Search for Superfluidity in Solid Hydrogen

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A torsional oscillator study of solid para-hydrogen has been carried out down to 20 mK in a search for evidence of superfluidity. We found evidence of a possible phase transition, marked by an abrupt increase in the resonant period of oscillation and onset of extremely long relaxation times as the temperature was raised above 60 mK. In contrast to solid ^{4}He, the change in the period for para-hydrogen is not a consequence of irrotational superflow. The long relaxation times observed suggest the effect is related to the motion of residual ortho-hydrogen molecules in the solid.

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A supersolid is a solid that possesses an element of superfluidity. The existence of supersolid ^{4}He was first suggested 67 years ago [1], while possible underlying mechanisms were discussed 30 years later [2]. Experimental evidence was reported by Kim and Chan (KC) only two years ago in a series of torsional oscillator experiments on bulk solid helium [3,4] and solid helium confined in porous media [5,6]. KC demonstrated that the torsional oscillator is an ideal tool for the detection of solid ^{4}He acquiring nonclassical rotational inertia (NCRI) [7]. NCRI is indicated by a drop in the resonant period of the oscillator below the transition temperature. The decrement in the period is proportional to the supersolid fraction in the limit of low oscillation speed [3]. These observations have since been replicated in three other laboratories [8]. This prompted us to address the question of whether or not the supersolid phase is present in any system other than ^{4}He.

Helium is the most quantum mechanical solid of all the elements. This is due to the combination of large zero-point energy of individual atoms and weak attractive interactions between them. A measure of the quantum nature of a substance in the condensed phases, i.e., liquid or solid, is given by the de Boer parameter, $\Lambda = h/\sigma\sqrt{m\epsilon}$, where σ and ϵ are fitting parameters for the interparticle potential energy [9]. Only helium and hydrogen isotopes have Λ greater than unity ($\Lambda_{3\mathrm{He}} = 3.0$, $\Lambda_{4\mathrm{He}} = 2.6$, $\Lambda_{\mathrm{H2}} = 1.7$, $\Lambda_{\mathrm{HD}} = 1.4$, $\Lambda_{\mathrm{D2}} = 1.2$). Therefore H_2, after ^{4}He, is the most likely system to exhibit superfluidity. The fact that the supersolid phase in ^{4}He persists up to at least 135 bar [4], where it is expected to be less quantum mechanical than at lower pressures, was further incentive to investigate solid H_2.

Our experimental configuration is similar to that used by KC [3]. A sample cell is suspended from the cooling stage of a ^{3}He-^{4}He dilution refrigerator by an annealed beryllium-copper torsion rod. The rod provides a restoring force to keep the cell in oscillatory motion and doubles as a fill line to the cell. Within the cell, solid H_2 takes the form of an annulus [Fig. 1]. The resonant period (τ_0) of the oscillator is determined by the moment of inertia (I) of the torsion cell and the torsion spring constant (κ) of the rod, such that $\tau_0 = 2\pi\sqrt{I/\kappa}$. The mechanical quality factor (Q) of the oscillator at low temperature is 1.1×10^6, which allows for the detection of changes in τ_0 of one part in 10^7.

Solid H_2 samples were grown at saturated vapor pressure from high purity H_2 gas containing very low levels of isotopic impurities: less than 10 ppm of both hydrogen deuteride (HD) and deuterium (D_2). However, for pure H_2 crystals there exist impurities of a second kind. The two lowest rotational energy states of each molecule are the para- and ortho- states, having angular momentum $J = 0$ and $J = 1$, respectively. The equilibrium concentrations of para-H_2 ($1 - x$) and ortho-H_2 (x) at 300 K are, respectively, 0.25 and 0.75. At temperatures (T) below 4 K the equilibrium value of x is approximately zero and the solid is essentially pure para-H_2. However, the conversion rate from ortho-H_2 to para-H_2 in the solid is very slow for $T >$ 500 mK (e.g., about three weeks of conversion are required for x to drop from 0.01 to 0.009). This rate can be increased

