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High-pressure triple point in helium: The melting line of helium up to 240 kbar

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A quasi-isochoric scanning method has been used to study the phase diagram of helium from 200 to 460 K and from 70 to 240 kbar. The melting line is shown to be a smooth curve that lies close to extrapolations from much lower pressure. Also, no anomalies were observed near room temperature, and thus there is no evidence for an fcc-bcc transition in the solid phase. On the basis of the experiments, it is concluded that the fcc-bcc-fluid triple point reported by previous investigators does not exist. The implications for the phase diagram are discussed.

Knowledge of the properties of helium under pressure is of great interest,[1] first, since it is a simple system on which theoretical calculations are relatively easy to perform. Second, using the law of corresponding states, the properties of other substances can be extrapolated to regions where experiments are very difficult to perform. Third, since large amounts of compressed helium are present, this knowledge will help us to understand our solar system. Over the last decade, helium has received increasing attention due to the advent of the diamond anvil cell (DAC) and especially because of the observation of a triple point[2] along the melting curve at 116 kbar and 299 K, since this implies that there is a new high-pressure solid phase other than fcc. The structure of this solid could not be determined experimentally. This has given rise to a number of theoretical papers[3] that favored the bcc structure as the high-pressure phase, except one that concluded that bcc is not thermodynamically stable under these conditions.[4] However, recent x-ray diffraction measurements by Mao *et al.*[5] have shown that solid He has an hcp structure at 300 K and pressures of 156 kbar and up. Thus it was proposed that the low-temperature hcp-fcc transition is connected to the high-pressure triple point, yielding an fcc-hcp-fluid triple point instead of an fcc-bcc-fluid triple point.

Recently, a study was undertaken in our laboratory[6] to investigate the three-phase line $S_{N2}+S_{He}+F$ in the system He-N_2, because a quadruple point was expected in the vicinity of the triple point of helium. The result showed a smooth phase line from 40 to 170 kbar with no evidence of a quadruple point. Furthermore, no evidence was found of a solid-solid transition in the helium-rich phase.

These facts prompted us to start an investigation of helium with three goals: (i) a search for the solid-solid phase transition of helium that intersects the melting line at the triple point. (ii) a comparison of the melting line with the three-phase line $S_{N2}+S_{He}+F$ in order to decide whether nitrogen is soluble in helium or not, and (iii) reproduction of the triple point in order to understand the absence of a quadruple point in He-N_2.

^{4}He does not solidify at ambient pressure, but solidifies into an hcp structure if pressure in excess of 25 bars is applied.[7] At 14.9 K and 1116 bars, there is a triple point along the melting line where an fcc structure occurs. The hcp-fcc transition line was investigated up to 10 kbar, where it shows a large hysteresis,[8] while the melting line was investigated up to 20 kbar.[9,10] In one of the earliest studies of the phase diagram performed in a DAC by Loubeyre *et al.*,[11] the pressure range from 100 to 170 kbar was investigated. These authors reported the existence of a triple point at 306 K and 130 kbar, as well as a new solid-solid phase line which they suggested was an hcp-fcc transition. A subsequent study[2] by the same research group revealed a clear cusp on the melting line at 116.5 kbar and 299 K, but no solid-solid phase transition. The new structure was tentatively specified as bcc. Another investigation[12] by this group showed that in the region between 110 and 150 kbar, melting may occur within a domain with a width of 10 K or 5 kbar. This domain was assigned to the presence of metastable phases and thus to a triple point in this range, although no cusp and again no solid-solid transition was observed. It was suggested that the new structure is bcc. At room temperature and pressures above 155 kbar, Mao *et al.*[5] have shown by x-ray diffraction that solid helium has an hcp structure.

The DAC and loading system used in this investigation are described in detail in another paper.[13] The sample space is loaded by pressurizing the DAC in a high-pressure vessel with a gas, after purging the vessel thoroughly. The gas used is of research-grade quality with a purity of 99.9999%.

The pressure was determined with the usual ruby technique, using the quasihydrostatic scale.[14] The temperature shift of the ruby lines was measured at ambient pressure in the experimental temperature range before and after each experiment, and the results were averaged.[15] After the third helium run from 170 to 240 kbar, the ruby chip was lost on unloading, so that for this run we used only the calibration up to 400 K performed before the experiment. The calibration was extrapolated to higher temperatures using earlier experiments. The ruby was excited with a HeCd laser, and we checked that no heating effects occurred. The error in pressure relative to the ruby scale was estimated to be ±0.5 kbar up to 400 K, increasing to ±2.0 kbar at the highest temperatures. The temperature was measured with a calibrated platinum resistance thermometer, with an accuracy of 0.5 K.

