Melting Pressure and α-γ Solid-Phase Transformation of He^4 near the Upper Lambda Point*

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Measurements are reported of the slope $(dP/dT)_m$ of the melting curve of He^4 over the temperature range -3×10^{-3}°K $<T-T_{\lambda'}<15\times10^{-3}$°K for the γ solid phase and 9×10^{-3}°K $<T-T_{\lambda'}<19\times10^{-3}$°K for the α solid phase, where $T_{\lambda'}$ is the temperature of the upper lambda point. The upper triple point, where the two solid phases and the liquid are in equilibrium, is $(10.00\pm0.10)\times10^{-3}$°K and 0.305 ± 0.003 atm above the upper lambda point. The slope of the α-γ transition line at the triple point is 14.3 ± 0.7 atm/°K. The temperature and pressure of the upper lambda point are 1.7632 ± 0.0001°K and 29.83 ± 0.02 atm, respectively, in satisfactory agreement with earlier measurements.

INTRODUCTION

THE body-centered cubic γ solid phase of He^4 was discovered by Vignos and Fairbank,[1] who found the upper triple point (T_t,P_t) (where the γ solid, the hexagonal close-packed α solid, and the liquid are in equilibrium) to be 13 mdeg above the upper lambda point $(T_{\lambda'},P_{\lambda'})$ (where the lambda line meets the melting curve). Grilly and Mills[2] reported both these points to be at 1.760°K. If this were correct, it could hardly be accidental; and it would seem to imply some connection between the lambda transformation in the liquid and the bcc-hcp transformation in the solid. Subsequently, Ahlers[3] observed both transformations calorimetrically and reported the triple point to be 10 ± 1 mdeg above the lambda point. In a previous investigation of the melting curve we[4] found no indication, at the upper lambda point, of the discontinuity in slope of the melting curve to be expected if a first-order transition were occurring in the solid; but we were prevented by experimental difficulties from continuing the measurements to high enough temperatures to observe the triple point. With a more careful experimental technique we have now been able to extend those measurements beyond the upper triple point and also to investigate the region around the upper lambda point in more detail.

EXPERIMENTAL

Except for the temperature measuring circuits, the apparatus used in these experiments is essentially the same as that used previously.[4,5] Therefore, it will be described only briefly here. It is shown schematically in Fig. 1.

Helium gas was purified in a trap (not shown) im-

mersed in liquid helium and was condensed into the sample compartment G through the low-temperature valve A, which was kept closed during measurements. G was isolated from the liquid-helium bath by the vacuum case B. Its temperature was controlled by the heater F and by pumping on liquid helium in E.

Changes in the pressure on the sample were measured by the oil manometer K and read with a cathetometer to 0.01 mm, which corresponded to about a millionth of an atmosphere. The absolute pressure was read to 0.01 atm on the Bourdon gauge P, which was calibrated against a dead-weight tester. The sample density could be changed by raising the oil in the left limb of the manometer, forcing gas to condense into G, or by letting more gas in through A.

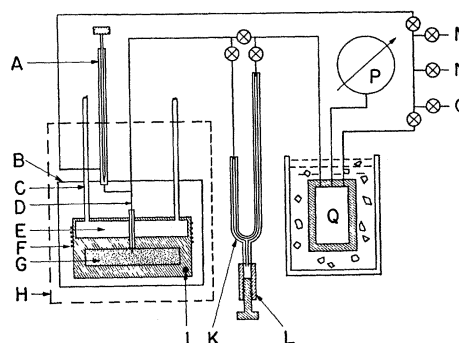Temperatures were measured with a Honeywell Series IV germanium resistance thermometer in an

FIG. 1. Schematic drawing of the apparatus. (A) needle valve; (B) vacuum case; (C) pumping and vapor pressure tubes (2) for (E); (D) 30% Cu-Ni capillary tubing, 0.1 mm i.d.; (E) temperature and vapor pressure compartment; (F) heater; (G) sample compartment packed with fine copper wire for rapid equilibrium (volume 39.83 cm³ at 1.76°K, height 10 mm to keep hydrostatic pressure differences small); (H) dashed lines enclose space immersed in liquid-helium bath; (I) germanium thermometer; (K) differential oil manometer, 0.060-in.-i.d. constant-bore glass capillary (left arm 40 cm long, right arm 90 cm long); (L) oil reservoir and leveling device filled with Apiezon B oil; (M) to He^4 supply tank and purifier; (N) to pump; (O) to atmosphere; (P) 25-cm-dial test gauge calibrated against a dead weight tester; (Q) ballast volume (1461 cm³) for balancing the right-hand side of K, held at constant temperature by an ice bath; $\otimes$ needle valves.

