

Calorimetric study of the transition between the close-packed phases of ^4He from the triple point to 3.9 kbar

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The hcp-fcc ^4He transition was studied using a calorimetric method from the triple point at 14.992 K and 1127 bar to a pressure of 3882 bar. The transition shows temperature hysteresis and a finite thermal width, both of which increase with increasing pressure. Erratic progress of the transition, including burstlike behavior leading to self-cooling during the heating transition and self-heating during the cooling transition was observed. The transition is most likely of martensitic type. Above about 15.8 K, the equilibrium phase line is linear with a slope of 550 bar/K. Between 15.8 K and the triple point, the phase line increases in slope, becoming very large and possibly infinite at the triple point. Transition entropy measurements give $(\Delta S)_{\text{tr}} = 18 \text{ mJ/mole K} \pm 10\%$ with no temperature dependence discernible within experimental scatter. The molar volume change is $0.33 \text{ mm}^3/\text{mole}$ above 15.8 K, this decreases to zero or near zero as the triple point is approached. The transition entropy and the molar volume change at 15.8 K and above are in good agreement with theoretical predictions. The data do not show, however, the predicted increase in slope of the phase line with increasing pressure.

I. INTRODUCTION

Since the work of Dugdale and Simon,¹ it has been known that ^4He can exist in either the hexagonal or the cubic close-packed (i.e., face-centered-cubic) form, both crystallographic phases occupying large parts of the phase diagram. Their work used the calorimetric method and followed the transition from the triple point near 1.1 kbar to a pressure near 2.2 kbar. The same method was also used to establish this transition in ^3He , but only a few points were taken near the triple point.^{2,3} The early x-ray work of Keesom and Taconis⁴ had shown the low-pressure phase to be hcp. The high-pressure phase, however, was only much later positively identified as fcc by the x-ray work at Los Alamos of Mills and Schuch.⁵ While x-ray measurements are certainly well suited to the crystal phase identification, they are much less useful for the establishment of the transition line due to the long exposure times needed. An attempt was made by Mills and Schuch⁶ along these lines, but their published phase diagram up to 4.5 kbar was of preliminary character only. Recently there have also been several inelastic neutron scattering investigations of the fcc phase of ^4He .^{7,8} In the course of these measurements the hcp-fcc transition was observed by Eckert⁹ near 4 kbar, but unfortunately with insufficient temperature resolution.

The helium isotopes are the only rare-gas solids (RGS) in which the transition between hcp and fcc is experimentally observed, all other noble gases crystallize only in the fcc form. Theoretical work on the

relative stability of the two close-packed phases is exceedingly difficult because of the weakness of the transition, which in the ^4He case has a transition entropy of only 0.018 J/mole K . The stability of the fcc phase at all densities in the heavier RGS is, however, surprising, since simple lattice energy considerations appear to favor the hcp phase at not too high densities.¹⁰ This problem has been recently reviewed by Niebel and Venables.¹¹

For the helium case it was realized since the work of Isenberg and Domb¹² and of Hoover¹³ that entropy considerations favor the fcc phase at sufficiently high temperatures. The entropy difference obtained by these two calculations is in fact in surprisingly good agreement with the experimental data. The relative stability at 0 K is much harder to decide since it involves the accurate calculation of the internal energy difference. This difference is influenced not only by two-body interactions, but by three-body and higher interactions, crystal-field effects, and by the difference in the zero-point energy. Uncertainties in the interatomic potential will also strongly affect the results, this potential is for helium still not sufficiently well known.^{14,15} Compared to the heavier RGS, however, there have to be factors in the case of helium which lead to an increased stability of the hcp phase. It was shown by the molecular dynamics calculations of Alder *et al.*¹⁶ that the zero-point energy difference can play this role. The initial calculations were made for a hard-sphere gas, subsequent work by Holian *et al.*¹⁷ extended this to more realistic interatomic potentials. Holian *et al.* proposed on the

basis of their work a phase diagram for ^4He which showed good agreement with the experimental data then known. At high pressures the phase line is proposed to assume negative slope leading to a hcp-fcc transition at 0 K at sufficiently high pressure (estimated to be in the range from 15 to 80 kbar). This feature of the proposed phase diagram is due to the fact that the static lattice energy heavily favors fcc at high densities for all reasonable interatomic potentials.

In the present investigation it was decided to locate the hcp-fcc transition in ^4He using a calorimetric method from the triple point to as high pressures as appeared feasible. The calorimetric method was chosen since it is inherently very sensitive; it has the further advantage of yielding the latent heat as well as the phase line. The most surprising result was the discovery that the transition is hysteretic,¹⁸ making a martensitic type of transformation likely. Other unexpected results were the singular behavior near the triple point,¹⁹ as well as the complicated kinetics of the transformation. Comparison with the calculations of Holian *et al.*¹⁷ show good agreement in some respects, but also serious discrepancies. It can be concluded that we have even now only an incomplete theoretical understanding of the equilibrium aspect of the transition. No theoretical treatments of the transition kinetics are at present available.

II. EXPERIMENTAL

A. Apparatus

The helium crystals were contained in the pressure cell shown in Fig. 1. The body of the cell was manufactured from hardened beryllium copper alloy (Berylco-25),²⁰ providing a helium space of 1.27-cm diameter and 5.8-cm length. The outside diameter of the cell over the lower part is 3.17 cm. The cell was sealed with a steel lens ring. Connection to the pressure system was made via Harwood 3M tubing²¹ (outside diameter 4.76 mm, inside diameter 0.64 mm), this tubing was connected to the cell using a standard cone seal. A copper piece was soft soldered to the bottom of the cell, as shown in Fig. 1, this piece carries a heater and a cooling coil. The volume of the helium space, with the pressure tube in place (i.e., in its experimental configuration) was determined at room temperature by weighing with either water or methanol, it was found at 7.51 cm³. The estimated error in this is about 1.5%. Corrections due to thermal contraction reduce this volume to 7.44 cm³ at temperatures below liquid nitrogen.²² For the range of molar volumes covered in this work, this volume contains between 0.63 and 0.80 mole of ^4He . The weight of the empty cell was 1.58 kg. Since Berylco-25 has about 2% beryllium and 98% copper by weight, the cell contains about 3.5 moles of beryl-

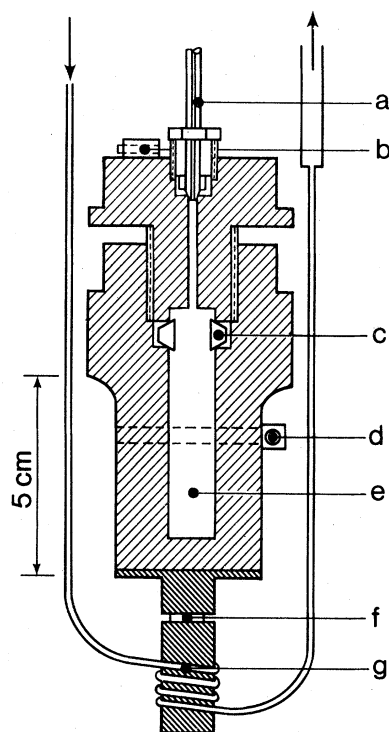


FIG. 1. The pressure cell: (a) pressure line; (b) heater; (c) lens ring; (d) thermometer; (e) helium space; (f) heater; and (g) cooling capillary.

lium and 24.4 moles of copper; the specific heat is therefore approximately that of pure copper. The Debye temperature of ^4He for the range of molar volumes investigated varies between 80 and 136 K, whereas the Debye temperature of copper is 344 K. It can therefore be estimated that the helium sample contributes at least 30% to the total heat capacity of the calorimeter. This ratio is sufficiently large to obtain clear signatures of the transition.

Two heaters were attached to the cell, at the top closure and in the bottom copper piece. The heater situated at the closure was used to heat the pressure tubing during the solidification of the helium sample. The second heater, of about 2000 Ω , was used as the working heater in experimental runs. The power input into this heater was derived from a stable dc circuit, it could be measured potentiometrically.

The working thermometer was a precalibrated germanium thermometer (Cryo-Cal).²³ It was attached about midway at the outside of the cell, so that it would be as close as possible to the helium crystal. In order to be independent of any pressure changes in the cell, the thermometer was attached to a 4-mm wide strip of copper, which in turn was soft soldered around the circumference of the cell, as shown in Fig. 1. Leads from the thermometer were attached to

the cell for a length of about 36 cm with GE 7031 varnish.

Since the transition to be studied is extremely weak, it was important to use a thermometer bridge of sufficient sensitivity. The circuit chosen is based on the conductance bridge developed by Adler *et al.* for tunneling studies²⁴; it is shown schematically in Fig. 2. The bridge power supply was a Hewlett-Packard model 4204A oscillator, operating at 1000 Hz. As a detector a PARR model HR8 lock-in detector was used. The off-balance output of the lock-in was observed on a strip-chart recorder. With power dissipation of about $0.02 \mu\text{W}$ in the thermometer, a temperature resolution of about 0.2 mK was achieved, which was sufficient to observe the transition in considerable detail. The chosen circuit incidentally also eliminates effects due to lead resistance to high order.

A general view of the cryostat is given in Fig. 3. Attached to the copper piece at the bottom of the pressure cell are several turns of 1-mm-diameter copper-nickel tubing. This tubing leads on one side to a needle valve in the external helium bath and on the other side to a vacuum pump. The intake of the needle valve is situated about 2.5 cm below the bottom of the vacuum can. This capillary is used to cool the cell when growing a helium crystal, its use is described in more detail in the next section. During measurements the needle valve was closed and the capillary pumped on.

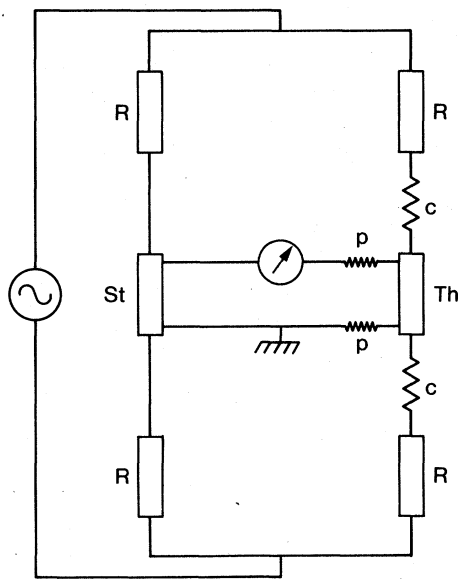


FIG. 2. The thermometer bridge, schematic. Th, thermometer; St, standard resistance; R, bridge resistors, 150 $\text{k}\Omega$; c, current leads; p, potential leads.

