New Disorder Induced Phase Transitions of Classical Rare Gases in Porous Vycor Glass

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We report the results of x-ray diffraction studies of Ar and Kr confined in Vycor glass. The freezing and melting temperatures of both Ar and Kr were suppressed well below their bulk freezing points. On solidification, both samples crystallized in a disordered hexagonal close packed structure similar to that observed in molecular dynamics simulations of confined solids. A new solid-solid phase transition is observed at a reduced temperature of $T/T_f \approx 0.5$ when confined to Vycor. Below this temperature the disordered hexagonal closed packed structure coexists with the fcc structure. [S0031-9007(98)06675-7]

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The effects of finite size and confinement on gases, liquids, and solids adsorbed in mesoporous materials, such as porous glasses and zeolites, is a topic of current interest for classical and quantum systems. For example, in classical systems the liquid-gas transition is enhanced with respect to the bulk [1,2] while the liquid-solid transition is suppressed [2,3]. Hysteresis, which appears to be a stable thermodynamic behavior, is also introduced into these transitions. Quantum transitions show equally dramatic behavior. For example, the superfluid transition of ^{4}He in Vycor is substantially suppressed while the critical exponents remain unchanged. However, confinement in aerogel results in only a small suppression but substantially different critical exponents [4,5]. ^{3}He, on the other hand, has superfluid phases in high porosity aerogels [6,7], but not in lower porosity confining geometries.

Microscopic structural studies of materials confined to mesoporous media have only recently been undertaken, and a variety of different behaviors have been reported. In some cases, such as Hg in Vycor [8], the structure of the confined solid is identical to that of the bulk while in other cases, such as H_2O and D_2 in Vycor [9,10], confinement stabilizes new structures not present in the bulk. Confinement can also suppress crystalline order, such as O_2 in xerogel [11], resulting in a glassy solid phase. Confinement has not, however, been observed to introduce new phase transitions in any systems that have been studied to date.

In this Letter, we report x-ray diffraction studies of Ar and Kr adsorbed in Vycor. As in many other systems, a suppression of the liquid-solid transition hysteresis between freezing and melting is observed. On freezing, both Ar and Kr are observed to form a disordered hexagonal close packed (dhcp) structure, characterized by random plane stacking, in contrast to the bulk fcc structure. A new phase transition, which is absent from the bulk phase diagram, occurs at roughly half of the freezing temperature below which both Kr and Ar exhibit coexistence of the dhcp and fcc phases. This solid-solid structural phase transition is repeatable on cycling and no appreciable hysteresis is observed. Thus, the coexistence phase appears to be a true disorder-induced thermodynamic phase, rather than a metastable phase.

The confining media used in these studies was Vycor glass. Vycor is produced by spinodal decomposition of a borosilicate glass followed by leaching of the boron-rich phase and has been extensively characterized [12–14]. The sample used in this study was a 14 mm diameter disk, 1.2 mm thick with a nominal pore diameter of 70 Å. The sample was cleaned using standard techniques [1] and transferred to a tightly fitting cell, designed to minimize the free volume surrounding the Vycor. The cell, which utilized beryllium windows to allow the passage of x rays, was mounted on a closed cycle refrigerator and the temperature was monitored with a silicon diode thermometer. The Vycor was filled to approximately 90% of capacity with the liquefied rare gases to avoid overfilling and the appearance of bulk sample.

The measurements were performed at the MATRIX (x18A) beamline at the NSLS, Brookhaven National Laboratory. A double Si(111) monochromator was employed to provide an incident energy of either 10 or 12 KeV. The incident beam was focused with a cylindrical platinum coated aluminum focusing mirror and collimated to 1×2 mm. Transmission geometry was used with the incident beam normal to the face of the Vycor disk at $\theta = 0$. Diffraction peaks from the Be windows were used to calibrate the instrument and to provide a measure of the instrumental resolution which was $\Delta Q/Q = 0.003$ at $Q = 3$ Å^{-1}.

