

be made and interpreted. First, these data are interpreted with kinematic scattering theory. Secondly, the high resolution of x-ray scattering enables straightforward analysis of 1000-Å correlation lengths. Finally, and perhaps most important, is that high signal rates are possible (50 000 cps for the FOR) with high signal-to-background ratio ($S/B = 500$ for the FOR). These capabilities should make this technique not only feasible but also practical and further experiments should stimulate advances in understanding two-dimensional phase transitions, the growth of thin films, and the behavior of small clusters on surfaces.

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^(a)Present address: Bell Laboratories, Holmdel, N. J. 07733.

^(b)Present address: Exxon Research and Engineering Company, Linden, N. J. 07306.

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High-Pressure Melting Curve of ⁴He

P. Loubeyre, J. M. Besson, and J. P. Pinceaux

Physique des Milieux Très Condensés, Université Pierre et Marie Curie, F-75230 Paris Cedex 05, France

and

J. P. Hansen

Laboratoire de Physique Théorique des Liquides, Université Pierre et Marie Curie, F-75230 Paris Cedex 05, France

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The melting curve $P(T)$ of ⁴He has been measured from 220 to 360 K (8 to 16 GPa); it is found to exhibit a well-defined cusp point at 299 K and 11.65 GPa. The cusp, together with estimates of the relative volume change, points to the existence of a triple point and a new high-pressure phase in solid ⁴He. The melting curve below this point is accurately fitted by theory on the basis of a modified Aziz interatomic potential.

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Knowledge of the thermodynamic behavior of helium at high densities is important not only because of the fundamental character of this ele-

ment, but also because it may serve as a model for the properties of highly compressed insulators. The law of corresponding states allows an

extrapolation of the properties of helium to other rare gases in regions of pressure and temperature which are not yet directly accessible by experiment. In this Letter we briefly describe experimental methods used to measure the melting curve of ^4He between 220 and 360 K (8 to 16 GPa) and to evaluate refractive indices and volume changes at melting. We find that the Simon equation which has been proposed earlier¹ is unsatisfactory at high densities. Our measurements show the existence of a cusp point on the melting line at 299 K and 11.65 GPa; this and other observations point to the occurrence of a new high-pressure structure, different from the fcc phase, for solid helium above this point.

The diamond cell, which as been described elsewhere,¹ is filled with ^4He (50 ppm impurity content), and then placed in a controlled temperature vessel. A thermocouple is attached to the Inconel 750 gasket. Temperature stability is 50 mK and absolute precision ± 0.3 K. Ruby chips, used as pressure gauges within the ^4He sample, are excited with a Kr^+ laser at incident powers below 50 mW. Wave-number shifts of the R_1 luminescence peak have been taken to be $-7.53 \text{ cm}^{-1} \text{ GPa}^{-1}$ and $-0.140 \text{ cm}^{-1} \text{ K}^{-1}$. Visual observation of the solid-fluid equilibrium was done under a microscope. With a suitable iris a small area ($15 \mu\text{m}$ in diameter) could be selected in the field and its transmittancy under white-light illumination was analyzed on a spectrometer. Maxima and minima in the spectrum of the Fabry-Perot interferometer formed by the anvil culets were recorded under pressure. The wave number ν_k of a given maximum of order k is given by $2ne\nu_k = k$ for a thickness e of the cell and refractive index n . Thus when the spot crosses the fluid-solid separation in the cell, the shift in ν_k represents the relative refractive-index difference between the two phases. Corrections for nonparallelism were measured in the fluid. Another type of measurement was done by keeping the anvils' position fixed with a blocking screw on the ram, and varying the temperature under isochoric conditions. The temperature interval ΔT between initiation and completion of the melting process along the melting line could thus be measured, and the isochoric P - T path drawn in the solid phase. Over the small temperature and pressure intervals (15 K, 1 GPa) where our observations were made, these conditions can be regarded as isochoric; this was checked over larger (50 K) temperature intervals in the solid phase, where no measurable thickness or area variation of the

cell could be detected.

In Fig. 1 the experimental results for the melting curve are compared with the theoretical analysis described below. In Fig. 2(a) the region around 300 K is enlarged to show the break in slope of $P(T)$ occurring at 299 K. This singularity, and the deviation from the best theoretical fit at lower pressures, are shown more clearly in Fig. 2(b). It should be noted that, although the absolute precision of the ruby scale is probably not better than 2% at 10 GPa, our error bars are only ± 15 MPa (0.15 kbars) which is the smallest pressure variation that we can detect. The behavior of the melting curve suggests the existence of a triple point, and thus of a new phase in solid ^4He above 300 K. Other observations point to the same conclusion:

(i) The variation of refractive index at melting can be related to the variation of density ρ by the Clausius-Mosotti equation:

$$\frac{n^2 - 1}{n^2 + 2} = F_{LL} \rho. \quad (1)$$

The Lorentz-Lorenz factor F_{LL} is known for helium at low densities ($0.52 \text{ cm}^3 \text{ mole}^{-1}$ at $\rho = 0.033 \text{ mole cm}^{-3}$).² Using scaling laws between Ar and He, known values for $F_{LL}(\rho)$ in Ar,³ and taking into account the number of electrons in the outer shells, we estimate F_{LL} to be about $0.25 \text{ cm}^3 \text{ mole}^{-1}$ at $\rho = 0.23 \text{ mole cm}^{-3}$, i.e., around 300 K.