[1] J. H. Vignos and H. A. Fairbank, Phys. Rev. Letters 6, 265 (1961); 6, 646 (1961).
[2] E. R. Grilly and R. L. Mills, Ann. Phys. (N. Y.) 18, 250 (1962).
[3] G. Ahlers, Phys. Rev. 135, A10 (1964).
[4] H. A. Kierstead, Phys. Rev. 138, A1594 (1965).
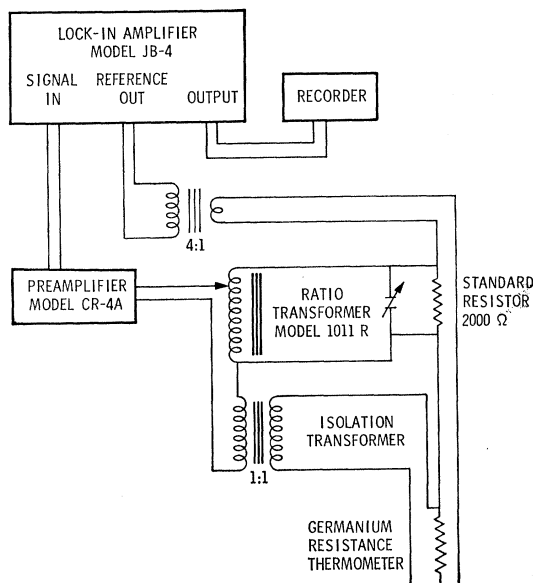[5] O. V. Lounasmaa, Phys. Rev. 130, 847 (1963).

FIG. 2. Ac potentiometer circuit for germanium
resistance thermometer.

ac potentiometer circuit, using a seven-dial Gertsch
model 1011R ratio transformer as the balancing ele-
ment and a Princeton Applied Research Corporation
model CR-4A low-noise amplifier and model JB-4
lock-in amplifier as null detector. The measuring
current was obtained from the internal reference
terminals of the Lock-in Amplifier. The frequency was
about 300 cps. The measuring circuit is shown in Fig.
2. At the upper lambda point the thermometer resist-
ance was 1218 Ω, and its sensitivity was 843 μdeg/Ω.
With about 6 μA of measuring current, the resistance
could be measured with a precision of 10^{-6}. The 2000-Ω
standard resistor had a temperature coefficient of 2
$\times 10^{-6}/°$C and was mounted in an insulated aluminum
block with a thermal time constant of over 6h.

The resistance thermometer was calibrated against
the vapor pressure of helium in E on the T_{58} scale,[6]
using a tube separate from the pumping tube. The
change in the thermometer resistance at the upper
lambda point after warming to room temperature and
recooling corresponded to a temperature change of less
than 10^{-5} °K. All temperatures were referred to the
upper lambda point in order to correct for small
changes in the thermometer or the measuring circuit.

For measurements on the melting curve the sample
was cooled below the upper lambda point, and the
pressure was raised until freezing began, as indicated
by an abrupt rise in temperature. Only a small amount
of solid was allowed to form, in order to ensure tem-
perature equilibrium and to avoid blocking of the 0.1-
mm capillary D. Then the temperature was raised,

and the increase in pressure was read from the man-
ometer. At each temperature no measurements were
recorded until equilibrium was established. If the capil-
lary became blocked by solid, it could usually be
cleared by warming a few mdeg and recooling very
slowly.

As the upper lambda point was approached, the
heater was adjusted for a very slowly rising tempera-
ture; and the heating curve was plotted on the recorder.
Because of the large change in thermal conductivity
at the lambda point, the heating curve showed a sharp
break, which could be located to within a microdegree.

