

†Permanent address: Faculté des Sciences, Orsay, France.

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Evidence for a New Phase of Solid He³ †

D. D. Osheroff, R. C. Richardson, and D. M. Lee

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850

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Measurements of the melting pressure of a sample of He³ containing less than 40-ppm He⁴ impurities, self-cooled to below 2 mK in a Pomeranchuk compression cell, indicate the existence of a new phase in solid He³ below 2.7 mK of a fundamentally different nature than the anticipated antiferromagnetically ordered state. At lower temperatures, evidence of possibly a further transition is observed. We discuss these pressure measurements and supporting temperature measurements.

On the basis of measured values of the solid-He³ spin exchange energy J , defined by $\mathcal{H}_{\text{ex}} = -2J \times \sum_{i < j} I_i \cdot I_j$, it has been assumed that near 2.0 mK solid He³ would order antiferromagnetically by a second-order phase transition.¹ In this Letter we present evidence that at 2.7 mK solid He³ undergoes a phase transition of a nature fundamentally different from that which had been expected, and that the ordered state is most probably not the simple antiferromagnetic one assumed. The refrigeration device, pressure transducer, and thermometry employed in our measurements are described, the evidence is presented, and a brief discussion follows.

The method of compressional cooling of He³ to obtain temperatures as low as 2 mK is by now well established.²⁻⁴ The present apparatus, shown in Fig. 1, employs a pressure amplifier which consists of a set of beryllium-copper bellows connected by a rigid piston. The pressure amplifier enables a moderate He⁴ pressure (< 10 atm) in the upper chamber, generated externally, to compress and solidify the He³ in the lower chamber. Although sufficient volume changes can be generated to solidify the entire 12-cm³ He³ sample, seldom was over 40% solid ever formed in the experiments to be discussed.

The apparatus was attached directly to the mixing chamber of a dilution refrigerator for pre-

cooling and thermal isolation.⁵ Above about 5 mK the compression process was highly revers-

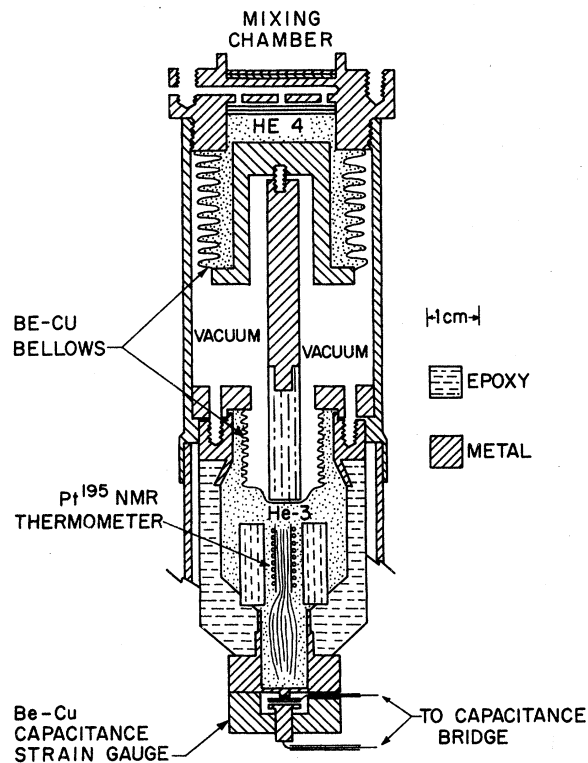


FIG. 1. Pomeranchuk cooling and pressure-measuring apparatus.

ible in the present device, and no heating associated with the motion of the bellows has been observed. Rates of compression (and decompression) producing solidification as rapidly as 2×10^{-2} mole/min were easily obtained. A typical rate of solidification, 1×10^{-3} mole/min, produced a cooling of about 0.25 mK/min.

