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THE HEAT CAPACITY OF SOLID He4 AT MOLAR VOLUMES BETWEEN 20.5 AND 21.1 cm³/MOLE

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Gardner, William Reavis.

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THE HEAT CAPACITY OF SOLID He$^4$ AT MOLAR VOLUMES BETWEEN 20.5 AND 21.1 cm$^3$/mole

William Reavis Gardner
(Ph.D. Thesis)
August 1966
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THE HEAT CAPACITY OF SOLID He\textsuperscript{4} AT MOLAR VOLUMES BETWEEN 20.5 AND 21.1 cm\textsuperscript{3}/mole

William Reavis Gardner

Inorganic Materials Research Division, Lawrence Radiation Laboratory, Department of Chemistry, University of California, Berkeley, California

August 1966

ABSTRACT

The heat capacity of He\textsuperscript{4} has been measured under constant-volume conditions from 0.32°K to the melting curve and at fourteen volumes ranging from 20.50 to 20.934 cm\textsuperscript{3}/mole. The measurements offer a significant increase in precision over other recently reported data and thus provide more definite answers to several outstanding questions. A linear term of 1.25 T millijoules/mole-°K was found in the heat capacity of the hcp phase, independent of volume and thermal history to within the precision of the measurements. Otherwise the hcp solid was found to be well-behaved and to have a Grünneisen constant of 3.2±0.1 in this region. The thermal expansion coefficient was found to be definitely positive throughout the hcp phase and 90 percent of the bcc phase, although the possibility of a negative coefficient near the low-temperature limit of the latter phase cannot be ruled out conclusively. The heat capacity of the bcc solid depends very strongly on density, exhibiting values of 8 to more than 30 for the Grünneisen γ. For this solid no discontinuity in C\textsubscript{v} is observed at the melting temperature, but the onset of melting is preceded by a narrow region of steeply increasing heat capacity which appears to be due to vacancy formation.
The PVT relations in the vicinity of the bcc phase have been studied by Grilly and Mills. The phase diagrams resulting from their work, with the hcp-bcc-liquid triple points adjusted to conform to the values obtained by other workers, are shown in Figs. 1 and 2. The justification for this adjustment will be discussed in detail in a later section.

The possibility of anomalous thermal properties immediately suggests the desirability of measuring the heat capacity of the bcc phase, and in 1963 Ahlers obtained $C_v$ data for three volumes lying near the high temperature, high density end of the phase. His experiments were restricted to volumes of less than 20.98 cm$^3$/mole and thus cover only about one fourth of the region of existence of the bcc phase. He concluded that at constant temperature $C_v$ increased with decreasing volume, requiring that the temperature derivative of $\alpha/\kappa$ be negative. By conventional notation $\alpha$ is the thermal expansion coefficient $V^{-1}(\partial V/\partial T)_p$ and $\kappa$ is the compressibility $V^{-1}(\partial V/\partial P)_T$. The precision of his data was such, however, that the results could be fit almost as well by a volume-independent heat capacity. Because of the limited extent of Ahlers' experiments and the inconclusiveness of his results, it was decided to complete the investigation of the bcc phase by constructing an apparatus which could contain a sample at any desired density.

In addition to providing direct information about the thermal properties of bcc He, heat capacity measurements along a series of isochorcs provide a means for completing the phase diagram in the volume-temperature plane. Grilly and Mills report only the volume of the liquid along the melting curve, the change in volume on melting $\Delta V_m$, and the volume change $\Delta V_{tr}$ for the solid-solid transformation.
Fig. 1. Pressure-temperature diagram of $^4$He in the region near the bcc phase.
Fig. 2. Volume-temperature diagram of He^4 in the region near the bcc phase.
The volumes of the two solid phases along the bcc-hcp transition curve are therefore left undefined except to the degree that they are specified by the extent of the bcc phase in the pressure-temperature plane and the approximate average compressibility reported by Grilly and Mills for the bcc phase. By observing the temperature limits of the solid phases along several isochores, as shown by discontinuities in the heat capacities, this part of the phase diagram could be completed.

It was also hoped that extension of $C_V$ measurements to lower temperatures would elucidate the volume-temperature relations for the hcp phase at temperatures below 1°K. The melting curve of hcp He$^4$ was established by Grilly and Mills down to 1.28°K, the volume at this temperature lying within the range encompassed by the bcc phase at 20.990 cm$^3$/mole. The nature of the volume-temperature relations at lower temperatures is of particular interest due to the recent discovery by Wiebes and Kramers$^9$ of a very shallow minimum in the melting pressure curve at 0.76°K, suggesting the possibility of a maximum in the hcp volume. This phenomenon, which for different reasons is also observed in He$^3$, was also predicted by Goldstein$^1$ and has since been studied more quantitatively by LeFair et al.$^{10}$ by Sydoriak and Mills,$^{11}$ and by Zimmerman.$^{12}$

The heat capacity of the hcp phase below 1°K is also of considerable interest. The only previous work in this region is that of Heltemes and Swenson,$^{13}$ who observe an anomalous contribution to the heat capacity in excess of that expected for a simple Debye solid. Within the precision of their data, this excess is fitted to an Einstein model having two volume-dependent energy levels of unspecified origin.

Franck$^{14}$ has interpreted his $C_V$ measurements in the temperature range above 1.5°K and at volumes of 10.8 to 16.3 cm$^3$/mole as showing a contribution
to the heat capacity which is linear with temperature. He has further concluded that the magnitude of this excess contribution is decreased by annealing, suggesting that it may be due to crystalline imperfections in the samples. Franck cites a theory by Granato in which such a linear specific heat term is derived for pinned line dislocations. An independent study of the heat capacity, preferably extending from well below 1°K up to the melting curve, was evidently needed to clarify this contradictory situation.

In an effort to answer as many as possible of these outstanding questions the decision was made to measure $C_v$ along several isochores, concentrating on the region around the bcc phase and the maximum volume of the hcp phase (20.9 to 21.1 cm$^3$/mole) and extending from approximately 0.3°K to the upper limit of the bcc solid.

Edwards and Pandorf have recently published the results of a similar series of experiments, but most of the questions raised above have been left unresolved.
II. EXPERIMENTAL TECHNIQUES

A. Calorimeter

A He³-cooled calorimeter, basically of conventional design but incorporating a unique sample container, was constructed for these experiments. The low-temperature portion of the apparatus is shown in schematic form in Fig. 3 and the supporting He³ system in Fig. 4.

The copper He³ chamber is thermally isolated from the He⁴ bath by making the pumping tube and other permanent connections of thin-section stainless steel. An air-actuated mechanical clamp serves to establish thermal contact between the He³ and He⁴ reservoirs when desired, and a similar mechanical switch is used to control thermal contact between the He³ heat sink and the sample container.

In order to avoid the various problems associated with use of the blocked-capillary technique for containing solid samples under pressure, a cell was constructed which featured an internal bellows-sealed needle valve. Arrangements were made so that the cell could be filled at cryogenic temperature, the valve closed by remote control, the actuating mechanism separated from the cell, and the filling tube evacuated. The design of this cell is shown in Fig. 5.

The cell was made from Beryllco 25 beryllium-copper alloy. All parts were hardened except the valve needle, which was left in the annealed state in order to allow it to deform against its seat and thus provide a better seal. In order to enhance the effectiveness of this seal, the valve needle was heavily plated with gold and the seating surface with nickel. This combination proved to be effective, as no leakage into the evacuated filling tube could be detected when the cell contained superfluid liquid He⁴ at pressures of nearly 30 atmospheres.
Fig. 3. Internal construction of calorimeter.
Fig. 4. He$^3$ system.
Fig. 5. Valved sample cell.
The most obvious advantage of this cell is its ability to effectively contain a sample of any desired density, limited only by the structural design pressure of the cell. It can therefore be used to obtain heat capacities of pure liquid phases or of liquid-solid mixtures, eliminating the necessity of correcting for a moving interface between the sample and a blocking plug in the capillary. The elimination of solid helium from the capillary also provides improved thermal isolation for the cell, as the solid plug in a blocked-capillary apparatus usually has a thermal conductivity much higher than that of the tube itself.

In order to further minimize the heat leak to the sample, the valve actuator was made in the form of a detachable shaft entering the vacuum space from room temperature through a Wilson seal. A square recess in the end of this shaft engages the square screw head on the cell assembly and serves to operate the valve, the cell being supported against the applied torque by closing the lower heat switch on a square shank.

The shaft is interrupted several inches from its lower end by a brass plug which acts as a trap for radiant heat coming from room temperature down the interior of the tubular shaft. This trap also has an exterior lip which, when the shaft is retracted from the cell, covers the end of the guide tube. Any radiant heat intercepted by this trap is transmitted to the He^4 bath by a short length of 1/8-inch copper braid.

The non-detachable connections contributing to the heat leak between the cell and the He^3 reservoir are two 0.010 in. thick Mylar support disks, twelve electrical leads of 0.0031 in. diameter manganin, and a stainless steel capillary about 12 in. long having an O.D. of 0.042 in. and an I.D. of 0.027 inches. The thermal conductance of these items is sufficiently small that temperature drifts were not a serious hindrance in
measuring the heat capacity of the empty cell. With a sample in the container, of course, the large heat capacity attenuates the temperature drifts even more.

B. Energy Measurement

The amount of heat put into the sample and its container during a heat capacity measurement is \( i^2 R t \), where \( i \) is the DC current passed through a heater, \( R \) is the resistance of the heater wire, and \( t \) is the duration of the heating period.