Following the determination of the upper lambda
temperature, melting pressure measurements were con-
tinued. Because the range of the oil manometer was
less than $\frac{1}{10}$ atm, the reference pressure had to be
changed about every 3 mdeg. Since pressure differences
could be measured more accurately than the absolute
pressure, results are reported as the temperature deriva-
tives $(dp/dT)_m$.

UPPER LAMBDA POINT

A number of absolute determinations of the upper
lambda point have been made, since this was used as
a reference point for the other measurements. In Table
I are listed 13 measurements of the temperature and
three of the pressure, made on different days and with
different amounts of solid in the cell.

The absolute accuracy of the temperature measure-
ment was limited by the calibration accuracy, which
was estimated to be better than 10^{-4} deg relative to
the T_{58} scale. As a check on this, the temperature of
the lower lambda point, which is a fixed point on the
T_{58} scale, was measured by the same technique, using
the helium in E. In each of three such determinations,
the error was less than 3×10^{-5} °K.

The absolute pressure measurement was limited by
the resolution of the gauge, about 0.01 atm. The gauge
calibration is subject to the same error, making the
over-all accuracy about 0.02 atm.

Other recent determinations of the upper lambda
point are listed in Table I. The present result agrees
very well with our previous determination, even though
an entirely different thermometer and measuring circuit
were used. With the exception of the values reported
by Grilly and Mills,[2] the other determinations of $T_{\lambda'}$
agree satisfactorily with ours, considering their proba-
ble errors. We know of no explanation for the large
deviation of Grilly and Mills's result. It has been
suggested[3,7] that there is a systematic error in their
temperature scale. Of the measurements of $P_{\lambda'}$, all but
Vignos and Fairbank's[1] are lower than ours. We can
only suggest that these limited-resolution experiments
have missed the rapid rise of pressure just below the
lambda point.

[6] H. Van Dijk, M. Durieux, J. R. Clement, and J. K. Logan,
Natl. Bur. Std. (U. S.), Monograph 10 (1960).

[7] D. O. Edwards and R. C. Pandorf (to be published).

TABLE I. Temperature and pressure of the upper lambda point.

Run No.	Temperature (°K)	Pressure (atm)
1804	1.76317	29.836
1806	1.76317	
1809	1.76316	
1811	1.76317	
1813	1.76316	
1815	1.76316	
1823	1.76313	
1824	1.76315	29.832
1825	1.76315	
1828	1.76315	
1829	1.76316	
1832	1.76316	29.830
1833	1.76315	
Mean	1.7632±0.0001	29.83±0.02
Kiersteadᵃ	1.7633±0.0001	29.84±0.02
Ahlersᵇ	1.763±0.001	
Grilly and Millsᶜ	1.760±0.001	29.67±0.01
Vignos and Fairbankᵈ	1.765±0.003	29.90±0.05
Lounasmaa and Kaunistoᵉ	1.762±0.001	29.71±0.01
Edwards and Pandorfᶠ	1.763±0.002	
Swensonᵍ (corrected to T_{58})	1.760±0.003	29.64±0.03

ᵃ Reference 4.
ᵇ Reference 3.
ᶜ Reference 2.
ᵈ Reference 1.
ᵉ O. V. Lounasmaa and L. Kaunisto, Ann. Acad. Sci. Fennicae: Ser. A VI, No. 59 (1960); Bull. Am. Phys. Soc. 5, 290 (1960).
ᶠ Reference 7.
ᵍ Reference 9.

UPPER TRIPLE POINT

As has been noted by Grilly and Mills,[2] it is difficult to obtain all three phases (α solid, γ solid, and liquid) in equilibrium. We have found that the γ form superheats 5 mdeg and the α form supercools 1 mdeg when in contact with the liquid. It was therefore not possible to observe the triple point directly but only as the intersection of the melting curves of the two solid phases. The γ form could be prepared by freezing at a low temperature or by cooling the α form below 1.772°K; and it could be maintained in equilibrium with the liquid up to 15 mdeg above the upper lambda point $T_{\lambda'}$ without conversion to the α form. The α form could be prepared by freezing at a high temperature or by heating the γ form above 1.779°K, and it could similarly be maintained down to 8.8 mdeg above $T_{\lambda'}$. The spontaneous transformation, once started, proceeded quite rapidly and was manifested by a large thermal effect and a falling pressure. The two forms could be distinguished by the slopes of their melting curves, which were quite different (see below).

