

Freezing and Pressure-Driven Flow of Solid Helium in Vycor

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The recent torsional oscillator results of Kim and Chan suggest a supersolid phase transition in solid ^4He confined in Vycor. We have used a capacitive technique to directly monitor density changes for helium confined in Vycor at low temperature and have used a piezoelectrically driven diaphragm to study the pressure-induced flow of solid helium into the Vycor pores. Our measurements showed no indication of a mass redistribution in the Vycor that could mimic supersolid decoupling and put an upper limit of about $0.003 \mu\text{m/s}$ on any pressure-induced supersolid flow in the pores of Vycor.

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In a recent torsional oscillator experiment [1], Kim and Chan observed an unexpected decoupling of ^4He from a porous Vycor matrix in a temperature and pressure range (below 175 mK and around 60 bar) where the helium was solid. The authors described the helium as a “supersolid” and speculated that its nonclassical rotational inertia (NCRI) might be associated with a high vacancy concentration in the confined helium. The same authors have subsequently observed [2] similar behavior for bulk helium, implying that supersolidity may be an intrinsic property of helium. The observation of NCRI in the bulk solid does not diminish the importance of the Vycor results. Mass can be transported in bulk crystals via the motion of extended defects like dislocations or grain boundaries. Such defects may be essential for supersolidity [3] but would be pinned in small pores and so would not explain the observed NCRI in Vycor. It is important that other experiments be done on this system, for example to see whether solid helium exhibits any of the other unusual flow properties typically associated with superfluidity, and to rule out alternative explanations of the NCRI in Vycor. These might include a persistent liquid layer [4] or a redistribution of mass due to some other transition in the confined helium. In this Letter we report on experiments in which we used a capacitive technique to study freezing of helium in Vycor and a new method to make the first measurements of the flow of solid helium in the pores in response to external pressure changes.

Vycor is a silica glass with about 28% of its volume consisting of a random interconnected network of pores with typical diameter about 7 nm. When helium is confined in its pores, a number of measurements [5,6] have shown that the freezing curve is shifted upward by about 10 bar. The measurements of Adams *et al.* [6] showed a reduced latent heat of freezing and they inferred a density change substantially smaller than in bulk. If this reflects incomplete freezing in the pores, then the decoupling seen in the torsional oscillator could be occurring in a liquid layer, rather than in the solid helium. It is also important to rule out explanations based on a redistribution of mass. Structural transitions have been seen in a number of ad-

sorbates in Vycor, including delayering in an argon layer near the pore surface [7] and crystallographic transitions in oxygen and argon [8]. Also, solid argon and krypton have been seen [9] to migrate out of the pores well below their freezing temperatures. Such effects can change the oscillator’s moment of inertia and mimic superfluid decoupling, as was shown for hydrogen [10] where a dewetting transition expelled mass from the Vycor. In the experiments described in this Letter, we used a capacitive technique to study the density changes associated with freezing of helium in Vycor and at the lower temperatures where Kim and Chan observed supersolidity. Our measurements confirm that the density change associated with freezing is smaller than in bulk helium, but show that it is independent of pressure. This implies that, if there is a remaining liquid layer, then it must be very difficult to freeze. We saw no evidence that solid helium spontaneously entered or left the pores at low temperatures, ruling out mass redistributions due to nonsuperfluid transitions as the explanation of the torsional oscillator results. It is therefore very interesting to see how solid helium flows in response to a pressure gradient. By suddenly increasing the pressure in a cell containing a Vycor sample, we were able to monitor the pressure-induced flow of solid helium in the pores. Near the melting temperature, solid helium did flow into the pores but the rate decreased rapidly with temperature; below about 700 mK no flow was detected. Our experiments extended below 50 mK, well into the temperature range where Kim and Chan observed NCRI. If the helium in Vycor is a supersolid, then either it does not respond to pressure differences or superflow occurs at a rate far slower than the critical velocities of the torsional oscillator measurements.

