Mobility Transition of Solid Rare Gases in Confined Environments

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We report the results of x-ray diffraction and small angle scattering studies of Ar and Kr confined in sol-gel and Vycor glasses. The confined liquid crystallizes in a disordered hcp structure on freezing. Upon further cooling a sharp transition occurs at a reduced temperature of $T/T_m \approx 0.65$, where the crystalline structure disappears and the total scattering decreases. This behavior marks the onset of a well-defined mobility transition, where the confined sample migrates out of the pore space.

The effects of confinement on the thermodynamic properties of imbibed liquid and solid phases have been extensively studied [1–3]. It has long been known that confinement can affect the thermodynamic behavior of imbibed liquids, such as suppressing the liquid-solid transition and introducing hysteresis between freezing and melting [4,5]. More recently, attention has focused on the microscopic structure of the adsorbed phases where confinement can not only change the microscopic structure, but also eliminate or introduce new transitions or stabilize new phases. Studies of confined water [6], Deuterium [7], and Ar and Kr [8] all report crystalline structures different from those in the bulk.

Simple rare gases, such as Ar and Kr, provide an attractive system to study the effects of confinement since they have been extensively studied and have both simple structures and uncomplicated phase diagrams. Recent studies have reported the surprising appearance of a solid-solid phase transition for Ar and Kr confined in porous Vycor glass [8]. Ar and Kr exhibit only fcc structure in the bulk [9], but when confined in Vycor, they crystallize into a disordered hexagonal close packed (dhcp) structure at high temperatures and undergo a solid-solid phase transition at $\sim T_m/2$ to a new phase characterized by a coexistence of dhcp and fcc structures. The dhcp component, both in the high and low temperature (high- and low-T) solids, has a correlation length comparable to the pore size. The fcc component, however, has a correlation length greater than 1000 Å. This large correlation length, along with strong orientation effects for the fcc peaks, suggested that the fcc component consisted of several large single crystallites spanning the pore network.

In this Letter, we report x-ray diffraction measurements of Ar and Kr confined in Vycor and sol-gel glasses that provide a surprising insight into the nature of this new confinement induced solid-solid transition. Our measurements have been carried out on powder samples in contrast to the monolithic sample employed in the previous studies. As in the previous studies, we observe the appearance of a dhcp structure on freezing at a temperature well below the bulk freezing temperature. We also observe a new transition in the solid phase near $T_m/2$, but of a very different nature

than the solid-solid transition reported by Brown *et al.* We observe a mobility transition characterized by a migration of the adsorbed phase out of the pores. This transition has a well-defined onset temperature and occurs at a low enough temperature such that traditional self-diffusion in the solid is negligible. This represents a new transition, induced by disorder and confinement, where the mobility of the solid increases by several orders of magnitude. Furthermore, we believe that the behavior observed by Brown *et al.* is a manifestation of this transition in a monolithic sample where migration of the sample is frustrated by the large sample dimensions.

The confining media used in these studies was Vycor [10–12] and Britesorb [13] glasses. Both of these glasses have a narrow pore size distribution; Vycor with a nominal pore diameter of 70 Å and Britesorb with a nominal pore diameter of 134 Å. Both glass samples were in powdered form with average particle sizes of 8 and 11 μm, respectively. The powders were tightly packed into a cylindrical cell with Be windows and mounted on a closed cycle refrigerator. The samples were filled with Ar and Kr such that the pores were 95% full when the vapor pressure was zero. All measurements were performed at the MATRIX (X18A) beam line at the National Synchrotron Light Source, Brookhaven National Laboratory, which has been previously described [8].

We first discuss the previous work of Brown *et al.* to provide a context of our new results. They measured the scattering from Ar and Kr confined in a monolithic Vycor sample, a disk with a diameter of 14 mm and a thickness of 1.2 mm. Their results for Ar in Vycor, with the scattering from the Vycor removed, are reproduced in Fig. 1a. Intense Bragg peaks, due to the Be windows and located at $Q = 3.1$ and 3.6 Å^{-1}, have been removed. At 85 K the confined Ar has a typical liquidlike S(Q), which is similar to that of bulk liquid Ar [14]. There is a broad peak at $Q \sim 2$ Å^{-1}, representing short-range correlations in the liquid, with several small oscillations (not seen here) at higher Q.