The beryllium-copper capacitive pressure transducer⁶ was calibrated at 1 K against a quartz secondary pressure standard. No hysteresis in the gauge greater than 2×10^{-3} atm, the reproducibility of the secondary standard, was observed during the calibration. The gauge reproducibility was better than 1×10^{-4} atm, and its resolution was better than 5×10^{-6} atm.

The thermometer shown in Fig. 1 consisted of 0.83 g of 0.001-in.-diam insulated reference-grade platinum wire obtained from the Sigmund Cohn Company. Temperatures were obtained by measuring the nuclear susceptibility of the platinum with a cw NMR spectrometer. A comparison of this thermometer with a similar one made of copper showed agreement better than 1% between 40 and 4 mK. Heating due to the applied rf signal caused less than a 2% temperature error at 3 mK, and the thermal relaxation time between the thermometer and the He³ bath was measured to be shorter than 3 min at 3 mK in a 1.5-kOe magnetic field.

The thermometer was calibrated using the He³ melting curve⁷ as measured by Johnson *et al.*,⁸ shifted downward in pressure by 0.24 psi to account for differences between pressure calibrations. From 30 to 3.5 mK, the melting curve obtained using the described apparatus agreed to better than 1% with the shifted curve of Johnson *et al.*⁸ Below about 3.5 mK the thermometer indicated temperatures above those given by the melting curve. A lowest measured temperature of 2.7 mK was obtained repeatedly with the thermometer shown in Fig. 1, and also with one other platinum and one copper thermometer in various experiments during the past year. It is assumed on the basis of the pressure measurements that much lower temperatures were generated in the cell, and that the behavior of the thermometers near 3 mK may be associated with changes in the properties of the solid He³ in contact with the thermometers.

Figure 2 shows the time evolution of pressure in the cell during a compression in zero (< 10 Oe) magnetic field, and serves to illustrate, as accurately as possible, the phenomena we observe. From $t = 0$ to point D, the rate of change of the

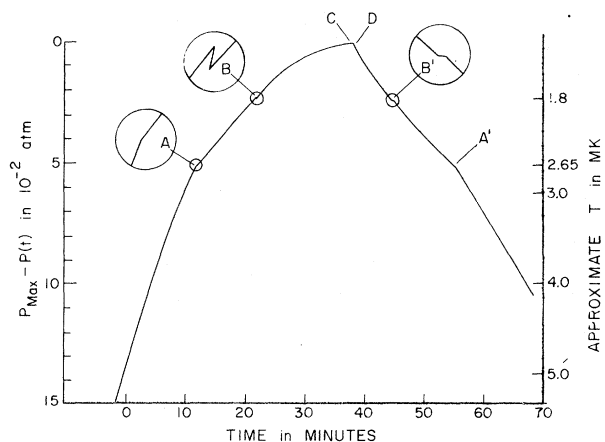


FIG. 2. Time evolution of the pressure in the Pom-eranchuk cell during compression and subsequent decompression.

cell volume with time (rate of compression) was constant and very uniform. The features of interest labeled A, B, and C are discussed below.

At point A, at 33.9053 atm, we observed an abrupt change in the slope of the pressure-versus-time (pressurization) curve. This pressure corresponds to a temperature of 2.65 mK on the shifted melting curve of Johnson *et al.*,⁸ extrapolated from 2.8 to 2.65 mK. The change in slope, by roughly a factor of 1.8, occurred within a pressure interval of less than 3×10^{-4} atm. The change was highly reproducible both upon warming and cooling, provided that the time interval over which the measurement was made was less than about 15 min. Because the solid He³ specific heat is immense below 3 mK, and its thermal conductivity poor, the bulk solid is thought never to reach thermal equilibrium with the liquid in these experiments. By working within a sufficiently short time period, the effects caused by the thermal relaxation of the solid are minimized.