Three experiments were performed with pure helium. The experimental techniques used were isochoric temperature scanning and visual observation. In a (quasi) isochoric scan,[16] the temperature of the DAC is varied under nearly isochoric conditions and a first-order phase transition manifests itself as a discontinuity in pressure. In carefully performed experiments, one can record pressure jumps of about 0.2 kbar, which correspond to volume discontinuities in the order of 0.1%.[17] The previous authors[2] reported a marked difference of 2 kbar in pressure jump on melting below and above the triple point, which is expected to be about the pressure jump of the solid-solid transition. From simulation data,[3] the fcc-bcc transition was expected to have a volume discontinuity of about 0.3%. For the hcp-fcc transition, only low-pressure data are known to us, showing a volume discontinuity[18] of about 0.004%. With visual observation, it was possible to distinguish the solid from the fluid phase through the presence or absence of interfaces, but it was hard to determine the exact transition temperature in this way.

An example of an isochoric scan of the melting line is shown in Fig. 1. It can be seen that in the solid phase the pressure is nearly constant up to a few degrees before the melting line (about 380 K), where it starts to increase slowly. Subsequently, we observe a marked increase over a larger interval due to melting (starting at 383 K) until, finally, the whole sample has melted near 392 K. We interpret the slow increase in pressure prior to the melting line as the premelting behavior observed by previous investigators.[2] Most of the scans were measured with increasing temperature (in steps of 1 K every 15 min), but some were recorded with decreasing temperature. There are no differences between these scans, indicating that no superheating or undercooling occurs. The cooling scans were started from the coexistence line, because when they were started from the homogeneous fluid phase, undercooling would occur, ranging from 10 to 35 K.

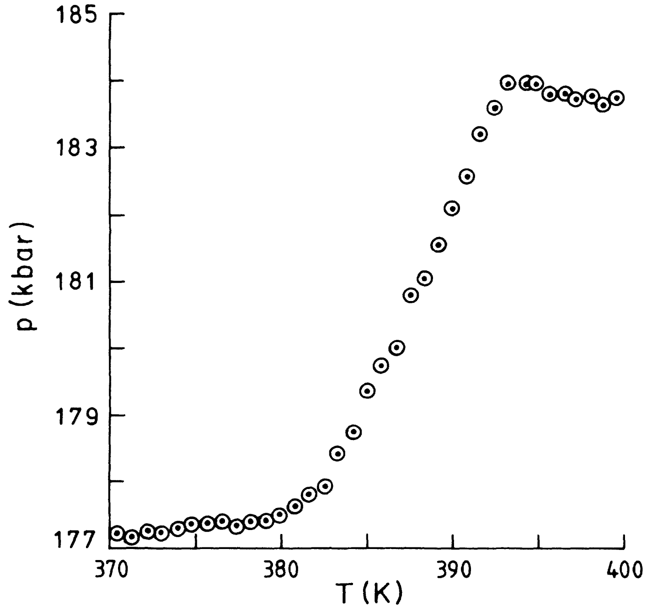

FIG. 1. Quasi-isochoric scan in helium.

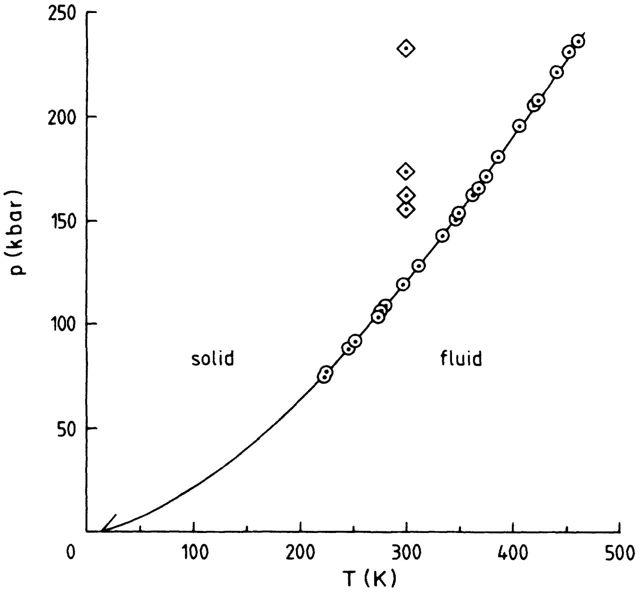

FIG. 2. Phase diagram of helium. Note the hcp-fcc phase line (Ref. 8) at low temperatures. The circles are our melting data, and the diamonds are the structural data from Mao *et al.* (Ref. 5).

