The change in entropy at the triple point is therefore:

$$\Delta S = \frac{L}{T} = (V - V_a)[\left(\frac{dp}{dT}\right)_{ac} - \left(\frac{dp}{dT}\right)_{ab}].$$  \hspace{1cm} (14)

The measured latent heats are consistent with the linear dependence on $V$ required by this equation, as is shown in Figure 22 in which the volumes of the three phases at $T_1$ and $T_2$ are those determined by Grilly and Mills (15). The maximum entropy changes $(\Delta S_1)_{\text{max}}$, $(\Delta S_2)_{\text{max}}$, which occur when $V$ equals $V_{\text{bcc}}$, are compared in Table 6 with values calculated with Eq. 14 from PVT data. As the table shows, agreement at $T_2$ between the present result, the one calculated from the slopes of the transition line and hcp melting curve (Grilly and Mills, 15), and the difference in melting curve slopes (Kierstead, 57) is excellent. At $T_1$ the agreement is poor but our value of $(\Delta S_1)_{\text{max}}$ is quite
Figure 22

The entropy change, $\Delta S/R = L/RT$, is shown at constant volume at the upper triple point, $T_2$, (circles) and at the lower triple point, $T_1$, (triangles) as a function of volume. The pairs of dashed lines are drawn to intersect the volume axis at the triple point volumes of the liquid and the hcp phases, measured by Grilly and Mills. At each triple point the pair of lines is drawn to intersect at the volume of the bcc phase, since the maximum entropy changes will occur when $V = V_{bcc}$. 

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TABLE 6. The temperatures of the bcc-hcp-liquid triple points, $T_1$ and $T_2$, and the upper $\lambda$ point, $T_\lambda$; the maximum constant-volume entropy change at the triple points, $(\Delta S_1)_{\text{max}}$ and $(\Delta S_2)_{\text{max}}$.

<table>
<thead>
<tr>
<th>Source</th>
<th>$T_1$</th>
<th>$T_\lambda$</th>
<th>$T_2$</th>
<th>$10^3(\Delta S_1)_{\text{max}}/R$</th>
<th>$10^3(\Delta S_2)_{\text{max}}/R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vignos &amp; Fairbank$^a$</td>
<td>1.449 ± 0.003</td>
<td>1.765 ± 0.003</td>
<td>1.778 ± 0.003</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>Grilly &amp; Mills$^b$</td>
<td>1.437 ± 0.006</td>
<td>1.760 ± 0.001</td>
<td>1.760 ± 0.004</td>
<td>22</td>
<td>33</td>
</tr>
<tr>
<td>Ahlers$^c$</td>
<td>1.464 ± 0.001</td>
<td>1.763 ± 0.003</td>
<td>1.773 ± 0.001</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.005</td>
<td></td>
</tr>
<tr>
<td>Kierstead$^d$</td>
<td>…</td>
<td>1.7633 ± 0.0001</td>
<td>1.7732 ± 0.0001</td>
<td>…</td>
<td>35.5 ± 2.0</td>
</tr>
<tr>
<td>Lounasmaa &amp; Kaunisto$^e$</td>
<td>…</td>
<td>1.762 ± 0.001</td>
<td>…</td>
<td>…</td>
<td>…</td>
</tr>
<tr>
<td>Present experiments</td>
<td>1.463 ± 0.002</td>
<td>1.763 ± 0.002</td>
<td>1.7715 ± 0.001</td>
<td>9 ± 1</td>
<td>32 ± 2</td>
</tr>
</tbody>
</table>

$^a$Reference 23.

$^b$Reference 15.

$^c$Reference 33.

$^d$Reference 57.

consistent with \((dp/dT)_{T1}\) obtained by Grilly and Mills at temperatures a little higher than \(T_1\), and it appears that their value at \(T_1\) itself, which is anomalously high, is in error.

Table 6 also gives the triple-point temperatures, \(T_1\) and \(T_2\), and the temperature of the intersection of the \(\lambda\) line with the melting curve \(T_\lambda\). In each case the result is the average of several determinations during different experiments with different densities, all of which are within the limits of error quoted. We are in very good agreement with the other authors except for Grilly and Mills (15), and we have therefore followed Ahlers (33) and added a correction

\[
\Delta T = 0.079 - 0.0375T_{GM} \tag{15}
\]

to Grilly and Mills' temperatures between \(T_1\) and \(T_2\) whenever we have had occasion to use their PVT data (as in Figures 16, 17, and 22), so as to bring their triple points into agreement with Ahlers' and our own values.

The Specific Heat

The heat capacities measured in the "pure" bcc phase are shown in Figure 23, both directly and as the effective Debye temperature \(\theta\), for several different volumes. Temperature rises of about 0.006 deg were used in the measurements. The data were obtained after heating the sample into the (liquid + bcc) region and allowing it to cool back into the bcc region of the phase diagram or after holding the temperature steady in the bcc region for half an hour or so. Otherwise the heat capacity was higher and not reproducible, and
Measurements of the specific heat at constant volume, $C_V$, of bcc He$^4$ for various molar volumes. The results are displayed both as $C_V$ and as $\theta$.

The samples in the present measurements are described in Table 7 and are shown as: $\bigcirc$, sample 1; $\square$, sample 2 ($V = 21.028 \text{ cm}^3$); $\triangledown$, sample 3 ($V = 21.208 \text{ cm}^3$); $\Delta$, sample 5 ($V = 20.998 \text{ cm}^3$); $\blacktriangle$, sample 7 ($V = 20.943 \text{ cm}^3$); $\theta$, sample 9 ($V = 20.927 \text{ cm}^3$); where the volumes quoted have been fitted to the melting line in the $V$-$T$ diagram of Figure 16 using the measured values of the melting temperature. Ahlers' measurements (see Reference 33) are for the following samples: $\bullet$, $V = 20.955 \text{ cm}^3$; $\times$, $V = 20.940 \text{ cm}^3$; $+$, $V = 20.921 \text{ cm}^3$; where the volumes have also been fitted at the melting line.
the heating curves showed small relaxation effects which were apparently due to small amounts of residual hcp phase which were able to remain for a considerable time. These were probably caused by pressure inhomogeneities: In particular, small regions of slightly higher pressure which were produced during the hcp-bcc transition and which slowly disappeared by the extrusion of the solid through the pores of the sintered copper calorimeter. When all traces of the residual hcp phase had been removed, it was possible to supercool the bcc solid about 10 mdeg or so below the lower phase boundary and to measure the temperature of the phase boundary with some precision (see Figure 24).

Unfortunately we were never able to superheat the bcc solid above its melting point, even after half an hour of annealing. Moreover, the increase in specific heat at melting was not completely sharp but showed a small "tail" up to 20 mdeg before the main discontinuity, although the data in this region were quite reproducible both on cooling and heating. These phenomena indicate that freezing probably left some small regions of slightly lower than normal pressure or density which we were unable to remove by annealing.

Figure 23 also shows the data of Ahlers (33) obtained at the high temperature end of the bcc phase. Both his data and ours lie rather close to one curve and can be represented to within about 3% of $C_V$ by a Debye formula with $\theta = 16.95^\circ K$ for all densities. This behavior is similar to that of the thermal conductivity measured by Berman and Rogers (58) which, when plotted against temperature, also lies on one curve irrespective of density. Ahlers has interpreted his specific heat results as indicating that the bcc phase has some
Figure 24

Temperature of the calorimeter vs time taken from a recorder tracing. At $t = 0$ the sample (number 5, Table 7) is in the (supercooled) bcc state and is cooling by heat loss through a superconducting indium thermal switch. At $t = 1.8$ min the heat capacity is determined in this supercooled state. Just after $t = 3$ min, hcp solid begins to appear and the calorimeter is heated slightly by the latent heat of transformation. At $t = 5.5$ min, the drift rate is steady once more and hcp and bcc are judged to be very near to equilibrium. Assuming that the rate of heat loss is constant over this small temperature range, extrapolation of the curves gives the bcc-hcp boundary in the absence of supercooling to be $1.612 \pm 0.001^\circ$K.
\[ AQ = 21.6 \text{ ergs} \]
anomalous properties in the high density part of the phase diagram, in
agreement with a theory of Goldstein (59) which predicts anomalous thermal
properties of the solid near the intersection of the $\lambda$ line with the melting curve.
Ahlers bases his conclusions partly on the fact that in his experiments the
specific heat appears to decrease with increasing molar volume at fixed
temperature (see Figure 23). In our experiments the tail or premelting effect
in the heat capacity makes the temperature and volume dependence of $C_V$ or $\Theta$
difficult to determine, but $C_V$ appears to increase with increasing $V$, which is
the behavior observed in bcc He$^3$ and in hcp He$^3$ and He$^4$.