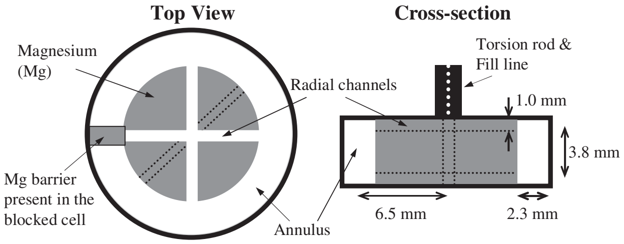

FIG. 1. Schematic of the torsion cell. The H_2 space in the cell is comprised of an open annulus and an axial fill line, which are connected by three channels that span the diameter of the cell. The annulus has an average radius, width, and height of 6.5, 2.3, and 3.8 mm, respectively. The radial channels and fill line have a diameter of 1.0 mm, a combined volume that constitutes 7% of the total cell volume, and contribute about 2% of the rotational inertia of all the H_2 in the cell. The "blocked cell" has the same geometry, with the addition of a barrier at one point in the annulus.

substantially by keeping H_2 in the liquid phase, i.e., $T > 13.8$ K, in the presence of a high surface area, magnetic material. In this way we attain $x < 0.01$. This process is irreversible so that the average x of each sample only decreases with time. Concentrations are determined by keeping the mixing chamber at 20 mK and measuring the temperature difference between the torsion cell and mixing chamber. Based on this measurement and the thermal conductance of the Be-Cu torsion rod, we can infer the amount of ortho-to-para conversion heat being released and hence x within the H_2 sample. The smallest measurable temperature gradient corresponds to $x = 0.01$. All H_2 samples discussed in this work have $x < 0.01$ (i.e., no observed gradient). To limit the uncertainty in the absolute value of x we measured the thermal conductivity of our Be-Cu rod, finding agreement with the literature [10] upon extrapolation to $T > 1$ K.

In Fig. 2(a) we have plotted τ_0 versus T for several samples. The empty cell period at 1 K ($\tau_{1\ K}$) is 709 700 ns, which decreases by only 3 ns, or five parts in 10^6, as the cell is cooled to 20 mK. This change is determined by the T dependence, if any, of I and κ. Based on earlier work [11], the small change in τ_0 depicted in Fig. 2(a) is due to small changes in I and/or κ rather than large, nearly compensating changes of each. For the H_2 sample in Fig. 2, τ_0 increases from the empty cell value by 2682 ns upon solidification, indicating that the cell is 88% full. The mass loading due to the heavier and denser isotope, HD, is 4675 ns, corresponding to 91% filling. Each data set has been shifted vertically for easy comparison. There is a slight difference in the slope of each curve shown, which has been observed in other torsional oscillator studies [3,5,11]. To our knowledge, no systematic investigation has been carried out to determine the precise origin of this feature.

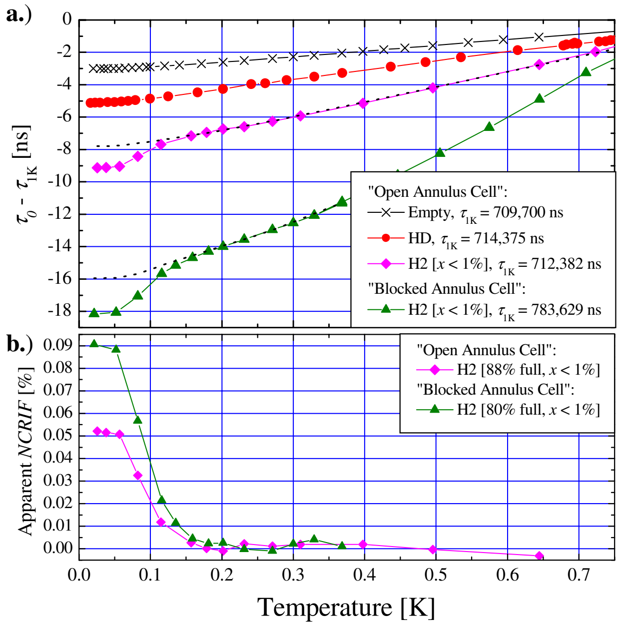

FIG. 2 (color online). (a) T dependence of τ_0 for both the open and blocked cells. All of the data shown were obtained at maximum rim velocities less than 40 μm/s. For the open annulus, data is plotted for the empty cell, cell containing HD, and cell containing H_2. H_2 data taken using the blocked cell exhibits the same qualitative features, including the long relaxation times. (b) T dependence of $\Delta\tau_0$, normalized by the total H_2 mass loading (NCRIF, the apparent NCRI fraction). The T dependence is similar to that observed in solid ^{4}He. However, the same effect is seen in the blocked cell.

