Solidification and Superfluidity of ^{4}He in Confined Geometries

E. D. Adams, K. Uhlig, Yi-Hua Tang, and G. E. Haas
Department of Physics, University of Florida, Gainesville, Florida 32611

(Received 19 March 1984)

The solidification of ^{4}He in Vycor glass and in sintered Ag powder has been studied between 0.8 and 2.5 K. At 0.8 K, elevation of the melting pressure by 12 bars is seen in Vycor and by 0.3 bar in the Ag sinter. In each material a range of melting pressures, corresponding to different pore sizes, is observed. The location of the λ transition in the liquid in Vycor is determined up to solidification pressure.

PACS numbers: 67.40.Kh, 67.80.Gb

Several studies have been made of the solidification and superfluidity of ^{4}He in confined geometries.[1-3] Experiments on helium in Vycor glass have indicated that it remained a liquid at pressures of ~15 bars above the bulk melting pressure.[2] Recently Beamish *et al.*[3] (BHTE) have observed solidification and the superfluid transition of helium in Vycor from changes in sound velocity. However, an accurate phase diagram has not been available because of uncertainties in the presence of the helium in the Vycor.

We report measurements of pressure versus temperature along isochores and of the cooling rate (related to the heat capacity) of helium in Vycor. We identify solidification, melting, and the λ transition and obtain a phase diagram up to $P = 60$ bars and $T = 2.5$ K. There is a range of pressures where both solid and liquid may exist, which, at $T = 0.8$ K, extends from 36.3 to 38.0 bars. Similar behavior is seen in the Ag sinter, but at only ~0.3 bar above bulk melting. The λ transition of helium in Vycor has been followed to above solidification pressure, made possible by supercooling of the liquid.

The cell is depicted in Fig. 1 (inset). Measurement of the pressure of ^{4}He in Vycor above bulk melting is difficult because of the long time constant required for communication to a transducer. We obtained a short time constant by grinding the Vycor into a powder with grains ≤ 74 μm (200 mesh sieve) thereby reducing the distance for pressure communication.[4] The powder *loosely* filled the cell to a filling factor of 0.5, allowing individual grains to move with the bulk helium surrounding them and to transmit pressure to the capacitive transducer.[5] Bulk helium existed in the spaces between grains which were ~10^4 times the dimension of the 60-Å pores in the Vycor.

A layer of 700-Å sintered Ag powder, pressed to a filling factor of 0.5, provided thermal contact to the helium. The cell was mounted on the still of a dilution refrigerator with a *weak* thermal link to allow slow cooling of the cell with a time constant ~500 times that for equililbrium within the cell. Temperatures were measured with a carbon resistor calibrated against the ^{4}He melting pressure.[6] Cooling along the bulk melting curve at $T = 2$ K was at a rate $|dT/dt| \approx 4$ mK/min, with the cell reaching 0.8 K in ~5 h. The cooling rate is related to the heat current from the cell $\dot{Q}$ by

$$\dot{Q}(T) = \left(c_l n_l + c_s n_s + \frac{dn}{dt}L\right)\left|\frac{dT}{dt}\right| = C_{\text{eff}}\left|\frac{dT}{dt}\right|,$$

where c_l and c_s are the specific heats of the liquid

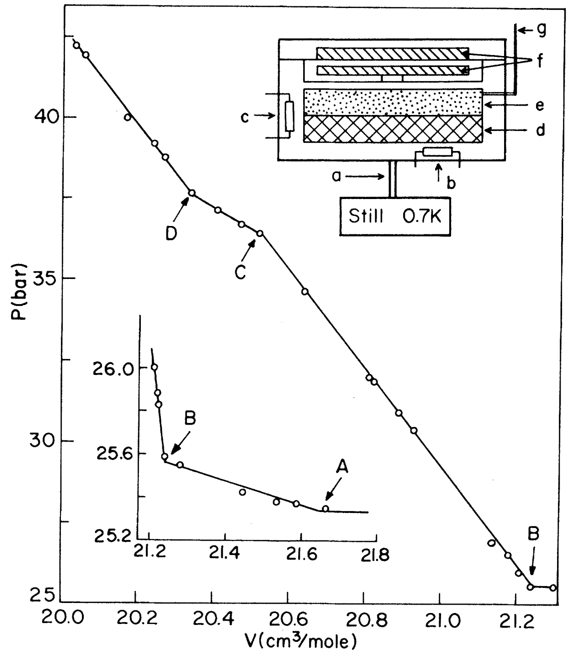

FIG. 1. Upper-right inset, the cell: (a) thermal link, (b) heater, (c) thermometer, (d) Ag sinter, (e) Vycor powder, (f) capacitance pressure gauge, (g) fill line. Main figure: P vs v at $T = 0.8$ K. Between points C and D, liquid and solid coexist in the Vycor. Lower-left inset: the coexistence region in the Ag sinter.

and solid phases, respectively, n the number of moles of one phase, and L the latent heat. Usually $\dot{Q}$ was just the flow of heat along the thermal link (see Fig. 1). The qualitative behavior of (dT/dt) indicated when the cell was following the melting curve of the bulk or confined helium or when the liquid in the Vycor was near the λ transition.