When the temperature is lowered below the freezing point of the confined solid, crystallization occurs as evidenced by the appearance of moderately sharp diffraction
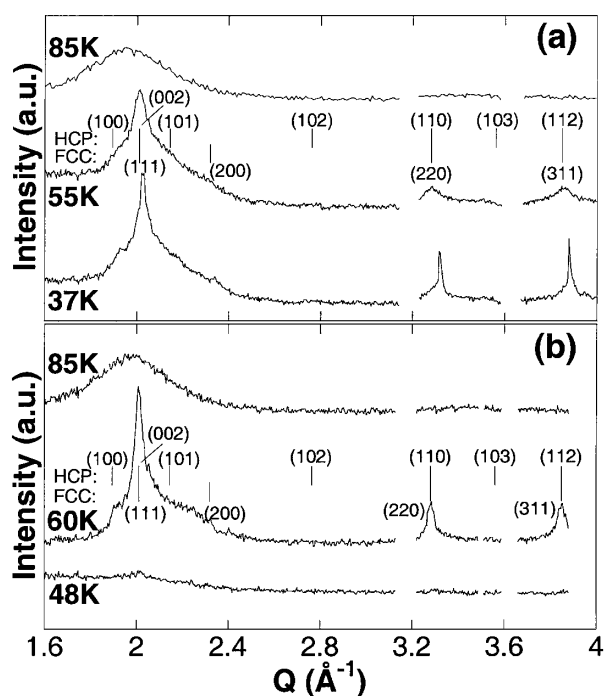
FIG. 1.   Scattering from Ar in a: (a) monolithic Vycor sample and (b) powdered Vycor sample, with the background removed. The curves are (top) liquid phase, (middle) high-T solid with dhcp structure, (bottom) low-T solid. Note the similarity in the liquid and high-T solid measurements for both substrates and the significant differences between the monolithic (a) and powdered substrate (b) for the low-T measurements. The vertical dashes mark the locations of the fcc and hcp structures.

peaks, shown in the 55 K measurement. These peaks can be indexed as the (111), (220), and (311) of an fcc structure. However, the (200) peak, which is very intense for the fcc structure, is missing. This is characteristic of the dhcp structure, which can be viewed as fcc with a maximum number of stacking faults. The width of these peaks gives a crystallite dimension of ~100 Å, comparable to the pore size of the Vycor.

A solid-solid phase transition occurs at low temperatures (37 K measurement) as can be seen by the appearance of sharp peaks atop the original dhcp peaks. With the appearance of the (200) reflection (not shown here), they were able to report the existence of a new crystalline phase. This new solid phase is characterized by a coexistence of an fcc structure with a large correlation length and a disordered hexagonal-close-packed (dhcp) structure with a short correlation length.

Our measurements from Ar in powdered Vycor are shown in Fig. 1b. This sample was obtained by crushing the original Vycor disk, used by Brown *et al.* The confined liquid structure at 85 K is identical to that reported by Brown *et al.* Upon cooling, diffraction peaks appear and a structure similar to that reported by Brown *et al.* appears. Our measurements show small (100) hcp and (200) fcc reflections implying that the stacking of the hexagonal planes, which is random for the dhcp structure, is no

longer fully random. Local regions must exist that slightly favor either the hcp or fcc stacking. No changes in this structure were observed with time or thermal cycling as long as the temperature remained above 54 K.

A phase transition occurs at ~54 K, similar in temperature to that reported by Brown *et al.,* but with a markedly different character. We find that on cooling below 54 K, the intensity of the diffraction peaks, which is characteristic of a crystalline solid in the pores, decreases with time. The bottom curve in Fig. 1b shows the scattering after 1–2 h, where the reduction in the diffraction peak intensity can be clearly seen. The diffraction peaks continue to diminish with time, and after several hours are no longer observable. However, the disappearance of the peaks associated with a crystalline solid in the pores is not accompanied by a reappearance of an amorphous, or liquidlike, component. In fact, we see a disappearance of the total scattering from the sample altogether. Thus, the confined solid phase is not simply undergoing a transition from a crystalline phase to an amorphous phase. Instead, a transition of a very different nature is occurring. This is in marked contrast to the measurements of Brown *et al.,* where they observed the appearance of a new crystalline phase.

Measurements of Kr in Vycor show similar behavior. Furthermore, measurements of both Ar and Kr in Britesorb exhibit this same behavior. The pore size and morphology of the Britesorb are similar to that of Vycor. In addition, we chose a sample where the particle size of the powder (11 μm) was comparable to that of the Vycore (8 μm). The scattering in the liquid and high-T solid phases of Ar in Britesorb is very similar to that of Ar in powdered Vycor. The primary difference is that the (100) and (200) peaks in the sol-gel sample are slightly more pronounced, indicating that the stacking order is less random in the larger pores of the sol-gel. Upon cooling, we observe a reduction of the diffraction peak intensity, without a corresponding increase in the intensity of the amorphous component, at a well-defined temperature. Thus, this new behavior is quite general and not dependent on the particular porous host employed.