Our Vycor sample was a disc with a diameter of 12.7 mm and a thickness $d = 0.52$ mm, onto which we evaporated circular copper electrodes (100 nm thick, area $A = 0.71 \text{ cm}^2$) to form a capacitor. Before depositing the electrodes, we dusted the Vycor with $40 \mu\text{m}$ cobalt powder (held in place by a magnet behind the sample). After deposition, the powder was removed, leaving an electrically continuous electrode with perforations (about 10% of

the area) to allow the helium easy access to the pores. At 4.4 K the empty sample had a capacitance $C_V = 3.7257$ pF, roughly what would be expected from the manufacturer's quoted dielectric constant for Vycor (3.1 at room temperature). If helium admitted to the pores acted as a uniform dielectric, then the capacitance change, ΔC_V would be proportional to the Vycor's porosity, $\phi \approx 0.28$, and to $\epsilon_{\text{He}} - 1$, the helium's contribution to the dielectric constant within the pores. Since $\epsilon_{\text{He}} - 1$ is proportional to the helium density, capacitance changes would provide a direct measure of the amount of helium in the sample. In a real porous medium, the contribution of a pore fluid to the dielectric constant depends on pore geometry through depolarization effects [11], but measurements with Ar and CO in Vycor have shown [12] that, except for very thin adsorbed films, this can be accounted for by including a simple geometric parameter so that the capacitance change is still proportional to the change in adsorbate density. We have confirmed this for liquid helium via a 1.8 K adsorption isotherm. For fillings greater than about two monolayers, the Vycor capacitance increased linearly with the amount of helium adsorbed.

For our initial freezing measurements, the Vycor capacitor was sealed into a copper pressure cell which included an *in situ* Straty-Adams pressure gauge. The cell had a volume much larger than the Vycor pores, so the bulk helium acted as a reservoir which kept the pressure essentially constant when the helium in the pores froze. Crystals were grown using the blocked capillary, constant volume technique. Temperatures were measured with a calibrated germanium thermometer above about 50 mK, with ^{60}Co nuclear orientation and ^3He melting curve thermometers for calibration at lower temperatures. The pressure and helium density were measured capacitively using an automatic bridge operating at 1 kHz (Andeen-Hagerling 2550 A). Most measurements were made with a 15 V excitation, after confirming that the few nW of dissipation in the Vycor capacitor (its resistance was greater than $3 \times 10^{10} \Omega$) did not cause any measurable sample heating down to 30 mK.

Figure 1(a) shows the thermodynamic path during a typical measurement. The bulk helium began to freeze at 2.75 K and 66.7 bar and the pressure then decreased, following the melting curve down to the point marked " T_B " (2.05 K, 39.4 bar) where bulk freezing was complete. At lower temperatures the pressure remained nearly constant and the helium in the Vycor pores did not begin to freeze until the point marked " T_F " (1.64 K). Figure 1(b) shows the corresponding capacitance, C_V , which reflects the helium density in the pores. Along the melting curve the capacitance decreased, since liquid helium left the pores as the pressure in the cell dropped, as can be seen in the lowest (39.4 bar) curve. The slower decrease between T_B and T_F is just the background temperature dependence of the dielectric constant of Vycor, due to "two level systems" (TLS) in the glass. Freezing in the pores was marked by the sudden increase in C_V at T_F , due to the