The Entropy

The specific heat measurements on some samples (3, 6, 8, and 9 in
Table 7) extend from the hcp phase past the lower triple point, $T_1$, and across
the two-phase hcp + bcc region. From these measurements we have been able
to obtain the entropy of the bcc phase of He$^4$ by integrating $C_V/T$ and adding the
appropriate entropy change at $T_1$. The results for the entropy at the transition
curve are given in Figure 25 as the square symbols. The experimental error
indicated in the graph is approximate and is based on the estimated 10%
accuracy of the heat capacity measurements in the two-phase region where the
thermal relaxation time is long. The figure also gives a value of $S$ at the lower
triple point, $T_1$ (the closed circle). This was obtained by adding $(\Delta S_1)_{\text{max}}$
(Figure 22) to the entropy of the mixture of hcp He$^4$ and liquid He$^4$ which
transforms to bcc He$^4$ at $T_1$. The entropy of the (hcp + liquid) mixture was
determined from the data on hcp He$^4$ given in Chapter III, the entropy of
TABLE 7. The samples of solid He$^4$. The table gives the initial or freezing pressure, $P_f$; the directly measured volume per mole of the sample, $V_{\text{meas}}$; the observed values of the bcc melting temperature, $T_{\text{melt}}$; the temperature at the hcp-bcc transition line, $T_{\text{tr}}$; and the freezing temperature, $T_f$. The volumes in parentheses below the values of $P_f$, $T_{\text{melt}}$, $T_{\text{tr}}$, and $T_f$ have been calculated from them using the PVT data of Grilly and Mills, corrected where necessary with Eq. 15.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>$P_f$ (atm) ±0.02 atm</th>
<th>$V_{\text{meas}}$ (cm$^3$) ±0.04 cm$^3$</th>
<th>$T_{\text{melt}}$ (°K) ±0.003</th>
<th>$T_{\text{tr}}$ (°K) ±0.002</th>
<th>$T_f$ (°K) ±0.002</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.0 (21.08)</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>2</td>
<td>46.2 (21.07)</td>
<td>...</td>
<td>1.632 (21.028)</td>
<td>1.561</td>
<td>...</td>
</tr>
<tr>
<td>3</td>
<td>46.3 (21.06)</td>
<td>21.11</td>
<td>1.632 (21.028)</td>
<td>...</td>
<td>2.237 (21.11)</td>
</tr>
<tr>
<td>4</td>
<td>46.3 (21.06)</td>
<td>20.97</td>
<td>1.632 (21.028)</td>
<td>...</td>
<td>2.242 (21.10)</td>
</tr>
<tr>
<td>5</td>
<td>47.3 (21.01)</td>
<td>21.04</td>
<td>1.674 (20.998)</td>
<td>1.612</td>
<td>2.260 (21.06)</td>
</tr>
<tr>
<td>6</td>
<td>47.3 (21.01)</td>
<td>...</td>
<td>1.685</td>
<td>1.627 ± 1</td>
<td>2.284 (21.01)</td>
</tr>
<tr>
<td>7</td>
<td>48.6 (20.94)</td>
<td>20.90</td>
<td>1.730 (20.943)</td>
<td>1.691</td>
<td>2.291 (21.00)</td>
</tr>
<tr>
<td>8*</td>
<td>48.6 (20.94)</td>
<td>...</td>
<td>...</td>
<td>1.708</td>
<td>...</td>
</tr>
<tr>
<td>9</td>
<td>48.7 (20.93)</td>
<td>20.86</td>
<td>1.746</td>
<td>1.712 ± 3</td>
<td>...</td>
</tr>
</tbody>
</table>

*This sample crossed the (hcp + bcc) boundary at 1.482 ± 0.003°K.
The entropy of bcc He\textsuperscript{4} at the hcp-bcc transition line. The solid squares show the entropy by integration of C\textsubscript{V}/T using the present C\textsubscript{V} measurements in the hcp, (hcp + liq), and (hcp + bcc) regions together with the value of the latent heat at T\textsubscript{1}. The solid circle gives the entropy at the lower triple point determined from the maximum value of the entropy change at T\textsubscript{1}, (\Delta S\textsubscript{l})\textsubscript{max}, the entropy of the liquid and the lower triple point from van den Meijdenberg \textit{et al.} (see Reference 60) and the entropy of hcp He\textsuperscript{4} at T\textsubscript{1} (see Chapter III).

The open triangles show S\textsubscript{bcc} = S\textsubscript{hcp} + \Delta V\textsubscript{tr} (dp/dT)\textsubscript{tr} using \Delta V\textsubscript{tr} and (dp/dT)\textsubscript{tr} from Grilly and Mills (see Reference 15 and S\textsubscript{hcp} from Chapter III); the closed triangle gives the same, but using (dp/dT)\textsubscript{tr} from Kierstead (see Reference 57).

The open circles show S\textsubscript{bcc} = S\textsubscript{liq} - \Delta V\textsubscript{m} (dp/dT)\textsubscript{m} - \Delta S' using S\textsubscript{liq} from van den Meijdenberg \textit{et al.}, and \Delta V\textsubscript{m} (dp/dT)\textsubscript{m} from Grilly and Mills. (\Delta S' is a small correction for the difference in entropy below on the melting line and the transition line). The straight line has been drawn through our values of the entropy.
freezing liquid helium at $T_1$ given by van den Meijdenberg, Taconis and Ouboter (60), plus the molar volume data given by Grilly and Mills (15). The inverted open triangles in Figure 25 represent values calculated from the formula $S_{bcc} = S_{hcp} + \Delta S_{tr} = S_{hcp} + \Delta V_{tr}(dp/dT)_{tr}$, where $(dp/dT)_{tr}$ and $\Delta V_{tr}$ were taken from Grilly and Mills. The uncertainty in these points is mainly in the value of $\Delta S_{tr}$ which was estimated to be ±10% by Grilly and Mills. The inverted, filled triangle at $T_2$ was obtained in the same manner but using the new measurements of Kierstead (57) for $(dp/dT)_{tr}$. The open circles in the figure were calculated from $S_{bcc} = S_{liq} - \Delta S_m - \Delta S'$, where $\Delta S_m = \Delta V_m(dp/dT)_m$ is from Grilly and Mills, $S_{liq}$ is from the data of van den Meijdenberg et al. (60), and $\Delta S'$ is a small correction for the difference between the entropy of the bcc phase at melting and at the transition line. $\Delta S'$ was estimated from the present heat capacity data and amounts to 4% of $S_{bcc}$ at most. As the figure shows, all the values of $S_{bcc}$ are in good agreement, within the expected errors, with the smoothed curve through the present data.

The entropy results together with the specific heat have been used to give some information about the possible temperature dependence of the Debye theta of bcc He$^4$ in the temperature range down to 0°K. In this region, of course, the hcp phase and the liquid are the thermodynamic equilibrium states but, in principle, the bcc solid could exist in a metastable "supercooled" state. The hypothetical temperature dependence of $\theta$ in this region has been studied by plotting the ratio of the entropy to the specific heat, $S/C_V$, versus a function of the specific heat, $T/\theta$, which is approximately proportional to the temperature.
The graphs for hcp He$^4$, for bcc He$^4$, and some results for bcc and hcp He$^3$ are all given in Figure 26. The specific heat measurements on the He$^3$ phases were made by the same technique as in the present work. The He$^3$ entropies were calculated by direct integration of the specific heat for $T/\theta \geq 0.025$. For $T/\theta < 0.025$, the Debye entropy was assumed, thus ignoring spin entropy and effects due to He$^4$ impurity. Figure 26 also shows graphs of $\theta/\theta_0$ versus $T/\theta$ for the different forms of solid helium. ($\theta_0$ is the value of $\theta$ at 0°K.) It may be seen that the entropy-specific heat curves reflect the dependence of $\theta$ on $T/\theta$ very well. The points for bcc He$^4$ lie very close to the curves for the other forms of solid helium, which all have very similar $\theta/\theta_0 - T/\theta$ curves, which suggests that the specific heat and Debye $\theta$ of "supercooled" bcc He$^4$ would have approximately the same temperature dependence as the other forms of solid helium. The agreement is closest with the $S/C_V$ curve for bcc He$^3$ of approximately the same molar volume ($V = 20.43 \text{ cm}^3$), so that we have used this curve to extrapolate our $\theta$ values for bcc He$^4$ to 0°K. The results of this calculation are given in Table 8.

<table>
<thead>
<tr>
<th>Molar volume $V (\text{cm}^3)$</th>
<th>20.927</th>
<th>20.932</th>
<th>20.988</th>
<th>21.028</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\theta_0$</td>
<td>21.2</td>
<td>21.1</td>
<td>20.95</td>
<td>20.8</td>
</tr>
</tbody>
</table>

TABLE 8. The Debye $\theta$ of bcc He$^4$ extrapolated to 0°K. Units are °K. The error is ±0.4°K.
Figure 26

$S/C_v$ versus $T/\theta$ for the various low-pressure helium structures; the dashed line gives the curve for the Debye model. The insert to the figure shows $\theta/\theta_0$ versus $T/\theta$ for hcp He$^4$ and bcc He$^3$ (hcp He$^3$ is nearly the same as hcp He$^4$ and is not shown).
\[ S/C_v \] versus \[ T/\Theta \]

- hcp He\(^3\)(18.31 cm\(^3\))
- bcc He\(^3\)(20.43 cm\(^3\))
- bcc He\(^4\)

DEBYE

References:
The calculated values of \( \theta_0 \) for "supercooled" bcc He\(^4\) have approximately the same dependence on \( V \) as the other solid helium allotropes in this volume range. These have a Gruneisen constant \( \gamma = 2.6 \), so that 
\[ \theta_0 \propto V^{-2.6} \]
It is interesting to compare the magnitudes of \( \theta_0 \) in the four low pressure forms of solid helium: the ratio \( \theta_0(\text{He}^3)/\theta_0(\text{He}^4) \) at a given volume is 1.17 for the hcp structure, much closer to the "classical" harmonic value \( \sqrt[4]{4/3} = 1.155 \) than that for the bcc structure which is 1.23.