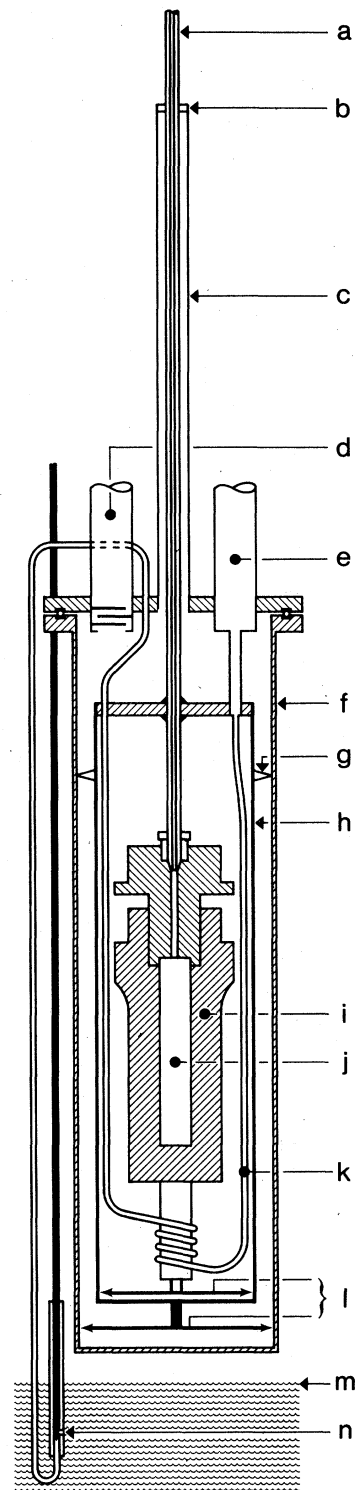


FIG. 3. The cryostat: (a) pressure line; (b) vacuum seal; (c) thermal standoff; (d) vacuum line; (e) pump line for cooling capillary; (f) vacuum can; (g) spacer; (h) adiabatic shield; (i) pressure cell; (j) helium space; (k) cooling capillary; (l) spacers; (m) helium bath; and (n) needle valve.

The pressure cell was surrounded by a thermal shield whose temperature could be controlled by a heater. Inside the shield the cell was supported by the pressure tubing and a stainless-steel spacer at the bottom. The major path for heat exchange is via the pressure tubing which was thermally anchored about 5 cm above the cell to the shield. The shield temperature was controlled manually so that the temperature drift of the pressure cell was less than about 1 mK/min before starting a run. Since the main purpose of the present study was to locate the transition it is not necessary to eliminate all heat exchange with the surroundings. What is required is that any extraneous heat exchange is constant in time during the transition, which was easily achieved. The present experimental arrangement is, however, not suitable for heat-capacity measurements, in particular, for the determination of the small difference in heat capacity between the two phases. Latent heat measurements, on the other hand, proved feasible if care was taken in the control of the shield temperature.

The pressure system used was a three stage gas compressor built by the Harwood Company.²¹ The gas was taken from a supply cylinder at 55 bar and compressed in the first two stages to about 850 bar. The last stage was an oil-driven intensifier of ratio 1:14, the oil being driven in turn by an air-operated diaphragm pump. A Heise pressure gauge in the high-pressure line served as a working gauge for operating purposes. After completion of solidification and the formation of a solid helium plug in the pressure line, the intensifier could be isolated from the pressure cell at a room-temperature high-pressure valve. The remaining pressure tubing at room temperature and the Heise gauge were maintained at the working pressure throughout the run in order to avoid any problems with plug slippage.

B. Experimental method

Helium of nominal purity 99.98% was used without further purification. It can be assumed that most impurities would condense out in bulk form before the helium is solidified (the highest melting temperature in this series of measurements was 34.4 K) and would therefore not influence the transition. In one run, at a pressure of about 1900 bar, helium of much higher purity was used (Linde ultrapure, 99.999% ⁴He, CH₄ < 3 ppm, O₂ < 2 ppm, N₂, Ne, and H₂ < 1 ppm). The results were in all respects indistinguishable from those obtained with the less pure source.

The pressure system was thoroughly flushed at room temperature and thereafter maintained at a pressure of at least 800 bar of helium to avoid contamination. When a run was started the helium pressure was raised at liquid-nitrogen temperature to the desired melting pressure for the run. Liquid helium

was then transferred into the outer Dewar to a level where it covered the intake of the needle valve but somewhat below the vacuum can (see Fig. 3). The top heater on the pressure cell was then used to keep the pressure line open. The cell was cooled by circulating cold helium gas drawn from the external bath through the cooling coil. The cooling rate of the cell could be adjusted by regulating the needle valve and the cell heater. The start of solidification was clearly noticeable via the reduced cooling rate. During solidification the pressure line was kept open and the pressure kept constant by judicious pumping. This way of operating allows the crystal to grow from the cell bottom upwards. The linear rate of crystal growth was varied from 0.01 to 0.4 mm/sec. No particular effort was made to produce single crystals, but in a number of runs the influence of various growing conditions on the transition was studied; this will be discussed in more detail in a later part of the paper. After the crystal had completely filled the cell, the cell heaters were switched off and the helium level brought up to cover the pressure line for at least a length of 20 cm, providing in this way a solid helium plug. All subsequent measurements were conducted therefore at constant volume; no problems with plug slippage were encountered.

The crystal was usually cooled to the vicinity of 4 K and held there for some time; this time could vary from 1 h to 24 h. After this the cell was brought gradually to the expected vicinity of the transition, and the shield heater adjusted to produce a drift of 1 mK/min or less of the cell temperature when the cell was not heated. A run was then started by heating the cell with constant power input to produce heating rates in the range 10 to 17 mK/min. These heating rates were sufficiently small to prevent serious overheating of the thermometer when the sample was solid. Measurements on the melting line, however, i.e., with solid and fluid present in the cell, required much smaller heating rates of about 1 mK/min. The cell temperature was continuously monitored on a strip-chart recorder. At the transition the heating rate slows down and the rate at which the transition progresses can be judged from the reduced heating rate. After the transition is completed the heating rate resumes its pretransition value since the specific heats of the two phases are very nearly the same. The heater power is then switched off and the return of the cell to temperature equilibrium observed. The thermal relaxation times were typically of the order 1.5 to 2 min; they depended somewhat on the density range. The observed transition temperatures were corrected according to these observations. In order to start a cooling run, the shield temperature was adjusted so that the cell was cooling at rates similar to the heating runs. The transition was observed in the same way as during a heating run. In a cooling run, the thermometer will be at a somewhat

lower temperature than the sample, similar to the overheating of the thermometer during a heating run. Corrections for this were made equal to those for a heating run with the same heating rate.

Figure 4 shows schematically the progress of a run. At the temperature T_h the transition in heating starts, it then proceeds during a temperature interval $\delta T_{tr,h}$, the width of the transition in heating. In cooling, the transition first starts at T_c , and again requires a certain temperature interval $\delta T_{tr,c}$ for its completion. In general, both heating and cooling transitions were observed several times in the same crystal. At the completion of a run the melting point of the crystal was observed, again by thermal analysis. The melting point was used to characterize the crystal and to obtain the molar volume and the pressure of the transition temperature from the published equation of state of helium. A total of 45 crystals were investigated in this way. Since the temperature hysteresis was discovered part way through this investigation, only heating transitions were observed in the first crystals measured; these will also be recorded but correctly identified as transitions in heating. Latent heat measurements were made on most crystals below transition temperatures of about 18 K. For higher-temperature transitions (i.e., larger densities) the transitions were too wide in temperature and ill defined to make this measurement possible. The rising background heat capacity of the cell and the helium crystal, coupled with the increasing width of the transition and the approximate constancy of the transition entropy, make it increasingly difficult to even observe the transition at higher densities. The largest pressure at which it was found practical to observe the transition by the thermal method was 4 kbar, at higher pressures other indicators of the transition should be used.^{25,26}

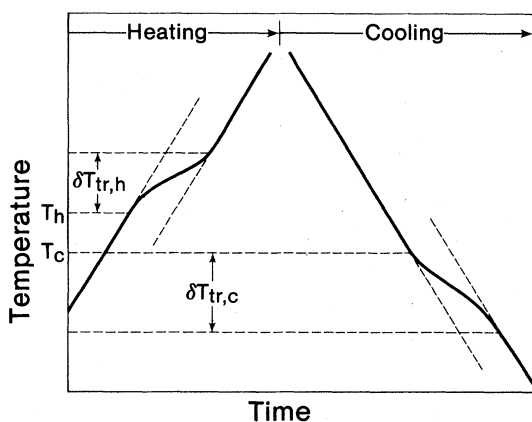


FIG. 4. Schematic of an experimental run. T_h , transition temperature in heating; T_c , transition temperature in cooling; $\delta T_{tr,h}$, transition width in heating; $\delta T_{tr,c}$, transition width in cooling.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Kinetic aspects of the transition

During the course of the investigation it became obvious that the transition is severely hysteretic and shows other irreversible characteristics. These effects are in themselves interesting, but a discussion of them is also necessary before progressing to the extraction of equilibrium data. The irreversible aspects include the temperature hysteresis, the finite width of the transition, and the progress of the transition. All these effects depend strongly on the density, and also in some, as yet not fully understood way, on the thermal history of the crystal. The general character of all these effects is very similar to those observed in martensitic transitions and it is therefore proposed that the transition is of this type.²⁷

1. Temperature hysteresis

The transition temperature in heating, T_h , is found in all crystals to exceed the transition temperature in cooling, T_c (see Fig. 4). The amount of temperature hysteresis is then defined as $(\Delta T)_{tr} = T_h - T_c$. Since always $T_h > T_c$, there is no overlap in temperature between the heating and cooling transition. In the temperature interval between T_h and T_c it was impossible to induce the transition. This was checked by waiting up to 6 h, and temperature cycling the crystal in this interval, both at large and small rates. One can therefore have either the hcp or the fcc phase in this temperature interval, depending on the thermal history of the crystal. The only exception to this was observed when measurements were made along the melting line, i.e., when the crystal was in equilibrium with the fluid. In this case, on two occasions, rapid heating (~ 200 mK/min) induced the transition near the estimated equilibrium transition temperature, rather than the transition temperature T_h normally observed when heating slowly (1 mK/min). The reason for this could possibly be that rapid heating along the melting line stresses the crystal severely because of the rapidly rising pressure ($dP/dT = 119$ bar/K on the melting curve at 15 K). This effect is much smaller along an isochore in the solid [typically $(dP/dT)_V = 10$ bar/K]. The fact that the transition can be induced by stress is well known for other martensitic transitions, and may offer an opportunity to come closer to the equilibrium transition temperature by deliberately stressing the crystal. This treatment was impossible in the present apparatus. Away from the melting curve it was always found that both T_h and T_c are independent of the heating or cooling rate. While the actual progress of the transition, once it was started, depended somewhat on the heating and cooling rate, respectively, and also on the thermal history of the crystal, there was very little influence

TABLE I. Influence of crystal preparation on transition temperatures. (See text for detailed description of crystals.)

Crystal	T_m (K)	T_c (K)	T_h (K)	ΔT_{tr} (mK)
A	27.263	17.508	17.768	260
B	27.238	17.450	17.733	283
C	27.542	17.463	17.818	355

on T_h and T_c , differences in the observed T_h and T_c upon thermal cycling being generally less than 10 mK. The value of these temperatures, however, did depend on the crystal quality. A study of this was made at a molar volume of $V = 10.18 \text{ cm}^3/\text{mole}$.