The most striking feature in Fig. 2(a) is the clear difference between H_2 and HD. The abrupt drop in τ_0 below 180 mK for the cell containing H_2 is absent for HD. This discrepancy is similar to that found between ^{4}He and ^{3}He, suggesting that the Bose or Fermi nature of the solid is important. The net period change ($\Delta\tau_0$) is obtained by subtracting the measured period from values extrapolated from high temperature. The change in τ_0 first becomes measurable below 180 mK, and saturates near 60 mK. While $\Delta\tau_0$ is more than an order of magnitude smaller than that in ^{4}He [3], its temperature dependence is similar [Fig. 2(b)].

There are, however, four puzzling features in the H_2 data. First, for solid ^{4}He, $\Delta\tau_0$ is accompanied by a minimum in the amplitude of oscillation at the temperature where τ_0 changes most rapidly [3]. There is no such minimum in oscillation amplitude near the transition region in the H_2 experiment. Second, for ^{4}He the measured NCRIF decreases once the maximum oscillation speed of the sample exceeds 10 μm/s [3]. This speed has been interpreted as the critical velocity of superflow. There is no evidence of this effect in solid H_2. We found $\Delta\tau_0$ to be independent of velocity up to 500 μm/s, the maximum within the linear response range of the oscillator.

Third, the apparent supersolid onset temperature ($T_C \sim 180$ mK) and saturation temperature ($T_S \sim 60$ mK) are remarkably close to the 230 mK and 50 mK values found for solid ^{4}He [3]. The similarity in these characteristic temperatures is inconsistent with the substantial difference in Λ_{4He} and Λ_{H2}. For solid ^{4}He in Vycor glass, very low ^{3}He impurity levels can significantly enhance the onset temperature [5]. While T_C for a sample containing 0.2 ppm of ^{3}He is about 175 mK, a sample with 10 ppm has $T_C \sim 370$ mK. This effect has also been observed in bulk ^{4}He [12]; thus the HD impurities may be responsible for the high T_C in solid H_2. However, we do not know the exact HD impurity level in our samples since this heavier isotope can preferentially adsorb onto surfaces in our gas handling system. Specifically, the capillary leading to the cell contains a chamber filled with a high surface area, FeO(OH) compound. Although we expect the actual HD concentration to be much less than the quoted value of 10 ppm, we cannot say with certainty. Thus, we cannot validate the $T_C = 180$ mK and $T_S = 60$ mK values we observe.