**The Phase Diagram**

We have already described the method of measuring the temperature of the (hcp + bcc) - (bcc) phase boundary, above and in the caption of Figure 24. The melting temperature of the bcc phase was more difficult to determine because of the tail or premelting before the main discontinuity in heat capacity and because of the size of the temperature intervals used in measuring the heat capacity. The melting point appeared as a very steep rise in heat capacity, less than a few millidegrees wide, giving values for the melting temperatures to about \( \pm 0.003^\circ\text{K} \). In order to make a meaningful comparison of these results with those of previous workers, we have fitted our melting points to the smoothed melting V-T curve for bcc He\(^4\) obtained by Grilly and Mills (15) (open circles in Figure 16), corrected using the formula suggested by Ahlers (33) (Eq. 15). This procedure was used to determine the molar volume by Ahlers, whose points are shown as open triangles. As Figure 16 shows, with the volumes normalized in this way the data from all three sources are in good agreement.
As explained in the description of experimental technique, we have also measured the molar volume of our samples directly by measurements on the gas at room temperature, and less directly, by determining the freezing point of the hcp phase and then using Grilly and Mills' melting curve data (15, 14). These values, which are given when available in Table 7, are in fair agreement with each other and the values used in Figure 16, although the discrepancies are slightly larger than 0.2% in V, the expected experimental accuracy.

The Compressibility

Since bcc He$^4$ exists over only a narrow range of density and temperature, one would expect that the compressibility $\chi = -(1/V)(\partial V/\partial p)_T$ is fairly constant over the whole bcc region of the phase diagram. Approximate values of $\chi$ can be calculated in a number of ways from the available experimental data:

(i) From the pressure, volume, and temperature (PVT) along the phase boundaries, one can calculate the average isothermal compressibility across the phase. In Figure 28 the curve marked PVT was calculated in this way by Ahlers (33).

(ii) From the discontinuous change in heat capacity, $\Delta C_V$, at the boundaries of the bcc phase using the thermodynamic equation (48, 49),

$$\chi = (T/V\Delta C_V)(dV/dT)^2$$ (16)
where \( \frac{dV}{dT} \) is the slope of the phase boundary in the V-T diagram (Figure 16). The \( \Delta C_V \) data for both boundaries of the bcc phase have been collected in Figure 27 which shows that Ahlers' (33) measurements and the present ones are in fairly good agreement. The compressibilities calculated with Eq. 16 from the smoothed curves for \( \Delta C_V \) and from \( \frac{dV}{dT} \) obtained from Grilly and Mills' (15) measurements are shown in Figure 28 as the curves \( A_t \) and \( A_m \). Here \( A_t \) refers to the bcc compressibility along the hcp-bcc transition line; \( A_m \) refers to the melting line. These curves are similar to the ones published by Ahlers but extend to lower temperatures.

(iii) From the variation of \( V \) with pressure along the phase boundaries, using the Gruneisen equation for the isobaric expansion coefficient, \( \alpha = \frac{1}{V} \left( \frac{3V}{3T} \right)_p = \gamma \frac{C_V}{V} \), to correct for the change in \( V \) caused by thermal expansion. This method results in the equation:

\[
x = \frac{\frac{dV}{dT}}{\gamma C_V - V \left( \frac{dp}{dT} \right)} \]

where \( \gamma \) is the Gruneisen constant which we have assumed to be approximately 2.6 (see the discussion above on the entropy of bcc \( \text{He}^4 \)). The values of \( x \) calculated from Eq. 17 for bcc \( \text{He}^4 \) along the melting curve are shown in Figure 28 by the curve \( B_m \).

(iv) The quantity \( \frac{dV}{dT} \) along the phase boundaries can be eliminated from the calculation of \( x \) by combining Eqs. 16 and 17:

\[
x = \frac{V \Delta C_V}{T \left[ \gamma C_V - V \left( \frac{dp}{dT} \right) \right]^2}
\]

This method gives the closed circles for the compressibility on the transition line and the closed squares for the melting line. The approximate experimental
Figure 27

The change in heat capacity at constant volume $\Delta C_V/R$ at the bcc phase boundaries as a function of temperature. The open symbols refer to the hcp-bcc transition line, the closed symbols to the melting line.
\[ \frac{\Delta C_v}{R} \]

- \( \circ \)-AHLERS
- \( \triangle \)-PRESENT

\( \text{bcc} \rightarrow (\text{bcc+liq}) \)

\( (\text{hcp+bcc}) \rightarrow \text{bcc} \)

\( T, (^\circ K) \)
The isothermal compressibility $\chi$ of bcc He$^4$ as a function of temperature. The points were calculated from Eq. 18. The squares refer to the melting line and the circles are for the hcp-bcc transition line. The line C represents some unpublished direct measurements of $\chi$ along the melting line by Grilly (see Reference 61). The other curves are explained in the text.
error indicated on these points has been estimated from the uncertainty in $\Delta C_V$ and $\gamma$. (The term in $\gamma$ has only a small effect on the results for $x$.) The average value of these points is $x = (3.8 \pm 0.2) \times 10^{-3}$ atm$^{-1}$.

Curve C in Figure 28 represents some unpublished, direct measurements (61) by Grilly. These extend from $x = 3.4 \times 10^{-3}$ atm$^{-1}$ at $1.48^\circ$K to $4.2 \times 10^{-3}$ atm$^{-1}$ at $1.74^\circ$K with a scatter of about 5% in $x$. Another direct measurement, by Kidder (62) and not shown in Figure 28, gives $(4.7 \pm 0.3) \times 10^{-3}$ atm$^{-1}$ between 1.55 and $1.7^\circ$K.

The values of $x$ from method (iv), i.e., from Eq. 18, are self-consistent within the experimental error in that the results for the transition line are the same as those along the melting line and are independent of temperature. They also agree with the preliminary direct measurements of Grilly. The wide variations in $x$, which are given by the first three methods described above, are probably due to small inaccuracies in the volume-temperature data which are not sufficiently accurate to give derived quantities like $dV/dT$.

The Expansion Coefficient

The isobaric expansion coefficient of bcc He$^4$ can, like the compressibility, also be estimated in a number of ways from the experimental data which are presently available. The methods are similar to the ones for the compressibility discussed above. For instance, the expansion coefficient can be obtained as an average across the bcc phase using Figures 16 and 17. Another way is by using values of $dV/dT$ and $\Delta C_V$ as in method (ii) for the
compressibility. Such calculations, which have been discussed by Ahlers (33),
give values of $\alpha$ which vary widely with temperature and volume and in some
cases give negative values of $\alpha$. The discussion of the compressibility above
has shown that the variation of $V$ with $T$ is not known sufficiently accurately at
present for such calculations to be at all reliable. Moreover, Kidder (62) has
shown by direct measurement that the isobaric expansion coefficient is positive
and less than $10^{-2}$ deg$^{-1}$ between 1.57 and 1.72°K. Self-consistent values of $\alpha$
can be obtained by eliminating $dV/dT$ from the input data. Using the equation
$dV/dT = V[\alpha - \chi(dp/dT)]$ with Eq. 16, one obtains:

$$\alpha = \chi(dp/dT) + (\chi \Delta C_v/V T)^{1/2}. \quad (19)$$

The result of applying Eq. 19 to the melting curve is shown as the squares in
Figure 29, while the results along the transition line are shown as circles.
These two sets of values are quite consistent with each other and also with those
from a completely different method, curve G, which was calculated from the
Gruneisen equation, $\alpha = \gamma \chi C_v/V$, using $\gamma = 2.6$.

**Elastic Anisotropy**

The elastic properties of bcc $\text{He}^4$ can be studied with the help of the
velocity of longitudinal sound measured by Vignos and Fairbank (23, 52), and
the recent measurements of the velocity of shear waves by Lipschultz and Lee
(63). The sound measurements are consistent with the values of the compressi-
bility in Figure 28 if we assume the samples studied in the sound experiments
were isotropic, since the equation $v_L^2 = (1/\chi p) + (4v_t^2/3)$, appropriate to an
The expansion coefficient $\alpha$ of bcc He$^4$ as a function of temperature. The continuous line $G$ is calculated from the Gruneisen equation, $\alpha = (\gamma \kappa C_v/V)$, assuming $\gamma = 2.6$. The points are calculated from Eq. 19, $\alpha = \kappa (dp/dT) + (\kappa \Delta C_v/VT)^{1/2}$. The circles are for the hcp-bcc transition, the squares for the melting line. The compressibility $\kappa$ was estimated from Figure 28, $V$ and $(dp/dT)$ from Grilly and Mills, $C_v$ and $\Delta C_v$ from Ahlers and the present work.
isotropic (or polycrystalline) solid gives a value of $3.8 \times 10^{-3}$ atm$^{-1}$, in excellent agreement with the present data. (It is estimated that the difference between the adiabatic and isothermal compressibilities is about 2%.)