Three crystals were grown: crystal *A* at a rapid rate of 0.40 mm/sec, crystal *B* was obtained by melting crystal *A* and then regrowing it with the pressure line blocked, probably producing a polycrystal. The third, crystal *C*, was grown by melting crystal *B*, and then regrowing it slowly at a rate of 0.07 mm/sec at constant pressure. The transition temperature and melting temperatures of these crystals are given in Table I. It can be seen that the crystal grown at the slowest rate shows the largest temperature hysteresis. Each heating and cooling transition was observed in each of these crystals at least three times and at heating and cooling rates varying from 15 to 60 mK/min; T_h and T_c were always found within 5 mK. It is therefore clear that differences in the crystal quality affect the temperature hysteresis with the crystal expected

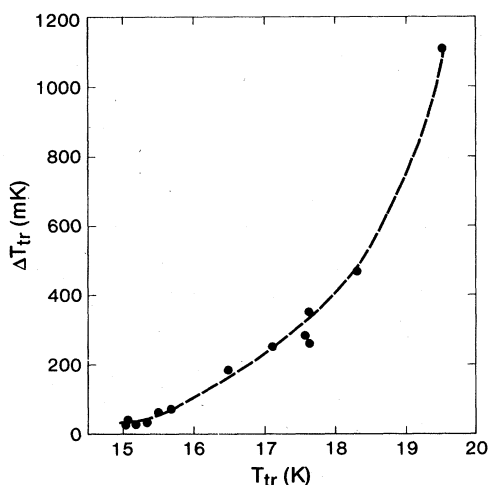


FIG. 5. Temperature hysteresis, $\Delta T_{tr} = T_h - T_c$, as function of average transition temperature, $T_{tr} = \frac{1}{2}(T_h + T_c)$.

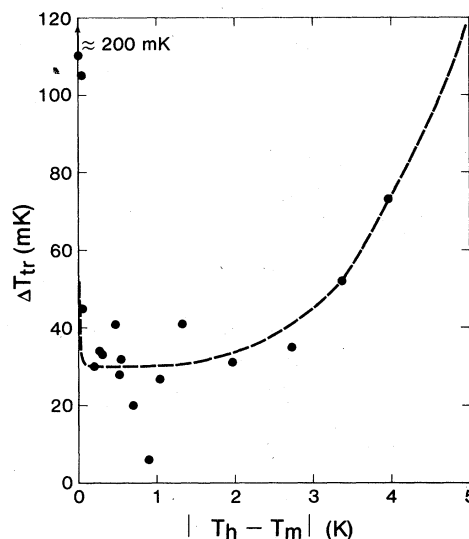


FIG. 6. Temperature hysteresis, $\Delta T_{tr} = T_h - T_c$, as function of temperature difference between transition in heating and melting temperature, $|T_h - T_m|$. The point plotted at $|T_h - T_m| = 0$ refers to a transition on the melting line.

to be the most ideal one (crystal *C*) giving the largest temperature hysteresis. It is probable that remaining stresses in crystals *A* and *B* aided the transition compared to crystal *C*.

Such a detailed analysis was not made at other densities, although crystals were generally grown slowly in order to obtain the maximum temperature hysteresis.

The amount of temperature hysteresis is strongly temperature dependent; it varies from 1 K at $P_{tr} = 4$ kbar, to nearly 30 mK slightly above the triple point. This is shown in Fig. 5. It was expected at first that the hysteresis might go to zero or be very small at the triple point, thus making it possible to experimentally obtain a well-defined triple point. It was found, instead, that the hysteresis increases again, reaching a value of about 200 mK when the transition is observed in a crystal in equilibrium with the fluid. This peculiar behavior is shown in Fig. 6, which gives the temperature hysteresis for transitions close to the triple point as a function of $|T_h - T_m|$.

2. Transition width

Since the transition is of first order and is observed at constant volume, it is expected to progress over a certain temperature interval from an initial temperature T_{in} to a final temperature T_{fin} . This thermodynamic width can be estimated from thermodynamic

data as

$$|T_{\text{fin}} - T_{\text{in}}| = \frac{(\Delta V)_{\text{tr}}/V}{\kappa(dP/dT)_{\text{tr}}} \quad (1)$$

where $(\Delta V)_{\text{tr}}/V$ is the relative volume change (about 3×10^{-5}) and κ the isothermal compressibility. It is always less than 1 mK for the density range of this work because of the extremely small volume change. The observed transition widths are shown in Figs. 7 and 8; they are much larger than the expected thermodynamic widths. A number of possibilities must be considered as a possible explanation for this. The most likely explanation would be given by the finite thermal relaxation time of the calorimeter, i.e., thermal smearing. This can be investigated by varying heating rates, reducing the heating rate should reduce the width of the transition. Careful investigation along this line has failed to produce any evidence that instrumental broadening of the transition is important at the heating rates used. In Fig. 9 is shown, e.g., the heating transition in a crystal with molar volume $V = 12.11 \text{ cm}^3/\text{mole}$. As can be seen, reducing the heating rate from 15 to 3 mK/min had no effect on the width of the transition. If anything, the slower heating rate gives a somewhat wider and more irregular phase transition. Even stopping the heating part way through the transition for times of about 20 min was not followed by the transition running to completion. It must therefore be concluded that instrumental smearing plays no role in the observed width of the transition. Another possibility is given by density variations in the helium sample. While there is, undoubtedly, some contribution from this source to the

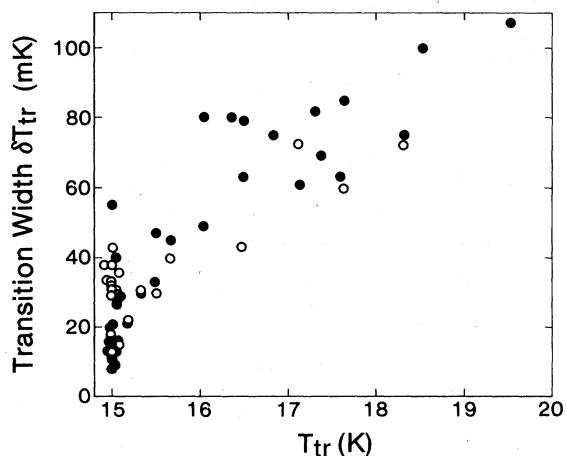


FIG. 7. Transition widths as function of average transition temperature, $T_{\text{tr}} = \frac{1}{2}(T_h + T_c)$. Full circles, transition in heating; open circles, transition in cooling.

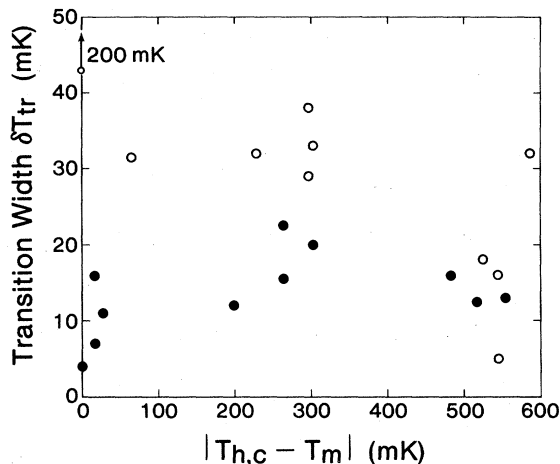


FIG. 8. Transition widths as function of temperature difference between transition temperature in heating, respectively, cooling and melting temperature. Closed circles, heating transition; open circles, cooling transition.

observed width, it must be quite small compared to other effects. The reason for this is the experimental observation that the heating and cooling transition widths are sometimes quite different, and even different passes through the transition in either heating or cooling will generally produce somewhat different transition width (see Figs. 10 and 11). The difference between heating and cooling transition width be-

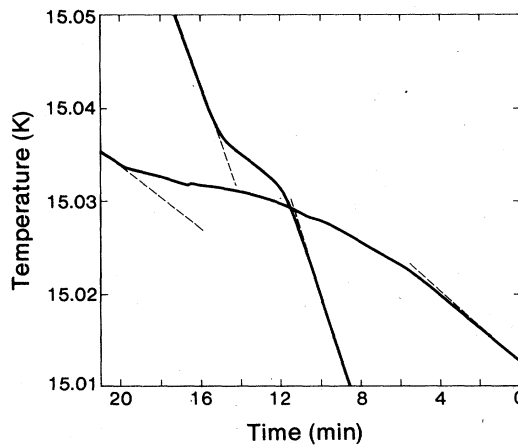


FIG. 9. Successive observations of the heating transition at different heating rates. Molar volume $V = 12.11 \text{ cm}^3/\text{mole}$.

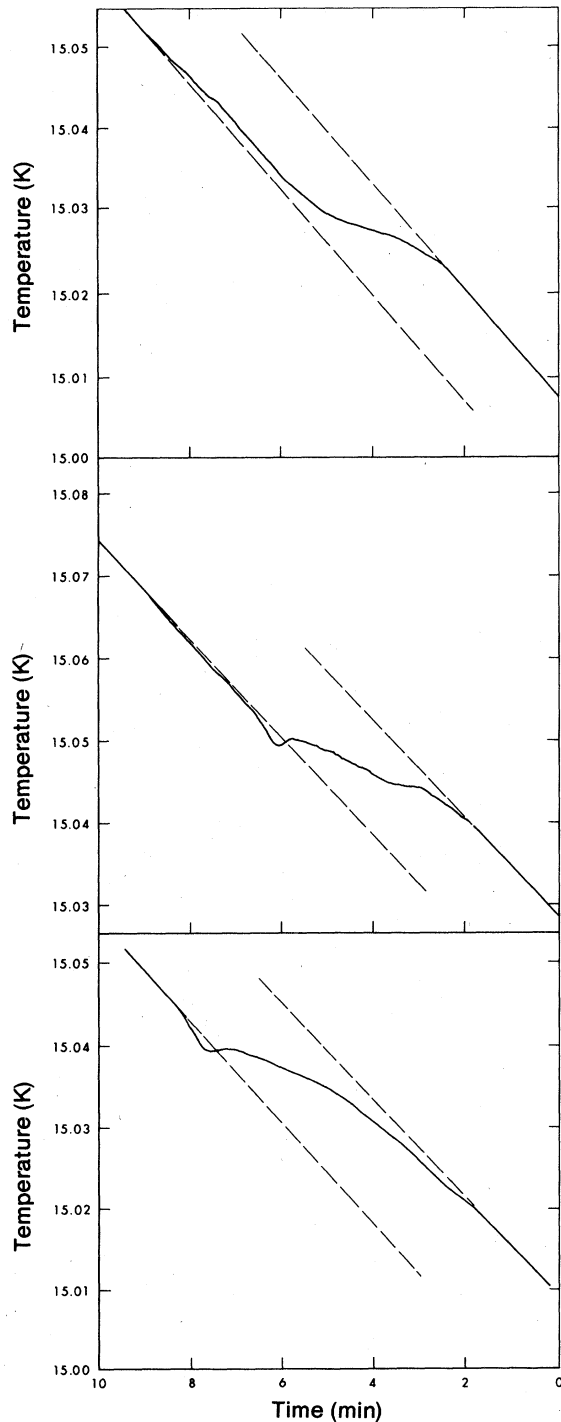


FIG. 10. Successive passes through the heating transition. Molar volume $V = 12.06 \text{ cm}^3/\text{mole}$. The transitions were observed in order from top to bottom. The second and third transition show self-cooling at the end of the transition.