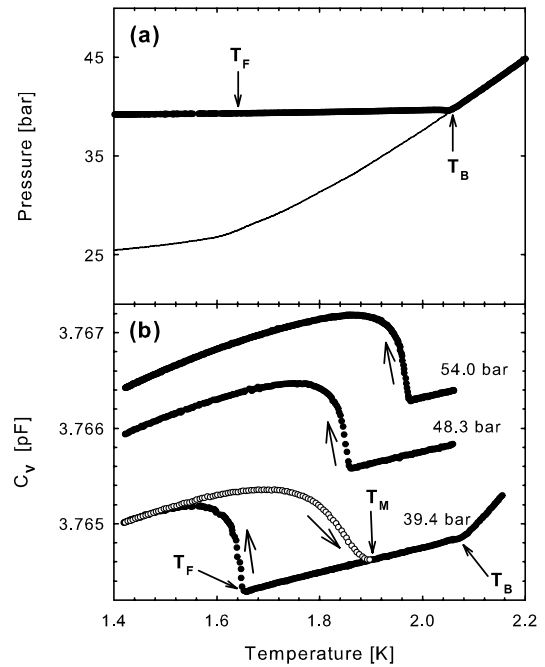


FIG. 1. Freezing and melting of helium in Vycor. (a) Thermodynamic path (pressure P vs temperature) during cooling. System follows the ^4He melting curve (solid line) until bulk freezing is complete at $T_B = 2.05$ K, $P = 39.4$ bar. (b) Lower curve: capacitance during cooling (solid symbols) and warming (open symbols) at 39.4 bar. Upper curves show the corresponding cooling data at 48.3 and 54.0 bar.

larger density of solid helium. When the sample was later warmed (open symbols) the helium melted at higher temperature, with melting complete at $T_M = 1.86$ K. The suppression of freezing and the hysteresis between freezing and melting are common features of adsorbates in small pores.

By extrapolating and subtracting the background temperature dependence of C_V we can extract the jump in capacitance, ΔC_V , associated with freezing in the pores. The jump in Fig. 1(b), $\Delta C_V = 0.0011$ pF, is about 2.8% of the 0.0395 pF capacitance change due to filling and pressurizing the sample with liquid helium, less than half the 6% density increase when bulk helium freezes at this pressure [13]. This may be due to an "inert layer" at the pore walls which does not participate in freezing and melting or may indicate that some of the helium remains liquid. In the latter case, we might expect the fraction of the helium which freezes to increase with pressure, with a correspondingly larger capacitance change. We made measurements at pressures ranging from 31.7 bar (where no freezing was seen down to 30 mK) up to 54 bar. Figure 1(b) includes freezing data at several pressures, all showing the same capacitance change, 0.0011 pF. If a persistent liquid layer remains after helium in the pores freezes, then it is remarkably stable and insensitive to pressure.

We next cooled the Vycor sample containing solid helium (at 39.4 bar) to look for any change in helium density

that might mimic superfluidity in a torsional oscillator. Figure 2 shows the capacitance data at low temperatures. The smooth minimum at 88 mK is typical of dielectric glasses and reflects coupling to the TLS, not changes in the helium density. For example, we saw the same behavior when the pores contained liquid helium at saturated vapor pressure. If there was a low temperature transition which resulted in helium being expelled from the pores, then it would show up as a sudden decrease in capacitance, but we saw no such change in the range below 200 mK where Kim and Chan saw decoupling. The bar in Fig. 2 shows the change that would be expected if 1% of the helium were to leave the pores. Since movement of helium in or out of the pores might occur slowly (Kim and Chan observed time constants of order 1 h for their oscillator period to stabilize), we waited overnight at our lowest temperature (about 30 mK) and then warmed our sample. The inset in Fig. 2 compares the capacitance during warming (open symbols) to the initial data during cooling. Within the resolution of our measurements, there is no difference, demonstrating that the density of the solid helium is constant to within 0.04% at low temperatures. Motion of solid helium into or out of the Vycor pores cannot explain Kim and Chan's observations, strengthening their interpretation in terms of supersolidity.

Since our measurements rule out some of the most obvious alternative explanations of the decoupling observed for solid helium in Vycor, it becomes interesting to see whether solid helium exhibits any of the other unusual flow properties of a superfluid. In our second experiment, by suddenly increasing the pressure in a cell containing the same Vycor sample, we were able to monitor the pressure-induced flow of solid helium in the pores. Since thermally activated vacancies can transport mass in a pressure gradient [14], we do expect to see flow at temperatures near the melting point of the helium in the pores, but this flow rate should decrease rapidly with temperature.