Since we have obtained more than 200 data points, only the midpoints of the melting transitions are shown in Fig. 2. Our data lie on a smooth curve that can be fitted with a Simon-Glatzel equation from the low-pressure hcp-fcc-fluid triple point to our highest data, yielding

$$p(\text{kbar})=0.016067T(\text{K})^{1.5650}-0.0 , \qquad (1)$$

with a standard deviation of 0.4 kbar. In Fig. 3, the difference between Eq. (1) and the data points is shown.

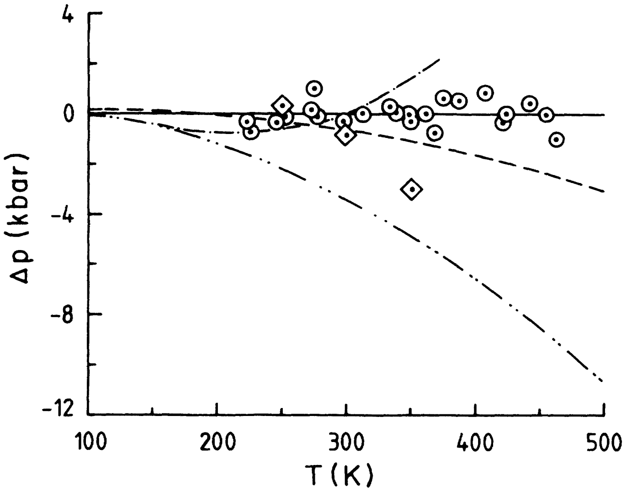

FIG. 3. Deviations of melting data from Eq. (1). The circles are our data, the diamonds are from Loubeyre *et al.* (Ref. 2), the dashed line is from Mills *et al.* (Ref. 9), the dashed-dotted line is from Besson *et al.* (Ref. 12), and the dash-double-dotted line is from Crawford and Daniels (Ref. 10).

No systematic deviations can be observed. From the same figure it can be seen that our results are in good agreement with the fcc-fluid line previously measured, fitted up to[12] 330 K. Our measurements do not agree as well with the bcc-fluid point from Ref. 2 at 350 K, which differs by 3 kbar. For comparison, we have corrected the previous measurements, evaluated with the linear ruby scale, to the quasihydrostatic pressure scale.[14] Our data are also in good agreement with a Simon-Glatzel equation, fitted to data up to 20 kbar by Mills *et al.*[9] From Fig. 3, one can see that even at 460 K, the discrepancy is less than 3 kbar, which is clearly inside the error of the ruby scale itself (probably around[19] 3% (7 kbar) in this region). With respect to the Simon-Glatzel equation fitted up to 10 kbar,[10] the discrepancy is somewhat larger, but still small considering the large extrapolation.

Compared to earlier experiments, some remarkable differences are observed. In the first place, no cusp was observed at 299 K. This is witnessed by the fact that the melting line is a smooth curve up to the highest pressures, as discussed above.

Furthermore, in this experiment, no enhancement of the scatter of the data points was noted in the range from 110 to 150 kbar (or from 280 to 350 K) as observed elsewhere.[12] This can be appreciated from Fig. 3, where it can be seen that the scatter in this range is less than 0.5 kbar. Entering the solid phase by increasing the pressure instead of cooling did not make any difference.

In one of the previous studies,[2] it was also observed that below 300 K, the premelting interval was about 3 K, while above 300 K it was about 10 K. As mentioned before, we also noted premelting behavior, which was investigated both in warming and in cooling scans. For all temperatures, the premelting interval was between 0 and 3 K, with no systematic tendencies.