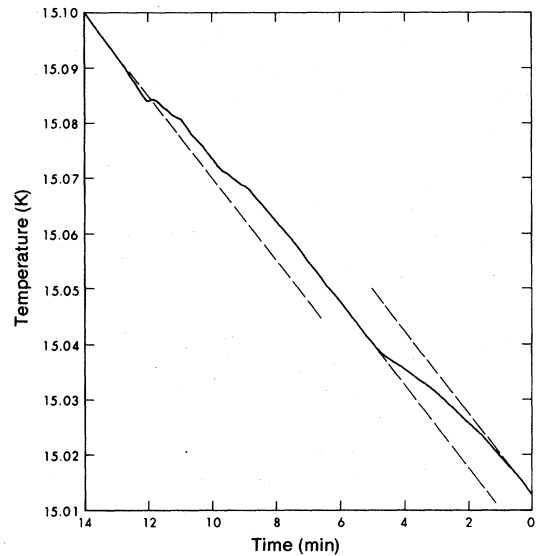


FIG. 11. Example of a heating transition that occurs in two separate stages. Same crystal as Fig. 10, molar volume $V = 12.06 \text{ cm}^3/\text{mole}$.

comes particularly large in the vicinity of the triple point (the cooling transition being wider). A special case is again provided when the transition is observed in a crystal in equilibrium with the fluid (i.e., on the melting line). On the melting line the expected thermodynamic width is zero. The heating transition at a heating rate of $1 \text{ mK}/\text{min}$ showed a width of only about 3 mK , the narrowest transition observed at any density. The cooling transition on the other hand is extremely wide and can be estimated to be of the order of 200 mK . All these observations indicate that density differences can be responsible for only a very small part of the observed transition width. Sluggishness of the transition, as one might expect if the transition proceeded via relatively slow diffusive processes, can also be ruled out. From Fig. 9 it can be seen already that time elapsed is definitely not the determining factor for the completion of the transition. When traversing the transition at even larger heating or cooling rates (up to $1 \text{ K}/\text{min}$) it was observed that the transition took place almost instantaneously. In more recent work at the University of Delaware,^{25,26} which uses an optical method for the detection of the phase transition, we were able to detect transitions which took at most 1.5 sec for completion.

The picture that experimentally emerges is then that the thermal width is essentially an inherent characteristic of the transition. At T_h in heating (or T_c in cooling) the transition starts, but it will run to

completion only over a finite temperature interval. At each point inside this temperature interval the transition takes place at high speed, but only up to a certain fraction of transformed substance. This aspect of the transition is similar to that observed in martensitic transitions and leads us, together with the observed temperature hysteresis, to claim this transition as being of martensitic type.

From our present understanding of martensitic transformations, it is likely that at each temperature within the transition width, different nucleation systems become unstable and grow rapidly to macroscopic size, without, however, filling the crystal matrix completely. The transition width and the progress of the transition are therefore indicators of the nucleation system present in the crystal, their complete identification is, however, impossible by thermal methods alone.

The progress of the transition in the transition interval can be judged from the slope of the temperature versus time curve. Since the thermal relaxation time of the calorimeter is about 60 sec, there will be a certain amount of thermal smearing; in spite of this it was possible to identify the occurrence of definite structure in the progress of the transition. The observed structure is density dependent and it is also dependent on the thermal history of the sample and on the heating rate. At high density the transition both in heating and cooling, appears to proceed quite smoothly through the transition interval. The width of the transition increases with density, as pointed out in the last paragraph. At lower densities the transition width becomes smaller and it increases again close to the triple point. When going to lower densities, structure in the transition becomes more pronounced. There is no very definite pressure at which structure sets in, but generally it was small above pressures of 2000 bar. This may, however, only mean that more careful observation might be needed to reveal it; this becomes increasingly difficult at high densities using the calorimetric method. There is, however, no doubt that structure is much enhanced as the triple point is approached. The structure can be described as either smoothly, or sometimes abruptly changing transition rate, including the split up of the transition into distinct steps. Examples for these various types of behavior are shown in Figs. 11 and 12. It is found that holding the sample for longer annealing times before going through the transition will generally reduce the transition width, without, however, completely eliminating it. At higher heating or cooling rates the transition will often appear to be smoother and slower heating rates show more structure. It looks as though at high heating rates the transition, once started, will keep on pushing on until completion. The dependence on thermal history and heating rate, although definitely observed, is of such a delicate manner, that it has

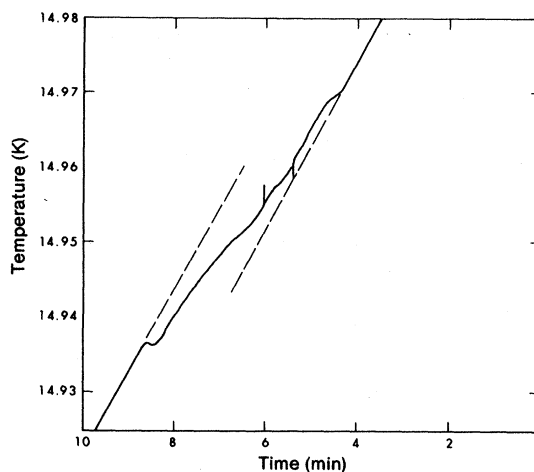


FIG. 12. Example of a cooling transition that occurs in two separate stages. Self-heating near the end of the transition. $V = 12.15 \text{ cm}^3/\text{mole}$.

been at present not possible to take these effects completely into hand. The observed structure is still to a large degree a matter of chance. One of the most surprising effects observed are those of self-heating and self-cooling. During heating it is sometimes observed that at the end of the transition the calorimeter cools. Obviously at this stage very rapid transformation takes place, resulting in adiabatic cooling. The progress of the transition has obviously reached a point where autocatalysis takes place. Equivalent effects were also observed during cooling runs, i.e., at the end of such runs adiabatic heating is observed due to the autocatalysis of the transformation. Examples of this behavior can be seen in Figs. 10–12. These effects were observed only at low densities, i.e., at molar volumes larger than $12.0 \text{ cm}^3/\text{mole}$. It is surprising that these effects can be resolved at all in spite of the thermal relaxation time of about 60 sec of the calorimeter. The actual self-cooling or self-heating of the helium crystal must therefore be much more dramatic than indicated in the heating or cooling curves. It should be mentioned that the very existence of self-cooling and self-heating are proof of the fact that the transition does not proceed at thermodynamic equilibrium.

It should not be surprising that it has not been proven possible so far to completely control the preconditions for a certain type of transition. The weakness of the transition coupled with its dependence on the nucleation and stress system in the crystal makes it likely that the actual state of the crystal is highly dependent on chance effects impossible to control.

B. Transition data

1. Transition temperature

The transition temperatures in heating, T_h , and in cooling, T_c , are reasonably well-defined experimental data in a given crystal, as was shown in the discussion of Sec. A. These two temperatures were observed about three or four times for each crystal.

They were generally reproducible within 10 mK although the following progress of the transition was sometimes quite different for successive passes through the transition. The crystal was then heated until the beginning of melting was observed at a temperature T_m ; this temperature characterizes the crystal. The temperatures T_h , T_c , and T_m constitute therefore the primary experimental data and they are given in Table II. For the first 15 crystals, only tran-

TABLE II. Transition data hcp ^4He -fcc ^4He .

T_m (K)	V (cm^3/mole)	T_c (K)	T_h (K)	P_{tr} (bar)	$(\Delta S)_{\text{tr}}$ (mJ/mole K)
13.946 ^a	12.07	≈ 14.84	15.049	1134	18.0
14.544 ^a	12.07	...	15.048	1134	...
15.506	12.11	...	15.045	1182	...
15.508	12.11	...	15.029	1182	17.2
15.908	12.02	...	15.024	1226	15.3
16.123	11.98	...	15.046	1250	15.9
16.507	11.90	...	15.100	1294	17.3
18.392	11.52	...	15.495	1517	...
20.940	11.07	...	16.040	1841	17.5
20.952	11.07	...	16.055	1841	...
22.204	10.87	...	16.367	2010	...
22.726	10.80	...	16.486	2081	...
23.889	10.63	...	16.850	2243	13.5
25.392	10.42	...	17.300	2460	11.6
25.705	10.38	...	17.374	2506	...
26.463	10.29	...	17.615	2618	6.9
28.060	10.09	...	18.091	2860	4.3
29.371	9.94	...	18.520	3062	...
31.550	9.71	...	19.271	3415	...
15.035	12.21	14.918	15.023	1131	...
15.042	12.21	14.971	15.016	1132	...
15.217	12.17	14.988	15.018	1151	14.5
15.273	12.16	14.973	15.007	1157	...
15.306	12.15	14.970	15.003	1160	...
15.490	12.11	14.965	15.006	1180	...
15.525	12.11	14.980	15.008	1184	...
15.567	12.10	14.980	15.012	1188	16.9
15.723	12.06	15.005	15.025	1206	13.7
15.923	12.02	15.020	15.026	1228	18.6
16.086	11.99	15.019	15.046	1246	15.4
16.419	11.92	15.043	15.084	1283	16.9
17.180	11.76	15.165	15.196	1371	18.1
18.088	11.58	15.318	15.353	1479	19.1
18.902	11.43	15.476	15.528	1579	18.9
19.672	11.29	15.633	15.706	1675	17.6
23.018	10.75	16.405	16.588	2119	13.7
25.381	10.43	16.994	17.246	2456	11.1
27.238	10.19	17.450	17.733	2731	...
27.263	10.19	17.508	17.768	2735	...
27.542	10.15	17.463	17.818	2778	...
29.857	9.89	18.088	18.559	3137	8.5
34.371	9.44	18.978	20.086	3882	17.5

^aThese entries refer to the observation of the transition on the melting line. V is the molar volume of the solid at $T = T_h$, and P_{tr} is the pressure at $T = T_h$.

sition temperatures in heating were observed, since at this stage the temperature hysteresis of the transition was not suspected. From the melting temperature T_m , the melting pressure P_m was calculated (in bar) using the melting curve published by Crawford and Daniels²⁸:

$$P_m = 17.83518 T_m^{1.54171} - 31.86 \quad (2)$$

Isochoric corrections were then made using the equation of state tabulations of Spain and Segall.²⁹ They varied from 6.1% of P_m at the highest pressure to 0% at the triple point. Subtracting the isochoric pressure correction from the melting pressures, one obtains the transition pressures at the transition temperature in heating, $P_{tr,h}$, and at the transition temperature in cooling, $P_{tr,c}$. These two pressures differ by only 5 bar at the highest pressure point, and less for lower pressures. In Table II we show therefore only the average transition pressure, \bar{P}_{tr} , which refers to the average transition temperature $\frac{1}{2}(T_c + T_h)$. The determination of the melting temperature by the calorimetric method is very sensitive; T_m was obtained with an error not exceeding 10 mK. This error in T_m introduces an error of at most 2 bar into P_m . The isochoric corrections are estimated by Spain and Segall to have errors of no more than 5%, which introduces at the highest pressure an uncertainty of about 13 bar in \bar{P}_{tr} , or about 0.3% of the total pressure. This assumes, of course, that the pressure varies along an isochore as expected from thermodynamic equilibrium behavior. That this is probably the case was shown earlier by Wright and Franck³⁰ in a different experiment which used a pressure sensing element embedded in the helium solid. It is seen, therefore, that the largest error for the transition pressure stems from the isochoric pressure correction. This error is somewhat below 0.5% at the highest pressure (~ 4 kbar) and it decreases with decreasing pressure. At the triple point the uncertainty in transition pressure is identical to the uncertainty in the helium melting curve which is estimated by Crawford and Daniels as about 2 bar.

