Inert-Gas Solids with Nanoscale Porosity

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The structure and thermal properties of novel mesoporous inert-gas solids were studied by synchrotron x-ray diffraction. The materials were prepared by injecting a jet of helium containing dilute amounts of inert atoms and molecules (Ne, Kr, N_2) into superfluid helium. The characteristic size of the constituent building blocks is ~ 60 Å, and the density is $\gtrsim 10^{20}$ impurity atoms per cm^3. The Kr and N_2 solids are stable outside of liquid He, up to temperatures above 10 K. These materials may find various applications as a new type of porous medium for fundamental physics, as well as in cluster physics, matrix isolation spectroscopy, and catalysis of low temperature chemical reactions. [S0031-9007(97)03981-1]

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Nanostructured materials are currently of intense interest in both fundamental and applied science. Examples include freestanding clusters [1,2] as well as materials with nanoscale porosity such as aerogels [3]. Rare gas solids are well suited to study phenomena associated with heterogeneity on a nanometer scale from a fundamental perspective, because the interaction potential between rare gas atoms is well known, they are chemically inert, and they form simple close packed crystal lattices. However, while a large amount of experimental and theoretical work has been focused on the properties of small clusters of inert-gas elements in dilute concentrations [1], mesoporous inert-gas solids have thus far not been produced. Here we report a novel method of producing solids with porosities on the nanometer scale of several inert chemical species (Ne, Kr, N_2) in bulk amounts. The characteristic size of the structural blocks in these materials (as determined by x-ray diffraction) is ~ 60 Å, the typical density is $\gtrsim 10^{20}$ cm^{-3}, and the materials are stable over a substantial temperature interval.

The technique for preparing the materials was pioneered by Gordon and co-workers [4–6] who showed that a transparent, gel-like substance forms when a jet of helium containing dilute amounts of impurity atoms or molecules (Ne, Ar, Kr, Xe, N_2, etc.) is injected into superfluid helium at $T = 1.5$ K. Superfluid helium is an excellent cooling agent and is also required because of its low vapor pressure; helium vapor disrupts the gas jet that is necessary to inject the impurities into the liquid without nucleation of microcrystallites. Remarkably, the samples were reported to be stable at temperatures up to 6–8 K. Mass spectrometry revealed the ratio of helium atoms to impurity atoms to be 12–60, depending on the type of impurity and the experimental conditions. However, microscopic structural information on these materials has thus far been lacking. We therefore assembled an experimental apparatus that allowed us to produce the materials inside a pumped ^{4}He cryostat ($T = 1.5$–300 K) designed for x-ray diffraction experiments. The cryostat was mounted on a two-circle goniometer, and the experiments were performed with 17.3 keV x rays on beam line X20B at the National Synchrotron Light Source.

Following Ref. [7], a jet of flow $(5–10) \times 10^{19}$ sec^{-1} consisting of gaseous helium and a small amount (0.5%–0.25%) of impurity gas was injected into superfluid helium held by a beryllium can inside the cryostat at $T = 1.5$ K. A sketch of the apparatus is provided in Fig. 1. In order to keep the liquid level constant, helium was continuously pumped into the can by means of a thermomechanical pump during the injection which lasted for typically 20–40 min. The jet source was a nozzle of diameter 0.75 mm located 16 mm above the liquid surface. After the beam injection, the resulting specimens could be kept in liquid helium at $T = 1.5$–4.2 K, or the liquid could be drained from the sample cell. In the latter case the temperature could be controlled in the range $T = 1.5$–300 K. Although due to geometrical constraints the gas-dynamical conditions of the earlier experiments could not be precisely replicated, bulk samples were successfully produced. X-ray photographs made for Kr-based samples (with high x-ray absorption) indicated that the samples occupied a substantial part of the can (a cylinder of diameter 11 mm and height 40 mm). Further, the diffraction pattern did not depend substantially on the position along the can probed by the x-ray beam, indicating the homogeneity of the samples.

We begin by discussing the results obtained for neon-based specimens. The x-ray diffraction pattern of one such sample, immersed in liquid helium soon after its preparation at $T = 1.5$ K, is shown in the inset of Fig. 2. Several features are apparent: The broad peak with the maximum at $2\theta \sim 13°$ is the well known liquid structure