The observed scattering from Ar in Vycor, with the scattering from the Vycor removed, is shown in Fig. 1. The Be windows contribute intense Bragg peaks at $Q = 3.1$ and 3.6 Å^{-1} which have also been removed. At 85 K the confined Ar is liquid and shows only a broad peak near the position of the bulk (111) peak due to short range order in the liquid. Confined Kr in the liquid phase gave qualitatively similar results.

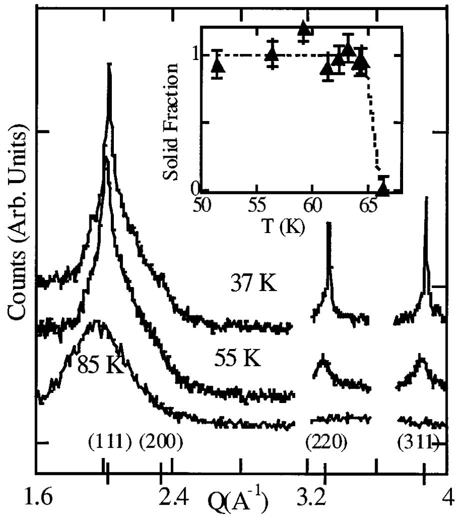

FIG. 1. Scattering from Ar (85, 55, and 37 K) confined to Vycor glass with the background removed. The vertical dashes mark the location of bulk solid Ar peaks. The inset shows the fraction of the sample in the crystalline state as a function of temperature on cooling, normalized to one at low temperature.

On cooling from the liquid phase, the Ar (Kr) developed relatively broad diffraction peaks signaling the onset of crystallization at 64 K (100 K). The diffraction pattern of Ar at 55 K, shown in Fig. 1, exhibits several Bragg peaks. The fraction of the sample in the crystalline state (inset in Fig. 1), as determined from the intensity of the diffraction peaks, shows a freezing transition that is quite sharp relative to the temperature steps taken (2 K). A broad component to the scattering also persists to low temperature due to the short range order of the sample in direct contact with the amorphous pore wall. Diffraction peaks corresponding to the (111), (220), and (311) of the bulk fcc structure are easily identifiable. The breadth of the (220) peak, 0.06 Å^{-1}, is indicative of an approximate crystallite dimension of ~100 Å, comparable to the pore size of Vycor. The diffraction pattern of Kr is qualitatively similar to that observed in Ar. The (200) peak, which should have an intensity comparable to the (111) and (220) peaks, is not present in the diffraction pattern of either confined solid.

With the exception of helium, the rare gas solids have been shown experimentally to crystallize in an fcc structure and exhibit no other structural phase transitions at moderate pressures. The solid phase of Ar and Kr in Vycor, just below the freezing temperature, is not consistent with the bulk structure due to the lack of the (200). The diffraction pattern is also inconsistent with an hcp structure, which is energetically very close to the fcc [15–17], differing only in the layer stacking order, and has been observed in a metastable state in vapor deposited crystals [18].

The missing reflection corresponds to an interlayer reflection suggesting that a large number of stacking faults are present. In fact, the observed scattering is consistent with the maximum number of stacking faults, corresponding to a dhcp structure [19]. The dhcp structure consists of hexagonal planes with a random stacking order, rather than the periodic stacking order of the hcp (*ABAB*...) or fcc (*ABCA*...) lattice. This structure was first considered [20] in conjunction with the structure of Cobalt and observed in systems of hard colloid spheres [21]. Molecular dynamics simulations of Lennard-Jones liquids solidifying in narrow channels bounded by molecular walls observed a solid with a hexagonal lattice within each layer [22]. However, no periodicity was observed in the stacking of the layers, reminiscent of the dhcp structure that we have assigned to the confined rare gas solids.

Figure 2 shows the scattering from Kr in Vycor at 94 K with the background removed and sample attenuation taken into account. The peak at $Q = 1.9$ Å^{-1} is comprised of a sharp component, due to Bragg scattering from a crystalline sample, and a broad component, due to amorphous layers on the surface of the pore [11]. The calculated diffraction pattern of a dhcp crystal with a volume of (100 Å)^3 is also shown. The relative intensities of the peaks, including the lack of the (200), as well as the widths of the peaks are in good agreement with the data. The broad component due to the amorphous layers has not been included in the model and is not reproduced in the calculation. The comparable widths observed in the experiment and the calculation strongly support our identification of the solid phase as a dhcp structure with average crystal dimension of 100 Å.