The molar volume, V , of the crystal was also calculated from the observed melting temperature T_m , as $V = V_s(T_m)$, where $V_s(T_m)$ is the molar volume of solid at the melting curve. For this purpose we again used the equation of state calculations of Spain and Segall²⁹ in the interest of consistency. Directly measured values of $V_{fl}(T_m)$ and ΔV_m , the fluid molar volume at the melting curve and the volume change on solidification, were published by Grilly and Mills,³¹ from which $V_s(T_m) = V_{fl}(T_m) - \Delta V_m$ can be obtained. The Grilly and Mills data are 1.4% lower than Spain and Segall at 1 kbar, and 1.0% lower at 4 kbar. This difference gives most likely an indication of the accuracy with which the molar volume is known. The molar volumes obtained in this way are

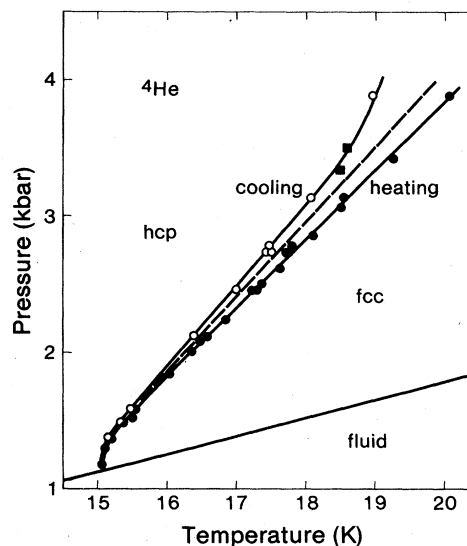


FIG. 13. Phase diagram of ^4He . Solid circles; transition temperature in heating, T_h ; open circles; transition temperature in cooling, T_c ; solid squares: mixed hcp-fcc crystal, Ref. 6; dashed line: estimated equilibrium line, slope 550 bar/K.

included in Table II. The molar content, n , of the cell is important for latent heat determinations (see next chapter) and it is given by $n = v/V$ where v is the cell volume.

The transition temperatures are shown in Figs. 13 and 14 in a (P, T) diagram. As can be seen, reason-

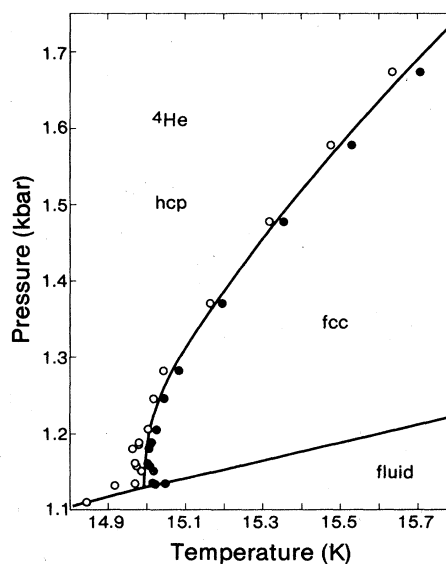


FIG. 14. Phase diagram of ^4He in the vicinity of the triple point. Solid circles, T_h ; open circles, T_c . Solid line, estimated equilibrium line. The two points shown on the melting curve refer to transitions in the presence of fluid ^4He .

ably well-defined curves are obtained for T_h and T_c in spite of their dependence on crystal quality. Deviations from a common curve are at most 100 mK at high pressures, going down to no more than 15 mK as the triple point is approached.

The transition curve in heating shows linear behavior above about 15.8 K, or 1.75 kbar, with a slope of 507 bar/K. Below 15.8 K, the heating transition curve increases gradually in slope, until about 35 bar above the melting curve where its slope is infinite. Heating transitions observed at lower pressures occur at higher temperatures again, the difference amounts to about 20 mK for transitions which occur only a few mK below the melting point. This peculiar behavior of the heating transition makes it difficult to determine the exact location of the triple point for the heating transition. It was therefore decided to observe the transition at a total density such that the pressure cell contained both fluid and solid helium. For this particular run the melting point was observed at 13.946 K and the heating transition at 15.049 K, which is again about 20 mK larger in temperature than for transitions that occur with only solid present, but in very close proximity to the melting point. The heating transition for this run is shown in Fig. 15, it is gratifyingly sharp, in spite of the fact that it is observed against the background of the latent heat of melting. The molar fraction of solid at the point where the transition is observed can be estimated as 52% of the total amount of helium in the cell. A second run, with a slightly larger total amount of helium in the cell was undertaken in order to test whether the heating transition is dependent on the amount of solid remaining at the transition. In this case the helium crystal started to melt at 14.544 K. The heating transition was observed at 15.048 K,

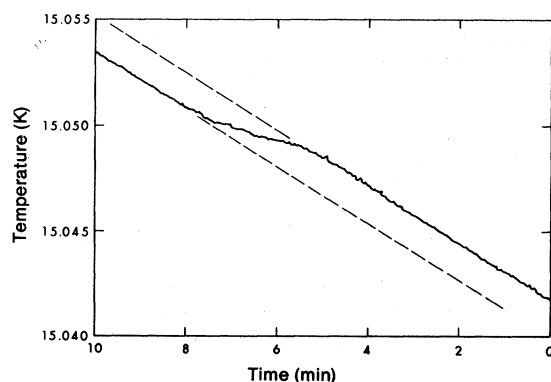


FIG. 15. Observation of the heating transition on the melting line. This helium sample started to melt at $T_m = 13.946$ K. Molar fraction of solid at the transition: $x_s = 0.52$.

in perfect agreement with the previous run. In this second run the molar fraction of solid helium was 80% at the transition. It appears, therefore, that one can speak about a "triple point in heating," which is defined as the start of the heating transition in a crystal in equilibrium with the fluid. It is found at 15.049 K and a pressure of 1134 bar. It is interesting that this point occurs about 20 mK higher than in a crystal where the transition occurs just below the start of melting. The physical difference between the cases is presumably that on the melting line the crystal is unconstrained. The experiments of Sanders *et al.*³² have shown striking differences in the elastic behavior of constrained and unconstrained hcp ^4He crystals. Any detailed explanation of the influence of this behavior on the transition temperatures has to await a clearer theoretical understanding of the transition kinetics.

The transition temperatures in cooling are also shown in Figs. 13 and 14. Between 15.8 and 17.5 K, and pressures of 1.77 and 2.8 kbar, they fall on a straight line with slope 592 bar/K. Above 17.5 K, the cooling transition shows increasing slope, as seen in Fig. 13. However, this increasing slope does not continue, according to recent measurements taken to higher pressures.²⁶ Below 15.8 K the cooling transition line shows gradually increasing slope and at the same time approaches the heating transition line. This continues until one reaches a situation where the heating transition is almost at the melting point (a few mK below). For these crystals the cooling transition moves, almost abruptly, to much lower values. This effect is extreme for the crystals measured on the melting line. Here the cooling transition temperature T_c is about 200 mK below the heating transition. Due to the extreme width of the cooling transition for unconstrained crystals, one can only approximately determine the "triple point in cooling." It lies near 14.84 K and a pressure of 1109 bar. This extreme asymmetry between the transitions in heating and cooling was totally unexpected. From our present understanding of more conventional martensitic transformations, one would expect that in unconstrained crystals there exists a very wide spectrum of rather small martensitic nuclei.

Only a few previous observations of this transition have been published. Dugdale and Simon¹ reported a triple point temperature of 14.9 K and a slope of 523 bar/K between 15 and 17 K. This is in fair agreement with the present results, considering that their data refer to the heating transition only. A slight increase in curvature with falling temperature is shown in the published phase diagram, although this effect appears to have been neglected. Dugdale and Franck³ published a single point at $T = 15.01$ K and $P_{tr} = 1283$ bar, again only a heating transition. This point is 70 mK lower than the present data would indicate. Mills and Schuch⁶ observed two cases, where

both hcp and fcc ^4He were present in their x-ray cell, at a temperature of 18.5 K and a pressure of 3.33 kbar. These points are shown in Fig. 13. The data of Mills and Schuch were taken at constant temperature. Because of the finite width of the transition, which at 3.33 kbar is about 80 mK, there is a finite *a priori* probability for observing both phases at a given temperature. From the description of their experimental procedure it can be assumed that their points refer to the cooling transition. As can be seen from Fig. 13, this interpretation leads to good agreement with the present cooling transition data. It can be concluded that previous observations of the transition are in at least fair agreement with the present results.

The equilibrium transition temperature between the two phases can be defined by the equality of the Gibbs free energy of the two phases in bulk, neglecting any contributions due to surface and strain energy. It is unfortunate that the temperature hysteresis makes it impossible to determine this temperature with certainty. It can be assumed, however, that this temperature lies somewhere in the interval between T_c and T_h . This assumption is supported by the fact that the transition in unconstrained crystals (i.e., on the melting line) could be induced in this interval, unfortunately only under rather nonideal experimental conditions. The situation is quite similar to that found in more conventional martensitic transformations. The most common assumption made is that the bulk transition temperature is approximately given by the average of cooling and heating temperature, i.e., $\frac{1}{2}(T_c + T_h)$. It was decided to follow this practice in the absence of more definite information.

Below 15.8 K, where the two transition lines approach each other closely, the possible error cannot be very large. The transition line shown in Fig. 14 was then drawn as a smooth curve, nearly everywhere halfway between T_c and T_h . The experimental data close to the melting line indicate a dramatic rise in slope, and the suggested equilibrium line was drawn with infinite slope at the triple point. Equilibrium transition data according to this phase line are tabulated in Table III. The experimental data available at present do not allow to distinguish between simply a very large or an infinite slope. The large decrease in the cooling transition temperature near and at the melting line was neglected when drawing the phase line. This brings the phase line closer to T_h than T_c near the triple point. The equilibrium triple point data obtained from this phase line are $T_{\text{triple}} = 14.992$ K, $P_{\text{triple}} = 1127$ bar, and $V_{\text{triple}} = 12.22$ cm³/mole. The triple point pressure is that obtained from the Crawford and Daniels melting curve,²⁸ and the molar volume was calculated using the tabulations of Spain and Segall.²⁹

Above 15.8 K the heating transition line is linear with slope 507 bar/K, and the cooling transition is linear with slope 592 bar/K up to a temperature of

TABLE III. Transition line between the triple point and 15.8 K, hcp \leftrightarrow fcc ^4He .

T_{tr} (K)	P_{tr} (bar)	$\left(\frac{dP}{dT}\right)_{\text{tr}}$ (bar/K)
14.992 ^a	1127	∞
14.996	1169	3745
15.000	1184	2740
15.100	1311	867
15.200	1386	729
15.300	1456	656
15.400	1520	610
15.500	1578	581
15.600	1636	562
15.700	1691	552
15.800	1745	550

^aTriple point.

17.5 K. Placing the equilibrium transition halfway between those lines we obtain

$$P_{\text{tr}} = 1745 + 550(T_{\text{tr}} - 15.8) \quad (3)$$

(bar), i.e., a slope of 550 bar/K. This line is shown in Fig. 13. Above 17.5 K, the cooling transition line shows increasing curvature. We have neglected this effect and extended the suggested equilibrium phase line to about 3.8 kbar with constant slope as shown in Fig. 13. This brings the equilibrium line somewhat closer to the heating transition line. This procedure may be defended by the observation that the cooling transitions were much more dependent on crystal quality, making them less well defined experimentally and possibly further removed from the equilibrium transition temperature than the heating transition. It is at least likely that an increasing slope of the equilibrium phase line would be reflected in an increasing slope of the heating transition line.