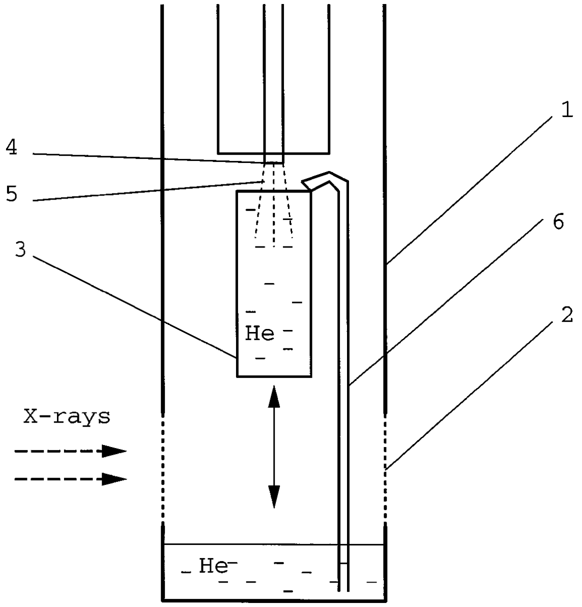

FIG. 1. Sketch of the apparatus: (1) cryostat, (2) x-ray windows, (3) beryllium can, (4) nozzle, (5) helium jet, (6) thermomechanical pump. The system is shown in the sample preparation mode. During the x-ray experiment, the beryllium can was lowered to the height of the x-ray windows (arrow).

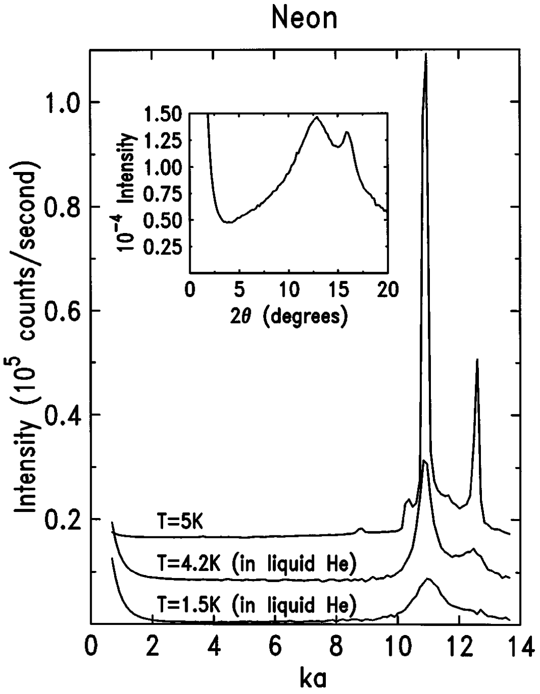

FIG. 2. X-ray diffraction patterns for the neon-based sample at different temperatures. The inset shows the raw data for the sample immersed in liquid; the helium background (when present) is subtracted in the main panel. k is the scattering vector; a is the lattice constant of bulk neon. Data taken at different temperatures were shifted along the y axis.

factor of helium [8]. The sharper structure near $2\theta \sim 16°$ and the intense small angle scattering signal below $2\theta \sim 3°$ arise from neon suspended in the liquid. The positions of the neon peaks are characteristic of the lattice spacing of crystalline neon, but their widths (which are much broader than the experimental resolution) point to the finite size of the neon fragments in the suspensions. The data can be corrected for the helium signal by repeating the scan with the entire can filled with helium. Figure 2 shows such background-corrected diffraction patterns taken on the same sample in the liquid at $T = 1.5$ K and $T = 4.2$ K, and after the evaporation of liquid helium at $T = 5$ K. Corrections for solid angle, polarization, and Debye temperature factors were also made. The data span the wave vector range near the (200) and (111) Bragg reflections of bulk neon. The samples in the liquid at $T = 1.5$ K were stable for many hours. At higher temperatures, but still in the liquid, the shape of the diffraction peaks changes markedly, heralding structural rearrangements within the suspensions. Outside of the liquid at $T = 5$ K the sample collapses into a collection of microcrystallites, which is indicated by resolution limited diffraction profiles corresponding to the structure of bulk neon.

In order to extract the size and density of the neon fragments in the suspensions, and to explore the origin of the structural rearrangements with temperature, we have numerically computed x-ray diffraction profiles from finite-sized neon clusters. We first consider the simplest model in which the clusters are isolated and approximately monodisperse; limitations of this model will be addressed below. A rough comparison of the width of the neon peak at $T = 1.5$ K with the results of earlier electron diffraction studies of argon clusters produced in supersonic beams [9,10] shows that the neon clusters contain at least 1000 atoms. It is believed that clusters of ~1000–5000 atoms have the structural characteristics of bulk neon, i.e., face centered cubic (fcc) [10,11], but contain stacking faults, predominantly twin plane faults [9]. We have therefore considered fcc clusters containing a specified number of twin plane faults. The diffraction pattern was averaged over the different positions of these faults in the cluster. The intensity at the scattering vector k was calculated using the Debye scattering equation [12]

$$I = I_0 \sum_m \sum_n f_m f_n \frac{\sin(k r_{mn})}{k r_{mn}} . \tag{1}$$

Here r_{mn} is the distance between mth and nth atoms, and $f(k)$ is the atomic form factor of neon. The best agreement with the experimental data was obtained for clusters consisting of ~5000 atoms (diameter ~60 Å). The calculated diffraction patterns, shown as dashed lines in Fig. 3, provide good descriptions of the data (shown as solid lines in the same figure) if the number of faults is allowed to decrease with increasing temperature while keeping the cluster size constant. The small angle scattering signal below $2\theta = 3°$ is also well reproduced by these calculations. Faults in the fcc structure are required to explain the data: The dotted line in Fig. 3 shows the calculated diffraction pattern of an *ideal*