The slopes of the melting curves of the two forms were measured in their respective regions of stability (or metastability), several determinations being made at about 10 mdeg above $T_{\lambda'}$, where preliminary measurements had indicated the triple point to be. These 10-mdeg measurements are summarized in Table II. The melting pressures of the two forms were then measured on the oil manometer, keeping the reference pressure P_0 constant, and corrected to $T-T_{\lambda'}=10$ mdeg by means of the measured slopes. In Table III are summarized three such determinations of the dif-

TABLE II. $(dP-dT)_m$ at the upper triple point.

Solid phase	$T-T_{\lambda'}$ (mdeg)	$(dP-dT)_m$ (atm-°K)
Alpha	10.3680	28.663
	10.4262	28.920
	10.4306	28.943
	10.4308	28.772
mean	10.4139	28.825
adjusted to 10 mdeg		28.77±0.10
Gamma	9.7217	30.959
	9.9022	31.013
	9.6178	30.843
	10.1742	30.813
	9.8903	30.889
	10.0274	31.027
mean	9.8889	30.924
adjusted to 10 mdeg		30.93±0.05

ference in melting pressures, $P_\gamma-P_\alpha$. The mean difference is less than the experimental error, so we have

$$T_t-T_{\lambda'} = (10.00\pm0.10)\times10^{-3}°K. \quad (1)$$

By integration of the γ-phase melting slopes (see below), we find

$$P_t-P_{\lambda'} = 0.305\pm0.003 \text{ atm.} \quad (2)$$

These differences are known somewhat more accurately than the absolute pressure and temperature, because of possible errors in the temperature scale and the Bourdon gauge calibration. However, using our measurements of $T_{\lambda'}$ and $P_{\lambda'}$ (Table I), we find

$$T_t = 1.7732\pm0.0002°K, \quad (3)$$

$$P_t = 30.14\pm0.02 \text{ atm.} \quad (4)$$

Using the Bourdon-gauge reading at the triple-point temperature, we calculate $P_t=30.15$ atm, in satisfactory agreement with the above value.

All known measurements of the triple point are listed in Table IV, expressed as $T_t-T_{\lambda'}$ and $P_t-P_{\lambda'}$ in order to minimize temperature scale and gauge calibration errors. All measurements agree with ours within their experimental errors, except for that of Grilly and Mills, which is almost certainly incorrect.

TABLE III. Relative melting pressures at $T-T_\lambda=10.0$ mdeg. P_0 is the reference pressure, which is different for each run.

Run No.	$P_\gamma-P_0$ (10⁻³ atm)	$P_\alpha-P_0$ (10⁻³ atm)	$P_\gamma-P_\alpha$ (10⁻³ atm)
1820	26.716	26.918	−0.202
1821	23.371	23.178	0.193
1830	20.823	20.784	0.039
mean			0.010±0.20

TABLE IV. Temperature and pressure of the upper triple point (T_t,P_t), referred to the upper lambda point $(T_{\lambda'},P_{\lambda'})$.

Source	$T_t-T_{\lambda'}$ (mdeg K)	$P_t-P_{\lambda'}$ (atm)
Vignos and Fairbank[a]	13±5	0.38±0.07
Grilly and Mills[b]	0±4	0
Ahlers[c]	10±1	
Edwards and Pandorf[d]	8.5±2	
This work	10.00±0.10	0.305±0.003

[a] Reference 1.   [c] Reference 3.
[b] Reference 2.   [d] Reference 7.