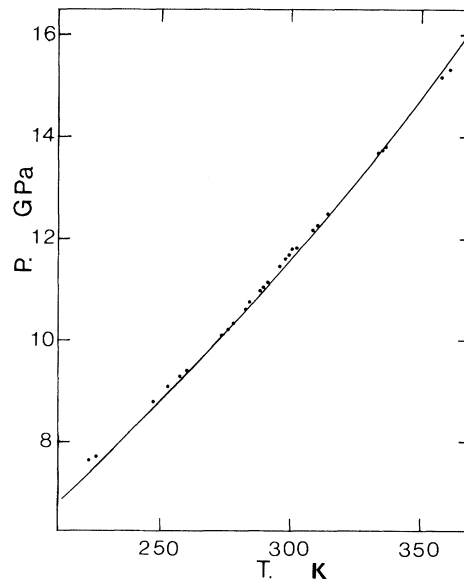


FIG. 1. Experimental (dots) and calculated (full line) melting curves of ^4He ; the calculated curve is the best fit based on the modified Aziz potential.

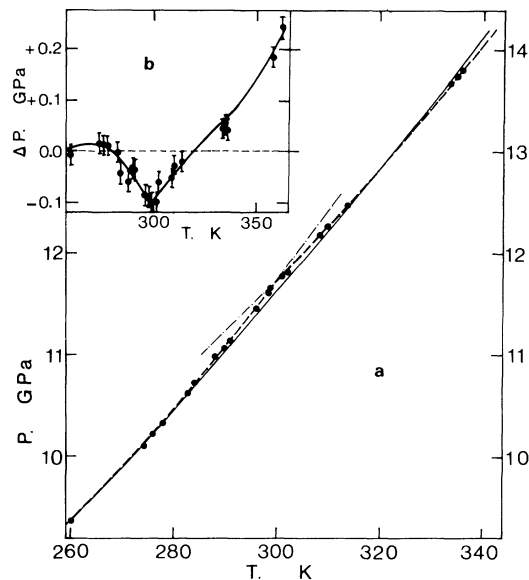


FIG. 2. (a) Enlarged plot of the experimental (dots) and calculated (full line) melting curves around 300 K; the dashed lines through the experimental points are a visual aid, as are the dashed-dotted tangents to the melting curve at the cusp point. (b) Calculated minus experimental melting pressures vs temperature for a clear visualization of the cusp.

Using now the relative index change at melting, $\Delta n/n$, from the shift of transmission extrema between the solid and the fluid, we can estimate the relative volume change $\Delta V/V$. This quantity is $(3.1 \pm 0.4) \times 10^{-2}$ between 265 and 280 K. The equation of state of Mills *et al.*⁴ predicts 2.9×10^{-2} in this range. Above 300 K, $\Delta V/V$ decreases strongly; it drops to $(1.0 \pm 0.3) \times 10^{-2}$ at 344 K as compared with a calculated⁴ value of 2.6×10^{-2} .

(ii) Direct measurement of ΔT , the temperature interval between initiation and completion of solidification along an isochore, will also yield an estimate of ΔV . In these experiments the initial temperature was taken with the cell still containing a very small crystal of solid He to avoid supercooling. The temperature was lowered until the solid occupied the entire cell. The temperature interval ΔT is related to ΔV by

$$\Delta V = \Delta T \left[\left(\frac{\partial V}{\partial P} \right)_T \frac{d\Phi}{dT} + \left(\frac{\partial V}{\partial T} \right)_P \right] = C \Delta T, \quad (2)$$

where $P = \Phi(T)$ along the melting curve. From the equation of state in Ref. 4 and our measurement of $\Phi(T)$, it can be verified that C increases by less than 15% between 260 and 335 K, and can be considered as constant for order-of-magnitude comparisons. ΔT is 8.2 ± 1.0 K between 255 and

290 K. It decreased down to 5 K at 310 K and 2 K at 335. From Clapeyron's equation this corresponds to a decrease of the latent heat by a factor of 3 between 280 and 335 K.