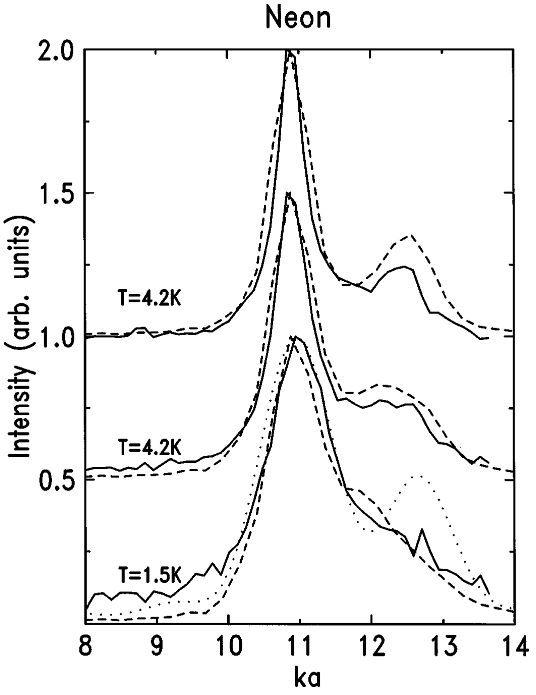

FIG. 3. X-ray diffraction patterns (solid lines) for the neon sample at different temperatures in liquid helium. The liquid helium signal is subtracted. The peak intensities were scaled to 1. The middle curve was taken immediately after the temperature was increased to 4.2 K. The top curve was taken ~30 min afterwards. The dashed lines are the results of calculations for clusters of 4590 atoms with seven, five, and three twin fault planes for the bottom, middle, and top curves, respectively. The dotted line shows the calculation made for an ideal fcc cluster of 450 atoms. The calculations were made for clusters of cubic shape, but spherical clusters gave essentially identical results.

fcc cluster containing 450 atoms, the number of atoms necessary to fit the observed (200) peak width. Clearly, this calculation does not reproduce the observed intensity ratio of the (200) and (111) reflections. Note that in the presence of defects there is no direct relation between the width of the diffraction profiles and the cluster size, as observed previously in the case of electron diffraction from Ar clusters [9].

A model based on fcc clusters of approximately uniform size around 60 Å, with stacking faults that are annealed out with increasing temperature, thus explains all features of the data. Of course we cannot rule out some polydispersity in the suspensions, or a slight temperature dependence of the characteristic size, but size distributions with standard deviations larger than about 20 Å are incompatible with the data. There are also some systematic errors associated with our determination of the characteristic cluster size of 60 Å. For instance, the data were corrected for the Debye-Waller factor (a ~10% correction in the k range of interest) based on the Debye temperature of bulk neon, 63 K. With a substantial fraction of the atoms residing near the cluster surfaces, the actual correction for thermal vibrations is likely to be larger. The assumed shape of the clusters does not significantly affect the characteristic size extracted from the data; the actual shape could be determined by detailed small angle scattering experiments. Overall, a conservative estimate of the characteristic cluster size is 60 ± 20 Å. The integrated intensities of the neon Bragg reflections, normalized to the helium signal, allow us to determine the density of the suspension. The ratio of helium to neon atoms varied from 120 ± 40 to 60 ± 20 as the temperature was increased from 1.5 to 4.2 K, presumably due to settling of the suspensions. This corresponds to a typical neon density of $\sim 10^{20}$ cm^{-3}, about 100 times lower than the density of crystalline neon.

We now turn to the N_2- and Kr-based suspensions which were obtained under the same conditions as the neon samples. After preparation, their diffraction patterns are very similar to those of neon. Although we did not perform calculations specifically for N_2 and Kr clusters, we conclude that these suspensions have a similar structure and density as those of Ne. However, the behavior of these samples is different from the behavior of the neon specimens in one important respect. Figure 4 shows diffraction profiles taken for a N_2-based sample at different temperatures. Clearly, the sample does not undergo any appreciable change on evaporation of liquid helium and in fact remains stable up to temperatures as high as 13 K. At still higher temperatures the sample abruptly collapses into a microcrystalline phase. The diffraction patterns of the Kr-based samples remain essentially unchanged up to about $T = 20$ K. We were thus able to obtain bulk samples whose constituent structural elements are characterized by a length scale of 60 Å, and which are stable outside of liquid helium over a substantial temperature range. In analogy with the Ne-based samples, we infer that the density of the samples outside of the liquid is $\gtrsim 10^{20}$ cm^{-3}.