A 91\% Pt-9\% W wire of 0.0009 in. diameter was wound non-inductively around the sample cell to serve as a heater. The wire, approximately 60 feet long, has a resistance of some 28,500 ohms. Four leads are provided to the heater so that its resistance can be measured without including that of the current leads. The lead resistance (about 10 ohms) is very small compared to the heater, and since only about half the heat generated in the leads goes to the sample, no correction has been considered necessary.

The heating current is measured by observing the voltage drop across a 100 or 1000 ohm standard resistor in series with the heater using a Leeds and Northrup K-3 potentiometer and a non-linear electronic null meter.

The lengths of heating pulses are measured to ±0.1 millisecond with a Hewlett-Packard electronic timer.

The sum of all cumulative errors involved in the energy measurements is approximately 0.05 percent, thus assuring that the more troublesome matter of accurately measuring relatively small changes in temperature constitutes the only significant source of error.
C. Temperature Measurement

Two Minneapolis-Honeywell germanium resistance thermometers were attached to the cell by soldering a strip of copper foil to the exterior wall, rolling the thermometers in this foil, and using General Electric 7031 varnish for thermal contact and mechanical security. The leads were wrapped twice around the cell and varnished in place.

Thermometer resistances were measured potentiometrically, the off-balance signal from the potentiometer being amplified and displayed on a chart recorder. A standard resistor of appropriate size was connected in series with each thermometer in order to provide a measure of the current. The basic elements of this system are shown in Fig. 6.

As each thermometer performs a quite specific function and their calibrations were handled somewhat differently, it seems desirable to describe them and their modes of use separately.

1. Low-resistance Thermometer:

Most germanium resistance thermometers are not useful below about 1°K because their resistances become intractably high. Since much of the work of this laboratory is done with He$_3$ cryostats operating from 0.25°K upward, several special low-resistance units have been obtained from Minneapolis-Honeywell for use in this temperature range. These thermometers characteristically have resistances of about 30 ohms at 4.2°K, increasing to some 300 to 500 ohms at 0.3°K.

The case of the thermometer used in these experiments was filled with an atmosphere of He$_3$ at room temperature, instead of the usual He$_4$, in an effort to improve the thermal contact between the thermometer capsule and the germanium crystal. Senozan$^{18}$ has established limits for the measuring current which may be passed through a similar He$_4$-filled
Fig. 6. Resistance thermometry system.
thermometer at various temperatures without overheating the germanium chip significantly. The behavior of the He\textsuperscript{3}-filled thermometer appears to be identical, as does that of a nitrogen-filled unit which has been used in this laboratory. The selection of the heat-exchange fluid seems to have little or nothing to do with the internal thermal transfer characteristics of the thermometer, leading one to the conclusion that thermal contact to the germanium chip must be established through its electrical leads. In view of these considerations, working currents were selected which did not raise the temperature of the resistance element more than $2 \times 10^{-4} \text{°K}$ above that of its surroundings.

The thermometer resistance was calibrated as a function of temperature between 1.1 and 4.2 \text{°K} by comparing it with the 1958 scale of He\textsuperscript{4} vapor pressures. Above the $\lambda$ point a vacuum-jacketed vapor pressure bulb was used, and below the $\lambda$ point the vapor pressure was measured in the space above the liquid helium bath.

The calibration was extrapolated to 0.24 \text{°K} with a Curie-law magnetic thermometer using a sphere machined from single crystals of cerium magnesium nitrate, Ce\textsubscript{2}Mg\textsubscript{3}(NO\textsubscript{3})\textsubscript{12} $\cdot$ 24H\textsubscript{2}O.

The thermometer was also calibrated up to 25 \text{°K} by comparison with hydrogen vapor pressures, a two-bulb helium gas thermometer, and a National Bureau of Standards platinum resistance thermometer.

The calibration data were fitted by the method of least squares to the equation

$$\frac{1}{T} = \sum_{i=0}^{5} a_i (\log R)_i^i$$

and the fractional residuals plotted and smoothed as a function of computed temperature. Temperatures derived from resistances via this equation and
deviation plot should differ from the 1958 He\textsuperscript{4} vapor pressure scale by no more than 0.001°K between 1.2 and 4.2°K. The validity of the temperature scale below this range has been established by Shen,\textsuperscript{19} who used a similar thermometer which was calibrated concurrently with this one to measure the heat capacity of pure copper. His results agree well with accepted values at all points between 0.3 and 4.2°K, the maximum deviation occurring at about 0.45°K where Shen's data are nearly 0.5% higher than expected.

2. High-resistance Thermometer:

A conventional He\textsuperscript{4}-filled germanium thermometer was included in the apparatus because of its greater sensitivity and was used primarily for measurements in the bcc phase. The resistance of this unit is about 1800 ohms at 4.2°K and approximately 23,000 ohms at 1.1°K.

This thermometer was calibrated at sixteen points between 1.09 and 2.16°K by comparing its resistance with that of the low-resistance thermometer.

While the heat transfer considerations described above limit the working current for this thermometer to about 1 microampere if the true resistance-temperature relation is desired, it was decided in the interest of increased sensitivity to use a current of 4.7µA in both the calibration and the experiments, relating the temperature to the apparent resistance of the thermometer. Although it is estimated that at the lower end of the temperature range the actual temperature of the germanium crystal was some 14 millidegrees above that of its surroundings, the measuring current in heat capacity experiments was kept very close to that used in the calibration so that the temperature did not depart from this apparent relation by more than a few microdegrees.
When a fitted equation is used in conjunction with a plot of smoothed differences to represent the relation between resistance and temperature, it can be shown that the error in computing a temperature difference (and thereby a heat capacity point) is dominated by the uncertainty in the slope of the difference curve. Working over such a limited temperature range, it seemed advisable to reduce the number of nodes and inflections in the difference plot by using an equation having the smallest workable number of arbitrary constants. The function

\[ T = 60.6286 R^{-0.3674669} \]

was found to represent the data to within 0.5 percent between 1.25 and 2.16°K, yielding a deviation plot having two nodes, one maximum and no inflections.

This approach made it possible to compute temperature differences to \( \pm 1 \times 10^{-5} \)°K or less and this, combined with the enhanced sensitivity (100 to 200 \( \mu \)V/millidegree in the bcc region) allowed the measurement of \( C_v \) over intervals of one to two millidegrees with a precision of \( \pm 1\% \) or better.

D. Heat Capacity of the Empty Cell

The heat capacity of the empty cell was measured several times down to 0.33°K. Attempts to fit the experimental heat capacity to the expression

\[ C = \gamma T + \alpha T^2 \]

failed unexpectedly, the experimental points being systematically high at low temperatures. Various other expressions were tried, and the equation

\[ C = 0.6371 + 2.044T + 0.2892 T^3 \text{ millijoules/°K} \]
was found to give an excellent fit between 0.33 and 2.0°K. Fractional deviations of experimental points from this fit are shown in Fig. 7, the different symbols distinguishing between separate experiments.

The cell had to be dismantled for repairs before run XII as a result of a bellows fracture, and it was therefore necessary to redetermine its heat capacity. Because of the thoroughness with which the functional form of the temperature dependence of the heat capacity had been established, one determination of the new heat capacity was considered sufficient. The fractional deviations of the experimental points from the fitted equation

\[ C = 0.6349 + 2.114T + 0.2234T^3 \ \text{millijoules/°K} \]

are shown in Fig. 8.

The rather large constant term seemed quite mysterious until it was learned that the Berylco 25 alloy contains some 0.2 to 0.3 weight percent cobalt. Crane and Zimmerman\textsuperscript{20} have observed large anomalies in the low temperature heat capacities of dilute alloys of Co in Cu, proportional to the cobalt concentration, which appear to be similar in nature to the unexpected heat capacity observed here in that they exhibit both an increase in the linear term over that for pure copper and a contribution which decreases at a less than linear rate with decreasing temperature.

Dr. J. C. Ho of this laboratory, using a Berylco 25 sample holder in other experiments, has recently observed similar behavior. Ho further has found that the application of a magnetic field increases the magnitude of this anomalous contribution, showing that the source of the anomaly must indeed be magnetic in character.\textsuperscript{21}

This constant term unfortunately constitutes approximately half the total heat capacity of the empty cell at 0.3°K and makes this total about equal to that of the enclosed hcp He\textsubscript{4} at that temperature. Typical scatter
Fig. 7. Heat capacity of empty cell shown as fractional deviations from fitted equation. Different symbols represent separate determinations.
Fig. 8. Heat capacity of empty cell after repairs shown as fractional deviations from fitted equation.
of ±0.5 percent in measurements of low-temperature heat capacities of hcp \( ^4 \text{He} \) could therefore be reduced by about half if the source of this contribution were eliminated. The seriousness of this problem decreases rapidly, of course, as the temperature is increased.

E. **Determination of Sample Densities**

1. **Gas Handling System:**

   A schematic drawing of the gas-handling system is shown in Fig. 9. Its main functions, purification and introduction of samples and determination of their molar volumes, are described below.

   High purity \( ^4 \text{He} \) gas was obtained from the University of California's liquid helium plant. The compressed gas, taken from the input stream of a Joule-Thomson liquefier, had been purified by passing it through silica gel at liquid nitrogen temperature. After prolonged storage in a conventional gas cylinder, however, it was considered prudent to repurify the gas before use, and a liquid nitrogen-cooled charcoal trap was placed in the supply line for this purpose.