If the bcc He$^4$ crystal were itself isotropic, the value of the Debye theta at 0°K, $\theta_0$, could be calculated from the equation:

$$
\theta_0 = \frac{\hbar}{k} \left( \frac{6\pi^2N_0}{V} \right)^{1/3} \left( \frac{2}{3v_t^3} + \frac{1}{3v_L^3} \right)^{-1/3}
$$

if $v_t$ and $v_L$ are the sound velocities at 0°K. This equation gives $\theta_0 = 35°K$, which is very high compared to the values of $\theta_0$ in Table 8 ($\sim 17°K$). This result demonstrates that bcc He$^4$ is elastically highly anisotropic. The scatter in the velocity of sound measurements from one specimen to another was quite small (23 52, 63), so that we can deduce that all the sound measurements were made on polycrystalline specimens containing a large number of crystals.

Recently, Nosanow and Werthamer (64) have developed a theory of the vibrational modes of both bcc and hcp solid helium and have given values for the principal sound velocities for He$^4$ and He$^3$ at various densities. Their theory shows that both structures should be very anisotropic. We have compared the present results with the theory by calculating the elastic constants $c_{11}$, $c_{12}$, and $c_{44}$ from the theoretical sound velocities. From these elastic constants we have obtained $\chi$, the compressibility at 0°K, and $\theta_0$, the Debye theta at 0°K. For $V = 21.00$ cm$^3$, the theoretical value of $\chi$ is about $3.4 \times 10^{-3}$ atm$^{-1}$, in good agreement with experiment; the theoretical value of $\theta_0$, obtained by the
"semi-analytic" method described by de Launay (65) is 24.5°K, again in fairly good agreement with the values in Table 8.

Conclusion

In summary, our data indicate that bcc He⁴ is probably not much different from the other forms of solid helium. This is based upon the following results discussed in detail above:

(a) The compressibility χ and the expansion coefficient α are well behaved. The expansion coefficient is positive and agrees with the Gruneisen equation with a Gruneisen constant γ = 2.6, which is the value found for the other low-pressure forms of solid helium and which is not inconsistent with the variation of the Debye θ with volume in the present measurements. As was illustrated in Figure 28, the V-T data available at present are not precise enough to use dV/dT to obtain either χ or α, so that earlier calculations which gave negative values of α are unreliable.

(b) The entropy of bcc He⁴ when plotted as S/Cᵥ versus T/θ (Figure 26) is found to be consistent with the values for the other low-pressure, crystalline forms of He⁴ and He³, indicating that the temperature dependence of θ and the lattice spectra are very similar.
APPENDIX A

Electronic Bridge

The temperature of the paramagnetic thermometer, cerium magnesium nitrate CMN, was inferred from the magnetic susceptibility by using Curie's law $\chi = C/T$ which is obeyed by CMN down to several hundredths of a degree K. The magnetic susceptibility was measured by a set of concentric solenoidal mutual inductance coils in the circuit of an electronic mutual inductance bridge of the Hartshorn type. This bridge which was originally used by Pillinger has been adapted for the present use. The bridge was used in conjunction with a recorder in order to give a continuous record of the temperature. This arrangement was similar to that used by J. L. Baum and A. S. McWilliams.

A simplified discussion of the electronics is presented here for those who may not be familiar with the principles involved. For a more exact and complete discussion the reader is referred to the above-mentioned references which are the bases of the present discussion.

By considering the simplified schematic diagram, Figure 30, the basic operation of the bridge can be understood by analyzing the voltages introduced into the secondary circuit of the bridge through the inductors, M, M_s, m, and the resistance network $r_1$, $r_2$, and R, when the variable parameters $\rho$
Figure 30

A simplified schematic diagram of the electronics for measuring the temperature of the cerium magnesium nitrate thermometer.
and R are adjusted for a null current in the secondary. The signal generator introduces a 150 cy/sec signal into the primary circuit which induces a voltage $\omega M_{ip}$ in the secondary circuit through the fixed mutual inductance of the "bucking" coil, M. A voltage $\omega M_{s} i_p$ is induced through the mutual inductance of the thermometer coil, $M_s$, which contains the paramagnetic salt pill. Furthermore, a signal $i_p \rho$ is introduced on the grid of the triode which introduces a signal in the artificial primary circuit $\omega G_{ip} \rho$ which in turn induces a voltage in the secondary circuit by the inductor $\mu$ of value $\omega m G_{ip} \rho$ (G is a constant, the effective transconductance). Finally through the resistive network $r_1$, $r_2$, and R, there is a voltage introduced in the secondary circuit of value $R_{\text{eff}} i_p$ ($R_{\text{eff}}$ is the resistance of the network). It should be noted that for ideal inductors the voltage induced in the secondary circuit through the inductor M is 180° out of phase with that induced by $M_s$, in phase with that induced by $\mu$, and 90° out of phase with the voltage introduced through the resistive network by the primary current. However, due to the non-ideality of the inductors there may be present in the secondaries of the inductors a "loss component" which is in phase with the primary current. The bucking coil is nearly identical to the thermometer coil so when the paramagnetic salt is removed from the coil, the voltages induced through M and $M_s$ nearly cancel. Then, when the paramagnetic salt is inserted in the $M_s$ coil, the voltage induced in the secondary circuit of the cryostat coils is due mainly to the paramagnetic susceptibility of the salt pill. The voltage induced in the cryostat coils by the presence of the paramagnetic salt can be cancelled in order to obtain a null current in the
secondary by adjusting the voltage induced through $m$ which is proportional to $\rho$. Furthermore, it can be shown that the susceptibility of the CMN pill will be directly proportional to $\rho$ (42). (It might be pointed out that in general with a null balance the value of $\rho$ is proportional to the susceptibility only for a spherical pill; however, CMN is such a weak paramagnetic salt that its shape becomes important only at the very lowest temperatures, for the present pill much below 0.1°K.)

Since the paramagnetic salt CMN obeys Curie's law $\chi = C/T$ in the temperature range of interest, and since $\chi$ is proportional to $\rho$ for a null balance, then we may write $\rho = A/T - B$, where the constants $A$ and $B$ are determined from a temperature calibration against the vapor pressure scale of liquid He$^4$.

The above method of measuring the temperature (i.e., by adjusting $\rho$ and $R$ to obtain a null in the secondary) is quite adequate for measuring the temperature if the temperature of the thermometer is steady or slowly varying. However, for specific heat measurements it is highly desirable to have a continuous record of the temperature; therefore, a recorder was used in conjunction with the bridge. To understand how the temperature was determined from the recorder trace, consider the paramagnetic salt at some temperature $T'$ with the bridge parameters $\rho$ and $R$ adjusted for null balance; then $\rho = A/T' - B$. If the temperature now changes to some new value $T' + \Delta T'$, an additional voltage $\Delta V$ will be induced on the secondary circuit which is directly proportional to the change in the susceptibility. The voltage $\Delta V$ is
picked up by the linear amplifiers, sent through the chopper to be converted to d.c., and then to the d.c. recorder. In response to $\Delta V$ the recorder indicates a deflection, $\Delta 1$, which is directly proportional to $\Delta \rho$, the amount $\rho$ is off null balance. Writing $\Delta \rho = \alpha \Delta 1$, the new temperature $T' + \Delta T' = T$ is obtained from the relation $\rho + \alpha \Delta 1 = A/T - B$. Solving for the temperature, $T = A/(\rho + \alpha \Delta 1 + B)$.

The phase shifter which is before the chopper is adjusted so that only the pure inductive component of the off-balance signal is received by the d.c. recorder. That is to say, the phase shifter is adjusted so that any resistive, "loss component," or the component due to the imaginary part of the susceptibility of the CMN which would be in phase with the primary current and which may be temperature dependent, will not contribute to the signal sent to the recorder. With the phase shifter adjusted as indicated above, one can see from the simplified schematic diagram that the X axis of the oscilloscope beam is swept back and forth in phase with the pure inductive component. Since the off-balance signal is fed into the Y axis of the oscilloscope one can see that a pure inductive off balance would produce a slanted line on the oscilloscope, while a pure resistive or "loss component" would produce an ellipse. By the shape of the figure on the oscilloscope one can then tell which components are present in the off-balance signal. This arrangement is a great aid in adjusting $R$ and $\rho$ to obtain a null balance.

Presented in Figure 31 is a block diagram of the electronics for the magnetic thermometer. The filters between the tuned Philbrick amplifier and
Figure 31

A block diagram of the electronic components used for measuring the temperature of the thermometer salt pill.
BLOCK DIAGRAM OF THE ELECTRONICS

AMPLIFIER AND PHASE SHIFTER

OSCILLATOR (GR 1301-A)

TRANSFORMER (UTC LS-33)

HARTSHORN ELECTRONIC BRIDGE WITH CRYOSTAT COILS

NULL BALANCE POTENTIAL AND RECORDER WHEELCO 8000-1600

OSCILLOSCOPE (DUMONT 304-AR)

TRANSFORMER (UTC LS-12X)

ATTENUATOR AND FILTER

TUNED AMPLIFIER (GERTSCH TNI-I)

BRIDGE PREAMPLIFIER

CHOPPER STEVENS-ARNOLD (NL 61296-1)

FILTERS

TUNED AMPLIFIER (PHILBRICK WITH TWIN T)
the chopper are a set of low-pass, high-pass filters used to reduce the 60 cycle pick-up and its harmonics. A schematic diagram of the Philbrick operational amplifier used in conjunction with a White "Twin T" filter in a feed-back loop which is tuned to 150 cy/sec is presented in Figure 32. The phase shifter, chopper, and cryostat coils are described by McWilliams (38). The remaining components are commercial products as indicated. A circuit diagram of the bridge pre-amplifier is presented in Figure 33.

