

Liquid-Solid Phase Transition in He³-He⁴ Mixtures,

P. M. Tedrow and D. M. Lee [Phys. Rev. 181, 399 (1969)]. Paragraphs on pp. 410 and 411 were inadvertently transposed. For convenience, both corrected pages are herewith reproduced in their entirety, and should be substituted for pp. 410-411 in the issue of note.

...three phases in accordance with the discussion of the phase rule. Figure 13 resembles an ordinary eutectic diagram with two liquids and one solid rather than two solids and one liquid coexisting.

Figure 14 is drawn for a pressure of 25.6 atm. The question of what happens as the He⁴-rich hexagonal close-packed (hcp) solid begins to form at about 25.0 atm is related to the melting curve minimum in pure He⁴. This is treated in detail by LePair *et al.*¹¹ and will not be discussed here. At 25.6 atm, the hcp solid stretches along the left side of the diagram and has isolated a pocket of liquid, L₁. Two more univariants have appeared, hcp-L₁-L₂ and hcp-bcc₁-L₁. The univariant hcp-bcc₁-L₁ appears twice because it is thought to have a minimum in the *P-T* plane, and the plane *P*=25.6 atm cuts it at two different temperatures. The projections of the hcp-L₁-L₂ and bcc₁-L₁-L₂ univariants in Fig. 14 onto the *P-T* plane are shown in Fig. 5. These figures show that hcp-bcc₁-L₁ and bcc₁-L₁-L₂ move to lower temperatures as *P*

increases while hcp-L₁-L₂ moves to higher temperatures.

In Fig. 15 at 26 atm the three univariants in Fig. 14 have met at about 0.37°K. At higher pressures, no He⁴-rich liquid L₁ can exist. This point is the quadruple point labeled Q₂ deduced from the experimental results earlier in the paper [Sec. IV(B)] corresponding to the coexistence of four phases, hcp, bcc₁, L₁, and L₂. The four intersecting univariants associated with this quadruple point are bcc₁-L₁-L₂, hcp-L₁-L₂, bcc₁-hcp-L₁, and bcc₁-hcp-L₂.

The interpretation of the experimental results obtained in this work in terms of a quadruple point is supported by observations by Zinovieva²² who visually detected the stratification of an 86.3% mixture into two liquid phases at temperatures of 0.30 and 0.35°K and a pressure of 26 atm with no solid being present. These observations agree qualitatively with the data in Fig. 5 and with the proposed phase diagram presented here if her observations were made in the two-phase region between hcp-L₁-L₂ and bcc₁-L₁-L₂ (Fig. 14). In the same manner that a triple point is useful in establishing a fixed temperature point in a single-phase system, a quadruple point in the He³-He⁴ system provides a fixed temperature point below 1°K, which is not a function of pressure or impurity content.

The location of the line bcc₁-hcp-L₂ is shown in Fig. 16 at 26.2 atm. This line also appears in Fig. 5. In the high-temperature region of the diagram, the univariant hcp-bcc₁-L₁ has disappeared and the boundaries of the two solid phases have met at the X=0 axis. This point corresponds to the lower triple point⁶ in pure He⁴.

In Fig. 17 at 26.5 atm, the solid-phase separation⁵ first appears and is thought to be a phase separation into two bcc phases labeled bcc₁ and bcc₂. This gives rise to another univariant, bcc₁-bcc₂-L₂. CP marks the critical point of the solid-phase separation. Along the pure He⁴ axis, the thin region of bcc solid⁶ in pure He⁴ is in evidence at about 1.5°K. The data points in this figure belong to the bcc₁-hcp-L₂ line and not to the bcc₁-bcc₂-L₂ univariant. The projection of the two univariants onto the *P-T* plane is shown in Fig. 20.

At 26.75 atm, in Fig. 18, the univariants bcc₁-bcc₂-L₂ and bcc₁-hcp-L₂ have met, giving rise to a second quadruple point, with the four phases bcc₁, bcc₂, hcp, and L₂ coexisting.

Again there must be four univariants meeting at this quadruple point. The other two, bcc₁-bcc₂-hcp and bcc₂-hcp-L₂, are shown in Fig. 19 at 30 atm. These surfaces, too, are shown in Fig. 20, projected onto the *P-T* plane. At 30 atm, pure He³ has begun to solidify, isolating a small pocket of L₂ in the lower right-hand corner. This is re-

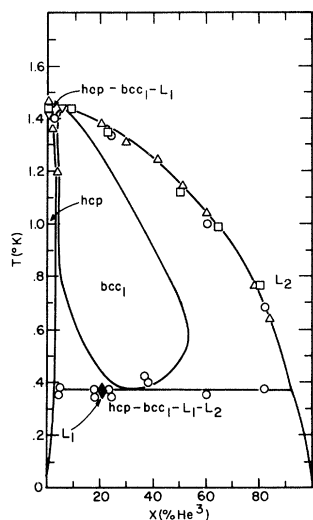


FIG. 15. At 26 atm and 0.37°K, the four phases, hcp solid, bcc₁ solid, liquid L₁, and liquid L₂ are in equilibrium, i. e., a quadruple point exists at this temperature and pressure. ○ This work; ▽ Vignos and Fairbank⁶; □ Le Pair *et al.*¹¹; △ Zinovieva²²; ▲ Lipschultz *et al.*³⁰

lated to the minimum in the He³ freezing curve.