Another phenomenon observed in one of the previous studies[2] was that the temperature interval of coexistence was 8 K below 300 and 5 K, decreasing to 2 K above 300 K. These temperature intervals correspond to pressure intervals of 5.0, 3.2, and 1.3 kbar, respectively. In our study, it was observed that the pressure intervals were about 6 kbar over the full temperature range as can be seen in Fig. 4. In this plot, we have not included pressure jumps from scans where the gasket clearly yielded, as inferred from decreases in pressure in the one-phase region.

In order to search for a solid-solid transition, we performed a series of long isochoric scans in the solid phase: two at about 103 kbar from 140 and 155 K to the melting line, one at 149 kbar from 200 K to the melting line, one at 161 kbar from 280 K to the melting line, and finally one at 230 kbar from 370 K to the melting line. In neither of these scans was a pressure jump or other sign of a phase transition observed.

The constant values of the pressure jumps and premelting trajectories as a function of melting temperature, the smoothness of the melting curve without an apparent cusp up to 240 kbar, and the small and constant scatter of the data points seem to indicate that there is no triple point within the present experimental range, as reported by others.[2,11,12] This is emphasized by the fact that our data are in very good agreement with a Simon-Glatzel equation, fitted for data up to 20 kbar.[9] These arguments lead to the conclusion that the melting line is still the fcc-fluid line. Another argument for this statement is the absence of a quadruple point between 40 and 170 kbar in the mixture[6] He-N_2, even though the corresponding three-phase line runs close to the melting line in the *p*-*T* plane. It is then expected that the quadruple point will be close to the triple point.

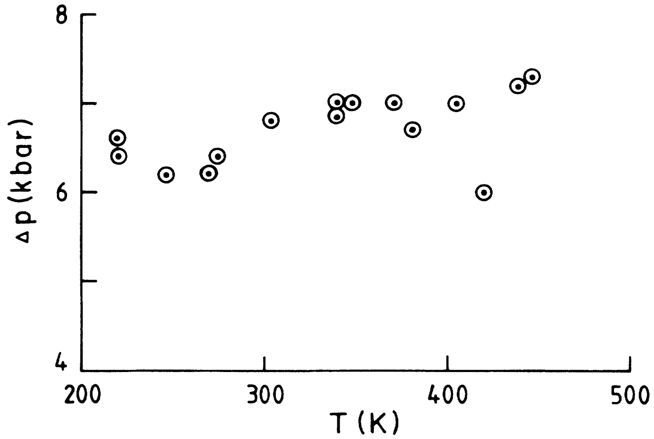

FIG. 4. Pressure jumps on melting vs temperature.

The absence of a solid-solid transition seems to contradict the results of Mao *et al*,[5] who observed that helium has an hcp structure at room temperature above 155 kbar. We have already noted that near the low-temperature triple-point[7] hcp-fcc fluid, the volume jump on going from hcp to fcc is only[18] 0.004%. This is much less than our detection limit. It is, therefore, not unexpected that no transition was observed. It then does not seem contradictory to propose that the low-temperature hcp-fcc phase line runs to higher pressures and temperatures, eventually meeting the melting line above 240 kbar. This can be more easily reconciliated with the data of Mao *et al.*[5] by realizing that at low temperature this transition shows a hysteresis[8] of 10% of the transition temperature and pressure, and that it is not quite clear from their paper whether Mao *et al.* had lowered or increased the pressure prior to their first experimental point.

On the other hand, it can not be excluded that a triple-point hcp-fcc fluid could remain unnoticed when looking at the melting line. This is also the case at the low-temperature triple point,[20] due to the small difference in thermodynamic properties of the two solid phases hcp and fcc. Here, the possible high-pressure triple point could be situated anywhere along the melting line.

In conclusion, contrary to previous investigations (Refs. 2, 11, and 12), no evidence has been found for a high-pressure fcc-bcc-fluid triple point on the melting line of pure helium up to 240 kbar. On the basis of our experiments, we state that the triple point reported by previous investigators does not exist. This is consistent with computer simulations.[4] The lack of a sign of a solid-solid transition is also in agreement with this conclusion. Finally, the present investigation confirms the recent conclusion[6] that the melting line lies at higher temperature than the three-phase line $S_{N2}+S_{\mathrm{He}}+F$ of the mixture He-N_2. Therefore and because of the absence of a quadruple point, the method of investigating solid solubility through the comparison of phase lines, which was successfully applied to the solubility of helium in solid nitrogen,[21] cannot be applied to the solubility of nitrogen in helium.

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