At B, at 33.9279 atm, 2.26×10^{-2} atm above $P(A)$, a sudden drop in pressure of about 3×10^{-4} atm was observed upon cooling, accompanied by no change in slope of the pressurization curve such as had been observed at A. By varying the rate of pressurization from 6×10^{-4} atm/min to 1×10^{-2} atm/min hysteresis of about 3×10^{-3} atm in B was observed. The effect observed at B', upon warming through decompression, showed no such hysteresis, and was basically different in nature from the effect at B, as is shown by the inset. B' always occurred at least 3×10^{-4} atm lower in pressure than B.

At C, 33.9575 atm, 5.22×10^{-2} atm above $P(A)$,

a maximum pressure was reached in the cell. This pressure, P_{\max} , is thought to be very near to the maximum in the ^3He melting curve. Not only was P_{\max} reproducible over a period of weeks, but it was independent of the rate of compression for sufficiently high rates. Further, the time evolution of the cell pressure upon warming from P_{\max} suggested that the melting curve might be nearly horizontal in the vicinity of P_{\max} .

At D in Fig. 2, the motion of the piston was reversed, and the features A' and B' already discussed were traced out by the pressure in the cell as a function of time.

All these features were highly reproducible, independent of the fraction solid in the cell, the position of the bellows, and the temperature of the dilution refrigerator mixing chamber. Even after the cell had been altered to accept a new thermometer, no changes in A , B , or C were observed.

The magnetic field dependences of A , B , and C have been studied in fields up to 13.4 kOe. Both A and C shifted to lower pressures, with $P(A) = -6.76 \times 10^{-3} H^2$, and $P(C) = -2.08 \times 10^{-2} H^2$ with P in atm and H in kOe. The hysteresis between B and B' became quite large, and the pressure drop at B increased in magnetic fields. The drop in pressure associated with B did not occur in fields above about 4 kOe, presumably having been shifted to a pressure above P_{\max} .

Because the He^3 melting curve is itself depressed in magnetic fields, the temperature shift associated with $P(A)$ is uncertain. Most likely, $T(A)$ is not shifted strongly in the fields applied in these experiments. In the course of this work, the magnetic field dependence of the melting curve was measured, and found to be in good agreement with calculations based on the high-temperature Heisenberg expansion of Baker *et al.*¹⁰ in fields up to 13.4 kOe, down to 5 mK. This result is in contradiction to the measurements of Johnson, Rapp, and Wheatley¹¹ which suggested a much stronger field dependence than theory predicts.

Although the platinum thermometer failed to follow the melting curve below 3.5 mK, direct evidence of the thermal nature of the transition at A in Fig. 2 was obtained using it. When the compression was stopped at a pressure near P_{\max} , and the melting pressure was allowed to drop slowly ($\dot{T} \approx 7 \mu\text{K}/\text{min}$) as the bulk solid relaxed thermally, the results shown in Fig. 3 were obtained. The upper curve, representing the cell pressure versus time, shows only a slight dimple

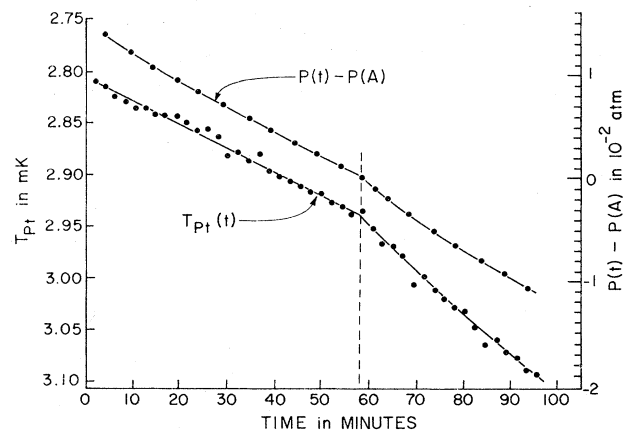


FIG. 3. Plots of pressure versus time and platinum temperature versus time in the neighborhood of the anomaly occurring at 2.65 mK.

at $P(A)$, but in the vicinity of this dimple, the characteristic change in slope by a factor of 1.8 is still easily measured. The lower curve, representing the temperature of the platinum thermometer during the same time interval, shows an abrupt change in slope at precisely the time that the cell pressure reached $P(A)$. This break in the warming curve of the platinum thermometer provides strong evidence that the phenomena observed with the strain gauge are related to the thermal properties of the helium under study.