The equilibrium transition line proposed is then given by Table III for $T \leq 15.8$ K, and by Eq. (3) from 15.8 to 19.7 K. This line is in disagreement with the phase line proposed by Mills and Schuch⁶ which was drawn before the temperature hysteresis of the transition was known. The phase line proposed here does not show increasing slope with temperature, at least to about 3.8 kbar. More recent work at the University of Delaware,²⁶ which extends this work to nearly 9 kbar, confirms this finding.

The increasing slope of the phase line as it approaches the triple point, is a new feature, although it might have been present in the original data of Dugdale and Simon as mentioned above. This result may also throw some new light on a rather anomalous

finding for the phase line between hcp and fcc ^3He . This line is based at present only on two points² taken close to the triple point, defining a slope of 1111 bar/K. At the time of those measurements it was assumed that the phase line should be linear for at least several kbar but it was not understood why the phase line in ^3He should have about twice the slope of the ^4He phase line. The present results remove this anomaly, making the slope for both isotopes nearly equal at the same reduced temperature $(T_{\text{tr}} - T_{\text{triple}})/T_{\text{triple}}$. It can be concluded that the slope of the ^3He transition line at higher pressures is presently not known, and should be established by experiment.

2. Latent heat and transition entropy

The latent heat, $(\Delta H)_{\text{tr}}$, of the transition was measured for several crystals. These measurements were only taken for the transitions in heating. From the observation of the cooling transition in these crystals it appears that the latent heat for the cooling transition is very similar, and probably equal, to the latent heat for the heating transition. The principle of the measurement is shown in Fig. 16. The cell was heated at constant power input. The adiabatic shield temperature was regulated for a drift below 1 mK/min for no power input, the drift was checked before and after traversing the transition. Both below and above the transition the heating curve is a straight line, the slope of these two lines is nearly equal for transitions of small width. These lines were extrapolated into the transition interval; the extra time necessary to traverse the transition, Δt , was determined at the midpoint of the transition. The extra energy needed to traverse the transition is then given by

$$\Delta E = \dot{Q} \Delta t, \quad (4)$$

where \dot{Q} is the power supplied. It is obvious there-

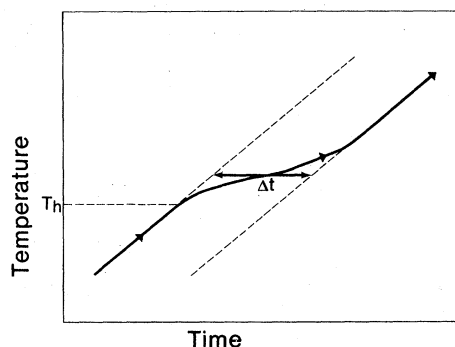


FIG. 16. Schematic for latent heat measurement.

fore that ΔE can be determined without separately measuring the background heat capacity. The molar content n of the pressure cell was obtained from the molar volume of the crystal (as calculated from the melting point) and the known volume of the pressure cell. Assuming that the transition was complete, the extra molar energy to traverse the transition is then given by $\Delta E/n$. This quantity is very nearly the latent heat of transition, $(\Delta H)_{\text{tr}}$. Corrections have to be applied, however, since the transition takes place at constant volume. The pressure rise during the transition can be estimated as

$$\Delta P = (\Delta V)_{\text{tr}}/V\kappa, \quad (5)$$

where κ is the isothermal compressibility and $(\Delta V)_{\text{tr}}/V$ the relative molar volume change. This pressure rise is extremely small due to the value of the volume change of the transition, which is only a few parts in 10^5 of the total molar volume (see next chapter). ΔP can be estimated at about 0.5 bar at a pressure of 4 kbar, it decreases from this value with falling pressure. The corresponding equilibrium temperature width of the transition is 1 mK at 4 kbar, it also falls with falling pressure. The transition is therefore nearly isobaric. It can be shown that the correction to obtain $(\Delta H)_{\text{tr}}$ from the measured $\Delta E/n$ is given by

$$(\Delta H)_{\text{tr}} = (\Delta E/n) [1 + (dP/dT)_V / (dP/dT)_{\text{tr}}], \quad (6)$$

where $(dP/dT)_V$ is the slope of the isochore and $(dP/dT)_{\text{tr}}$ the transition line slope. The correction varies between 0 and 2% between the triple point and $T_{\text{tr}} \approx 16$ K.

The foregoing analysis assumes, of course, that the transition takes place under equilibrium conditions, whereas in fact it takes place over a much wider temperature interval than estimated from the equilibrium behavior and at temperatures above the equilibrium transition temperature. Let us first assume that the transition takes place completely at a single temperature $T_h > T_{\text{tr}}$. The enthalpy difference between the phases can then be obtained as

$$\begin{aligned} \Delta H &= \int_0^{T_h} C_{P,\text{fcc}} dT - \int_0^{T_h} C_{P,\text{hcp}} dT + (\Delta H)_0 \\ &= (\Delta H)_{\text{tr}} + \int_{T_{\text{tr}}}^{T_h} (C_{P,\text{fcc}} - C_{P,\text{hcp}}) dT. \end{aligned} \quad (7)$$

(We treat for this analysis the transition as isobaric, which is very nearly correct.) The correction term is therefore

$$\int_{T_{\text{tr}}}^{T_h} (C_{P,\text{fcc}} - C_{P,\text{hcp}}) dT = \int_{T_{\text{tr}}}^{T_h} C_{P,\text{fcc}} \left[1 - \frac{C_{P,\text{hcp}}}{C_{P,\text{fcc}}} \right] dT. \quad (8)$$

The temperature interval from T_{tr} to T_h is about $(\Delta T)_{\text{tr}}/2$, i.e., it is 50 mK or less for the density range of this work. One can then approximately

write the correction term as

$$\left(1 - \frac{C_{p, \text{hcp}}}{C_{p, \text{fcc}}}\right) \int_{T_{\text{tr}}}^{T_h} c_{p, \text{fcc}} dT = \frac{\Delta C_p}{C_p} \int_{T_{\text{tr}}}^{T_h} C_p dT \quad (9)$$

The reduced temperature T/Θ_D (Θ_D the Debye temperature) at the transition can be estimated (see below) to vary from 0.183 at the triple point to about 0.148 at 3.9 kbar. Using a Debye approximation this gives a specific heat at the transition varying between 7.9 and 5.2 J/mole K. The relative difference in specific heat between the two phases, $\Delta C_p/C_p$, is not experimentally available, but can be estimated at least to an order of magnitude from the calculations of Domb and Isenberg¹²; their calculations give $\Delta C_p/C_p = 0.01\%$ at the triple point and 0.07% at 3.9 kbar. We estimate then, that the correction term to $(\Delta H)_{\text{tr}}$ varies between 0.02 mJ/mole (at the triple point) and 0.2 mJ/mole (at 3.9 kbar). This can be compared with the measured, uncorrected, value for $(\Delta H)_{\text{tr}}$, which varies between 274 and 360 mJ/mole. It can be seen that the correction term is entirely negligible. The temperature width of the transition can be taken into account by assuming that over each interval of the transition width a certain fraction of the helium is transformed. This has the effect of increasing the temperature interval (T_{tr}, T_h) to about $(T_{\text{tr}}, T_h + \frac{1}{2}\delta T_{\text{tr}})$ to a maximum of about 90 mK. The correction term is therefore about doubled, and still insignificant.

The values of the latent heat $(\Delta H)_{\text{tr}}$, obtained in the way described, can be used to calculate the transition entropy

$$(\Delta S)_{\text{tr}} = (\Delta H)_{\text{tr}}/T_{\text{tr}} \quad (10)$$

The value for T_{tr} used in this calculation was the average of the cooling and heating transition temperature, $T_{\text{tr}} = \frac{1}{2}(T_c + T_h)$. Any errors because of a deviation of the true equilibrium temperature from the T_{tr} used are of the order of a few tenths of 1% and therefore negligible. The results for the transition entropy so obtained are included in Table II and are shown in Fig. 17. It can be seen that from about 15.2 to 16 K the transition entropy is remarkably constant at a value of about 18.3 mJ/mole K. Above 16 K the transition entropy appears to drop, although the transition entropy measured at the highest density, at a transition temperature of 19.53 K, is again almost in agreement with the data at lower densities. Transitions between 15.2 K and the triple point also give generally smaller transition entropies, although not always, as the measurements of $(\Delta S)_{\text{tr}} = 18.6$ mJ/mole K for $T_{\text{tr}} = 15.023$ K shows. All reported measurements of $(\Delta S)_{\text{tr}}$ are averages of two or three successive determinations of $(\Delta S)_{\text{tr}}$. The differences between different determinations on the same crystal was generally within $\pm 10\%$, although in some crystals it was as small as $\pm 5\%$. The estimated error bar in

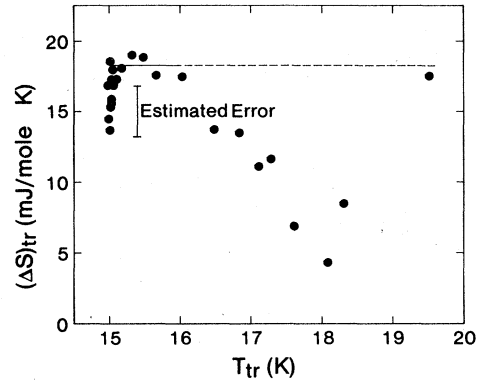


FIG. 17. The transition entropy as function of average transition temperature, $T_{\text{tr}} = \frac{1}{2}(T_h + T_c)$.

Fig. 17 is based on a random error of $\pm 10\%$ and this is obviously much larger than the corrections discussed earlier.

In order to obtain a value for the transition entropy at the triple point, it was attempted to measure the latent heat on an unconstrained crystal, i.e., a crystal in equilibrium with the fluid. As was shown earlier (Fig. 15) the heating transition in such a crystal can be quite narrow and well defined. The molar content of the cell for this particular run was such that melting started at $T_m = 13.946$ K. The hcp-fcc transition was observed at $T_{\text{tr}} = 15.049$ K with a width of only 3 mK. The excess energy for the hcp-fcc transition was obtained as before; an independent determination of the latent heat of melting is not necessary. In order to obtain molar quantities, one has to estimate the molar amount of solid helium, n_s , present in the cell at the transition. This quantity can be calculated using the condition of constant cell volume and constant total molar content n :

$$n_s = (v - nV_{\text{fl}})/\Delta V_m \quad (11)$$

In here v is the cell volume, V_{fl} the molar volume of fluid, and $\Delta V_m = V_{\text{fl}} - V_s$ the molar volume change on melting, both taken at the transition temperature. The total molar content was obtained in the usual way, $n = v/V_s(T_m)$. For the validity of this relation it is important that no plug slippage occurred, at least up to the observation of the transition. This was checked by observing the full melting interval. The temperature at the end of the melting interval was found as $T_{mf} = 16.525$ K. The width of the melting interval at constant volume, $T_{mf} - T_f$, is given by the relation

$$V_s(T_m) = V_{\text{fl}}(T_{mf})$$

or

$$V_{\text{fl}}(T_m) - V_{\text{fl}}(T_{mf}) = \Delta V_m(T_m) \quad (12)$$

Direct experimental determinations of V_{tr} and ΔV_m were reported by Grilly and Mills,³¹ using their data we predict $T_{mf} = 16.405$ K. This is in reasonable agreement with the measured T_{mf} , making it likely that the melting interval was traversed without plug slippage. Anomalous effects on the observed heating curve, which might be an indication of plug slippage, were also not observed. Using now the data of Grilly and Mills one calculates that $n_s = 0.31$ mole at T_{tr} , corresponding to a molar fraction of solid $x_s = n_s/n$, of 52%.³³ Molar transition entropies obtained in this way for two different passes of the transition were 15.4 and 20.5 mJ/mole K, giving an average of 18.0 ± 2.5 mJ/mole K. It is gratifying that this small entropy change can be obtained against the background of the much larger melting entropy (ca. 7.0 J/mole K); this is possible only because the experiment is performed at constant volume, extending the melting interval over about 2.5 K. The transition entropy on the melting curve is in good agreement with the data for transition temperatures in the range 15.2 to 16 K.