   Samples are delivered to this trap from the storage cylinder via a high-pressure regulator and then admitted directly to the cell. Two bourdon tube gauges show the pressures in the trap and in the output line, the output pressure being measured to ±1.5 psi by means of a 0-1500 psi Heise instrument.

   In these experiments the cell was filled with liquid \( ^4 \text{He} \) at 4.22°K using the PVT data of Hill and Lounasmaa \(^{22}\) to estimate the pressure required to provide the desired molar volume. The predicted density could then be used in conjunction with the molar content of the sample, the measurement of which is described below, to calculate the volume of the cell. An average
Fig. 9. Gas-handling System.
of six such determinations yielded a cell volume of 11.773 cm$^3$ with a standard deviation of ±0.009 cm$^3$.

2. Determination of Sample Densities from Gas Volume Measurements:

After most experiments the calorimeter was warmed to liquid nitrogen temperature and the sample released into a pair of copper tanks having a combined volume of 11.798 liters. These tanks are housed in a wooden box, insulated with a sheet of aluminum foil and an inch of styrofoam, and are connected to a constant-volume manometer. The temperature of the tanks and the pressure shown by this manometer give the number of moles in the sample. The necessary correction for the dead volumes (cell, supply line, and high-pressure manifold) in the system was determined by evacuating these volumes, expanding the gas remaining in the tanks into them, and measuring the resulting decrease in pressure.

As mentioned above, these measurements of sample content, when used in conjunction with sample densities predicted from the temperature and pressure of filling and the PVT data of Hill and Lounasmaa$^{22}$ provide a means of determining the volume of the cell. The effects of random errors in the measured quantities are reduced by averaging over several such determinations, and the average cell volume thus obtained can be used to compute the molar volume of any individual sample from the number of moles of gas released.

The standard deviation of 0.08 percent in the cell volume is the result of several random error sources, only one of which is the measurement of gas volumes. Once a value for the cell volume is adopted, however, its uncertainty may be regarded as a systematic error contributing to the inaccuracy, but not to the imprecision, in sample densities. Molar volumes determined in this way are therefore limited in precision only by random errors in the
measurement of gas volumes and must be somewhat more precise than ±0.08 percent. In any case the precision is adequate for use in the computation of molar heat capacities, and the number of moles obtained from gas volume measurements has been used for this purpose when available.

3. Molar Volumes from the Melting Curve:

For purposes of computing derivatives of thermodynamic functions with respect to volume, however, the measurements described above are not sufficiently precise. The entire range of existence of the bcc phase is only about one percent in volume, so the accurate calculation of volume derivatives in this region requires an extremely high degree of precision in volume measurements. The phase boundaries in the V-T plane are so nearly flat and the bcc region so narrow that samples differing in volume by 0.1 percent (0.02 cm$^3$/mole) or less may have no region of overlap in temperature whatever and may have melting points which differ by as much as 40 millidegrees.

This aspect of the phase diagram can be turned to advantage, however. Since melting points were determined to at worst ±0.002°K and in most cases ±0.001°K, comparison of these temperatures with the melting curve reported by Grilly and Mills yields molar volumes with a precision of ±0.001 cm$^3$/mole (±0.005%) or better.

Before Grilly and Mills' phase diagram can be thus used, however, the discrepancies between their values of the triple point temperatures and those reported by other workers must be resolved. Table I gives the values reported by various authors$^{2,6,7,17,23,24}$ for the three triple points involving bcc He$^4$, T$_1$ and T$_2$ designating respectively the lower and upper limits of occurrence of the bcc phase and T$_{mA}$ indicating the intersection of the λ line with the melting curve.
Table I. Triple point temperatures of bcc He\(^4\) (°K): \(T_1\) (hcp-bcc-liquid II), \(T_2\) (hcp-bcc-liquid I), and \(T_{mA}\) (bcc-liquid I-liquid II).

<table>
<thead>
<tr>
<th>Source</th>
<th>(T_1)</th>
<th>(T_{mA})</th>
<th>(T_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vignos and Fairbank(^a)</td>
<td>1.449±0.003</td>
<td>1.765±0.003</td>
<td>1.778±0.003</td>
</tr>
<tr>
<td>Grilly and Mills(^b)</td>
<td>1.437±0.006</td>
<td>1.760±0.001</td>
<td>1.760±0.004</td>
</tr>
<tr>
<td>Ahlers(^c)</td>
<td>1.461±0.001</td>
<td>1.765±0.003</td>
<td>1.773±0.001</td>
</tr>
<tr>
<td>Kierstead(^d)</td>
<td></td>
<td>1.763±0.0001</td>
<td></td>
</tr>
<tr>
<td>Lounasmaa and Kaunisto(^e)</td>
<td></td>
<td>1.762±0.001</td>
<td></td>
</tr>
<tr>
<td>Edwards and Pandorf(^f)</td>
<td>1.463±0.003</td>
<td>1.765±0.002</td>
<td>1.771±0.001</td>
</tr>
<tr>
<td>This work</td>
<td>1.462±0.001</td>
<td>1.760±0.001</td>
<td>1.772±0.001</td>
</tr>
</tbody>
</table>

\(^a\) See Ref. 2
\(^b\) See Ref. 6
\(^c\) See Ref. 7
\(^d\) See Ref. 23
\(^e\) See Ref. 24
\(^f\) See Ref. 17
Ahlers had attributed the discrepancies in $T_1$ and $T_2$ to errors in Grilly and Mills' temperature scale and has applied a linear correction to their temperatures before using their phase diagram to determine his sample volumes in the manner described above. His correction function is defined as

$$T_{\text{Ahlers}} - T_{\text{GM}} = 0.079 - 0.0375 \ T_{\text{GM}} \ (°K)$$

which by definition gives the correct values at $T_1$ and $T_2$. His example, while admittedly a bit arbitrary, was followed by Edwards and Pandorf. While this treatment does not destroy the self-consistency of the melting curve as a basis for volume comparisons, it seems quite unlikely for several reasons that the apparent discrepancies in triple points are due to errors in temperature measurements.

First, an error in the temperature scale alone could not account for Grilly and Mills' conclusion that $T_{\text{m}1} = T_2$. Another error of some sort would be required to cause these two transitions, which occur some 12 millidegrees apart, to appear indistinguishable.

Furthermore, the apparent discrepancy of 22 millidegrees at $T_1$ is not of reasonable magnitude for an error lying solely in temperature measurement, particularly considering the nature of Grilly and Mills' procedures and their extensive experience with low-temperature techniques. Their experimental cell was immersed directly in a liquid $\text{He}_4$ bath (superfluid in this region) and their temperatures were taken from the vapor pressure as measured directly above the bath. Only moderately careful manometry would thus have been required to give temperatures within 2 or 3 millidegrees of the $T_{\text{m}8}$ scale.
Thirdly, and in this lies the resolution of the dilemma, only one of
the triple points was determined directly by Grilly and Mills and it is the
only one for which they claim high accuracy. This point, $T_{mA}$, is seen from
Table I to be in good agreement with the values reported by all other in-
vestigators, strongly suggesting the Grilly and Mills temperature scale is
correct. The solid-solid-liquid triple points were both determined by an
extrapolation procedure in which the authors themselves have limited faith,
as they state that "the triple points in the phase diagram of He$_4$ are
difficult to pinpoint...".

In order to understand the nature and the shortcomings of these extra-
polations, it is necessary to first examine Grilly and Mills' experimental
procedures. Their approach was to determine the pressure-volume relations
along a series of isotherms and establish phase boundaries by the breaks
and discontinuities in these curves. Figure 10 shows the idealized appear-
ance of two such isotherms, curve b passing through the bcc phase between
$T_1$ and $T_{mA}$, and curve a representing a temperature below $T_1$. These curves
were constructed directly from Grilly and Mills' reported values of liquid
volume, $\Delta V_m$, $\Delta V_{tr}$, and approximate pure-phase compressibilities.

The triple points must be obtained from this type of data by extra-
polation of the width of the bcc phase, either in pressure or volume, to
the temperatures at which the width vanishes. The range of volume over
which the bcc phase exists at a given temperature is sufficiently ill-defined
by these experiments that Grilly and Mills decline to report a value for it,
giving instead only the volume change $\Delta V_{tr}$ accompanying the solid-solid
transformation. In fact, it will be shown later that their values for $\Delta V_{tr}$
are also considerably in error. This imprecision in establishing the low-
volume limit of the bcc solid may presumably be attributed to the difficulty
Fig. 10. Idealized isotherms for He\textsuperscript{4} constructed from quantities reported by Grilly and Mills.\textsuperscript{6}
of achieving complete homogeneity in a sample undergoing a solid-solid transition.

The extrapolations for determining the triple points must therefore be performed using the pressure range of the pure bcc phase, \( P_{tr} - P_m \). While this difference is large compared to Grilly and Mills' experimental uncertainties and thus measurable with fair accuracy (±5%) over most of the bcc region, it varies only slowly with respect to temperature except very near the ends of the phase and is therefore extremely difficult to extrapolate reliably.