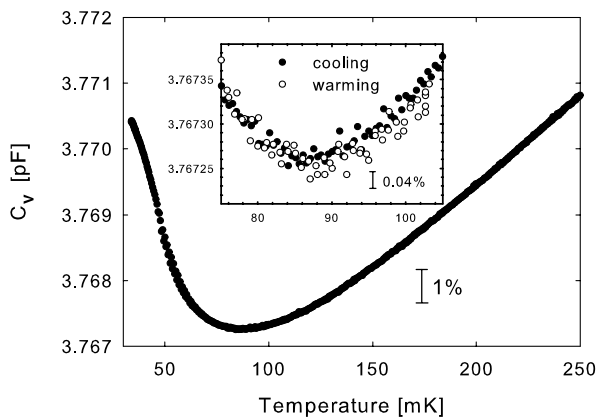


FIG. 2. Low temperature capacitance of the Vycor/solid helium sample. Bar shows the capacitance change for a 1% change in the density of the helium in the pores. Inset is a blowup of the data around the capacitance minimum at 88 mK and includes data taken during warming from 30 mK (open symbols).

For the pressure/flow measurements we built a beryllium copper “squeezing cell” with a flexible diaphragm machined into one end and an external piezoelectric actuator designed to compress the helium by up to 1%. We again started at a pressure high enough to completely freeze the helium in the pores (at $T_F = 2.05$ K for the 57 bar data shown below) and cooled to a temperature between 2 K and 30 mK. We then suddenly (in about 10 sec) compressed the helium by applying a voltage to the piezoelectric actuator while monitoring the helium density in the Vycor. Figure 3 shows the results of such “squeezes” at five temperatures between 1.8 and 0.5 K. At 1.1 K and above, the capacitance (i.e., the solid helium density in the pores) responded to the pressure step in two stages. First, there was an immediate capacitance jump of about 0.133 fF, which occurred within the measurement time of our capacitance bridge, i.e., during the 10 sec taken to increase the pressure. Second, there followed a slower, temperature-dependent increase. The time constant associated with the slower increase varied from less than 30 seconds at 1.8 K to more than an hour at 1.1 K. Below 700 mK (e.g., the 500 mK data in Fig. 3) there was no measurable capacitance change following the initial jump.

The initial 0.133 fF jumps in Fig. 3 are simply due to the elastic compression of the capacitor. Even if no helium flows into the pores, a pressure change ΔP will elastically compress the capacitor and produce a geometric change $\Delta C_V/C_V$. This temperature independent change is immediate and can be calculated from Vycor's dielectric and elastic constants (Young's modulus $E = 1.8 \times 10^{10}$ Pa; Poisson's ratio $\nu = 0.20$). For uniaxial compression in our cell, we expect $\Delta C_V/C_V = (1.0 \times 10^{-10} \text{ Pa}^{-1}) \Delta P$; our 0.133 fF jump corresponds to a pressure increase of about 3.5 bar. If solid helium subsequently flows into the Vycor to equalize the pressures after compression, then the capacitance will increase further, but at a slower rate which depends on the flow velocity. This capacitance change depends on the compressibility of the helium in the pores,

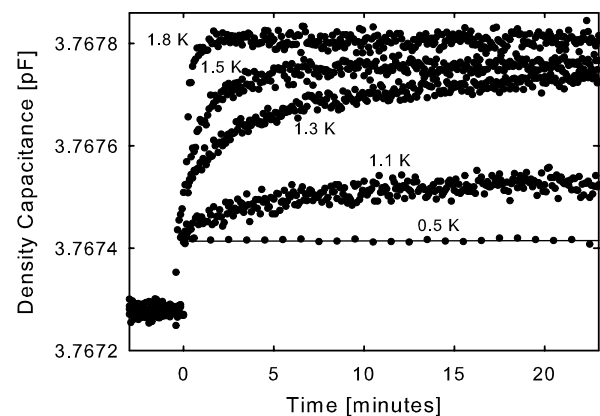


FIG. 3. Capacitance response to a rapid compression of the surrounding helium. From top to bottom, the curves correspond to temperatures 1.8, 1.5, 1.3, 1.1, and 0.5 K. Horizontal line through the 0.5 K data is a guide to the eye.

