NEW SOLID PHASE IN He^4†

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Recent measurements of the longitudinal velocity of first sound in solid He^4 have revealed a first order phase transition, and hence a new solid phase (designated the γ phase), between 1.45°K and 1.78°K in a narrow range of pressure adjoining the melting curve. The transition between the previously established hexagonal close-packed α phase[1-3] and the inferred γ phase was detected by observing the discontinuity in the velocity of sound at the phase boundary. Subsequent measurements of a change in molar volume across the phase boundary and a discontinuity in the slope of the melting curve at the lower liquid–solid α–solid γ triple point have substantiated that this is indeed a first order phase transition.

The standard ultrasonic pulse technique at a carrier frequency of 10 Mc/sec has been employed to measure the longitudinal velocity of sound in solid as well as liquid He^4. First order phase transitions can also be explored since there is a discontinuous change in velocity on crossing the transition. The melting curve of He^4 has been investigated in this manner and is shown in Fig. 1 (solid circles). Investigation of the velocity of sound in the solid region near the melting curve indicated the existence of another first order phase transition. The locus of the discontinuity in velocity observed in this region is shown in Fig. 1 (open circles). This discontinuity was found to be reversible in both temperature and pressure. The locations of the liquid–solid α–solid γ triple points are given by $T_u = 1.778 \pm 0.003$°K, $P_u = 30.28 \pm 0.05$ atm and $T_l = 1.449 \pm 0.003$°K, $P_l = 26.18 \pm 0.05$ atm. The velocity of sound in the solid α region, both along the melting curve from 1°K to the lower triple point and along the α-γ phase boundary, was found to be essentially constant and equal to 478 m/sec. Throughout the solid γ region the velocity has values ranging from 520 m/sec to 545 m/sec, these two extremes being the predominant values. We attribute this variation to different orientations of a single crystal or a few large crystals. This tendency for helium to form large crystals is consistent with previous observations.[1-3] For reference the velocity of sound in the liquid at the melting curve is 365 m/sec from 1°K to the λ point and then climbs to 380 m/sec at 1.8°K. The lambda line shown in Fig. 1 (solid triangles)

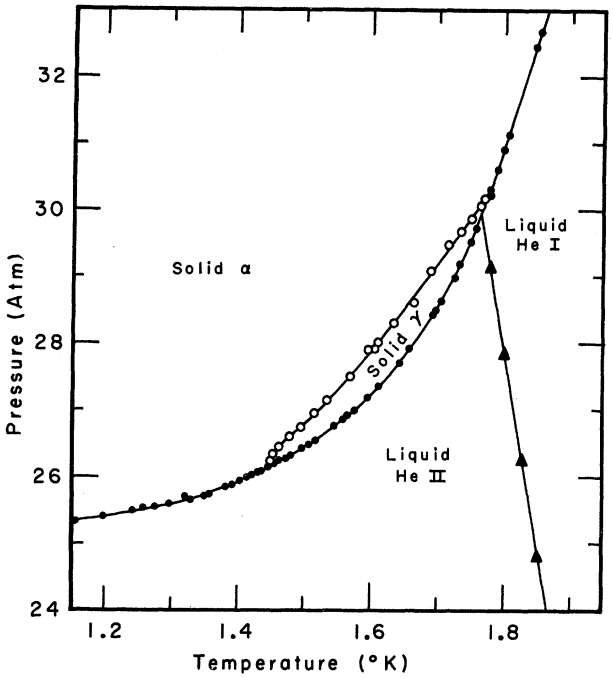

FIG. 1. The phase diagram of He^4 showing the melting curve (closed circles), the solid α-solid γ transition (open circles), and the λ transition (triangles).

was determined by noting points of maximum sound absorption in the liquid. The lambda line–melting curve triple point is given by $T_\lambda = 1.765 \pm 0.003$°K, and $P_\lambda = 29.90 \pm 0.05$ atm. From 1°K to 2°K our melting curve and lambda line lie about 0.2 atm above those determined by Swenson.[4]

The gas-handling system employed allows a measure of the flow of gas into or out of the sample chamber; consequently we were able to measure, though very roughly, the change in molar volume in passing from one phase to the other. The volume of the γ phase was larger than that of the α phase. At 1.50°K the change in volume at the transition was 0.07 cc/mole, which corresponds to a 0.3% change in the molar volume. The slope of the α-γ transition curve (Fig. 1) at 1.50°K is 9.3 atm/°K and hence by the Clapeyron equation the difference in entropy of the phases $(S_\gamma - S_\alpha)$ is 0.016 cal/deg mole.