It is therefore concluded that the apparent discrepancies at the upper and lower triple points are much more likely to be due to errors of interpretation than to actual errors in temperature measurement. On the basis of this conclusion, the melting curve as reported by Grilly and Mills has been used in this work for establishing the molar volumes of bcc samples. Only the ends of the bcc phase have been modified to concur with the proper triple points. This adjustment was made by plotting the smoothed data reported by Grilly and Mills (from 1.44°K to 1.76°K in steps of 0.04°K) and drawing a smooth curve through the points. This curve was then truncated at 1.462°K (\( T_1 \)) and extended as smoothly as possible at the other end to 1.772°K (\( T_2 \)).

In order to provide a consistent basis for comparison of experimental results, the molar volumes of samples reported by Ahlers and by Edwards and Pandorf have been re-evaluated on this same basis. The old and new values for their sample volumes are collected in Table II.

It should be mentioned that the molar volumes obtained in these experiments from gas volume measurements yield a melting curve for the bcc phase which appears to deviate systematically from that reported by Grilly.
Table II. Molar volumes of previously measured bcc \( ^4 \text{He} \) samples: reported volumes based on Ahlers' adjustment of Grilly and Mills' melting curve; modified volumes determined directly from Grilly and Mills' curve to conform with present experiments.

<table>
<thead>
<tr>
<th>Source</th>
<th>Run</th>
<th>Reported volume</th>
<th>Modified volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ahlers(^a)</td>
<td>1</td>
<td>20.962</td>
<td>20.946</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20.955</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>20.940</td>
<td>20.927</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>20.921</td>
<td>20.909</td>
</tr>
<tr>
<td>Edwards and Pandorf (^b)</td>
<td>2</td>
<td>20.028</td>
<td>21.017</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>20.998</td>
<td>20.984</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>20.988</td>
<td>20.973</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>20.943</td>
<td>20.928</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>20.932</td>
<td>*</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>20.927</td>
<td>20.913</td>
</tr>
</tbody>
</table>

* Reported volume based on hcp transition

a. See Ref. 8
b. See Ref. 17
and Mills. The two sets of data are in reasonably good agreement at the upper triple point, but at the lower triple point the present measurements of volume seem to be about 0.3 percent high. Due to the relatively large scatter in the present experiments this apparent discrepancy is regarded as more provocative than conclusive, and Grilly and Mills' melting curve is retained as a basis for assigning molar volumes. This shows the desirability of an independent redetermination of the PVT relations in this region, either by a refinement of the method used here or by some other technique.
III. SUMMARY OF EXPERIMENTS

Fourteen successful heat capacity experiments were performed at molar volumes ranging from 20.50 to 21.10 cm$^3$/mole. Six runs originated in the hcp phase, ten passed through the bcc phase, and two involved measurements of both solids. All the experiments involving the hcp phase and four of the others extended to below 0.4°K. These experiments are listed, along with their observed transition temperatures, in Table III. For the sake of convenience, the commonly used abbreviated phase notations $\alpha$(hcp) and $\gamma$(bcc) are introduced here.

A. The Phase Diagram

The results of the various molar volume determinations for all samples are collected in Table IV. For all isochores passing through the bcc phase, the melting point $T_{\gamma,m}$ of this solid has been used as previously described to define the nominal volume. Determinations of $T_{\gamma,m}$ from cooling curves were found to be imprecise and dependent upon the direction of heat flow, so these temperatures were derived instead from curves of experimental heat capacities over very small increments in the vicinity of the melting point.

It can be seen from Table IV that the volumes predicted from filling pressure in conjunction with Hill and Lounasmaa's PVT data for the liquid are systematically higher than those obtained from Grilly and Mill's phase diagram by about 0.2 percent. While this is slightly outside the range of known experimental uncertainty, it could easily be due to any of several potential sources of systematic error present in the cell-filling process and is therefore not believed to indicate a significant discrepancy between the two sets of PVT data. Furthermore, the discrepancy between predicted volumes and those derived from the upper limit
Table III. Observed values of transition temperatures:

\[ T_{\alpha,\text{tr}} (\text{hcp} \rightarrow \text{hcp} + \text{bcc}), \quad T_{\gamma,\text{tr}} (\text{hcp} + \text{bcc} \rightarrow \text{bcc}), \]
\[ T_{\gamma,\text{m}} (\text{bcc} \rightarrow \text{bcc} + \text{liquid II}), \quad T_{f} (\text{hcp} + \text{liquid I} \rightarrow \text{liquid I}). \]

The source of the value of \( V \) is given in Table IV.

<table>
<thead>
<tr>
<th>Run</th>
<th>( V ) cm(^3)/mole</th>
<th>( T_{\alpha,\text{tr}} ) (^\circ)K</th>
<th>( T_{\gamma,\text{tr}} ) (^\circ)K</th>
<th>( T_{\gamma,\text{m}} ) (^\circ)K</th>
<th>( T_{f} ) (^\circ)K</th>
</tr>
</thead>
<tbody>
<tr>
<td>IX</td>
<td>20.58</td>
<td>1.829*</td>
<td>-</td>
<td>-</td>
<td>N.D.</td>
</tr>
<tr>
<td>X</td>
<td>20.50</td>
<td>1.864*</td>
<td>-</td>
<td>-</td>
<td>2.533</td>
</tr>
<tr>
<td>XI</td>
<td>21.006</td>
<td>-</td>
<td>1.587</td>
<td>1.648</td>
<td>N.D.</td>
</tr>
<tr>
<td>XII</td>
<td>20.999</td>
<td>-</td>
<td>1.596</td>
<td>1.656</td>
<td>2.253</td>
</tr>
<tr>
<td>XIII</td>
<td>20.78</td>
<td>1.656</td>
<td>-</td>
<td>-</td>
<td>2.382</td>
</tr>
<tr>
<td>XIV</td>
<td>20.86</td>
<td>1.544</td>
<td>-</td>
<td>-</td>
<td>2.327</td>
</tr>
<tr>
<td>XV</td>
<td>20.919</td>
<td>1.475</td>
<td>1.705</td>
<td>1.739</td>
<td>2.306</td>
</tr>
<tr>
<td>XVI</td>
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<td>-</td>
<td>1.504</td>
<td>1.548</td>
<td>2.225</td>
</tr>
<tr>
<td>XVII</td>
<td>21.067</td>
<td>-</td>
<td>1.497</td>
<td>1.536</td>
<td>2.231</td>
</tr>
<tr>
<td>XVIII</td>
<td>20.934</td>
<td>1.415**</td>
<td>1.683</td>
<td>1.724</td>
<td>2.297</td>
</tr>
<tr>
<td>XIX</td>
<td>20.987</td>
<td>-</td>
<td>1.609</td>
<td>1.670</td>
<td>2.254</td>
</tr>
<tr>
<td>XX</td>
<td>20.988</td>
<td>-</td>
<td>N.D.</td>
<td>1.669</td>
<td>N.D.</td>
</tr>
<tr>
<td>XXI</td>
<td>20.910</td>
<td>N.D.</td>
<td>1.720</td>
<td>1.749</td>
<td>2.303</td>
</tr>
<tr>
<td>XXII</td>
<td>21.034</td>
<td>-</td>
<td>1.541</td>
<td>1.605</td>
<td>2.235</td>
</tr>
</tbody>
</table>

* \( \text{hcp} \rightarrow \text{hcp} + \text{liquid I} \)

** \( \text{hcp} \rightarrow \text{hcp} + \text{liquid II} \)

N.D. - Not determined in this experiment
Table IV. Molar volumes of samples as determined by different methods in units of cm$^3$/mole.

Source of Volume Determination

<table>
<thead>
<tr>
<th>Run</th>
<th>Transition Temperatures</th>
<th>Filling Pressure</th>
<th>Gas Volumes</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Limit of hcp</td>
<td>Melting bcc</td>
<td>Freezing point</td>
</tr>
<tr>
<td>IX</td>
<td>20.555</td>
<td>-</td>
<td>N.D.</td>
</tr>
<tr>
<td>X</td>
<td>20.481</td>
<td>-</td>
<td>20.50</td>
</tr>
<tr>
<td>XI</td>
<td>-</td>
<td>21.006</td>
<td>N.D.</td>
</tr>
<tr>
<td>XII</td>
<td>-</td>
<td>20.999</td>
<td>21.07</td>
</tr>
<tr>
<td>XIII</td>
<td>20.769</td>
<td>-</td>
<td>20.80</td>
</tr>
<tr>
<td>XIV</td>
<td>20.851</td>
<td>-</td>
<td>20.92</td>
</tr>
<tr>
<td>XV</td>
<td>20.906</td>
<td>20.919</td>
<td>20.95</td>
</tr>
<tr>
<td>XVII</td>
<td>-</td>
<td>21.067</td>
<td>21.11</td>
</tr>
<tr>
<td>XVIII</td>
<td>20.927</td>
<td>20.934</td>
<td>20.98</td>
</tr>
<tr>
<td>XIX</td>
<td>-</td>
<td>20.987</td>
<td>21.06</td>
</tr>
<tr>
<td>XX</td>
<td>-</td>
<td>20.988</td>
<td>N.D.</td>
</tr>
<tr>
<td>XXI</td>
<td>-</td>
<td>20.910</td>
<td>20.96</td>
</tr>
<tr>
<td>XXII</td>
<td>-</td>
<td>21.034</td>
<td>21.10</td>
</tr>
</tbody>
</table>

* Volumes derived from PVT data of Grilly and Mills. See references 5 and 6.