(iii) Under the isochoric conditions used to measure ΔT at melting, the plot of $P(T)$ with decreasing temperature can be extended into the solid phase in the vicinity of the melting curve. The isochore is tangent to the melting curve and, for a measurable temperature interval, it is not separated from the melting curve by more than 1 kbar (0.1 GPa) although the cell is entirely filled by the solid phase. Upon further lowering of the temperature, the isochore flattens out, as expected. The magnitude of this temperature interval is a gauge of the softening of the crystal prior to melting (increase of the compressibility and of the thermal expansion coefficient) which has been reported before in ⁴He (Ref. 5) and in other crystals.⁶ The premelting behavior extends over 3 K below 299 K and over about 10 K above. We take this observation again as evidence for a new solid phase above 299 K.

The measured melting curve up to the triple point can be reproduced within experimental accuracy by a variational calculation based on a modified Aziz interatomic pair potential $v(r)$ [Eq. (1) of Ref. 7]; this potential is softer than the 12-6 Lennard-Jones potential which is known to be too stiff at short interatomic distances. The Helmholtz free energies F of the fluid and the solid are calculated from the Gibbs-Bogoliubov inequality:

$$F(\rho_1 T) \leq F_0(\rho_1 T) + 2\pi N\rho \int_0^\infty g_0(r)[v(r) - v_0(r)]r^2 dr, \quad (3)$$

where F_0 is the free energy of a reference system of N atoms interacting, at the same density and temperature, via the pair potential $v_0(r)$, and $g_0(r)$ is the corresponding pair distribution function. In view of the softness of the Aziz potential, we have chosen a reference system with $v_0(r) = \epsilon(\sigma/r)^{12}$, the thermodynamics and pair distribution function of which are accurately known from Monte Carlo simulations over a wide range of the single variable $\xi = \rho\sigma^3(k_B T)^{-1/4}$ in both fluid and solid phases.⁸ The variational program of Eq. (3) was carried out by minimizing the free energy on the right-hand side with respect to σ (or ξ); this procedure improves upon a similar calculation by Ross and Young.⁹ Quantum corrections to the classical free energy F^{cl} estimated from Eq. (3) are not negligible even at 300 K.¹⁰ The leading

\hbar^2 term in the Wigner-Kirkwood expansion is evaluated from

$$F = F^{c1} + \frac{1}{12} \lambda^2 \rho N \int_0^\infty g_0(r) \nabla^2 v(r) r^2 dr, \quad (4)$$

where $\lambda = h(2\pi m k_B T)^{-1/2}$ is the de Broglie thermal wavelength. This expansion converges rapidly for $\lambda < \rho^{-1/3}$, i.e., for $T \gtrsim 100$ K along the ^4He melting curve. From the isothermal plots of the free energy versus molar volume we get the melting pressure and molar volumes of the coexisting phases by a Maxwell double-tangent construction. The agreement with experiment is reasonably good if the original Aziz potential parameters⁷ are used. Decreasing the exponent α in the exponential repulsion of this potential from 13.35 to 12.98 yields the best fit to the experimental results up to 300 K (cf. Table I). This calculation cannot account for a possible triple point on the melting curve, since the Monte Carlo results in the solid are for the fcc structure, which is always stable in the inverse-12 reference system.

The modified effective pair potential reproduces the experimental data for the melting pressure of ^4He within 2% over the entire range which was studied. This is at the present time within the precision of the ruby scale used for pressure measurements.¹¹ Above 300 K we do not expect our fit to be significant, since the shape of the experimental melting curve indicates the existence of a triple point at 299 K and thus of a new structure above this temperature. Although this finding is supported by the difference in volume variation and in premelting behavior above and below this point, we have not obtained *direct* experimental evidence of the solid-solid phase transition. If this transition indeed exists, it should be noted that the enhanced premelting behavior above 300 K is reminiscent of the specific-heat anomalies in bcc ^4He prior to melting, at low temperatures.⁵ Moreover, the large difference in ΔV 's at melting, above and below 299 K, would not fit in with an fcc-hcp phase transition. To reconcile our observations with the low-temperature behavior of ^4He ,¹² a speculative phase diagram of ^4He along the melting curve would show an hcp up to 1 kbar, then an fcc modification up to 11.65 GPa (299 K), and finally a bcc phase.

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TABLE I. Theoretical and experimental melting pressures (in GPa) as functions of temperature; the theoretical results are for the original and modified Aziz potentials, respectively. Experimental values at 50 and 100 K are from Ref. 4. The others are from our measurements.

T (K)	Aziz ($\alpha = 13.35$)	Aziz ($\alpha = 12.98$)	Experiment
50	0.756	0.751	0.740
100	2.279	2.142	2.177
150	4.264	4.005	...
200	6.667	6.370	...
250	9.375	8.797	8.93
300	12.517	11.620	11.72
350	15.913	14.826	14.65
400	19.678	18.369	...

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