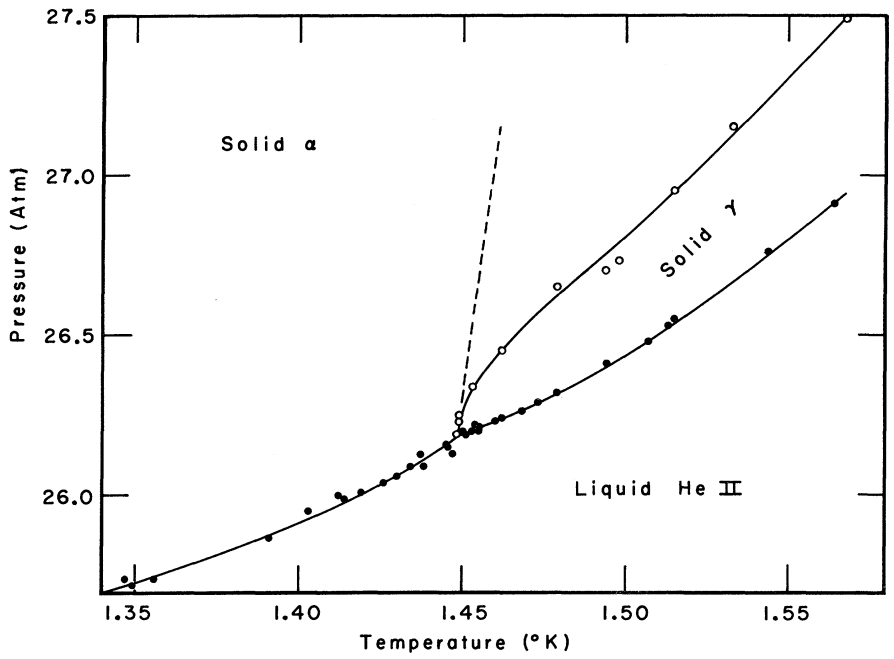

FIG. 2. The phase diagram of He^4 in the vicinity of the lower triple point. The slope of the $\alpha - \gamma$ transition curve at the triple point calculated from Eq. (1) is shown by the dashed curve.

An enlarged graph of the phase diagram in the vicinity of the lower triple point is shown in Fig. 2. It is seen that at the lower triple point there is an abrupt change in slope of the melting curve. From the Clapeyron equation applied to each transition at the triple point it is seen that such a discontinuity is required, its magnitude being given by

$$\left[\left(\frac{dP}{dT}\right)_{\alpha,l} - \left(\frac{dP}{dT}\right)_{\gamma,l}\right]$$

$$= \left[\left(\frac{dP}{dT}\right)_{\alpha,\gamma} - \left(\frac{dP}{dT}\right)_{\alpha,l}\right](\Delta V_{\gamma,l}/\Delta V_{\alpha,\gamma}), \quad (1)$$

where the subscripts l, α, and γ refer to the liquid, solid α, and solid γ phases, respectively, and $\Delta V_{x,y} \equiv V_y - V_x$. Using our values of slope for the two liquid-solid transition curves, our value of $\Delta V_{\alpha,\gamma}$ at 1.50°K, and Swenson's[4] value of $\Delta V_{\gamma,l}$ at the triple point, we have calculated from Eq. (1) the value of $(dP/dT)_{\alpha,\gamma}$ (shown by the dashed curve in Fig. 2) and find it to be consistent with the experimental value. At the upper triple point Eq. (1) would predict a change in slope of the melting curve of only 2%, assuming $\Delta V_{\alpha,\gamma}$ to be about that observed at 1.5°K. This is in agreement with the observed data of Fig. 1 where the change in slope of the melting curve is immeasurably small.