The sample transmission can provide valuable information on the amount of material and its arrangement inside the pores [15]. The transmission for porous materials with adsorbates imbibed in the pores, or any multicomponent system in general, depends not only on the number and type of scatterers but also on their arrangement. A collection of rods of perfectly absorbing material arranged in a close packed array illustrates the dependence on shape as well as substance. If these are aligned along the direction of the incident beam, then the transmission through the inter-rod spaces will be large. However, if they are aligned perpendicular to the beam, the transmission will be zero. Even though the number of scatterers in the beam doesn't change, the transmission changes dramatically by simply rearranging the material.

The sample transmission for Ar confined in sol-gel was measured by monitoring the intensity of the diffraction peak from the Be window on the back of the cell. Be has a strong diffraction peak at $Q = 3.1$ Å^{-1} and, due to the spatial separation of the two windows, the peak from the rear window can be independently monitored. Figure 2 shows the sample transmission as a function of time at several temperatures. Once the solid has formed, one would expect that there would be little change in the transmission. This is confirmed for the intensities at 56 and 55 K. Indeed, as long as the temperature remains above 54 K, the sample transmission is independent of time or temperature. Upon cooling below 55 K, the sample transmission abruptly begins to increase. This increase in the transmission continues as the temperature is lowered. The upper inset shows the normalized intensity of the x rays scattered from the Ar as a function of time at a temperature of 48 K. As can be seen, the temporal variation of the intensity is well described by an exponential decay with a time constant of ~5000 s. An exhaustive survey of this time constant as a function of temperature has not been carried out. However, time constants for a number of different temperatures have been measured, as shown in the lower inset.

The dramatic change in the sample attenuation, like the dramatic disappearance of the diffraction peaks, clearly marks the onset of some new behavior. The Vycor glass nearly fills the free volume of the cell and the pores are nearly filled with Ar. We find it unlikely that material is leaving the scattering volume—at least to the extent that our measurements indicate. Thus, the only explanation remaining for the change in transmission is that the Ar is rearranging itself within the porous material. The most probable scenario is that material is leaving the pores and forming a thin film over the outer surface of the glass powder. Model calculations of the attenuation support this interpretation for the data. Furthermore, we may use the time dependence of the transmission to characterize the dynamics of the migration out of the pores. Lacking a more detailed theory we may assume that this is a diffusive process [16]. The characteristic size (particle diameter) is of the order of 10 μm and the characteristic time is of the order of 5000 s yielding a diffusion constant of $D = x^2/t \sim 10^{-10}$ cm^2/s. This is considerably smaller than the diffusion of liquid Ar at 85 K, $D \sim 10^{-5}$ cm^2/sec [17] but it is many orders of magnitude larger than self diffusion of solid Ar, $D \sim 7 \times 10^{-15}$ cm^2/s [18].

In light of the diffusion rate reported here, it is not surprising that Brown *et al.* did not see the Ar leave the pores. Our powder samples had a particle diameter of approximately 10 μm and a time constant of ~5000 s. In their sample the Ar would need to travel on the order of 1 mm corresponding to a time constant of nearly 2 yr, which would certainly not have been seen in the time allotted for each measurement.

Our interpretation of the diffraction and transmission measurements, in terms of migration of the material out of the pores, was confirmed using small angle x-ray scattering (SAXS). SAXS provides information on the macroscopic distribution of scattering density of the constituents of the sample. The intensity observed in a SAXS measurement is sensitive to both the amount of material within the pore volume and its distribution in space. Migration of the adsorbed phase out of the pores will be reflected in the measured SAXS intensity.

Figure 3a shows SAXS measurements of Britesorb filled with Ar at various temperatures as well as an empty sol-gel scan. After filling the pores, the scattering decreases and changes shape. The change in both intensity and shape reflects the fact that the primary scatterer is now Ar and no longer the sol-gel matrix. The liquid (85 K) and two high-T solid measurements are quite similar in shape, although the intensity is slightly less in the solid due to its higher density.