**Filament Supply Circuit**

The accuracy of the temperature measurements depends upon the stability of the electronic circuits and the most critical component of the whole system is the electronic bridge and specifically the electronic tube which controls the artificial primary current. Good stability required that the filament voltage be controlled to about 2 parts in $10^5$. In order to get this degree of stability at a reasonable cost, the circuit presented in Figure 34 was used. A battery eliminator in parallel with a lead storage battery being charged at about 20 ma provided a rather stable voltage supply. The stability of the voltage supply was monitored by a micro-ampere meter and dry cell battery placed in parallel with the voltage supply (see Figure 34). The battery eliminator, the resistor $R_1$, and the resistor $R_2$ were adjusted so that the lead storage battery was changed at a rate of about 30 ma while the dry cell battery was being discharged at a rate of 2 $\mu$a. Any significant drift in the stability of the voltage supply could be observed on the micro-ampere meter and corrected
Figure 32

The circuit diagram of the tuned amplifier as used in Figure 31. The operational amplifier was made by the Philibrick Manufacturing Company and the "Twin T" filter was made by the White Instrument Laboratories.
Figure 33

The circuit diagram of the bridge pre-amplifier.
Figure 34

Filament supply circuit used to control the filament supply voltage to about 2 parts in $10^5$. 
FILAMENT SUPPLY CIRCUIT

1.8 Ω

50 mA

±50 μA

LOAD

S1

S2

S3

1.0 Ω

R1

20 Ω

6 V.
STORAGE
BATTERY

R2

100 Ω

6 V.
DRY CELL

BATTERY
ELIMINATOR 6V

50 mA

Thesis - K. C. Pandorf
by adjusting $R_1$ and $R_2$. Through switch $S_1$ the lead storage battery could be charged directly. The switch $S_2$ was placed in the circuit to short out the 50 ma meter.
APPENDIX B

Calorimeter Heater Circuit

In performing specific heat measurements it is necessary to dissipate a known quantity of energy in the calorimeter of such magnitude that the temperature of the calorimeter will rise by an increment appropriate to its temperature. For the present experiments this requires that energy be dissipated in the calorimeter at a rate ranging from 1 erg/sec to $10^6$ ergs/sec (depending on the value of the specific heat) over an accurately measured period of time of the order of 3 sec. The circuit as presented in Figure 35 was designed to meet this requirement.

There are two current loops of the circuit for dissipating electrical energy in the calorimeter heater. With switch $S_H$ "on," Figure 35, the current loop through the battery (of voltage $V$), the resistance box (of value $Z$), the 1K standard resistor, and the calorimeter heater (of resistance $R$) will dissipate energy in the heater at a rate $W = \frac{RV^2}{(Z + X)^2}$. $X$ is the resistance of the standard resistor, the heater, and lead resistance. This loop of the circuit is used to heat the calorimeter during a specific heat measurement, and the length of time of the heating pulse is measured by the timer. The timer measures the time interval between two events when the two events are represented by voltage changes on separate input channels. Thus, in flipping switch $S_H$ "on,"
Figure 35

The calorimeter heater circuit diagram.

The components of the circuit consist of the following:

1. 12.6 V lead storage battery.

2. Keithley Model 660 d. c. differential voltmeter with a quoted error of 20 µV in the range 100 µV to 10 mV and ±0.02% in the range 100 mV to 500 V.

3. Hewlett-Packard 5233L electronic counter used as a timer.

4. Resistance box Z₀ (Model C-37) made by the Electro-Scientific Industries with a quoted accuracy ± 0.03%.

5. Resistance box Z made by General Radio with a quoted accuracy of ± 0.05%.

6. 1K ohm standard resistor made by Leeds & Northrup with a quoted accuracy of ± 0.005%.
Figure 35, a voltage is applied to start input channel of the timer and to the heater at the same instant. At the end of the heating period switch $S_H$ is thrown "off" and a voltage is applied to the stop input channel of the timer. The timer then counts the time in milliseconds that electrical power was delivered to the calorimeter heater through the resistance box $Z$. The capacitors are used in the timer circuit to eliminate d.c. leakage to the ground.

On the other hand, with $S_H$ "off" and $S_A$ "on", there is the auxiliary current loop through the battery, the resistance box (of value $Z_0$), the standard resistor, and the heater which will dissipate energy into the heater at a rate $W_0 = RV^2/(Z_0 + X)^2$. This loop of the circuit is used to control the rate of temperature drift of the calorimeter due to heat leakage into the cooling salt pill through the indium heat switch.

Circuits are also provided for determining the resistance $R$ of the calorimeter heat by measuring the current flow through the calorimeter heater and the voltage drop across it. Also a circuit for measuring the voltage $V$ of the lead storage battery is provided.

The calorimeter heater was made from polyurethane coated Evanohm wire made by the Wilbur B. Driver Company. The heater resistance was about 1000 ohms at room temperature but was temperature dependent below 4°K (see reference 66). In computing the heating rates $W$ and $W_0$, this dependence was taken into account. Separate potential and current leads were used up to the calorimeter vacuum jacket while (superconducting) 0.003" niobium current
leads were used from the vacuum jacket to the Evanohm heater. The niobium leads were spot welded at all joints.
APPENDIX C

Molar Volume Measurement

In order to compute the specific heat of a sample it is necessary to know the number of moles of substance contained in the calorimeter during the experiment. Knowing the volume of the calorimeter and the molar volume of the sample, the number of moles contained in the calorimeter can be determined. The molar volume of the sample can be determined in a number of different ways. Using the PVT melting curve data, the molar volume can be determined from the melting temperature as well as the freezing temperature of the sample. Also, since the helium sample is solidified at constant volume using the blocked capillary method, the molar volume can be determined from the freezing pressure by using the melting curve data. In addition to the above methods of determining the molar volume, which depend on the melting curve data, the molar volume can be determined directly by expanding the solid helium sample into a known volume; then from the temperature and pressure the molar volume can be computed. This latter method used to directly measure the molar volume of the sample in the calorimeter will now be described.

After the completion of the specific heat measurements, the state of the system would be such that solid helium would exist in the calorimeter and in the section of the filling tube between the calorimeter and the top of the vacuum
jacket. The section of the filling tube between the top of the vacuum jacket (which was at 1.2°K) and the top of the cryostat (at room temperature) was enclosed in a vacuum, and provisions were made to heat this section of tubing with an electric current; therefore, this section of the filling tube contained mostly gaseous helium at high pressure. In view of these circumstances it was assumed that all the helium sample below the top of the vacuum jacket, denoted by volume $V_J$ (Figure 36), was in the solid phase while all the helium above the top of the vacuum jacket in volume $V_D$ was in the gaseous phase. The cryostat and system for measuring the molar volume is illustrated in Figure 36. Due to the small cross-sectional area of the filling tube, an error of 10 cm in estimating the boundary between the solid and gaseous helium in the filling tube would cause an error in the determination of the molar volume of about 0.3%.

Any gas let out of the high pressure part of the system (i.e., from volumes $V_D + V_J$) into the low pressure part was let into the volumes consisting of the volume of the known standard volume $V_S$, the volume of the connecting tube $V_G$, and the volume of the pressure side of the mercury manometer $V_M$ (which was directly proportional to the pressure). The volume of the low pressure section was thus given as $(V_S + V_G + V_M)$. The molar volume of the helium sample was determined by measuring the total number of moles $n_t$ of helium in the volume $V_D + V_J$ in a manner that revealed the number of moles $n_D$ of gaseous helium in the volume $V_D$. The molar volume of this sample was then given as $(n_t - n_D)/V_J$. 
An illustration of the experimental arrangement for measuring the molar volume which includes the helium cryostat, a pressure strain gauge, a standard (known) volume, $V_s$, and a mercury manometer.
The number of moles $n_D$ was determined by letting the high pressure gas in $V_D$ into the volume $(V_S + V_M + V_G)$ in a series of steps continuing up to the point the solid helium began to melt. Letting $n_{Di}$ represent the number of moles of gas allowed into the volume $(V_S + V_M + V_G)$ after the $i$th step, then

$$n_{Di} = \pi_i (V_S + V_M + V_G)/RT,$$

where $\pi_i$ is the pressure as read on the mercury manometer. Moreover, the number of moles $n_{Di}'$ of gas remaining in $V_D$ after the $i$th step can be written as $P_i V_D/ZRT$ where $P_i$ is the strain gauge pressure.

By the conservation of matter $n_D = n_{Di} + n_{Di}'$, so that $n_{Di} = n_D - n_{Di}'$, and from the above we may write $n_{Di} = \pi_i (V_S + V_M + V_G)/RT = n_D - (P_i/Z)V_D/RT$.

A graph of the $n_{Di}$ versus $P_i/Z$ was then made for the five or six points taken, and $n_D$ was determined by extrapolating $P_i/Z$ to zero.

The total number of moles $n_t$ of helium occupying the volume $V_S + V_D$ was measured by letting all the helium sample into the volume $(V_J + V_D) + (V_S + V_M + V_G)$ and allowing the calorimeter to warm up to near room temperature. The total number of moles was then given as

$$n_t = \pi (V_J + V_D + V_S + V_M + V_G)/RT,$$

where $\pi$ was the pressure as read on the mercury manometer. The number of moles $n_J$ was then given as $n_J = n_t - n_D$.