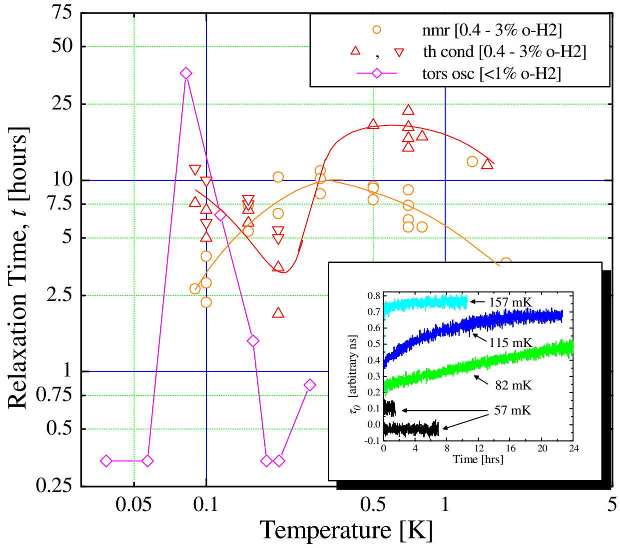

FIG. 3 (color online). T dependence of measured relaxation times, including NMR and thermal conductivity data from the literature [18]. ○ signify the growth ($T < 1$ K) or decay ($T > 1$ K) rates of isolated orho-H$_2$ molecules. △ and ▽ are, respectively, the exponential decay and growth rates of the thermal conductivity. In the present study, -◇- are extracted from τ_0 versus time data. The sharp increase in t coincides with the observed τ_0 shift. The largest t values are observed near 80 mK. Near 180 mK, a minimum in t exists for both the oscillator and conductivity measurements. Inset: τ_0 versus time curves for different T. The lower $T = 57$ mK curve, from a previous sample, clearly demonstrates the time independence at low T. The curves are shifted vertically for clarity.

The final and most unusual feature of the H$_2$ data, compared to ^{4}He, is the exceedingly long relaxation time (t) of the period [Fig. 3]. The e^{-1} time constant required for thermal equilibration increases with decreasing T and typically reaches 15 min below 50 mK. Since the mechanical Q is on the order of 10^6, the necessary time to allow for mechanical equilibrium is about 10 min. Therefore it is necessary to wait at least 75 min after each temperature step before collecting τ_0 data. This protocol was used in the solid helium experiments to ensure reproducible data upon warming and cooling. However, in gathering data on H$_2$ we observe t values as long as 40 h just above 60 mK. There is no such evidence of relaxation in the HD sample or for the empty cell, for which τ_0 equilibrates within 75 min at all T. We will return to the issue of t values below.

We have carried out a crucial control experiment to ascertain whether the observed effect in solid H$_2$ is a signature of superfluidity. We constructed another sample cell, identical to the first except for the addition of a barrier at one point in the annulus [Fig. 1]. Its purpose is to make the path for the irrotational superflow much more tortuous, leading to a predictable decrement in NCRI [13,14], thus reducing $\Delta\tau_0$. This control experiment provides a convincing case for the supersolid phase of ^{4}He. It was found that when the annulus was blocked, $\Delta\tau_0$ was reduced by a factor of 70 from the open annulus value [3]. This reduction is in agreement with what is expected for irrotational superflow [14]. The result of the control experiment for solid H$_2$ is plotted alongside the data of the "open annulus cell" in Fig. 2(a). The period drop below 180 mK is still present for the "blocked annulus cell." In fact, we find the magnitude is larger in the latter. One possible reason for this is that, while each sample has $x < 0.01$, the exact ortho-concentrations of the two samples may differ. Regardless, this result clearly indicates that the $\Delta\tau_0$ in H$_2$ is not related to superfluidity. We note that, as in the open cell, long relaxation times are observed just above the saturation temperature of 60 mK.

Long equilibration times are typical in studies of ortho-H$_2$ diffusion in solid para-H$_2$ [15]. In the dilute limit where x is less than several percent, isolated ortho-H$_2$ molecules (singles) cluster together below 1 K even though thermally activated diffusion is severely limited. The ortho-H$_2$ impurities effectively propagate throughout the lattice via the transferral of J from molecule to molecule [16], rather than by particle exchange. The "equilibrium" state of the solid thus involves a T-dependent distribution of singles, pairs (two neighboring ortho-H$_2$ molecules), and larger clusters of ortho-H$_2$. At several kelvin, all of the ortho-H$_2$ molecules are randomly distributed as singles. As the temperature is lowered the number of isolated singles decreases in favor of the formation of pairs and larger clusters. Since ortho-H$_2$ and para-H$_2$ have different densities, in the limit of zero temperature the system prefers to be in a macroscopically phase-separated state.