Above 55 K, the SAXS measurements in the high-T solid phase ($T > 55$ K) are independent of both temperature and time. However, when the temperature is lowered below 55 K, the SAXS spectra begin to evolve with time. Figure 3b shows SAXS measurements of the previous empty sol-gel, liquid, and high-T solid, as well as a measurement at 48 K for three different times in the Guinier (low Q) region. The time evolution of the spectra is quite clear. As can be seen, the spectra evolve from the characteristic form of the high-T solid towards the liquid, or even the empty sol-gel. We were able to extract a time constant of ~5000 s from the time evolution of the Guinier region, similar in value to the time constant found with transmission measurements. This is consistent with
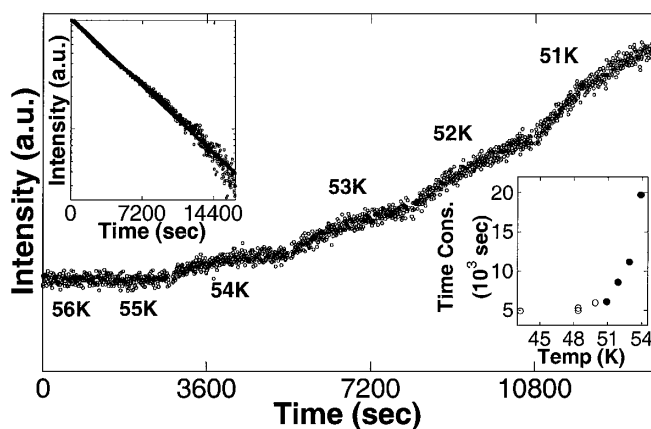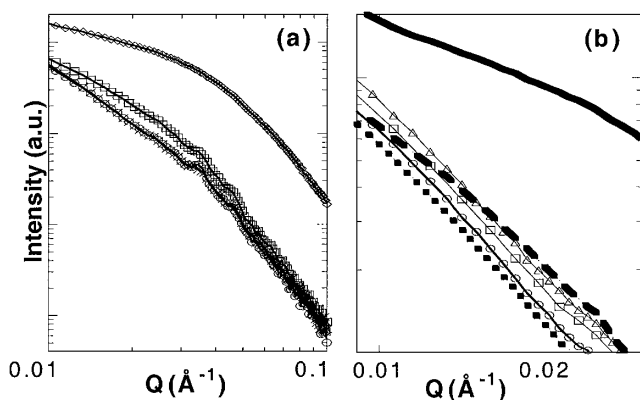
FIG. 2. Measurement of the sample attenuation of Ar in Britesorb as a function of time at several different temperatures. Note that the intensity is constant above 54 K and changes with time when lowered below 55 K. The upper inset shows a semilog plot of the scattered intensity from Ar as a function of time at 48 K. The lower inset shows the time constant as a function of temperature. [The higher temperature data (●) are time constants extracted from the main figure, while the lower temperature data (○) are from single temperature measurements as in the upper inset.]

FIG. 3. (a) SAXS measurements of Ar in Britesorb for the empty sol-gel ($\diamond$), 85 K ($\square$), 70 K ($\bigcirc$), and 60 K ($\times$). (b) SAXS measurements of empty sol-gel (solid line), Ar in Britesorb at 85 K (dashed line), 60 K (dotted line), 48 K after 0.5 h ($\bigcirc$), 48 K after 2.0 h ($\square$), and 48 K after 3.5 h ($\triangle$).

our model that material is migrating out of the pores in the low-T phase.

The experimental evidence from diffraction, transmission, and SAXS measurements paints a consistent picture of a transition with a sharp onset where the solid develops an enhanced mobility and migrates out of the pores. Nonwetting behavior has been studied both experimentally [19] and theoretically [20] and appears to depend on the interplay between short and long-range interactions. The behavior in our measurements is more reminiscent of a dewetting transition. As the temperature is decreased, it is no longer thermodynamically favorable for a liquid to wet the surface of a solid. The nature of such a dewetting transition for a solid imbided in porous media has not been explored to our knowledge. However, many studies have indicated that there is an amorphous layer at the pore wall, mirroring the structure of the confining glass, and a crystalline solid in the pore interior, mirroring the order in the bulk solid. The incompatibility of these two structures coupled with the competition between adsorbate-adsorbate and adsorbate-surface interactions must lead to a highly strained system. As the temperature is lowered the crystalline solid tries to contract relative to the glass matrix and the strains can only increase. Perhaps the transition we are observing is associated with diffusion of atoms through this highly disordered and strained system when a critical value of the strain is reached on cooling. Further experimental and theoretical work will be required to clarify the nature of this transition.

To summarize our results, we find that the solid crystallizes into a dhcp structure in both the sol-gel and Vycor. We also observe a sharp mobility transition at lower temperatures, where the material begins to leave the pores. The

movement of the material out of the pores is slow, with a time constant of ~ 5000 s, below the transition temperature, but is still several orders of magnitude faster than can be explained by traditional self-diffusion in the solid. This transition is reminiscent of a dewetting transition. However, the exact nature of the transition and the mechanism by which the material migrates out of the pores remains an open question.

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