After the cell was filled to the desired molar volume at a temperature above the bulk melting point,[6] the blocked fill line kept the quantity of helium constant. Then as the cell slowly cooled along an isochore, $P(t)$ and $T(t)$ were recorded on a strip chart recorder or on a digital oscilloscope. Also, $P(T)$ was measured along isochores for both warming and cooling, while regulating the temperature of the cell. Usually thermal and pressure time constants were short, so that the $P(t)$ and $T(t)$ data agreed with $P(T)$.

The state of the helium at $T = 0.8$ K is seen from the isotherm $P(v)$ (constructed from the isochores) in Fig. 1. At large v, P is constant at 25.3 bars, the bulk melting pressure. As v is decreased, the bulk volume becomes filled with solid at point A (inset) where $v = 21.63$ cm^3/mole. This is greater than $v_{s,\mathrm{bulk}} = 20.98$[6] because there is still liquid in the Ag sinter and in the Vycor. As v is decreased further, freezing occurs in the Ag sinter (between points A and B, Fig. 1). The slope here corresponds to freezing in progressively smaller channels in the Ag sinter. The freezing pressure with the Ag sinter just filled with solid (point B) is elevated by 0.27 bar.

Upon further decrease in v, P rises rapidly until point C where the pressure is 36.3 bars, just sufficient for some solid to form in the Vycor. Because of supercooling (discussed later), the melting pressure in Vycor may be somewhat less than 36.3 bars. As more material is added, the solidification pressure rises, with freezing occurring in smaller pores until point D, where solidification is complete. Again the slope between points C and D indicates the elevation of melting pressure with decreasing pore size in the Vycor. Thus the melting pressure acts like a "spectrometer of pore size."

In Fig. 2(a) and 2(b) are portions of $P(t)$ and $T(t)$ for two different isochores. Initially these are along the bulk melting curve, with a rapid drop in $P(t)$ and slow cooling rate resulting from the latent heat of freezing. At point A, bulk solidification is completed. For isochore (a), the Vycor helium remains all liquid to the lowest temperature. The λ point is indicated by: (1) a minimum in $P(t)$ followed by an inflection point similar to that seen in bulk helium near T_λ, and (2) a decrease in the cooling rate as a result of the large heat capacity of the Vycor helium near its λ point. From the inflection point in $P(t)$ for several isochores, $T_{\lambda,\mathrm{Vycor}}(P)$ was determined, with the results shown in Fig. 3. Below bulk melting pressures, this temperature is somewhat above that for the onset of superflow, which accounts for the offset in $T_{\lambda,\mathrm{Vycor}}$ at bulk melting.[7] For isochore (b), which is at a higher pressure, freezing occurs in the Vycor helium between points B and C, where (dT/dt) is small because of the latent heat of freezing. As discussed below, there was always substantial supercooling prior to freezing. Along isochores which had a mixture of liquid and solid at $T = 0.8$ K, supercooling revealed the λ point in the liquid above the melting pressure.