N.D. Not determined in this experiment.
T_{x, tr} of the hcp phase averages only about 0.1 percent, or approximately the expected experimental error. Adoption of nominal volumes based on filling conditions for those experiments (IX, X, XIII, and XIV) involving only the hcp phase will therefore give rise to no serious errors, particularly since these samples are much more widely spaced in volume than the bcc samples.

The volumes based on gas pressure measurements with the vaporized samples follow the same trend, of course, being computed using a cell volume derived from densities predicted from filling pressures.

Figure 11 shows the volume-temperature phase diagram for He in the immediate vicinity of the bcc phase. The experimental points on the lower boundary of the bcc phase and on the hcp transition curve are shown, including those observed by Ahlers and by Edwards and Pandorf.

The boundaries of the bcc phase are essentially now completely defined with the drawing of a smooth curve through the points shown on the lower volume-temperature curve. While additional information near the ends of the phase would be welcomed, as would an independent verification of the absolute accuracy of the volumes, the boundaries are believed to be defined with a precision of ±0.002°K and ±0.003 cm³/mole.

The experimentally determined points along the hcp phase boundary above 20.9 cm³/mole, the volumes of which are taken from the melting curve of the bcc phase, are seen to be systematically high with respect to Grilly and Mills' curve. Ahlers also reports points along this boundary, determined in the same way, and his results agree very well with the present work. These results lead one to the conclusion that the values obtained by Grilly and Mills for the volume change \( \Delta V_{tr} \) between the two solid phases are too large by about 10 percent. While
Fig. 11 Volume-temperature diagram for He\textsuperscript{4} in the vicinity of the bcc phase: \textbullet{} - this work; \textquotedblleft{}\text{\textbullet}{}\textquotedblright{} - Edwards and Pandorf (ref. 17); \textsquare{} - Ahlers (ref. 8).
this discrepancy is only twice their stated maximum error for this quantity, it is felt that the experiments reported here provide a quite definitive measure of the relation between the transition curves and thereby define the hcp boundary more accurately than the $\Delta V_{tr}$ measurements of Grilly and Mills. However, independent PVT measurements capable of resolving this question unambiguously seem to be in order.

The onset of freezing observed during initial cooling of the samples provides in principle another means of determining molar volumes. While values obtained by comparing the freezing temperatures $T_f$ with the liquid volume data of Grilly and Mills yielded values which were consistent with those obtained by other means, the existing data were so sparse in the region of interest that the curve was not defined with the desired precision. The results of these experiments may, conversely, be used to improve the definition of the liquid boundary between 2.0 and 2.5°K, and points on the smoothed freezing curve in this region are tabulated in Table V.

**B. Entropy Change at the Lower Triple Point**

At constant volume, a triple point such as the lower limit $T_1$ of the bcc phase appears calorimetrically to have the properties of an ordinary first-order phase transition. In addition to a discontinuous change in the heat capacity, such a triple point also exhibits a latent heat. At $T_1$ and in the range of volumes between $V_\alpha$ and $V_\gamma$ the isothermal addition of energy causes the transformation from hcp + liquid II to the hcp + bcc equilibrium.

This energy change was measured at five volumes by performing a heat capacity measurement (or series of measurements) passing from $T < T_1$ to $T > T_1$. The energy required to warm the hcp + liquid II sample from
Table V  The freezing curve of He from 2.0 to 2.5 K. $V_f$ = molar volume of liquid I in equilibrium with the bcc solid

<table>
<thead>
<tr>
<th>$T$, °K</th>
<th>$V_f$, cm$^3$/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>21.608</td>
</tr>
<tr>
<td>2.05</td>
<td>21.488</td>
</tr>
<tr>
<td>2.10</td>
<td>21.369</td>
</tr>
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<td>2.15</td>
<td>21.251</td>
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<td>2.20</td>
<td>21.137</td>
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<tr>
<td>2.25</td>
<td>21.024</td>
</tr>
<tr>
<td>2.30</td>
<td>20.921</td>
</tr>
<tr>
<td>2.35</td>
<td>20.822</td>
</tr>
<tr>
<td>2.40</td>
<td>20.729</td>
</tr>
<tr>
<td>2.45</td>
<td>20.637</td>
</tr>
<tr>
<td>2.50</td>
<td>20.545</td>
</tr>
</tbody>
</table>
the starting point to $T_1$ and the hcp + bcc mixture from $T_1$ to the final temperature was computed from heat capacity measurements lying wholly in the separate two phase regions and subtracted from the total heat input. Correction was also made for any leakage of heat between the cell and its surroundings during the time required for the measurements. The resulting value of $\Delta E = T \Delta S$ is estimated to be accurate to ±2 percent, except for the point nearest $V_{\alpha}$ where the corrections constituted the largest part of the total heat involved, and this is supported by agreement between repetitions of several measurements.

The entropy change at the triple point is a function of the average molar volume, vanishing at $V_{\alpha}$ and $V_{\text{liquid}}$ and increasing linearly on both sides to a maximum at $V_{\gamma}$. The results of the present measurements are shown in Fig. 12, along with those reported by Edwards and Pandorf. From this plot of $\Delta S/R$ against $V$ it is seen that $(\Delta S/R)_{\text{max}} = \Delta S/R(V_{\gamma}) = (10.15 \pm 0.1) \times 10^{-3}$. Edwards and Pandorf's results, while somewhat less precise, are shown by the figure to be essentially correct. Their value for $(\Delta S/R)_{\text{max}}$ of $(9 \pm 1) \times 10^{-3}$ also agrees satisfactorily with the present work.

C. Heat Capacity Discontinuities

Discontinuous changes in heat capacity are observed in passing from a pure phase into a two-phase region at constant volume, and Lounsmaaa has shown\textsuperscript{25} that these discontinuities may be used in conjunction with PVT data to calculate the compressibility $\kappa$ and thermal expansion coefficient $\alpha$ of the pure phase at such a boundary. The discontinuities $\Delta C_v$ observed at the limits of the hcp and bcc phases are listed in Table VI. The limit of experimental error in these values is approximately ±4 percent.
Fig. 12 Entropy change at the lower triple point.
Table VI. Heat capacity discontinuities observed at transition curves. Values for melting of bcc solid obtained by extrapolation procedure as explained in text.

<table>
<thead>
<tr>
<th>Run</th>
<th>$V_{cm^3/mole}$</th>
<th>$\Delta C_v$ at transitions, joules/mole°K</th>
<th>hcp → hcp+bcc</th>
<th>hcp+bcc→bcc</th>
<th>bcc→bcc+liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>20.50</td>
<td>N.D.</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IX</td>
<td>20.58</td>
<td>1.07&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XIII</td>
<td>20.78</td>
<td>1.94</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XIV</td>
<td>20.86</td>
<td>1.42</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>XXI</td>
<td>20.910</td>
<td>N.D.</td>
<td>1.85</td>
<td>6.40</td>
<td>-</td>
</tr>
<tr>
<td>XV</td>
<td>20.919</td>
<td>0.985</td>
<td>-</td>
<td>5.12</td>
<td>-</td>
</tr>
<tr>
<td>XVIII</td>
<td>20.934</td>
<td>0.79&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.70</td>
<td>3.99</td>
<td>-</td>
</tr>
<tr>
<td>XIX</td>
<td>20.987</td>
<td>-</td>
<td>1.27</td>
<td>1.81</td>
<td>-</td>
</tr>
<tr>
<td>XX</td>
<td>20.988</td>
<td>-</td>
<td>N.D.</td>
<td>1.81</td>
<td>-</td>
</tr>
<tr>
<td>XII</td>
<td>20.999</td>
<td>-</td>
<td>1.25</td>
<td>1.34</td>
<td>-</td>
</tr>
<tr>
<td>XI</td>
<td>21.006</td>
<td>-</td>
<td>1.20</td>
<td>1.35</td>
<td>-</td>
</tr>
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<td>21.034</td>
<td>-</td>
<td>1.09</td>
<td>0.86&lt;sup&gt;a&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>XVI</td>
<td>21.061</td>
<td>-</td>
<td>0.912</td>
<td>0.411</td>
<td>-</td>
</tr>
<tr>
<td>XVII</td>
<td>21.067</td>
<td>-</td>
<td>0.882</td>
<td>0.436</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup> hcp → hcp + liquid I (above upper triple point)

<sup>b</sup> hcp → hcp + liquid II (below lower triple point)

N.D. Not determined in this experiment
Figure 13 shows $\Delta C_v$ plotted as a function of temperature for the three transitions, including the data of Ahlers and of Edwards and Pandorf along the bcc boundaries.

It should be remarked here that the discontinuities at the melting curve of the bcc phase do not in fact exist, but are obtained artificially by extrapolating the heat capacity of the solid from near its lower boundary up to the melting point. In every bcc sample a "tail" was observed in the heat capacity, starting some 10 to 25 millidegrees below the melting point $T_{\gamma,m}$ and rising sharply in such a way that $T_{\gamma,m}$ was marked by a discontinuous change in slope but not in the heat capacity itself. Figure 14 displays a typical example of this phenomenon, the horizontal bars on the points denoting the extent of each point in temperature. This phenomenon was also observed by Edwards and Pandorf, but they did not report the nature of the effect in detail.
Fig. 13  Heat capacity discontinuities at phase boundaries: closed symbols - this work; open symbols - Edwards and Pandorf (ref. 17).
Fig. 14  Heat capacity of a typical bcc sample.