The location of all of the univariant surfaces is summarized in Fig. 20 where their projections on the *P-T* plane are shown. The parts of the surfaces which have been measured in this laboratory have data points shown.

A few words must be said concerning the extrapolation of some of the univariants beyond the region where they have been measured. The ways of terminating univariants were mentioned earlier in this section. They can terminate at critical point lines or pure substance lines, and at quadruple points where four must meet.

The *bcc*₁-*hcp*-*L*₂ univariant has been drawn so that it meets the pure He³ melting curve at high pressure and low temperature. This must be the case if the *hcp* solid is essentially inert and does not affect the situation at all. Then nearly pure solid He³ (*bcc*₁) and nearly pure liquid He³ (*L*₂) are what determine the path of *bcc*₁-*hcp*-*L*₂. Since pure liquid He³ and pure solid He³ are in equilibrium along the He³ melting curve, the behavior shown in Fig. 20 is reasonable if the *hcp* solid is pure He⁴ at absolute zero.

The *hcp*-*L*₁-*L*₂ curve is shown merging into the pure He⁴ melting curve as the temperature approaches zero. If Fig. 14 is correct, then as the pressure decreases from 25.6 atm and the *hcp*-*L*₁-*L*₂ line moves toward lower temperatures, *L*₁ and *L*₂ become purer until at absolute zero the pure *hcp* solid will be in equilibrium with the pure He⁴ and pure He³ liquids assuming complete phase separation at absolute zero. In this condition the solid will be at the bottom of a container with the He⁴ liquid above it and the He³ liquid on top. If phase separation is complete at absolute zero, He³ atoms cannot spontaneously pass into either liquid He⁴ or solid He⁴ whereas the He⁴ atoms can move freely from liquid to solid. Thus it seems reasonable that the three-phase equilibrium curve *hcp*-*L*₁-*L*₂ should extrapolate to the He⁴ melting curve. If the liquid phase separation is incomplete at absolute zero, as is the case for saturated vapor pressures^{3,4} that is, if *L*₁ can have finite concentration of He³ at absolute zero, then the situation can be quite different. If the *hcp* solid meets the liquid phase separation surface in such a way that it "traps" a region of *L*₁ on the low-temperature side, then the univariant *hcp*-*L*₁-*L*₂ will have a minimum. Figure 21 shows a series of *T-X* diagrams for incomplete phase separation which leads to a minimum in the *hcp*-*L*₁-*L*₂ line on the *P-T* diagram.

The other univariants end more routinely. Figures 11 and 12 show why *bcc*₁-*L*₁-*L*₂ must end at the peak of the liquid phase separation. The termination of *bcc*₁-*bcc*₂-*L*₂ at the critical point

of the solid phase separation can be understood by noticing how Fig. 17 evolves from Fig. 16. Less is known about the termination of *bcc*₁-*bcc*₂-*hcp*. It is thought that the critical curve (labeled CP) for the solid phase separation is nearly independent of pressure.⁵ As the pressure is increased the *hcp*-*bcc* phase transition occurs at higher He³ concentrations. As the *hcp*-*bcc* transition moves across toward higher He³ concentrations, it carries *bcc*₁-*bcc*₂-*hcp* with it until it hits the peak of the curve, CP in Fig. 19. At this point on the *P-T* diagram *bcc*₁-*bcc*₂-*hcp* should terminate. Very little is known about the solid phase separation, however, so this statement lacks verification. Finally, the *bcc*₁-*hcp*-*L*₁ line must end at the pure He⁴ melting curve at the lower triple point. In Fig. 20, points shown on the *bcc*₁-*hcp*-*L*₁ univariant were obtained by Lipschultz *et al.* in ultrasonic experiments.³⁰ From the shape of the *T-X* diagrams in Figs. 10-19, the location of the azeotropic line on the *P-T* diagram is also clear.

Large portions of the phase diagram and the existence of many of the three-phase surfaces have not been verified experimentally suggesting the need for further experiments.

Alternative diagrams have been suggested by several other groups.^{11,22,31} The diagram proposed by LePair *et al.*¹¹ mainly agrees with the one presented here. In addition, they discuss the . . .

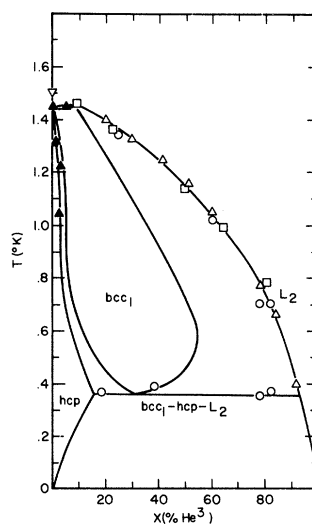


FIG. 16. At 26.2 atm only the univariant *bcc*₁-*hcp*-*L*₂ remains. *L*₁ cannot exist at this pressure. The lower triple point of pure He⁴ is at about 1.45° K.⁶ ○ This work; ▽ Vignos and Fairbank⁶; □ Le pair *et al.*¹¹; △ Zinovieva²²; ▲ Lipschultz *et al.*³⁰