Two factors are likely to contribute to the remarkable stability of these mesoporous materials. First, the heat of absorption of helium on the surface of the impurity species (60 K for the absorption of a helium atom on a neon surface [13], and even higher for nitrogen and krypton) is large compared to the experimental temperatures. It was therefore suggested [4–6] that impurity particles formed in the gas jet become surrounded by van der Waals shells of helium atoms upon entering liquid helium. Helium remains physisorbed on the cluster surfaces even outside of the liquid and prevents their coalescence. While our diffraction experiment did not allow us to detect a small amount of helium in the materials outside the liquid, independent observations [5] indicate that helium is indeed present. Second, the self-diffusion coefficient D_s for rare gas solids is given by $D_s = D_0 \exp(-Q/kT)$, where $D_0 = 0.12$–0.15 cm^2/sec, $Q = 945$ cal/mole for neon and $D_0 = 5$ cm^2/sec, $Q = 4800$ cal/mole for krypton [14]. A rough estimate of the characteristic time for local rearrangements of the lattice is $\tau = a^2/D_s$, where a is of the order of the lattice constant. Significant kinetic barriers (with characteristic rearrangement times larger

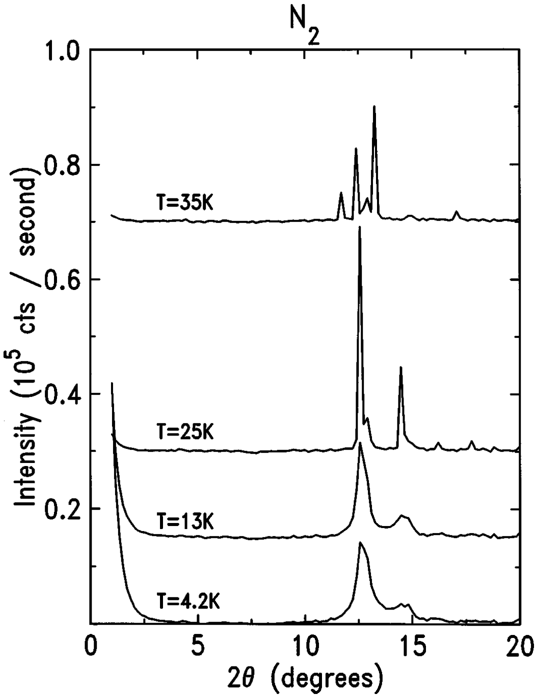

FIG. 4. X-ray diffraction patterns for the nitrogen sample at different temperatures. Mesoporous N_2 is stable up to at least $T = 13$ K. At $T = 25$ K the diffraction pattern indicating large crystallites of the cubic phase of nitrogen is observed. Between $T = 25$ K and $T = 35$ K these microcrystallites undergo a well known cubic-hexagonal transition.

than ~1 min) exist below $T \sim 15$ K for neon, and below $T \sim 70$ K for krypton.

The diffraction data are well described by model calculations for a collection of independent clusters. It thus appears that (at least inside the liquid) a substantial fraction of the inert-gas clusters are isolated from each other by helium shells. Weakly interacting rare gas clusters of well controlled size can also be produced by supersonic beam techniques [15], but the cluster concentrations achievable in such beams are small (typically between 10^{12} and 10^{14} atoms per cm^3 [9]). These concentrations are high enough to allow the use of mass spectroscopy, laser spectroscopy, and electron diffraction techniques which have elucidated a rich variety of phenomena, but too small to allow application of other important experimental techniques such as x-ray diffraction. Further, the temperature of the clusters produced in the beams cannot be easily varied and is often not very well defined [16,17]. At higher densities it is difficult to prevent coalescence of the clusters. The techniques described here achieve this and provide a new avenue for detailed structural investigations as a function of temperature. A possible complication requires further investigation: x-ray photographs of Kr-based samples immersed in the liquid as well as direct visual inspection in a cryostat equipped with optical windows show gel-like objects with a finite shear modulus, which presumably indicates that some fraction of the clusters form a loosely connected continuous network even inside the liquid. Thus not all of the clusters appear to be weakly interacting. However, a very wide range of experimental parameters controlling the density and size of the clusters remains unexplored in these initial studies, and it seems certain that this situation will improve with further work.

Independent of their detailed mesostructure, the novel materials described here will open up new opportunities in various scientific contexts. For instance, the superfluid transition of helium could be studied in a constrained geometry with well characterized helium-wall interactions. The extremely high surface area may also prove useful in initiating or catalyzing low temperature chemical reactions.

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