He$^4$

$V=21.061$ $\text{cm}^3$/mole
IV. PROPERTIES OF THE HEXAGONAL CLOSE-PACKED PHASE

The heat capacity of the hcp solid was measured along six isochorces ranging from 20.50 to 20.93 cm³/mole. All of these experiments began below 0.4°K and extended to the upper limit of the phase. The melting (or transition) temperatures for these samples ranged from 1.445 to 1.864°K (see Table III). These temperatures were readily obtained with good precision from discontinuities in $C_v$ or in slopes of cooling curves. Temperature increments for $C_v$ measurements were limited to $T/10$ or less so that the temperature dependence of $C_v$ could be analyzed in a meaningful fashion.

A. Linear Term in the Heat Capacity

One of the samples was investigated exhaustively down to 0.32°K in an effort to test the contention of Franck and of Heltemes and Swenson that the limiting behavior of $C_v$ at low temperatures is not adequately represented by the Debye theory. The lowest volume sample (Run X, 20.50 cm³/mole) was chosen for this investigation because its heat capacity remained uncomplicated by phase transitions until the onset of melting at 1.864°K.

Figure 15 shows the experimental results in the form of $C_v/T^3$ as a function of temperature. The presence of a well defined minimum in the data is clear evidence that the expansion of $C_v$ in powers of $T$ must contain a term with an exponent less than 3. The Debye theory, therefore, does not adequately represent the heat capacity of this sample. As proof of the reality of this effect, the dashed curves in the figure indicate the form the data would take if the heat capacity of the empty cell were in error by the unlikely amount of 5 percent in either direction.
Fig. 15  Heat capacity of hcp He$^4$ at 20.50 cm$^3$/mole as $C_V/T^3$ vs $T$. Dashed lines show effect of adding or subtracting 5 percent of empty calorimeter heat capacity.
The failure of Edwards and Pandorf to observe this phenomenon is explained by Fig. 2 of their paper wherein they demonstrate that a decrease of 1 percent in the empty calorimeter correction would produce a marked maximum in Debye $\Theta$ throughout the range of their hcp sample volumes ($16.90 - 20.93 \text{ cm}^3$/mole).

If, as reported by Franck, the heat capacity at low temperatures is represented by

$$C_v = AT + BT^3$$

a plot of $C/T$ vs $T^2$ should give a straight line with a slope of $B$ and an intercept at $T^2 = 0$ of $A$. The experimental points for this sample are displayed in this fashion in Fig. 16, clearly showing a finite intercept and thus a contribution to the heat capacity linear in temperature.

This linear term, $1.25 \pm 0.05 \text{ T millijoules/mole} - \text{oK}$, constitutes some 12 percent of the total heat capacity of the lowest-temperature points and is several times greater than the uncertainty in the extrapolation. Furthermore, Shen's measurements of the heat capacity of copper provide evidence that this scale contains no irregularities of a magnitude sufficient to change this intercept significantly. In fact, any small adjustment of the temperature scale which could be justified on the basis of his data would tend to increase the linear contribution rather than decrease it.

The coefficient of the linear term obtained from this experiment is comparable in magnitude to the values obtained by Franck. However, since the molar volume of this sample was considerably higher than any of his, and since the source of this linear term is not understood, it is impossible to estimate the relationship which should exist between this linear term and his.
Fig. 16  Heat capacity of hcp He$^4$ at 20.50 cm$^3$/mole as $C_V/T$ vs $T^2$.  

$C_V = 1.25 T + 85.1 T^3$
B. Effect of Annealing

The present experiments allow determination of the coefficient of the linear term with far greater precision than any previous work and should therefore provide a very sensitive test of the annealing effect reported by Franck. While the heat capacity points themselves are somewhat more precise, the main factor in reducing the uncertainty in the intercept $A$ is the extension of the data to lower temperatures. The extrapolated function is linear in $T^2$, so extending the data down to $0.32^\circ K$ instead of Franck's $1.5^\circ K$ reduces the length of the extrapolation by a factor of about 16.

The various symbols in Fig. 16 indicate measurements made on the lowest-volume sample with different thermal histories. The key to the symbols is as follows:

- $\bigcirc$ frozen as quickly as possible
- $\Delta$ annealed within $0.1^\circ K$ of melting temperature for 16 hours
- $\Box$ annealed within $0.18^\circ K$ of melting temperature for 24 hours
- $\nabla$ annealed at $0.95 \pm .2^\circ K$ for 42 hours

It can be seen from the figure that all the data lie along the same line, the total scatter in the points being $\pm 0.5$ percent.

The magnitude of the linear contribution to the heat capacity is therefore independent of the thermal history of the sample unless, as may be argued, the most quickly frozen sample was already well annealed. The rate of freezing was limited by the thermal transfer capability of the mechanical heat switches, and the formation of solid from the liquid took place over some six to eight hours. While it was thus impossible to
test whether a truly rapid quenching of this sample would produce an even larger linear term by freezing mechanical defects into the crystal, the results show quite clearly that the observed anomaly is not subject to elimination by annealing. It is therefore highly unlikely that the source of this contribution is related to the presence of crystal defects in non-equilibrium concentrations.

The small scatter in the data for this run and the lack of divergence due to annealing are also clearly seen in Figs. 15 and 17. In Fig. 17 values of the Debye theta computed from that portion \( C_L \) of the heat capacity remaining after subtraction of the linear term are shown as a function of temperature. The most striking feature of this figure is the failure of the data to approach a constant value, while Edwards and Pandorf indicate that at this volume \( \Theta \) should not change significantly below about 0.06°K. The experimental values appear to be parabolic in temperature up to about 1.1°K. Extrapolation of the parabola shown in Fig. 17 to \( T = 0 \) yields \( \Theta_o = 28.45°K \), corresponding to a \( T^2 \) coefficient of 84.4 millijoules/mole·°K

The narrow temperature interval of \( T^3 \) (constant \( \Theta \)) behavior is not too surprising for a solid such as \( \text{He}^4 \) having very large vibrational displacements. If the vibrational spectrum of \( \text{He}^4 \) is similar to that observed in other solids, the deviations from a \( T^3 \) dependence should be approximated by the addition of a term in \( T^5 \), or

\[
C_L = C_v - AT = BT^3 + DT^5.
\]

If so, then

\[
\frac{C_L}{T^3} = B + DT^2
\]

and a plot of \( C_L/T^3 \) vs \( T^2 \) should yield a straight line with an intercept
Fig. 17: Debye theta of hop He\(^{++}\) at 20.50 cm\(^3\)/mole.
of B and a slope of D. Such a plot is shown in Fig. 18, from which it is seen that this approximation is valid within experimental error up to about 1°K, above which higher-order terms are required. The intercept, or $T^3$ coefficient, is $84.6\pm0.4$ millijoules/mole-°K$^4$. This is equivalent to a value for $\Theta_0$ of $28.43\pm0.1$°K, in excellent agreement with that obtained from Fig. 17 and consistent with the slope of $C_v/T$ vs $T^2$ in Fig. 16.

C. Volume Dependence of the Heat Capacity

The experiments involving hcp samples at higher volumes are seen from Fig. 19 to be consistent with the same linear term observed for the 20.50 cm$^3$/mole sample. While the data for these samples are not so extensive at low temperatures, all appear to have a finite intercept and none clearly requires extrapolation to an intercept appreciably different from 1.25 millijoule/mole-°K$^2$. Over the limited volume range covered by this series of experiments, therefore, the coefficient of the linear contribution appears to be independent of volume.

For most solids, the variation of heat capacity with volume can be adequately expressed in terms of a value for the Grüneisen constant

$$\gamma = -\left(\frac{\partial \ln \Theta}{\partial \ln V}\right)_T.$$ 

The value of $\gamma$ may be obtained by measuring the slope of a logarithmic plot of $\Theta$ vs $V$ as shown in Fig. 20. The values of $\Theta_0$ were obtained from plots of $(C_v - 1.25T)/T^3$ vs $T^2$ similar to Fig. 18. The one point from Edwards and Pandorf's work lying within this volume range is included in the figure for comparison and is seen to be considerably low, as expected from the neglect of the linear term in their analysis. The slope of the line in Fig. 20 gives $\gamma = 3.2\pm0.1$, higher than Edwards and Pandorf's value of 2.60 and the 2.24 reported by Heltemes and Swenson but within
Fig. 18 Heat capacity of hcp He$^4$ at 20.50 cm$^3$/mole as $(C_v - 1.25T)/T^3$ vs $T^2$. 

$$C_v = 1.25T + 84.6T^2 + 10.9T^5$$

($\theta_0 = 28.43 ^\circ$K)
Fig. 19 - Heat capacity of hcp He$^4$ with most of the lattice contribution subtracted:

- $\bigcirc - V = 20.50 \text{ cm}^3/\text{mole}$;
- $\square - V = 20.78 \text{ cm}^3/\text{mole}$;
- $\triangledown - V = 20.86 \text{ cm}^3/\text{mole}$;
- $\lozenge - V = 20.919 \text{ cm}^3/\text{mole}$;
- $\blacktriangle - V = 20.58 \text{ cm}^3/\text{mole}$. 
Fig. 20 Volume dependence of Debye theta \((T = 0)\) for hcp \(\text{He}^4\): 0 - this work; \(\triangle -\) Edwards and Pandorf (Reference 16).
the range of values obtained by Ahlers. It has been pointed out elsewhere\textsuperscript{16} that $\gamma$ is not really a constant for solid helium but increases with increasing volume. In view of this fact the observed value of $\gamma$ seems reasonable. The Debye theta at zero temperature is therefore represented by

$$\theta_0 = (4.484 \times 10^5) V^{-3/2}$$

over the range of the present measurements.