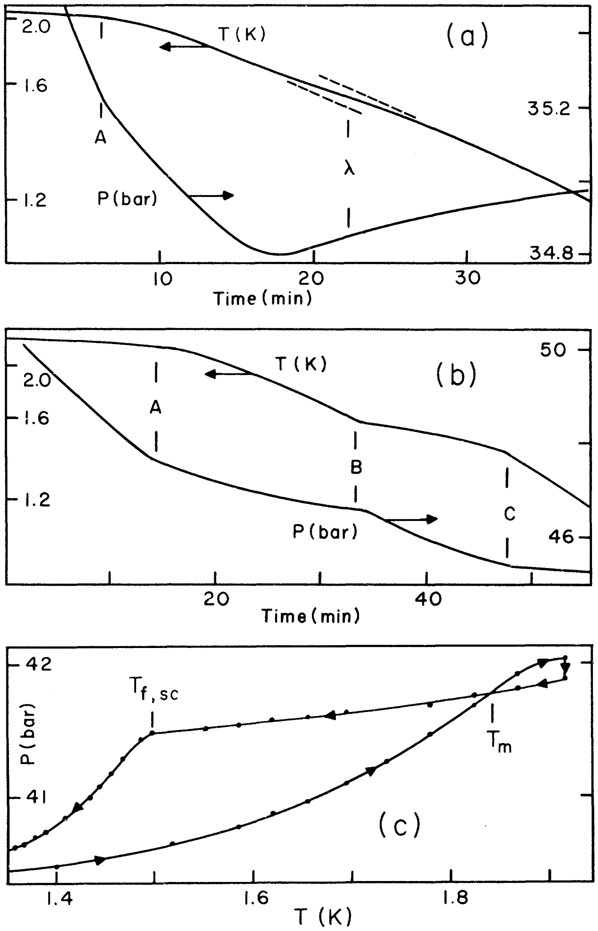

FIG. 2. (a) and (b) $P(t)$ and $T(t)$ for various isochores. λ, λ transition; A, end of bulk freezing; B, freezing in Vycor; C, end of freezing in Vycor. (c) $P(T)$ for warming and cooling: $T_{f,\mathrm{sc}}$ freezing of supercooled liquid; T_m, melting.

Because of the pore-size dependence of the melt-

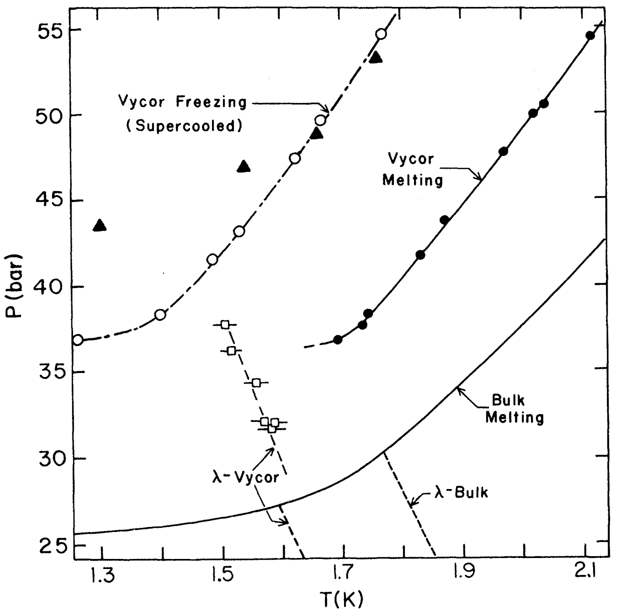

FIG. 3. P-T phase diagram of helium in Vycor and of bulk helium. Triangles, Ref. 3; all other points, this work. Error limits, where not shown, are about the size of the points.

ing pressure, liquid and solid coexist over a *surface* bounded by an all-solid line (equilibrium freezing curve) and an all-liquid line (melting curve). (Gibb's phase rule requires one additional degree of freedom.) The melting point on an isochore was identified by the procedure shown in Fig. 2(c). On warming, equilibrium was very fast until T_m and data could be taken as soon as the temperature was stabilized by the regulator (about 1 min). At T_m time constants for pressure equilibrium increased drastically (~ 10 min), $C_{\rm eff}$ became large, and dP/dT changed discontinuously, indicating melting. It was easier to locate the melting point by rapidly heating past T_m [in which case dP/dT was continuous as in Fig. 2(c)], wait for equilibrium near bulk melting, then take $P(T)$ on cooling where time constants were short. The intersection of the warming and cooling isochores located the melting points which are shown in Fig. 3. Since no solidification occurred at $P < 36.3$ bars (point C, Fig. 1), the melting line could not be located below 1.7 K. Whether it becomes horizontal in this vicinity could be determined using a two-compartment cell to change the pressure at constant temperature.

The onset of freezing from the *supercooled* liquid $T_{f,\,\rm sc}$ was an easily identifiable and reproducible point in either the $P(t)$ and $T(t)$ data or in the $P(T)$ data taken on cooling as shown in Fig. 2. However, the reproducibility of $T_{f,\,\rm sc}$, depended on complete remelting of the solid: upon cooling again after warming above the melting point only briefly so that some solid was still present, freezing took place at a higher temperature. The dot-dashed line of Fig. 3 locates $T_{f,\,\rm sc}$ (not the equilibrium freezing curve, because of supercooling). Although the liquid was in a metastable state, there was no indication of freezing until $T \approx T_{f,\,\rm sc}$. Once initiated, freezing occurred rapidly; however, there was never an "avalanche" with the transition taking place at once. This is understandable since nucleation of solid in one pore in the Vycor could not propagate readily to others to produce instant freezing.