The transition entropies given in Table II and Fig. 17 can be regarded as true molar quantities provided that the following conditions are also met: (i) the transition is complete, i.e., it proceeds from 100% hcp to 100% fcc ^4He ; (ii) the analysis shown schematically in Fig. 16 takes in the complete transition interval; and (iii) none of the transition energy is stored elastically, as, e.g., in thermoelastic martensite. None of these conditions can be conclusively ruled on by thermal measurements alone. It should be noted, however, that each of these possibilities for error would make the measured transition entropy appear too small, so that in general the largest measured values should be preferred. The first of the possibilities can most probably be ruled out. In both x-ray work^{5,6} and neutron work⁹ no cases were observed for incomplete transformation. In an earlier paper¹⁸ the present author suggested that partial transformation might be the cause for the dropoff of the measured transition entropies above 16 K. It is now believed that the second case, i.e., incomplete account of the transition interval is the most likely cause for these findings. This error source becomes more serious at higher densities where the transition width increases quickly. When the main part of the transition has taken place, it is therefore difficult to decide whether the high-temperature slope of the heating curve is solely due to the heat capacity of cell and helium crystal, or whether it also still contains part of the transition running to completion over a considerable temperature interval. Recent optical investigations at the University of Delaware^{25,26} have shown that such slow completion of the transition does indeed sometimes occur. Partial elastic storing of the transition energy is also a possibility, but cannot be proven. Further confirmation for the argument that the drop-

off of the measured transition entropies above 16 K is spurious comes from the measurement at the highest density of this work. Here a $(\Delta S)_{tr}$ of 17.5 mJ/mole K was found at a transition temperature of 19.53 K. This value is in good agreement with the data below 16 K. Similar arguments can also be extended concerning the apparent dropoff of $(\Delta S)_{tr}$ between 15.2 K and the triple point. In this range the transition becomes wider again and erratic, as shown before. It was observed, in particular, that in many cases the transition seemed to run to completion only at the beginning of melting. This effect shows itself as extra structure in the heating curve at the melting point. That the apparent dropoff in $(\Delta S)_{tr}$ is again most likely spurious is shown again by the measurements at $T_{tr} = 15.023$ K, which gave $(\Delta S)_{tr} = 18.6$ mJ/mole K, and by the result for $(\Delta S)_{tr}$ on the melting curve discussed above.

The foregoing discussion can be summarized by stating that the largest measured values of $(\Delta S)_{tr}$ give the true molar transition entropy. Within the random error estimate of about $\pm 10\%$ there is no indication of any temperature dependence of these data from the triple point to 19.5 K. The best estimate of $(\Delta S)_{tr}$ over this temperature range is $(\Delta S)_{tr} = 18.3 \pm 2$ mJ/mole K. The calculation of derived thermodynamical properties will be based on this value.

Several theoretical estimates for the transition entropy have been given. Isenberg and Domb¹² published a calculation of the difference in specific heat between a fcc and hcp lattice as a function of reduced temperature, T/Θ , where Θ is the Debye temperature. The difference $\Delta C_V = C_V(\text{fcc}) - C_V(\text{hcp})$ is positive everywhere, it has a maximum at $T/\Theta = 0.07867$ and becomes quite small above $T/\Theta = 0.2$. The Debye temperature of solid helium for the molar volume corresponding to the triple point ($V = 12.22$ cm³/mole) is about 82 K, so that the triple point occurs at $T/\Theta = 0.183$. Numerical integration of $\Delta C_V/T$ gives a transition entropy of $(\Delta S)_{tr} = 11.9$ mJ/mole K at the triple point. The transition line moves to lower values of T/Θ with increasing density. At the highest density of this work we have a transition temperature of $T_{tr} = 19.53$ K and an estimated Debye temperature of $\Theta = 132$ K, or $T/\Theta = 0.148$. At this reduced temperature, the Isenberg and Domb calculations give $(\Delta S)_{tr} = 11.5$ mJ/mole K. Very little temperature dependence of $(\Delta S)_{tr}$ is therefore predicted. Later calculations were given by Hoover¹³ for a nearest-neighbor harmonic oscillator model [$(\Delta S)_{tr} = 12.5$ mJ/mole K], and by Alder *et al.*¹⁶ for a hard-sphere particle in the Wigner-Seitz cell of the respective lattice [$(\Delta S)_{tr} = 16.6$ mJ/mole K]. The most recent and detailed calculations of Holian *et al.*,¹⁷ who use a realistic cell potential in the Wigner-Seitz cell of the two lattices, give $(\Delta S)_{tr} = 18.3$ mJ/mole K. The experi-

mental data agree therefore quite well with all these calculations and, in particular, with the predictions of Holian *et al.*, although the excellent agreement in this case is no doubt somewhat fortuitous.

3. Derived thermodynamic data

a. *The molar volume change.* The molar volume change associated with the transition, $(\Delta V)_{tr}$, can be obtained from the Clausius-Clapeyron equation

$$\left(\frac{dP}{dT}\right)_{tr} = \frac{(\Delta S)_{tr}}{(\Delta V)_{tr}} \quad (13)$$

In order to evaluate $(\Delta V)_{tr}$, we use a constant transition entropy of 18.3 mJ/mole K from the triple point to about 16 K. The equilibrium phase line in this range is given by Table III. The molar volume change obtained in this way is given in Table IV and shown in Fig. 18. The steep increase of the transition line slope as the triple point is approached is reflected in the fall of $(\Delta V)_{tr}$ to quite small values, and possibly zero, at the triple point. The smoothed data of Table III assume, in fact, that the phase line becomes infinitely steep at the triple point, the molar volume change obtained by using this assumption will therefore go to zero at the triple point. The experimental data, as discussed in Sec. III B 1, are at present not sufficiently precise, however, to distinguish between a very large slope and an infinite one; as a consequence the molar volume change at the triple point may be finite, but at least an order of magnitude smaller than above 16 K. Near 16 K, where the phase line assumes its linear part, the molar volume change becomes constant at $(\Delta V)_{tr} = 0.33$ mm³/mole, which is equivalent to 27 ppm of the molar volume at the triple point. This value will continue to hold to about 4 kbar, if the transition entro-

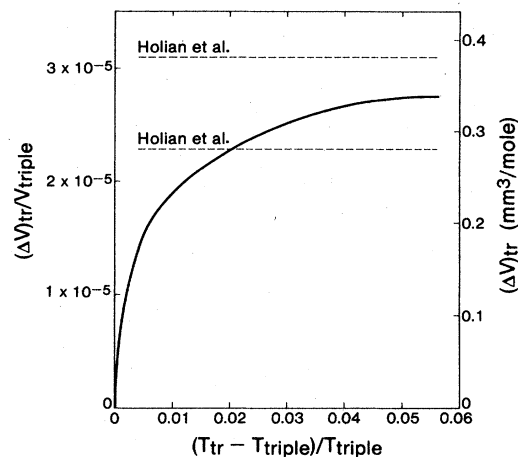


FIG. 18. Smooth values of the molar volume change as function of reduced temperature. $T_{triple} = 14.992$ K, $V_{triple} = 12.22$ cm³/mole. The dashed lines are theoretical estimates of Holian *et al.* (Ref. 17).

py stays constant over this range, which is probably the case (see the discussion in the previous paragraph). While the relative variation of $(\Delta V)_{tr}$ with temperature depends only on the accuracy with which a smooth phase line can be drawn, it should be remembered that the actual accuracy of $(\Delta V)_{tr}$ depends on the uncertainty in $(\Delta S)_{tr}$, which is about $\pm 10\%$. The high-temperature limiting value of $(\Delta V)_{tr}$ should therefore be quoted as 0.33 ± 0.04 mm³/mole. The only previous experimental value of $(\Delta V)_{tr}$ in ⁴He is due to Dugdale and Simon,¹ who found 0.4 mm³/mole as an average value between the triple point and 2 kbar, in good agreement with the present data. For the corresponding transition between hcp and fcc ³He a value of $(\Delta V)_{tr} = 0.14$

TABLE IV. Smoothed transition data, hcp \leftrightarrow fcc ⁴He. [$\Delta = (\text{fcc}) - (\text{hcp})$.]

P_{tr} (bar)	T_{tr} (K)	$(\Delta V)_{tr}$ (mm ³ /mole)	$(\Delta H)_{tr}$ (mJ/mole)	$(\Delta U)_{tr}$ (mJ/mole)	$-(\Delta F)_{tr}$ (mJ/mole)
1127 ^a	14.992	0	274	274	0
1150	14.993	0.026	274	271	3
1200	15.006	0.085	275	264	10
1300	15.087	0.202	276	250	26
1400	15.219	0.257	279	243	36
1500	15.368	0.293	281	237	44
1600	15.537	0.320	284	233	51
1700	15.717	0.332	288	231	56
1750	15.809	0.333	289	231	58

^aTriple point.

mm³/mole was given by Dugdale and Franck,^{2,3} based on two transition points (in heating) close to the triple point of ³He [$T_{\text{triple}}(^3\text{He}) \approx 17.80$ K]. The lower $(\Delta V)_{\text{tr}}$ value in ³He was a direct consequence of the larger transition line slope observed in ³He compared to the average slope for ⁴He between triple point and 2 kbar, since the measured latent heat was almost identical for both isotopes. It was not understood at the time why ³He should have a $(\Delta V)_{\text{tr}}$ so much lower than that found in ⁴He; or put another way, why the transition line slope should be so much larger in ³He. If, however, the steepening of the transition line on approaching the triple point, observed for ⁴He, should also occur in ³He, then these results become compatible. The average reduced temperature on which the transition line slope of ³He was based, can be estimated as $(T_{\text{tr}} - T_{\text{triple}})/T_{\text{triple}} \approx 0.003$. At this reduced transition temperature, the ⁴He transition has a $(\Delta V)_{\text{tr}}$ of 0.15 mm³/mole, in almost perfect agreement with the ³He result. This comparison suggests that the behavior of the two isotopes at the hcp-fcc transition is indeed very similar. It is clear that a detailed study of the phase line of ³He should be undertaken.