If the dependence on volume and temperature of the "lattice" heat capacity $C_L(V,T) = C_v - 1.25T$ may be adequately described by the variation of $\theta_0$ with $V$ and a single function $C_L(\theta_0/T)$, as assumed in the derivations of the Debye theory and of the Gr"uneisen relation, it can be shown that the reduced Debye theta $\theta/\theta_0$ is a universal function of the reduced temperature $T/\theta_0$ regardless of volume. Experimental values of $\theta/\theta_0$ are plotted against $T/\theta_0$ in Fig. 21, including for readability only the highest- and lowest-volume samples and one of intermediate density. The data are seen to be coincident within experimental error, indicating that this condition is satisfied throughout the range of these experiments.

This conclusion is not sufficient to show that the heat capacity $C_L$ fits the Debye theory, as the Debye model further requires that the function $C_L(\theta_0/T)$ have a particular form. It does, however, demonstrate the validity of the Gr"uneisen relation

$$\alpha/\kappa = \gamma C_L/V$$

for that portion of the heat capacity remaining after subtraction of the volume-independent term $1.25T$.

The reduced Debye theta curve is qualitatively similar in shape to those reported by other workers for helium and other solidified rare gases\textsuperscript{3,16}.
Fig. 21  Debye theta in reduced form:

- $\circ$ - $V = 20.50 \text{ cm}^3/\text{mole}$;
- $\triangle$ - $V = 20.78 \text{ cm}^3/\text{mole}$;
- $\square$ - $V = 20.93 \text{ cm}^3/\text{mole}$. 
but a detailed comparison with other $^4$He work is not justified because of the differences of interpretation involved in the extraction of $\Theta_0$ values. Numerical values defining this curve are given in Table VII, and these may be combined with the equation for $\Theta_0$ and the linear term $1.25T$ millijoules/mole$^{-2}$K to reconstruct the heat capacity of the hcp phase at any temperature and volume in the range of these experiments.

D. Calculation of the Entropy

Smooth curves drawn through the experimental data were integrated numerically using the cubic form of Simpson's Rule in order to evaluate the entropy

$$S(T) = \int_0^T \left( C_v / T \right) \, dT.$$ 

The resulting values for the entropy of the hcp solid along the phase boundary are shown in Fig. 22, including for comparison the first of several values obtained by Edwards and Pandorf and data below the lower triple point derived by the relation

$$S_{\alpha,m} = S_f - \Delta V_m \frac{dP_m}{dT}.$$ 

Here $S_f$ is the entropy of the liquid along the freezing curve as reported by van den Meijdenberg et al. $^{26}$ and the values of $dP_m/dT$ and $\Delta V_m$ are those obtained by Grilly and Mills. The agreement with Edwards and Pandorf's calorimetric work is satisfactory, but the other values appear to be lower than those obtained here by about two-thirds. The values derived from liquid entropies are inherently uncertain, however, being the small difference between two large numbers, neither of which is known more accurately than $\pm 3$ percent.
Table VII. Temperature Dependence of Debye Theta in Reduced Form.

<table>
<thead>
<tr>
<th>$T/\theta_0$</th>
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</tr>
</thead>
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<tr>
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<td>0.060</td>
<td>0.8620</td>
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</table>
Fig. 22. Entropy of hcp He$^4$ along the transition curve: O - integrated from heat capacities; $\Delta$ - computed from entropy of freezing liquid.
Smoothed values of the entropy in the hcp region are tabulated at convenient volume intervals in Table VIII in terms of the dimensionless quantity \( S/R \), where \( R \) is the gas constant. The heat capacity is presented in the same fashion in Table IX.

E. Expansion Coefficient and Compressibility

If the phase boundaries are known with sufficient precision that temperature derivatives of \( P \) and \( V \) may be extracted, the compressibility \( \kappa \) and the thermal expansion coefficient \( \alpha \) along the boundaries can be computed from the heat capacity discontinuities \( \Delta C_V \) observed at the boundaries.

The compressibility was computed from the relation

\[
\kappa = \frac{1}{V \Delta C_V} \left( \frac{dV}{dT} \right)^2,
\]

taking for the total derivative along the phase boundary the slope of Grilly and Mills' hcp transition curve. These calculations resulted in \( \kappa \) values of \((3.0 \pm 0.4) \times 10^{-3} \text{ atm}^{-1}\) over the range of these experiments, in good agreement with previously reported values.\(^6,16\)

Straightforward thermodynamic calculation of the thermal expansion coefficient is not quite so satisfactory as it involves the difference between two terms of comparable size, each of which contains at least one imprecisely known derivative. In order to resolve the possibility of \( \alpha \) becoming negative, however, it is only necessary to establish the behavior of the ratio \( \alpha/\kappa \), the compressibility being always positive. This ratio may be obtained from available data via the Gruneisen relation

\[
\alpha/\kappa = \gamma \sigma_L/V \quad (1)
\]
### Table VIII. Entropy of hcp He$^4$ as S/R

<table>
<thead>
<tr>
<th>V</th>
<th>20.5</th>
<th>20.6</th>
<th>20.7</th>
<th>20.8</th>
<th>20.9</th>
</tr>
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<tbody>
<tr>
<td>cm$^3$/mole</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2°K</td>
<td>0.00037</td>
<td>0.00043</td>
<td>0.00049</td>
<td>0.00055</td>
<td>0.00063</td>
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<td>0.4</td>
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</tr>
<tr>
<td>1.8</td>
<td>0.02739</td>
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</tr>
</tbody>
</table>

### Table IX. Heat Capacity of hcp He$^4$ as C$_V$/R

<table>
<thead>
<tr>
<th>V</th>
<th>20.5</th>
<th>20.6</th>
<th>20.7</th>
<th>20.8</th>
<th>20.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm$^3$/mole</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2°K</td>
<td>0.00111</td>
<td>0.00114</td>
<td>0.00118</td>
<td>0.00123</td>
<td>0.00125</td>
</tr>
<tr>
<td>0.4</td>
<td>0.0072</td>
<td>0.0075</td>
<td>0.0079</td>
<td>0.0082</td>
<td>0.0084</td>
</tr>
<tr>
<td>0.6</td>
<td>0.00241</td>
<td>0.00250</td>
<td>0.00260</td>
<td>0.00272</td>
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<tr>
<td>0.8</td>
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<td>0.00601</td>
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<td>0.00662</td>
<td>0.00699</td>
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<tr>
<td>1.0</td>
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<td>0.01235</td>
<td>0.01297</td>
<td>0.01358</td>
<td>0.01438</td>
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<td>0.0229</td>
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<td>1.4</td>
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<td>0.0398</td>
<td>0.0421</td>
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<tr>
<td>1.6</td>
<td>0.0621</td>
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</tr>
<tr>
<td>1.8</td>
<td>0.1037</td>
<td>0.1052</td>
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</table>
the validity of this relation having been demonstrated in the previous section. Calorimetric measurements along two or more isochores may be used to obtain $\alpha/k$ on a completely general basis from the thermodynamic relation

$$\alpha/k = \left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T.$$  \hspace{1cm} (2)

Equation (1) always produces positive value of $\alpha/k$ for this solid, as $\gamma$ and $V$ are positive and $C_L > 0$ at non-zero temperatures. The curve generated by Eq. (1) for sample X, $V = 20.50$ cm$^3$/mole, is shown in Fig. 23 as a typical example. It is evident from Figs. 19 and 20 that $(\partial C_V/\partial V)_T > 0$ throughout the range of the experiments, requiring that the entropy also increase with increasing volume. Positive values of $\alpha/k$ are therefore obtained also from Eq. (2). No evidence whatever was therefore found for the existence of the predicted region of negative thermal expansion.
Fig. 23  Ratio of thermal expansion coefficient to compressibility for hcp He\textsuperscript{4}, $V = 20.50$ cm\textsuperscript{3}/mole.
V. PROPERTIES OF THE BODY-CENTERED CUBIC PHASE

A. Volume Dependence of the Heat Capacity

The heat capacity $C_v$ of the bcc solid was measured at ten volumes ranging from 20.910 to 21.067 cm$^3$/mole, covering some three-fourths of the volume range over which the phase exists. The results of these measurements are shown in Fig. 24 in the form of $C_v$ vs $T$. Runs XII and XX were omitted from this figure because their volumes are so close to those of XI and XIX.

The pre-melting heat capacity "tail" is clearly seen to be present for each of the samples. The mechanism responsible for this anomaly, probably vacancy formation similar to that observed by Beaumont et al. for other rare gas solids, appears to be a reversible process. The heat capacity in this region was the same for a given volume and temperature whether the sample had been just frozen, warmed from the solid-solid region, annealed, or cycled part way through the anomalous interval. Contrary behavior reported by Edwards and Pandorf is believed to result from very slow establishment of pressure and density homogeneity in their sintered copper calorimeter.

The most notable feature of this figure, however, is the fact that throughout the range of the experiments the heat capacity increases with increasing volume. The bcc solid therefore appears to possess no energy levels which are abnormal in the sense of exhibiting a negative volume dependence. While this result contradicts the early conclusions of Ahlers, the effect is several times larger than the experimental uncertainty and therefore appears to be quite unambiguous. Edwards and Pandorf have already demonstrated the inconclusiveness of Ahlers' work, but the precision of their experiments would not enable them to
distinguish between the behavior observed here and a neutral volume dependence.