To interpret the results we have obtained, we have had to make some basic assumptions. The most important of these, already discussed above, is that in the rapid compression-decompression experiments, the dominant thermal reservoir being cooled by the solidification process is that of the liquid He^3 , and not the solid. The very lengthy solid thermal relaxation times we have measured during compression experiments, coupled with the independence of the phenomena observed on the rate or sense of the compression, and the extremely sharp nature of the transition observed at A , all support this hypothesis. If one also assumes that no large changes in the molar volume of the solid occur at A , the discontinuity in dP/dt at A in Fig. 2 must be caused by a discontinuity in dP/dT .

A microscopic description of the solid which exists below 2.7 mK cannot be obtained from these measurements. On the other hand, several surprising features of the new solid phase can be inferred from the data by means of the Clausius-Clapeyron equation,

$$\left(\frac{dP}{dT}\right)_{\text{melt}} = \frac{S_{\text{sol}} - S_{\text{liq}}}{V_{\text{sol}} - V_{\text{liq}}}.$$

First, since the liquid entropy is negligible at 2.7 mK, a sudden change in the slope of the melting curve, dP/dT , corresponds to a large change in the solid entropy. The estimated decrease in entropy is from $S \sim 0.6R$ above the transition to $\sim 0.45R$ below the transition. In rapid compression experiments in zero magnetic field, the narrow pressure interval over which the change takes place, less than 3×10^{-4} atm, corresponds to a temperature interval of approximately $10 \mu\text{K}$. It is therefore quite likely that the effect corresponds to a first-order phase transition.

The second observation is that the pressure change we measure from 2.7 to 0 mK, $P(C) - P(A) = 5.22 \times 10^{-2}$ atm, is too large to be consistent with a simple antiferromagnetic transition at A . In fact, the pressure change we observe is twice as large as that calculated by Johnson *et al.*⁸ on the basis of an antiferromagnetic transition. In order to obtain sufficient pressure change from 2.7 to 0 mK through integration of the Clausius-Clapeyron equation,

$$\Delta P = \int \frac{(S_{\text{sol}} - S_{\text{liq}}) dT}{V_{\text{sol}} - V_{\text{liq}}} \approx \int \frac{S_{\text{sol}}}{\Delta V} dT,$$

to agree with the value presented above, one is forced to hold the solid entropy nearly constant over a broad temperature region below the 2.7-mK transition temperature. This possible behavior of the solid entropy is, in fact, also suggested by the nearly constant slope of $P(t)$ between A and B in Fig. 2. We know of no physical system which furnishes a precedent for the entropy behavior we postulate here.

Finally, in the experiment of Sites *et al.*⁴ and in subsequent work, we have measured values of the nuclear magnetic susceptibility of solid He³ which are too large to be consistent with an antiferromagnetic transition at 2.7 mK. Perhaps the transition at 2.7 mK corresponds to a crystallographic phase change, induced by a complex coupling between the spin and phonon systems. The new crystallographic phase might have quite different magnetic properties from the high-temperature phase. The sharp break in the warming curve of the platinum thermometer shown in Fig. 3 seems to support this hypothesis. The thermometer can only measure the temperature of the phonon bath surrounding it. In the disordered solid, the temperature of the phonon bath is most

strongly influenced by the temperature at the solid liquid interface. Once the liquid is below 2.7 mK, the phonon system becomes locked by spin interactions to the temperature of the interface between the two solid phases. The fact that the limiting temperature measured by the platinum thermometer was never below 2.7 mK suggests that the solid phase interface never reached the platinum wires.

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