At the triple point, the slope of the α-γ transition line is given by[8]

$$(dP/dT)_{\alpha\gamma}=(dP/dT)_{\alpha l}-(V_l-V_\gamma)(V_\gamma-V_\alpha)^{-1}$$
$$\times[(dP/dT)_{\gamma l}-(dP/dT)_{\alpha l}],\quad (5)$$

where $(dP/dT)_{\alpha l}$ and $(dP/dT)_{\gamma l}$ are the slopes of the melting curves of the α and γ solid phases at the triple point, and V_α, V_γ, and V_l are the molar volumes of the α, γ, and liquid phases at the triple point. Using Grilly and Mills's volumes[2] and our slopes (Table II), we find

$$(dP/dT)_{\alpha\gamma}=28.77-(1.35/0.201)(30.93-28.77)\quad (6)$$

$$=14.3\quad 0.7\ \text{atm}/°\text{K}.\quad (7)$$

This is in good agreement with a value of 13.9 atm/°K obtained graphically from Vignos and Fairbank's[1] data, but is 25% larger than Grilly and Mills's value[2] of 11.6 atm/°K and Edwards and Pandorf's[7] 11.5 atm/°K. Edwards and Pandorf calculated the slope of the transition line from the equation [their Eq. (2), rearranged]

$$(dP/dT)_{\alpha\gamma}=(dP/dT)_{\alpha l}-\Delta S_{\text{max}}/(V_\gamma-V_\alpha),\quad (8)$$

where ΔS_{max} is the entropy change when pure γ solid transforms at constant volume to a mixture of α solid and liquid. They used their value for ΔS_{max} with Grilly and Mills's values for $V_\gamma-V_\alpha$ and $(dP/dT)_{\alpha l}$. Using instead our value for $(dP/dT)_{\alpha l}$, we calculate $(dP/dT)_{\alpha\gamma}=15.1$ atm/°K, in satisfactory agreement with our calculation.

MELTING CURVE

The slope of the melting curve $(dP/dT)_m$ is plotted against temperature in Fig. 3. In the region between

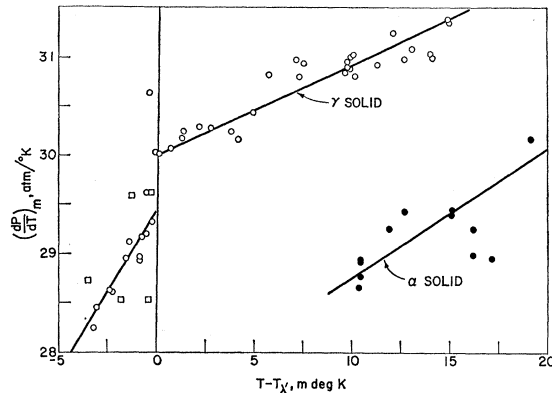[8] E. R. Grilly and R. L. Mills, Ref. 2., Eq. (2).

FIG. 3. Slope of the melting curve $(dP/dT)_m$ of He⁴.
○ γ solid; ● α solid; □ Kierstead (Ref. 4).

8.8 and 15 mdeg above $T_{\lambda'}$ it was possible to measure the slopes for both solid phases.

The straight line drawn through the points below the lambda point is the one reported previously,[4] i.e.,

$$(dP/dT)_{\gamma l}=29.43+326(T-T_{\lambda'}).\quad (9)$$

Our new data fit this line even better than the old. The line drawn for the γ solid above the lambda point fits the equation

$$(dP/dT)_{\gamma l}=30.00+93(T-T_{\lambda'}),\quad (10)$$

while the line for the α solid fits the equation

$$(dP/dT)_{\alpha l}=27.47+130(T-T_{\lambda'}).\quad (11)$$

The apparent discontinuity at the lambda point, which would imply a first-order transition in the liquid, is presumably not real; and, in fact, a few of the measurements in this region suggest that the melting slope rises rapidly just below the lambda point. To define the curve in this region would require a higher resolution than we were able to achieve.

In our earlier paper[4] we discussed other measurements[1,2,9] of the melting pressure in this temperature region. No valid comparison is possible since the other measurements are tabulated at intervals which skip over the entire region of our measurements.

[9] C. A. Swenson, Phys. Rev. 89, 538 (1953).