Clustering was first observed by monitoring the time evolution of the nuclear magnetic resonance (NMR) absorption spectra for ortho-H$_2$ singles and pairs after rapid warming or cooling of solid H$_2$ crystals [17]. Representative growth (above 1 K) and decay (below 1 K) rates of the singles spectrum [18] are presented in Fig. 3. The singles decay rate exhibits a nonmonotonic T dependence, decreasing dramatically between 300 and 100 mK. Well below 100 mK the decay of singles is on a time scale of minutes rather than hours, rendering the measurement impossible. The pair spectrum also shows an enhancement in its decay rate at low T but time constants are at least 1 order of magnitude longer, e.g., on the order of 10 h at 25 mK [19]. Also included in Fig. 3 are relaxation times obtained from simultaneous thermal conductivity measurements [18]. The time evolution of the thermal conductivity depends strongly on T. For $T > 300$ mK the time dependence is described by a simple exponential. However, contrary to the singles decay rate, a sum of two exponentials best fits the conductivity data below 300 mK. This difference may be related to the presence of ortho-H$_2$ clusters at lower temperature. Since it is difficult to resolve the spectra of triples or larger clusters [20], NMR studies cannot quantify the degree of mobility of larger ortho-H_2 clusters that form at low T. Their presence, however, has been detected for solid H_2 crystals held at 25 mK for only 24 h [21].

Our torsional oscillator data are obtained using the following protocol. Upon cooling H_2 samples to 20 mK, one to two weeks are allowed for equilibration, during which time τ_0 drops smoothly until finally stabilizing to within 0.05 ns, our limiting resolution. We note that the rate of irreversible ortho-to-para conversion is enhanced for $T < 200$ mK since local x values are higher in clustered regions [22]. However, upon stabilizing at 20 mK, we observe no long term drift in the τ_0 reading. After complete equilibration the temperature is raised in successive steps, for each of which τ_0 is measured as a function of time [Fig. 3 inset]. We find for all samples that τ_0 equilibrates quickly for any $T < 60$ mK. However, further increase in T leads to extremely slow relaxation. Near and above 180 mK we find that t shortens, returning to a value of about 15 min, the usual e^{-1} equilibration time. When the temperature sweep is complete the system is returned to 20 mK and allowed to reequilibrate. Our measured t values are presented in Fig. 3.

Associating the motion of ortho-H_2 impurities with the data in Fig. 3 explains the absence of this unusually long relaxation in HD, ^{4}He, and ^{3}He. In our experiment we allow clustering to ensue for up to two weeks at 20 mK so that no isolated ortho-H_2 singles or pairs remain in our samples at the beginning of each temperature sweep [18,19]. Thus, we are able to follow the unclustering process upon gradual warming of the torsion cell.

The moment of inertia and hence τ_0 are extremely sensitive to the radial density profile of the sample. Changes in τ_0 require the rearrangement of ortho-H_2 within the torsion cell in such a way as to reduce or enhance the density at large radii. A possible explanation for the observed $\Delta\tau_0$ below 180 mK is the formation of large clusters of nearly pure ortho-H_2 in the center of the cell (fill line and radial channels), increasing the purity of para-H_2 in the annulus. Since the density of ortho-H_2 is 1.7% higher than that of para-H_2, clustering of ortho-H_2 toward the center can effectively reduce I. An extreme case is where all of the ortho-H_2 molecules cluster to the center of the torsion cell, which may take place below 60 mK. If we take $x = 0.01$ as the upper limit, the reduction of τ_0 is 1.7×10^{-4} of the total H_2 mass loading. This is on the same order of our observations [Fig. 2], i.e., 5.5×10^{-4} and 9.0×10^{-4} in the open and blocked cells, respectively. However, one would expect this extreme case to be an overestimate. Since $\Delta\tau_0$ is too large, one must consider the possibility of additional effects.

It is known that solid H_2 does not wet many metal substrates [23]. It is possible the contact angle of a sample (with a free surface within the annulus) is determined by the local ortho-para composition near the surface. During clustering either ortho-H_2 or para-H_2 can concentrate at the walls and possibly lead to an additional change in I.

In conclusion, a resonant period shift in our torsional oscillator containing solid H_2 is observed. While the phenomenon shares some features with the supersolid transition in ^{4}He, there are several dissimilarities. Most notable is the presence of the period drop in both the open and blocked cells, ruling out superfluidity. We believe the abrupt rise in τ_0, accompanied by a sudden increase in t near 60 mK, is consistent with a transition from a phase-separated configuration to one that is unclustered at high temperature.

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