Upon further cooling of the confined Ar a new solid-solid phase transition occurs which has no analog in the bulk phase diagram. This transition is manifested by the appearance of very sharp (i.e., resolution limited) peaks at the position of the bulk (220) and (311) peaks as shown in Fig. 1. Scans of the cell orientation (ω-scans) in the high (43 K) and low (37 K) temperature phases of confined Ar with the detector fixed on the (311) peak are shown in Fig. 3. At 43 K, the (311) peak is present but the scattering displays no structure in ω, characteristic of a powder

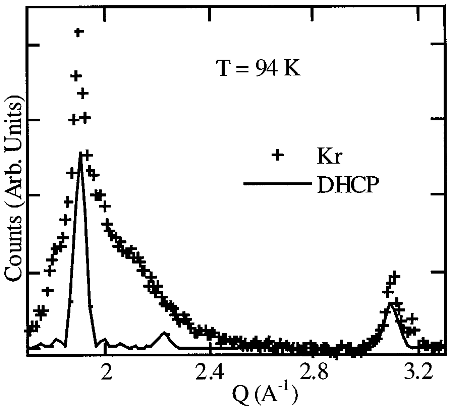

FIG. 2. Calculated scattering from a dhcp crystal with volume of 100 Å^3 (solid lines), and data taken on Kr at 94 K with background removed (+).

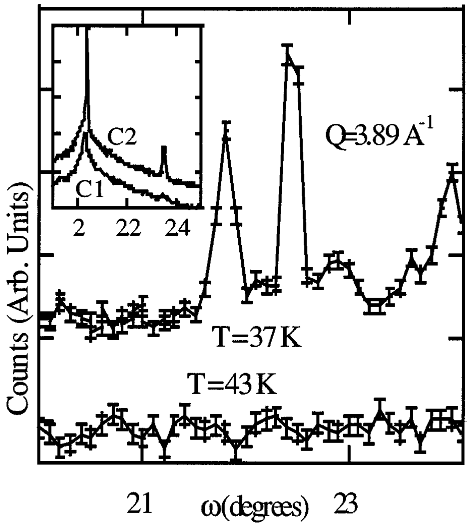

FIG. 3. Scan of the orientation of the cell (ω scans) with the detector fixed on the (311) peak. The inset shows the diffraction pattern in the low temperature phase from consecutive cooling cycles ($C1$ and $C2$). Note the difference in intensity of the (111) and (200) between cycles.

sample. At 37 K, peaks in ω are present, indicating that the portion of the sample that is responsible for the sharp peaks is not a powder, but rather a collection of a finite number of single crystallites.

A very small peak has also developed in the scattering of the Ar at the position of the bulk (200) peak as shown in Fig. 1. The inset of Fig. 3 shows the scattering from the low temperature solid phase of Ar on consecutive cooling cycles. Sharp components of the (111) and (200) peaks are present on the second cooling cycle which were not observed on the first. This indicates that the orientation of the crystallites is not held fixed between cooling cycles.

The scattering from confined Kr also developed a small (200) peak at low temperature, indicating that the Kr had experienced the same solid-solid phase transition as Ar. The other sharp peaks which are present in the low temperature Ar diffraction pattern were initially absent, however. The reason for this is now clear. The missing sharp peaks were found only after correctly (auspiciously) orienting the cell such that the Bragg condition was satisfied for a least one of the crystallites in the low temperature phase. The observed scattering from the Kr in the low temperature phase, with the cell orientation set to half of the scattering angle $[\omega = (1/2)2\theta]$, that is, with the sharp peaks absent, is consistent with that observed by Schafer *et al.* in sol-gel glasses of similar pore size [23] at 40 K.

The orientation of the single crystallites associated with the low temperature phase is not the same on consecutive cooling cycles. Therefore, it is nontrivial to place the exact temperature of the appearance of the large crystallites on cooling as the sharp peaks are difficult to find without prior knowledge of their orientation. The transition occurs between 40 and 44 K on cooling in the case of confined Ar.