The structure of the new γ phase in solid He^4 has not yet been established; however, there is reason to believe that it is body-centered cubic. A phase transition has been observed in solid He^3, above about 100 atm,[5] which is similar to the $\alpha - \gamma$ transition in solid He^4 in its pressure and temperature dependence and in the change in molar volume. In He^3 the higher pressure phase (β) is hcp and the lower pressure phase (α) is bcc.[6] In the case of He^4 the higher pressure phase (α) is also hcp, and hence one is led to believe by analogy that the lower pressure phase (γ) is most likely bcc. Why a stable bcc lattice is found in He^3 (and possibly He^4) and in no other solid dielectric element is not yet clear.[7,8] It is very unlikely that nuclear spin effects are responsible for the transition in He^3 if the new γ phase in He^4 does prove to be bcc.

The first order phase transition to the β phase in solid He^4 above 15°K and 1100 atm, inferred from the specific heat measurements of Dugdale and Simon,[9] is probably a transition to a cubic close-packed structure and is unrelated to the low-pressure transitions in solid He^3 and He^4 discussed above.

In summary, a new γ phase has been shown to exist in solid He^4. It has a larger volume and entropy than the adjacent hexagonal close-packed α phase, as required by thermodynamics, and a larger longitudinal sound velocity. By analogy

with solid He^3 it seems likely that the new γ phase is body-centered cubic.

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COMPRESSIBILITY, ZERO-POINT ENERGY, AND SPECIFIC HEAT IN SUPERCONDUCTORS*

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Keesom and Bryant[1] showed that the specific heat of indium in the superconducting state at the lowest temperatures is considerably smaller than the lattice specific heat deduced from measurements in the normal state. The work of Boorse, Hirschfeld, and Leupold[2] and of Zavaritskii[3] indicates a similar effect in niobium and tin. Such a phenomenon would be easily understood if there were correspondingly large differences in the elastic constants and in the Debye characteristic temperatures, θ_D, of the two states. Work by Chandrasekhar and Rayne[4] has now confirmed the generally accepted view in ruling out the possibility of any differences in θ_D greater than 1 part in 10^4. We wish to show here that even the very much smaller changes in θ_D which are known to exist can influence the zero-point energy enough to allow an explanation of the observations.

The total energy, E, of a Debye solid at low temperatures may be written

$$E = 1.125 R\theta_D + 58.5 RT^4/\theta_D{}^3, \qquad (1)$$

where R is the gas constant. The first of these terms is usually known as the zero-point energy of the lattice. If θ_D is constant, we obtain the well-known expression for the T^3 lattice specific heat, C_g, at low temperatures:

$$C_g = \partial E/\partial T = 234 RT^3/\theta_D{}^3. \qquad (2)$$

An attempt to explain the observed differences in specific heat using this formula requires complicated and unlikely changes in the phonon spectrum.

On the other hand, it is well known that the difference in compressibility between the two states is temperature dependent and given by[5]

$$\frac{1}{V}\left(\frac{\partial V_n}{\partial p} - \frac{\partial V_s}{\partial p}\right) = \frac{1}{4\pi}\left(\frac{\partial H_c}{\partial p}\right)^2 + \frac{H_c}{4\pi}\frac{\partial^2 H_c}{\partial p^2}, \qquad (3)$$

where V_n and V_s are the volumes in the normal and superconducting states, H_c is the critical magnetic field, and p is the pressure. The compressibility in one of the states at least must then be temperature dependent, and θ_D must clearly be so, too.

Such a temperature dependence of θ_D affects the zero-point energy and contributes to the specific heat, which now becomes

$$C_E = \partial E/\partial T = 1.125R(\partial\theta_D/\partial T) + 234RT^3/\theta_D{}^3 \times[1-(3T/4\theta_D)(\partial\theta_D/\partial t)]. \qquad (4)$$

It is obvious that even a very small value of $\partial\theta_D/\partial T$ at the lowest temperatures may produce effects comparable with the value of C_g given by Eq. (2).

The expressions (3) and (4) and the known dependence of θ_D on compressibility can be used to calculate the difference between the lattice specific heats, C_{gn} in the normal and C_{gs} in the superconducting states, from the pressure de-