The heat capacity of this phase exhibits an unexpectedly large sensitivity to density. While the volume dependence cannot be determined meaningfully near the melting curve because of the large pre-melting effects, the heat capacity curves appear to be reasonably parallel over the low-temperature half of the isochores. Values of the Grüneisen constant have been computed in the regions of overlap and should be valid at or near the lower boundary of the phase. The values of \( \gamma \) obtained are extremely large near the extremities of the phase and pass through a minimum near 1.6°K. Even at the minimum \( \gamma \) values of about 8 are obtained, about 3 to 4 times normal values and 2.5 times that obtained in these experiments for hcp He\(^4\). Figure 25 shows \( \gamma \) as a function of temperature. Since the heat capacity differences from which \( \gamma \) values were derived are only a few percent, the Grüneisen constant is uncertain by about \( \pm 10 \) percent as a result of experimental scatter and limited regions of overlap. This uncertainty is far from being great enough, however, to alter the above conclusions concerning the general features of the volume dependence of the heat capacity.

B. Entropy of the bcc Solid

As with the hcp phase, the entropy was obtained by integration of the heat capacity data for all samples for which measurements were begun below 1°K. The resulting entropy values along the solid-solid boundary and the melting curve of the bcc phase appear to be smooth within \( \pm 2 \) percent, as shown in Figs. 26 and 27, respectively.
Fig. 25  Grüneisen constant for bcc He.
Fig. 26. Entropy of bcc He\textsuperscript{4} along the solid-solid equilibrium curve: ○ - This work; Δ - $S_{\gamma, \text{tr}} = S_{\alpha, \text{tr}} + \Delta S_{\text{tr}}$ using $S_{\alpha, \text{tr}}$ from this work and $\Delta S_{\text{tr}}$ from Grilly and Mills (Reference 6); □ - Edwards and Pandorf (Reference 17).
Fig. 27  Entropy of bcc He$^4$ along the melting curve:
$\bigcirc$ - This work; $\Delta s_{\gamma m} = s_f - s_m$ using $s_f$
from van den Meijdenberg et al (Reference 26) and $s_m$ from Grilly and Mills (Reference 6).

$$S_{\gamma m}/R$$

$T$ ($^\circ$K)
Along the transition line the entropies derived in this way may be compared with the calorimetric results of Edwards and Pandolfi and also with values obtained from the hcp transition entropies observed in these experiments. The latter comparison involves the relation

\[ S_{γ, tr} = S_{α, tr} + ΔV_{tr} \left( \frac{dT}{dP} \right) \]

and the transition properties reported by Grilly and Mills. These comparisons are included in Fig. 26 where it can be seen that the agreement between all three sources is satisfactory except for the lowest-temperature point in the present series, which appears to be high by about 12 to 15 percent. There is no apparent reason to doubt the validity of this point except this lack of agreement with other work, however, and further high-precision heat capacity measurements near the high-volume end of the phase would be required to resolve the discrepancy.

A comparison between the calorimetric entropies at the melting curve and values derived from the entropy of freezing liquid is shown in Fig. 27. The liquid entropy data of van den Meijdenberg et al.\(^{26}\) and that of Lounasmaa\(^{25}\) are combined with the transition data of Grilly and Mills according to the relation

\[ S_{γ, m} = S_{f} - ΔV_{m} \left( \frac{dT}{dP} \right) \]

where \( S_{f} \) is the entropy of the freezing liquid. As in the case of the hcp – hcp + liquid transition this calculation involves the evaluation of a small difference between two large numbers, thus magnifying the experimental uncertainties in the original quantities. In view of the fact that in this region just below the \( λ \) point \( S_{γ, m} \) is only about 15 percent of \( S_{f} \), and also considering that the combined uncertainties
reported for $S_f$ and $\Delta S_m = \Delta V_m \frac{dP_m}{dT}$ total ± 7 percent, the observed discrepancy of 20 percent between these calculations and the directly measured entropies is not surprising.

C. Expansion Coefficient and Compressibility

The data obtained in these experiments can be used to calculate the mechanical properties of the bcc solid along both boundaries by the same techniques described for the hcp phase. In addition, the narrowly separated boundaries of the bcc phase may be considered to define incremental isobars and isotherms from which average values of $\alpha$ and $\kappa$ across the phase may be computed.

All calculations of the compressibility $\kappa$ yielded positive values, as expected, clustered between 0.003 and 0.004 atm\(^{-1}\). No direct measurements of $\kappa$ have been made with good precision, but the values obtained here agree within experimental error with two crude experiments which have been reported\(^{28,29}\) and also with previous estimates from calorimetric data.\(^{8,17}\)

Thermal expansion coefficients computed along the bcc boundaries by the equation

$$\alpha = \kappa \frac{dP}{dT} - \left( \frac{\kappa \Delta V}{VT} \right)^{1/2}$$

and those obtained as averages across the phase both show a drop to small or negative values near the low-temperature end of the phase. Figure 28 shows the results of these calculations. The broken lines representing the expansion coefficient along the phase boundaries have little quantitative significance, especially near the ends of the phase, as they represent differences of as little as 10 percent between two terms, each containing derivatives of experimental quantities. The
Fig. 28  Thermal expansion coefficient of bcc He\textsuperscript{4}.

---, average across phase;

---------------, along solid-solid transition curve;

--- --- ---, along melting curve.
PVT averages, which should be the most accurate of the several values, are in good agreement with the values reported by Edwards and Pandorf above 1.55°K but drop off sharply below that temperature, becoming negative below about 1.54°K. While the extremities of the bcc region are the least well defined by available PVT data, including that obtained in these experiments, there does not appear to be enough latitude in the definition of the phase boundaries to draw them in such a way as to eliminate this negative expansion coefficient. Estimated uncertainty limits in this region are shown by the vertical bars in Fig. 26.

The Grüneisen relation

\[ \frac{\alpha}{\kappa} = \frac{\gamma C_v}{V} , \]

while it always gives positive values when applied to the data of these experiments, is probably not valid for testing the sign of \( \frac{\alpha}{\kappa} \) due to the proximity of the entire bcc phase to the melting curve and the subsequent importance of premelting phenomena. The thermodynamic expression

\[ \frac{\alpha}{\kappa} = \left[ \frac{\partial S}{\partial V} \right]_T \]

is valid, however, and there are fortunately data available near 1.5°K which may be conveniently used for this purpose.

Runs XVI and XVII differ in volume by only 0.006 cm³/mole (21.061 and 21.067 cm³/mole, respectively), yet their heat capacities are clearly distinguishable (see Fig. 24). Since these two experiments did not extend to low temperatures, it is necessary to extrapolate the bcc entropy at the transition curve into this temperature range before comparing entropies for the two samples. The steepest possible slope
of $S_{\gamma, tr}$ consistent with Fig. 26 was chosen in order to insure that the minimum value of $(\partial S/\partial V)_T$ was obtained. Figure 29 shows the resulting entropy curves for the two samples, clearly demonstrating that $(\partial S/\partial V)_T = \alpha/k > 0$ above 1.50°K. If the thermal expansion coefficient of the bcc solid is negative at all, therefore the phenomenon must be limited to the lowest 38 millidegrees of the existence region.
Fig. 29. Entropy of bcc He$^4$ at 21.061 (XVI) and 21.067 (XVII) cm$^3$/mole.
VI. CONCLUSION

The results of these experiments, while in substantial agreement with previous findings, provide a considerably more precise definition of the heat capacity and other thermodynamic properties of bcc and hcp solid He\textsubscript{4} at low densities.

The existence of a contribution to the heat capacity of the hcp phase varying linearly with temperature was firmly established, and this contribution appears to be independent of volume over the narrow range of these investigations. This linear term appears to be an equilibrium property of the solid, as several attempts to reduce or eliminate it by extensive annealing were unsuccessful. Apart from this unexplained feature, the heat capacity of the hcp phase appears to be that of a well-behaved though highly anharmonic normal solid from the lowest temperatures to well above 1\textdegree{}K. No evidence for the predicted negative thermal expansion coefficient was observed for this structure, and its properties could be adequately described by a law of corresponding states with a Grüneisen constant of 3.2.

The phase boundaries and thermodynamic properties of the bcc solid have now been established over the entire region of existence except at the very extremities. While calculations of the thermal expansion coefficient based on the shape of the phase boundaries indicate that $\alpha$ should become negative near the low-temperature end of the phase, no such phenomenon exists above 1.50\textdegree{}K. The remaining possibility that such a situation may exist between 1.462 and 1.50\textdegree{}K is one of several features indicating the need for more precise PVT data on He\textsubscript{4}. The properties of bcc He\textsubscript{4} exhibit an exceptionally large volume dependence, values ranging upward from $\gamma = 8$ being observed for the Grüneisen constant. All bcc
samples showed an enormously steep rise in heat capacity over a 10 to 25 millidegree range preceding the onset of melting, and no discontinuous change in \( C_v \) was observed at the melting curve. This behavior is presumed to be a result of the formation of large numbers of lattice vacancies just prior to melting.

While several opportunities still exist for profitable research in the areas covered by this work - notably heat capacity and PVT work in the hcp phase even nearer the volume limit, detailed study of pre-melting phenomena, and improved direct measurement of mechanical properties - it is felt that the work presented here is as definitive within its scope as present techniques of cryogenic calorimetry allow.
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