Knowing the volume of the calorimeter $V_C$, the number of moles $M$ contained in the calorimeter was $M = n_J V_C/V_J$, and the molar volume was given as $V_J/n_J$.

In Figure 37 is presented a diagram of the helium handling and storage system.
Helium sample storage and handling system. The low pressure section consists of the storage bottles X, Y, Z, P₁, P₂, A, B, C, D, E, 1, 2, 3, 4, the liquid nitrogen charcoal trap (for removing condensible vapors), a mercury manometer and standard volume (used to calibrate unknown volumes of the system), the Toepler pump (used to transfer helium gases and also used as one of the known volumes), and a vacuum pumping system consisting of a mercury diffusion pump and a rotary pump (used for pumping the manometer and purging the system of unwanted gases). The high pressure section consists of the calorimeter, a pressure strain gauge (used in determining the sample pressure at freezing and in measuring the dead volume gas), the small dead volume high pressure valves 1 and 2, a bourdon gauge (used as a convenience to indicate the pressure) and the condensing system used to liquefy the low pressure helium gas sample for producing high pressure.
APPENDIX D

Analysis of the Recorder Record of a Specific Heat Point

The method used to compute the specific heats from the recorder record was basically the same as that used by J. L. Baum (46) and A. S. McWilliams (38); however, to illustrate some of the limitations and assumptions of this method a brief analysis will be given.

When the temperature of the calorimeter was below 0.7°K, the isolation of the calorimeter from the surrounding was reasonably good; however, as the temperature of the calorimeter was raised above 0.7°K, the isolation became progressively worse mainly due to the heat conduction through the indium thermal switch; for above 0.7°K the conductivity of the normal and superconducting states of pure indium approach each other rapidly. The temperature drift of the calorimeter due to this heat leakage was controlled by electrical power supplied to the calorimeter by an auxiliary circuit (Figure 35) at a rate $W_0$. Below 0.7°K additional forms of heat leakage, however, attributed a greater share of the total (for example, electromagnetic pick-up, mechanical vibration, conduction along leads, supports and filling tube, conduction due to the residual exchange gas and adsorption and desorption on the walls of the calorimeter). The total rate of leakage $W_L$ due to these various sources was assumed to be of the form $W_L = K(T^n - T_0^n)$ where $K$, $T_0$, and $n$
are constants and \( T \) the temperature of the calorimeter. Due to the good thermal contact between the copper calorimeter and the thermometer and between the calorimeter and its contents, the observed temperature \( T \) was assumed to represent the temperature of the calorimeter along with its contents at all times.

Illustrated in Figure 38 is an exaggerated example of a case in which heat conducted out of the calorimeter caused it to cool rapidly which would have made it difficult to obtain an accurate specific heat measurement, so at time \( t_0 \) heat was supplied to the calorimeter at a rate \( W_0 \). The temperature-time course of the calorimeter was then observed long enough to predict its course of travel. At time \( t_1 \) the power supplied to the calorimeter was increased from \( W_0 \) to \( W \). (This was controlled by switch \( S_H \), Figure 35, which turns off the auxiliary heating \( W_0 \) and turns on the heating \( W \) and the timer.) At time \( t_2 \) the power delivered to the calorimeter was reduced from \( W \) to \( W_0 \) again, and the temperature-time course of the calorimeter was observed long enough to predict the course of the calorimeter. From this record the specific heat of the calorimeter and contents were determined by constructing an ideal heating curve (dotted line, Figure 38) from which the temperature rise \( T_{c'} - T_{a'} \) corresponding to the heat pulse \( (W - W_0)(t_2 - t_1) \) could be determined. The ideal path was constructed as depicted in Figure 38 by drawing a line parallel to the temperature axis such that the area \( aa' \) equaled the area \( cc' \). The specific heat for the ideal curve is given as \( C = \frac{\Delta Q}{(T_{c'} - T_{a'})} \) where \( \Delta Q \) is the heat injected into the calorimeter to cause the instantaneous temperature rise.
Figure 38

An illustration of the temperature of the calorimeter as a function of the time during a specific heat measurement in the temperature range 1 to 2°K. The scale has been distorted and exaggerated in order to give equal emphasis to all the main features.
RAPID COOLING OF CALORIMETER

HEATING INTERVAL 
($t_1$ to $t_2$)

AUXILLARY HEAT
SUPPLIED TO
CALORIMETER

TIME

TEMPERATURE OF CALORIMETER

IDEAL PATH

$t_0$ $t_1$ $t_2$
from \( T_a' \) to \( T_c' \). A justification for these latter remarks will now be given.

From Figure 38 it is apparent that the total heat which entered the calorimeter along the actual path abc must equal the total heat which would enter the calorimeter along the ideal path aa'bc'c. Thus:

\[
\int_{t_1}^{t_2} (W - W_L) dt = \Delta Q + \int_{t_1}^{t_2} (W_o - W_L) dt
\]

where the subscripts A and I indicate integration over the actual and ideal paths respectively. Solving this equation for \( \Delta Q \), one obtains:

\[
\Delta Q = (W - W_o)(t_2 - t_1) + \int_{t_1}^{t_2} (W_L) dt - \int_{t_1}^{t_2} (W_L) dt.
\]

Setting \( W_L = K(T^n - T_0^n) \) and writing \( T^n = (T_a' + \Delta T)^n = T_a^n(1 + n\Delta T/T_a' + \ldots) \), one can show for \( \Delta T/T_a' \ll 1 \) that the two above integrals cancel when the areas aa'b and cc'b are equal.

The recorder record of the specific heat point was in terms of the bridge parameter \( R_0 \) (or \( \rho \)) versus time; however, since \( T = A/(R_0 + B) \), one can show for \( \Delta T/T_a' \ll 1 \) that \( \Delta T \) is directly proportional to \( \Delta R_0 \). Therefore, the ideal heating curve can also be constructed on the \( R_0 \) vs t recorder record using the equal area scheme to determine the initial and final value of \( R_0 \) which corresponds to the heating pulse \( (W - W_0)\Delta t \). In order to keep the error in the specific heat due to the temperature interval within 1%, the interval was held within the limit \( \Delta T/T = \Delta R/(R + B) < 1/20 \).
Calculation of the Specific Heat by Computer

Upon completion of an experiment it is highly desirable to know the results before the next experiment in order to evaluate the operation of the apparatus and the experimental procedure so that possible improvements and preparations may be made in the next experiment so as to bring out significant aspects of the data. Since the hand calculation of the specific heat results is a long, laborious and highly repetitive job, it was decided to systematize the computations of the specific heat calculation by programming it on a computer, thereby greatly shortening the time between the experiment and its results which meant in most cases that the results of an experiment were available before the next experiment.