which can be found from the data of Fig. 1(b). Between 48.4 and 54 bar, we estimate the solid's compressibility (at 1.45 K) as $2.0 \times 10^{-8} \text{ Pa}^{-1}$, slightly less than the corresponding value for bulk helium ($2.3 \times 10^{-8} \text{ Pa}^{-1}$ at 54 bar [15]). For a 3.5 bar pressure step, equilibrating the pressure inside and outside the pores would produce a change of about $3 \times 10^{-4} \text{ pF}$, roughly what we observe after the initial jump.

The flow-induced capacitance changes in Fig. 3 occurred more slowly as the temperature was reduced. This is consistent with mass transport via a thermally activated process, presumably the diffusion of vacancies in the solid helium or in a disordered layer at the pore walls. Above 1.3 K, the capacitances approached similar final values within the time shown; at 1.1 K the changes continued for much longer and we did not wait long enough to determine the asymptotic value. At 0.5 K we saw no flow at all. The flow behavior depended slightly on the thermal history of the sample and differences between the final capacitance values may reflect defect creation associated with deformation of the bulk solid and annealing at the higher temperatures. Although the results of Fig. 3 are not systematic enough to provide a precise activation energy (the data between 1.1 and 1.8 K indicate a value around 9 K), the essential result is that solid helium near its melting point flows in Vycor when an external pressure is applied, but this flow is negligible at temperatures below about 0.7 K.

The most interesting question is whether the solid helium in the Vycor responds to a pressure difference when cooled below 175 mK (the range where Kim and Chan saw decoupling). Figure 4 shows our capacitance results at 88 mK when the pressure was raised, held for about 4 h, and then returned to its original value. By taking data at the capacitance minimum of Fig. 2 (88 mK), we eliminated effects of the small temperature changes caused by heating in the piezoelectric actuator. There is no indication of any density change inside the Vycor following the initial capacitance jump. About 0.5% of the helium decoupled in Kim and Chan's Vycor measurements. If this fraction were to flow from the surface to the center of our sample at their critical velocity (of order $100 \mu\text{m/s}$), then a 1% density change outside the pores would be transmitted throughout the pores within a few seconds. Figure 4 shows that any pressure-induced helium flow in our experiments must occur at much lower speeds. Assuming that helium can flow into the Vycor through the electrode's perforations and at its edges (about 30% of the sample's outer surface), we find that the flow velocity must be less than about $0.003 \mu\text{m/s}$. We extended our squeezing measurements down to 48 mK with no indication of mass flow. Below this temperature, dissipation in the piezoelectric actuator heated the cell slightly and prevented accurate measurements.

The NCRI observed in Kim and Chan's torsional oscillator measurements appears to be a fundamental property of solid helium at low temperatures. Our measurements

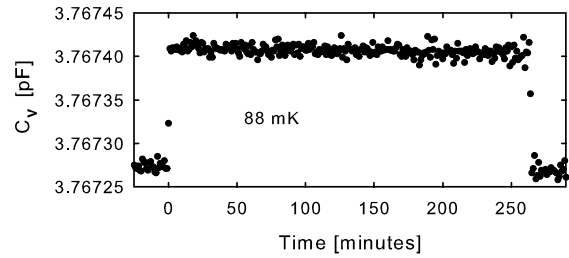


FIG. 4. Capacitance change for a compression at 88 mK, followed by a decompression 260 min later.

rule out alternative explanations of their results based on redistribution of mass in Vycor rather than supersolid decoupling. However, we do not see any evidence of pressure-induced flow in the temperature range where they observed supersolidity. This is consistent with previous experiments by Greywall [16] which put a similar limit ($0.002 \mu\text{m/s}$, using Kim and Chan's bulk supersolid fraction [2], 1.5%) on pressure-induced flow of bulk solid helium through capillaries. If a supersolid exists, then its flow properties must be quite different from that of superfluids, since the chemical potential difference created by a pressure change does not appear to produce superflow.

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