The equilibrium freezing line (all solid) $T_f(P)$ must intersect the $T = 0.8$-K isotherm of Fig. 1 at point D. However, location of $T_f(P)$ either by detection of its intersection with isochores or by construction of additional isotherms, as in Fig. 1, was not possible because of the supercooling. As shown in Fig. 1, the freezing and melting pressures at 0.8 K differ by only 1.7 bars. Thus the equilibrium freezing line is probably near the melting line. The phase diagram for helium in Vycor (and bulk helium) is shown in Fig. 3. The freezing points of BHTE, which should be the same as our $T_{f,\,\rm sc}$, are shown for comparison. Only their 1.3-K point is more than their uncertainty from our curve. This discrepancy vanishes if their pressures are corrected for the decrease ~ 1 bar which occurs after bulk solidification.

Our data are sufficient to determine the molar volume of the Vycor helium since we know the fraction of the volume in the pores, the molar volume in the cell, and the bulk molar volume (treating the Ag sinter as bulk).[6] Relative to bulk helium, liquid in Vycor has a higher density, is less compressible, and changes volume less on freezing (e.g., $\Delta v_{ls,\,\rm Vy} = 0.55 \pm 0.1$ cm^3/mole at $P = 37$ bars vs 1.44 for the bulk).[8] These results are plausible since much of the helium in Vycor has a high density because of the Van der Waals attraction by the walls.

The model which has been applied to freezing at elevated pressures in confined geometries[1,3] employs the lack of wetting of the glass surface by solid helium and the interfacial tension between the liquid and solid, α_{ls}.[9] Thus to nucleate a seed crystal of radius r limited by the pore size requires an excess pressure

$$\Delta P = 2\alpha_{ls} v_s / (\Delta v_{ls} r).$$

Using the previous ΔP to calculate α_{ls} has given values a factor of 2 greater than the measured α_{ls}.[1,3,9] However, with our observed $\Delta v_{ls,\,\rm Vy}$ at $P = 37$ bars and $T = 1.3$ K (instead of $\Delta v_{\rm bulk}$),[10] we obtain $\alpha_{ls} = 0.05$ erg/cm^2, a factor of 3 less than the observed $\alpha_{ls} = 0.15$.

Further tests of this model could be made if α_{ls} were available at higher temperatures where a considerable increase in elevation of the freezing pressure occurs. Just how the *melting* pressure enters into the model is not clear. We note that $T_{\text{melt}} - T_{f,\text{sc}} \approx$ constant, which may suggest that temperature difference is the relevant quantity in determining freezing of the supercooled liquid.

We acknowledge useful discussions with Bob Guyer, Gary Ihas, and Pradeep Kumar. This work was supported by the National Science Foundation under Grant No. DMR-8312959. One of us (K.U.) acknowledges partial support from Deutsche Forschungsgemeinschaft, West Germany.

---

[1] E. N. Smith, D. F. Brewer, Cao Liezhao, and J. D. Reppy, Physica (Utrecht) **107B**, 585 (1981).

[2] D. F. Brewer, Cao Liezhao, C. Girit, and J. D. Reppy, Physica (Utrecht) **107B**, 583 (1981).

[3] J. R. Beamish, A. Hikata, L. Tell, and C. Elbaum, Phys. Rev. Lett. **50**, 425 (1983).

[4] In the small channels involved, pressure transmission is expected to be by diffusion rather than Poiseuille flow. Thus the time constant should decrease as the square of the distance.

[5] G. C. Straty and E. D. Adams, Rev. Sci. Instrum. **40**, 1393 (1969).

[6] E. R. Grilly, J. Low Temp. Phys. **11**, 33 (1973).

[7] D. F. Brewer, J. Low Temp. Phys. **3**, 205 (1970).

[8] Full results of the molar volumes in Vycor will be presented elsewhere.

[9] S. Balibar, D. O. Edwards, and C. Laroche, Phys. Rev. Lett. **42**, 782 (1979); J. Landau, S. G. Lipson, L. M. Määttänen, L. S. Balfour, and D. O. Edwards, Phys. Rev. Lett. **45**, 31 (1980).

[10] It appears that BHTE (Ref. 3) used Δv_{ls} appropriate for the bulk melting *temperature,* rather than for the freezing *pressure* in Vycor.