The computer program was set up on an IBM 7094 to determine for each experimental point the specific heat of the contents of the calorimeter, the temperature and the Debye $\theta$. The symbols used in the computer program are sometimes necessarily different from the symbols used in the previous discussion; therefore, definitions of the symbols used in the program, as well as in the previous discussion are given in Table 9. The following is an abstract of the program requirements.
### TABLE 9. Definition of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALPHA, α</td>
<td>Calibration of the recorder chart in terms of ( R_0 ) (or ( \rho )).</td>
</tr>
<tr>
<td></td>
<td>( \alpha = \Delta R_0 / \Delta L ).</td>
</tr>
<tr>
<td>AL1, L1</td>
<td>The value of the chart recorder immediately before a supposed ideal specific heat measurement.</td>
</tr>
<tr>
<td>AL2, L2</td>
<td>The value of the chart recorder immediately after a supposed ideal specific heat measurement.</td>
</tr>
<tr>
<td>C</td>
<td>The specific heat of the calorimeter and its contents in ergs/°K.</td>
</tr>
<tr>
<td>CC, C_C</td>
<td>The specific heat of the empty calorimeter in ergs/°K.</td>
</tr>
<tr>
<td>CH</td>
<td>The specific heat of the calorimeter helium sample in ergs/°K.</td>
</tr>
<tr>
<td>CD</td>
<td>The specific heat as ( CD = C_V / 3R ) (( R = ) gas constant).</td>
</tr>
<tr>
<td>CVIR</td>
<td>The specific heat of the helium sample in units of ( R ), i.e., ( C_V / R ).</td>
</tr>
<tr>
<td>DT, ΔT</td>
<td>The temperature interval °K of the specific heat point.</td>
</tr>
<tr>
<td>IRTS</td>
<td>A control symbol for the ( R ) vs ( T ) table which indicates when a new table is to be introduced (( R = ) heater resistance).</td>
</tr>
<tr>
<td>KA, A</td>
<td>The slope of the CMN thermometer calibration curve when plotted as ( R_0 ) vs 1/T.</td>
</tr>
<tr>
<td>KB, B</td>
<td>The negative of the ( R_0 ) intercept of the CMN thermometer calibration curve when plotted as ( R_0 ) vs 1/T.</td>
</tr>
<tr>
<td>KX, X</td>
<td>The value of the lead resistance plus the calorimeter heater resistance ( R ) at 4°K plus the standard resistor of the heater control circuit (Figure 35) in units of ohms.</td>
</tr>
<tr>
<td>KPNT</td>
<td>The number assigned to the specific heat point for identification.</td>
</tr>
<tr>
<td>N</td>
<td>The number of specific heat points in a given experiment.</td>
</tr>
<tr>
<td>NEXP</td>
<td>The number of experiments in a given run with the computer.</td>
</tr>
<tr>
<td>NTB1</td>
<td>The number of points in the CC vs T table.</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>NTB2</td>
<td>The number of points in the CD vs X table.</td>
</tr>
<tr>
<td>OM, M</td>
<td>The number of millimoles of helium sample contained in the calorimeter.</td>
</tr>
<tr>
<td>Q</td>
<td>The number of ergs of heat supplied to the calorimeter during a specific heat measurement.</td>
</tr>
<tr>
<td>R</td>
<td>The resistance in hecto-ohms of the calorimeter heater which is a function of temperature.</td>
</tr>
<tr>
<td>RO, R₀, ρ, r</td>
<td>The setting of the electronic bridge decade potentiometer which controls the artificial primary current of the bridge and which is proportional to the susceptibility of the CMN thermometer at null balance.</td>
</tr>
<tr>
<td>T</td>
<td>The average temperature °K of the calorimeter during a specific heat measurement.</td>
</tr>
<tr>
<td>THETA, θ</td>
<td>Debye θ, deg K.</td>
</tr>
<tr>
<td>TM</td>
<td>The length of time in milliseconds of the heating interval during a specific heat measurement.</td>
</tr>
<tr>
<td>T₁, T₂</td>
<td>The temperature of the calorimeter immediately before the supposed ideal specific heat measurement.</td>
</tr>
<tr>
<td>T₀, T₂</td>
<td>The temperature of the calorimeter immediately after the supposed ideal specific heat measurement.</td>
</tr>
<tr>
<td>V</td>
<td>The voltage of the battery supplying the power to the calorimeter heater (Figure 35).</td>
</tr>
<tr>
<td>W</td>
<td>The power supplied to the calorimeter heater during a specific heat measurement.</td>
</tr>
<tr>
<td>W₀</td>
<td>The power supplied to the calorimeter heater in order to control its temperature drift.</td>
</tr>
<tr>
<td>X</td>
<td>X = θ/T.</td>
</tr>
<tr>
<td>Z</td>
<td>The value in kilo-ohms of the resistance box (Figure 35) used to control the power supplied to the calorimeter heater during a specific heat measurement.</td>
</tr>
<tr>
<td>------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>ZO, Z₀</td>
<td>The value in kilo-ohms of the resistance box used to control the power supplied to the calorimeter heater in order to control its temperature drift.</td>
</tr>
</tbody>
</table>
Program abstracts: For each series of experiments there exist tables of quantities CC vs T and CD vs X. Each experiment is characterized by the fixed run parameters: KA, KB, N, V, KX, OM, and the table R vs T. In each experiment there are the variable input quantities KPNT, AL1, AL2, TM, RO, Z, ZO, ALPHA, which take on N successive values. For each of the N values of the variable input quantities the program computes and prints the output quantities: KPNT, T1, T2, DT, Q, C, CH, CVIR, T, THETA. The quantities KPNT, CVIR, T, and THETA are punched out on cards. One obtains the output quantities from the input quantities by the following definitions:

\[ T_1 = \frac{KA}{(RO + KB + ALPHA*AL1)} \]
\[ T_2 = \frac{KA}{(RO + KB + ALPHA*AL2)} \]
\[ T = \frac{(T_1 + T_2)}{2} \]
\[ DT = T_1 - T_2 \]
\[ Q = (W - WO)*TM \]

where \( W = \frac{R*V^2}{(Z + KX* .001)^2} \) and \( WO = \frac{R*V^2}{(ZO + KX* .001)^2} \). The quantity R is obtained by making a linear interpretation from a table of R vs T.

\[ C = \frac{Q}{DT} \]
\[ CH = C - CC \]

CC is obtained by making a linear interpolation from the table CC vs T.

(Continued...
where $X = (77.927/CD)^{1/3}$ for $CD < .023$. For $CD > .023$ the value $X$ is obtained by making a linear interpretation from the table $CD vs X$.

If for some reason the computer is not able to compute all the output quantities for a given set of variable input, the computer prints out those output variables which it is able to compute and then continues to the next set of variable input. Upon completion of the computation of the set of $N$ variable input for a given experiment, the computer continues to the next experiment and performs the same operations until all experiments have been computed.

The operations as outlined above have been written in machine operations as outlined in the flow chart (Figure 39) and as stated more exactly in the program tables (Table 10). For the convenience of the user the card formats are illustrated in Table 11, and the deck order is presented in Figure 40.
Figure 39

7094 Scatran flow chart for the computation of the specific heat and Debye $\theta$
SUMMARY OF VARIABLE AND LABEL USAGE

MAIN PROGRAM

STATEMENT LABELS

SPHC LCOP1 WR1 LOOP2 TOR M1 MP2 CCOK MP3 XOR

F1 F2 F3 F4 F5 F6 F7 F8 F9

INTEGER VARIABLES

NTB1 I NTB2 NEXP J KA KB N KK IR1S

FPNI ISW

FLOATING POINT VARIABLES

HEAU T CC CD X TI KT TMN V OM

ALI AL2 TM K I Z ZC ALPHA TI F2 DT

K W M U C U CH CVIR THETA

GENERAL STORAGE ASSIGNMENTS

HEAU T CC CD X TI KT SPHC F1 NTB1

F1 F2 I VR2 F3 F4 VEXP LOOP1 J F6

F5 F7 KA KH V U KK OM IR1S WR1

F12 VR11 TP F11 F12 F9 LOOP2 F10 FPNI AL1

AL1 TM K I Z ZC ALPHA TI 12 DT TOR

K W MP1 W MP2 C L ISW J CCOK

F12 F17

SUBPROGRAM LABELS

STATEMENT LABELS

T1P1 TH1 S1CH1 TH1 TH2 S1CH1 F1N F85 F87 F86
INTEGER VARIABLES
NO ISW L VU
FLOATING POINT VARIABLES
U GVU FND FFND
UNIVERSAL VARIABLES
LOOP ? TMN KPN
GENERAL STORAGE ASSIGNMENTS
L TNP1 TNP2 TNP3 TNP4 TNP5 TNP6 TNP7 TNP8 TNP9 TNP10 TNP11 TNP12 TNP13 TNP14
FND FND FND FND FND FND FND FND FND FND FND FND FND FND FND FND
DUMMY CALLING PARAMETERS
U INC GVU FND ISW
SUBPROGRAM "HINT"
STATEMENT LABELS
LOCATE
INTEGER VARIABLES
L
FLOATING POINT VARIABLES
K T T T T T T T T T T T T T T T T T
GENERAL STORAGE ASSIGNMENTS
LOCATE I I K I I I I I I
DUMMY CALLING PARAMETERS
A T T T K
SUMMARY OF EXTENSION NAME USAGE
FLOATING POINT EXTENSION NAMES
RINT TABLE ENDJON
SOURCE LANGUAGE EXTENSION NAMES
RINT TABLE
INPUT OUTPUT EXTENSIONS
KESYS KMPLS PUNCH
SOURCE LANGUAGE STATEMENTS