Once the sharp peaks are found, however, it is a simple matter to follow them until they disappear on warming as the crystallite orientation varies little with temperature. Figure 4 shows the intensity of the (200) peak of both confined Kr and Ar plotted versus the reduced temperature, $t = T/T_f$, where T_f is the bulk freezing point. The sharp peak indicative of long range translational order clearly disappears at a reduced temperature of approximately $t = 0.5$.

Enough of the peaks indicative of the fcc structure have been observed in the low temperature phase to conclude that a portion of the confined solid has transformed into a finite number of large crystallites having an fcc structure. Indeed, with the resolution of the instrument maximized, the breadth of the sharp peaks is approximately 0.002 Å^{-1}, corresponding to an average crystallite dimension well above the limit of the Sherrer formula [24] of 1000 Å. Such a large correlation length indicates that the long range order of the fcc structure is propagated through many pores. Similar behavior has been reported for D_2 in Vycor. The broad peaks of the dhcp structure are still present in the low temperature phase, indicating a coexistence of the fcc and dhcp structures. Kr and Xe grown by vapor deposition below about $0.65T_f$ exhibited coexistence of the hcp and fcc phases [18], while above this temperature only the fcc structure existed. In this case, the hcp structure is frozen into the quench condensed solid since the atoms lack the mobility at low temperature to anneal into the stable fcc structure. Upon warming to greater than $0.65T_f$, the hcp phase is lost and does not reappear on subsequent cooling, characteristic of a metastable phase. In contrast, the solid-solid phase transition observed here is present with repeated cycling, indicating that it is indeed a stable thermodynamic phase.

Qualitatively, the disorder-induced phase transition may be understood by considering the free energy of the system. The system tries to minimize its free energy,

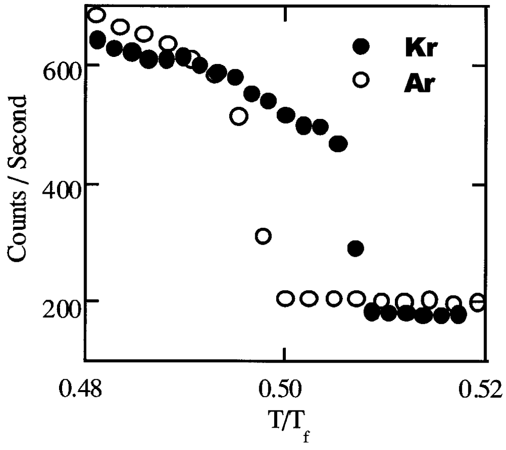

FIG. 4. Intensity of (200) peak of the low temperature phase of both Ar (○) and Kr (●) as a function of reduced temperature.

given by $G = U - TS$, where U is the internal energy of the system and S is the entropy. At high temperature the entropy associated with the disorder of the confining matrix dominates the free energy and is maximized through the formation of the dhcp structure. On cooling the importance of the entropy term decreases, allowing part of the sample, presumably at the pore center, to transform into an fcc structure minimizing U.

An alternative explanation of the origin of the fcc crystalline phase is bulk material solidifying between the face of the Vycor glass and the Be windows. We have performed microdiffraction studies on the sample by reducing both the incident and detector slits to fractions of a mm, allowing us to focus on only 0.3 mm^3 entirely within the porous matrix. This procedure reduced the breadth of the sharp Ar (311) peak while completely eliminating the scattering from the windows. This shows conclusively that the large fcc crystallites which are responsible for the sharp peaks are located within the Vycor, rather than on the surface of the Be window.

In summary, we have found that the freezing and melting transitions of Ar and Kr, when confined to the pores of Vycor glass, are significantly suppressed and hysteresis exists between melting and freezing. On solidification, both rare gas solids crystallized into a dhcp structure and, with further cooling, a new solid-solid transition into a phase where fcc and dhcp structures coexist, which has no analog in the bulk solid. We attribute this phase behavior to the balance of maximizing the entropy at high temperature and minimizing the internal energy at low temperatures.

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