Theoretical estimates of $(\Delta V)_{\text{tr}}$ have been given only by Holian *et al.*¹⁷ who quote for the transition close to the triple point two values, $(\Delta V)_{\text{tr}} = 0.28$ and 0.38 mm³/mole, depending on the interatomic potential used. The high-temperature value of $(\Delta V)_{\text{tr}}$ is therefore in excellent agreement with these predictions. The sharp fall of $(\Delta V)_{\text{tr}}$ as the triple point is approached, and therefore also the large increase in transition line slope, are, however, unexpected. This aspect of the transition has been discussed in a previous paper.¹⁹

b. Internal and free energy differences. The enthalpy difference (i.e., the latent heat) at the transition is given by

$$(\Delta H)_{\text{tr}} = T_{\text{tr}}(\Delta S)_{\text{tr}} \quad (14)$$

From this we can obtain the difference in internal energy between the two phases as

$$(\Delta U)_{\text{tr}} = T_{\text{tr}}(\Delta S)_{\text{tr}} - P_{\text{tr}}(\Delta V)_{\text{tr}} \quad (15)$$

and the difference in Helmholtz free energy F as

$$(\Delta F)_{\text{tr}} = -P_{\text{tr}}(\Delta V)_{\text{tr}} \quad (16)$$

The experimental error in these quantities is essentially that of $(\Delta S)_{\text{tr}}$, i.e., $\pm 10\%$. The differences refer here to the difference between the phases at the transition, i.e., at constant T_{tr} and P_{tr} , and $\Delta = (\text{fcc}) - (\text{hcp})$. The various energies are tabulated in Table IV, and shown in Fig. 19 as a function of transition pressure. The internal energy difference is found at 0.274 J/mole at the triple point, it gradually decreases to 0.230 J/mole at 15.9 K. Above 15.9 K the phase line has constant slope for the range of

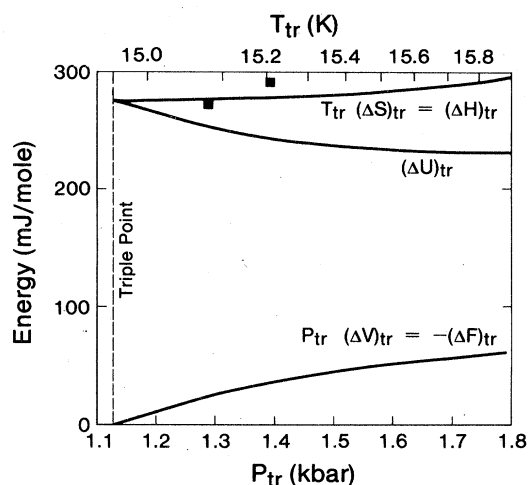


FIG. 19. Differences in thermodynamical functions from the triple point to a transition pressure of 1.8 kbar. Black squares: theoretical estimates of $(\Delta H)_{\text{tr}}$, Holian *et al.* (Ref. 17).

these measurements. If the transition entropy also stays constant, which is probably the case, then $(\Delta U)_{\text{tr}}$ will remain constant above 15.9 K at 0.23 J/mole. This can be seen from the equivalent expression for $(\Delta U)_{\text{tr}}$:

$$(\Delta U)_{\text{tr}} = (\Delta S)_{\text{tr}} \left[T_{\text{tr}} - P_{\text{tr}} \left(\frac{dT}{dP} \right)_{\text{tr}} \right] \quad (17)$$

$$\frac{d(\Delta U)_{\text{tr}}}{dP_{\text{tr}}} = -(\Delta S)_{\text{tr}} P_{\text{tr}} \left(\frac{d^2T}{dP^2} \right)_{\text{tr}} \quad (18)$$

The experimental energy differences can at present only be compared with the calculations of Holian *et al.*¹⁷ which are tabulated in Table V for the two molar volumes within the range of the present work. In Table V, $\Delta\phi$ is the lattice potential-energy difference as calculated by Holian *et al.* using the interatomic potential of McLaughlin and Schaefer.³⁴ ΔU_0 are internal energy differences at 0 K and ΔE_0 are zero-point energy differences, where $\Delta U_0 = \Delta\phi + \Delta E_0$. For the calculation of ΔE_0 lattice dynamics corrections were included in case c, but not in b, leading to the two different values of ΔU_0 , case b and c (notation of Holian *et al.*). Estimates for the internal energy difference at the transition temperature T_{tr} were also given by Holian *et al.* For their case b, they equated this quantity with ΔU_0 (case b), whereas in case c they added an estimation of the thermal part of ΔU to ΔU_0 , and the result is given in Table V as $(\Delta H)_{\text{tr}}$ (case c). The identification of the calculations for the internal energy difference at the transition temperature with the enthalpy difference can be made because the calculations were made at

TABLE V. Energy differences between fcc and hcp ^4He . V in cm^3/mole , energies in mJ/mole , $\Delta = (\text{fcc}) - (\text{hcp})$. All entries, with the exception of the last column, are from Holian *et al.* (Ref. 17). Case *b*: cell model internal energy; case *c*: lattice dynamics correction to cell model internal energy included. Last column: experimental data of this work. The various terms are explained in the text.

V	$\Delta\phi$	ΔU_0 (b)	ΔU_0 (c)	ΔE_0 (b)	ΔE_0 (c)	$(\Delta H)_{\text{tr}}$ (c)	$(\Delta H)_{\text{tr}}$ (expt.)
11.5	74.8	291	166	216	91	273	277
9.5	108.1	416	166	308	58	318	351

constant volume. One has in general

$$(\Delta H)_{\text{tr}} = (\Delta U)_{\text{tr}} + P_{\text{tr}}(\Delta V)_{\text{tr}}, \quad (19)$$

where

$$(\Delta U)_{\text{tr}} = U_{\text{fcc}}(T_{\text{tr}}, V + \Delta V) - U_{\text{hcp}}(T_{\text{tr}}, V).$$

Since $(\Delta V)_{\text{tr}}$ is small, one can develop

$$\begin{aligned} (\Delta U)_{\text{tr}} = \Delta U(T_{\text{tr}}, V) &+ \left[\frac{\partial U_{\text{fcc}}}{\partial V} \right]_T (\Delta V)_{\text{tr}} \\ &+ \frac{1}{2} \left[\frac{\partial^2 U_{\text{fcc}}}{\partial V^2} \right]_T (\Delta V)_{\text{tr}}^2 \end{aligned} \quad (20)$$

or

$$(\Delta U)_{\text{tr}} = \Delta U(T_{\text{tr}}, V) - P_{\text{tr}}(\Delta V)_{\text{tr}} - \frac{1}{2} \left[\frac{\partial P}{\partial V} \right]_T (\Delta V)_{\text{tr}}^2. \quad (21)$$

The quadratic term can be estimated as $\sim 10^{-5}$ times the linear term, so that

$$\Delta U(T_{\text{tr}}, V) = (\Delta U)_{\text{tr}} + P(\Delta V)_{\text{tr}} = (\Delta H)_{\text{tr}}. \quad (22)$$

Direct comparison with experiment is possible only at the transition temperature, since experimental estimates of the thermal part of the internal energy difference are not available. (This would require the measurement of the specific-heat difference from 0 K to T_{tr} , the fcc phase being maintained in metastable equilibrium.) As Table V shows, the experimental and theoretical data compare quite favorably. Case *c*, with lattice dynamical corrections to ΔE_0 and the thermal part of ΔU included, appears to be closer to the experiment.

The energy relation giving the experimental latent heat can now be written as

$$(\Delta H)_{\text{tr}} = \Delta\phi + \Delta E_0 + \Delta U_{\text{th}}, \quad (23)$$

where the terms on the right-hand side refer to constant volume and have been defined before. "Exper-

imental" values of ΔE_0 could only be quoted with confidence if both $\Delta\phi$ and ΔU_{th} were known with sufficient accuracy. From Table V we see that ΔU_{th} is theoretically estimated at 60 to 90% of ΔU_0 . No estimate of the presumed accuracy of this term is available, but it cannot reasonably be expected to be better than $\pm 10\%$, possibly worse. Uncertainties in $\Delta\phi$ are also large because of the uncertainty in the interatomic potential of helium, but are at present difficult to estimate. Any "experimental" value of ΔE_0 would reflect these uncertainties.

In the theoretical calculations of ΔE_0 , one can further divide ΔE_0 into two parts, corresponding to contributions from the cell model, and contributions from lattice dynamics

$$\Delta E_0 = \Delta E_{0,\text{cell}} + \Delta E_{0,\text{latt}}. \quad (24)$$

In here the cell part is found to be positive by Holian *et al.* The lattice dynamical contribution, on the other hand, can be seen from Table V to be negative, in agreement with the earlier conclusions of Isenberg and Domb.¹² Neglect of the cell part of the zero-point energy differences would lead to much lower estimates of ΔU_0 , and therefore also of $(\Delta H)_{\text{tr}}$, in disagreement with experiment. The experimental data can then be interpreted as giving support to this positive contribution to ΔE_0 , although little can be said about its value.

IV. SUMMARY

The first-order transition between hcp and fcc ^4He was studied using a calorimetric method from the triple point to about 3.9 kbar. Several new interesting properties of this transition were observed. Features connected with the kinetics of the transition are the following: Each crystal shows a quite well-defined transition temperature in heating, T_h , and in cooling, T_c . Temperature hysteresis is always observed, with T_h always larger than T_c . The amount of tempera-

ture hysteresis, ΔT_{tr} , is somewhat dependent on crystal preparation, with T_c more susceptible to change than T_h , and much more strongly dependent on pressure (i.e., density). At the largest pressure of 3.9 kbar $(\Delta T)_{tr}$ is about 1.1 K, it then decreases with falling pressure to about 30 mK close to the triple point. In the immediate vicinity of the triple point, the temperature hysteresis increases again, to about 200 mK for transitions observed in crystals in the presence of fluid. The transition, both in heating and cooling, has a definite thermal width; this width is also dependent upon the crystal preparation, and the density. In general it is found that large temperature hysteresis implies also a large thermal width, so that its dependence on pressure follows that of the temperature hysteresis. The thermal width is further dependent upon the thermal treatment of the crystal; it is in general not reproducible for different passes through the transition, nor is it the same for heating and cooling transition. In some cases, the transition occurs in several stages; it also shows burstlike behavior leading to adiabatic cooling for the heating transition and adiabatic heating for the cooling transition. These more irregular characteristics are most pronounced at low pressures, close to the triple point. Since these kinetic aspects are similar to those that are commonly observed in martensitic transitions, it is proposed that the transition proceeds via a martensitic mechanism. Further studies of the kinetic aspects of the transition would therefore be of considerable interest, some studies of this kind have already been done using an optical method.²⁵ Theoretical investigations of the transformation kinetics of this transition have so far not been published, they will have to follow the considerable body of work available for other martensitic transitions.²⁷

The equilibrium features of the transition are as follows: Above about 15.8 K and 1.75 kbar, the phase line appears to be linear with a slope of 550 bar/K. The phase line therefore does not show the

theoretically predicted increase in slope with pressure.¹⁷ Below 15.8 K, the phase line shows increasing slope with falling pressure, leading to infinite or nearly infinite slope at the melting line. This feature is completely unexpected. Several suggestions can be advanced for the explanation of this phenomenon, since the weakness of the transition makes its equilibrium behavior susceptible to quite small contributions to the free energy. Such contributions can, e.g., come from thermally activated vacancies as the melting line is approached. Other possibilities are small contributions to the bulk internal energy, that might be connected with the rapidly increasing vibration amplitude when approaching the melting line. The case of any of these possibilities can, however, only be convincingly put if it is backed up by detailed numerical calculations.

Measurements of the transition entropy are in good agreement with theoretical calculations, probably over the total density range investigated. In particular, the transition remains of first order at the melting line. The molar volume change of the transition is also in agreement with theory above 15.8 K, i.e., for the linear part of the phase diagram. The increasing slope of the phase line at low pressures, however, leads to a much reduced molar volume change, which will vanish, or at least be reduced by an order of magnitude, at the melting line. A theoretical understanding of this effect is related to an understanding of the phase line behavior at low densities.

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