1 C NENT=NUMBER OF ELEMENTS IN T, CC TABLES -

2 C NTH1 = NUMBER OF ELEMENTS IN T, CC TABLES -

3 C NTH2 = NUMBER OF ELEMENTS IN CD, X TABLES -

4 C NEXP = NUMBER OF EXPERIMENTS -

5 C PROGRAM PRINTS AND Punches EACH NEW CASE -

6 DIMENSION (HEAD(12),1(100),CC(100),CD(200),X(200),111(I0),PI(1)) -

7 SPHC READ INPUT ,F1,(WH1,IM1).

8 READ INPUT ,F2,(1T(I),CC(I),I=1,1,LE.NTH1)) -

9 READ INPUT ,F1,(NTB2) -

10 READ INPUT ,F3,(CD(I),X(I),I=1,1,LE.NTB2)) -

11 READ INPUT ,F4,(NEXP) -

12 DU THROUGH (LOOP1),J=1,1,J.LE.NEXP -

13 READ INPUT ,F6,((HEAD(I),1=1,1,1.LE.12)) -

14 WRITE OUTPUT ,F5,((HEAD(I),1=1,1,1.LE.12)) -

15 READ INPUT ,F7,(KA,KB,N,V,KX,OM,IKTS) -

16 TRANSFER (WH1) PROVIDED (IKTS.E.0) -

17 READ INPUT ,FF0,(NENT,(IT(I),RT(I),I=0,1,1.LE.NENT)) -

18 WH1 WRITE OUTPUT ,F8,(KA,KB,V,KX,OM) -

19 WRITE OUTPUT ,FR11,((IT(I),1=1,1,1.LE.NENT)) -

20 WRITE OUTPUT ,FR12,((NT(I),1=0,1,1.LE.NENT)) -

21 WRITE OUTPUT ,FV -

22 DU THROUGH (LOOP2),J=1,1,J.LE.N -

23 READ INPUT ,F10,(KPNT,AL1,AL2,TM,RC,Z,20,ALPHA) -

24 T1=KA/(KU+KB+ALPHA*AL1) -

25 T2=KA/(KU+KB+ALPHA*AL2) -

26 T=(T1+T2)/2.0 -

27 DT=T2-T1 -

28 TRANSFER (TOR) PROVIDED (T.L.TT(I0).OR.T.G.TT(NENT-I)) -
R=RI NT . (TT,RT,T) –
W=R*(V/(Z+K*X*.001))*(V/(Z+K*X*.001)) –
TRANSFER TO (MP1) PROVIDED (Z0=L.0.0) –
W0=K*(V/(Z0+K*X*.001))*(V/(Z0+K*X*.001)) –
TRANSFER TO (MP2) –
MP1 : W0=0.0 –
MP2 : Q=(W-W0)*TM –
C=Q/DT –
ISW=0 –
U=TABLE . (NTB1,T,CC,ISW) –
TRANSFER (CCOK) PROVIDED (ISW,E.0) –
WRITE OUTPUT ,FCCER , (KPNT,T1,T2,DT,Q,C,T) –
TRANSFER (LOOP2) –
CCOK : CC=U –
CH=C-CC –
CD=CH/(2*51C,0*UM) –
CVIR=3.0*CD –
TRANSFER TO (MP3) PROVIDED (CD,L.023) –
ISW=0 –
U=TABLE . (NTB2,CD,X,ISW) –
TRANSFER (XOK) PROVIDED (ISW,E.0) –
WRITE OUTPUT ,FXER , (KPNT,T1,T2,DT,Q,C,CH,CVIR,T) –
TRANSFER (LOOP2) –
XOK : X=U –
TRANSFER TO (MP4) –
MP3 : X=(77.927/CD) . P . 33333333333 –
MP4 : THE ETA=X*T –
WRITE OUTPUT , TEMP , (CC,X) –
WRITE OUTPUT , F11 , (KPNT,T1,T2,DT,Q,C,CH,CVIR,T,THE ETA) –
PUNCH CARDS, F12, (KPNT, GVNR, T, THETA) -

LOOP2 CONTINUE -

LOOP1 CONTINUE -

CALL SUBROUTINE (1=ENDJOB, 1) -

FUNCTION (U)*TABLE. (NO,GVN,FND,ISW) -

DIMENSION (GVN(200), FND(200)) -

UNIVERSAL (LOOP2, TMIN, KPNT) -

L = 1 -

TRANSFER TO (TBPI) PROVIDED (GVN(1), G. GVN) -

TRANSFER TO (TBEI) PROVIDED (GVR(I), F. GVN) -

DO THROUGH (SKCM), i = 1, i = L, i = G

END LOOP 1

TRANSFER TO (TBEI) PROVIDED (GVNI(1), G. FGN) -

SKCM CONTINUE -

YJ = L -

TRANSFER TO (TBEI) -

TB1 TRANSFER TO (TBEI) PROVIDED (GVNI(I), E. GVN) -

TB2 GO THROUGH (SKCH), L = 1, L = L, L = 10 -

TB3 TRANSFER TO (TB4) PROVIDED (GVNI(L), E. GVN) -

SKCH CONTINUE -

ISW = 1 -

NORMAL EXIT -

TB4 TRANSFER TO (TBEI) PROVIDED (GVNI(L), E. GVN) -

TB5 TRANSFER TO (TBS) PROVIDED (GVNI, G. TMIN) -

FND = FND(L - 1) -

TB6 TRANSFER TO (TB7) -

TB7 FND = FND(L - 1) -

U = ABS. (ABS. (FND(L - 1)) - I. ABS. (GVNI-GVNL - 1)) / (I. ABS. (GVNI(GVNL - 1))) + FND -

TB6 NORMAL EXIT -
97   TEP1  PU THRU (SKCH1),L=1C,F10,F2,LE+NO-
98   N3-L=9-
99   TRANS: X 10 (Tan) PROVIDED (GVV(L),LE,GV4)-
100  SKCH1  CONTINUE -
101  N4-L=9-
102  TRANS: X 10 (Tan2)-
103  T31  TRANS: X 10 (Tan) PROVIDED (GVV(L),LE,GV4)-
104  FL3  Do THRU (SKCH2),L=1D,F10,F2,LE+40-
105  TRANS: X 10 (Tan) PROVIDED (GVV(L),LE,GV4)-
106  SKCH3  CONTINUE -
107  N3=L=1-
108  no-ADL X A -
109  TRANS: X 10 (Tan2)-
110  T41  TRANS: X 10 (Tan)-
111  P1  END SUBPROGRAM -
112  F F1  (15, F7, 4) -
113  F F2  (4F6,2,1X,F9,0,1X))- -
114  F F3  (4F9,7,1X,F6,1,1X))- -
115  F F4  (1X)- -
116  F F5  (1H1,12L6)-
117  F F6  (12L6)-
118  F F7  (1K,1X,15,1X,13,1X,F7,5,1X,14,1X,F6,2,1X,T)-
119  F F8  (1H0,4,2H8*15,4X,2HB*16,4X,2HB*7,3,4X,2HB*15,4X,2HB*F6,2.1)-
120  F F9  (1T/7 HM NP-PT,5X,2HT1,10X,2HT2,10X,2MST1,12N,1M0,13X,1HG,12X,2HCH,T,12X,4HCF/R,11X,1HT,8X,5HMETAF/- 1-
121  F F10  (15X,1F6,2,1X,F4,2,1X,F5,0,1X,F6,0,1X,F5,1,1X,F5,1,1X,F6,0)-
122  F F11  (2X,13,4X,F8,5,4X,F8,5,4X,11L,5,4X,F10,0,3X,F10,0,4X,F11,8,4X,F8,5,3X,F7,2)-
116 F F12 (2X, 14, 3X, F11.8, 3X, F8.5, 3X, F7.2) -
117 F TEMP (2X, 3HCC=F9.0, 2Hx=F6.1) -
118 F FFO (I1,4(F7.1,F6.2)) -
119 F FF1 (2X, 13,4X, F8.5,4X,F8.5,4X, F8.5,4X, 1(1H*),4X, 10(1H*), 3X, 10(1H*), 4X, 11(1H*), 4X, F8.5,3X,7(1H*)) -
120 F FRTT (IH0,6X, IHT, 4X, 10(F10.3)) -
121 F FKT2 (1X,1HR,4X,10(F10.3)) -
122 F FCCER (2X,13,4X,F8.5,4X,F8.5,4X,F8.5,4X,E11.5,4X,F10.0,3X,10(1H*),4X,11(1H*),4X,F8.5,3X,7(1H*)) -
123 F FXER (2X,13,4X,F8.5,4X,F8.5,4X,F8.5,4X,E11.5,4X,F10.0,3X,F10.0,4X,E11.8,4X,F8.5,3X,7(1H*)) -
124 FUNCTION (R)=RINT.(T),(RT,T,T) -
125 DIMENSION (TT(0),RT(0)) -
126 LOCATE DO THROUGH (LOCATE),I=1,1,(I.G.TT(1)) -
127 W=TT(I)-TT(I-1) -
128 H=RT(I-1)-RT(I) -
129 W1=TT(I)-I -
130 HT=W1*H/W -
131 R=RT(I)+HT -
132 NORMAL EXIT -
133 END SUBPROGRAM -
134 TOR WRITE OUTPUT ,FF1,(KPNT,T1,T2,DT,T) -
135 TRANSFER (LOOP2) -
136 END PROGRAM (SPHC) -
### CARD FORMATS FOR SPECIFIC HEAT COMPUTATIONS - 7094 SCATRAN

#### F1
| 1 | 3 | F13 |

#### F3
| 13 | F97 | F61 | F97 | F61 | F97 | F61 | F97 | F61 |

#### F5
| CD1 | CD2 | X11 | CD3 | X12 | CD4 | X13 | CD5 | X14 |

#### F7
| 14 | 15 | 13 | 11 | F13 | 10 | F62 | 9 |

#### F9
| NHT | NT | NT | NT | NT | NT | NT | NT | NT |

#### FF0
| 11 | F71 | F63 | F71 | F63 | F71 | F63 | F71 | F63 |

### DEBYE THETA TABLE

### RUN PARAMETERS

### HEATER RESISTANCE vs TEMPERATURE TABLE

### SPECIFIC HEAT POINTS

| 13 | F42 | F32 | F50 | F60 | F51 | F31 | F60 |

### TITL AND HEADING CARD

### NT21 TMAP
Figure 40

Deck order for the specific heat program.
7094 SCATRAN
DECK ORDER
FOR SP. HT.
COMPUTATIONS

To be repeated
for each experiment
except as noted.*

*The R vs T table may be deleted for succeeding experiments in which case IRTS must
be 0. If a new table is to be used (as is always true for the first experiment),
IRTS must be 1.


18. R. H. Sherman and E. J. Edeskuty, Symposium on Liquid and Solid He$^3$ (Ohio State University, Columbus, 1957), p. 44.
19. R. L. Mills and E. R. Grilly, Symposium on Liquid and Solid He\textsuperscript{3} (Ohio State University, Columbus, 1957), p. 100.


42. W. L. Pillinger, Ph.D. Thesis (Ohio State University, 1958).
46. J. L. Baum, Ph.D. Thesis (Ohio State University, 1961).
47. O. V. Lounasmaa, Cryogenics 1, 212 (1961).


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