

- 19. Mao-Bell diamond cells [H. K. Mao, P. M. Bell, K. J. Dunn, R. M. Chrenko, R. C. Devries, Rev. Sci. Instrum. 50, 1002 (1979)] were used with either Re or spring-steel gaskets to compress the samples, which consisted of cryogenically loaded Xe along with Fe powder (<20 µm grain size) and less than 10 volume % fine-grained ruby (<5  $\mu$ m grain size); the latter is used for pressure calibration [H. K. Mao, P. M. Bell, J. W. Shaner, J. Steinberg, J. Appl. Phys. 49, 3276 (1978)]. Samples were heated inside the diamond cell by means of a Quantronix 117 continuous-wave Nd:YAG laser operated in the TEM\_{00} mode, with average temperatures ranging from 1860 (±180) to 3080 (±300) K being documented by imaging spectroradiometry [R. Jeanloz and A. Kavner, Philos. Trans. R. Soc. London Ser. A 354, 1279 (1996)].
- 20. Diffraction patterns were obtained at high pressures and room temperature (before and after laser heating) using a Rigaku 12 kW/mm<sup>2</sup> rotating anode source of monochromatized Mo K<sub>α</sub> x-rays. The diffraction patterns were collected in angular-dispersive mode with film and analyzed by methods described elsewhere [J. H. Nguyen and R. Jeanloz, *Rev. Sci. Instrum.* 64, 3456 (1993)].
- 21. The calculations were carried out for the static lattice, corresponding to zero temperature and no zero-point vibrations, with the electron-ion core interaction represented by norm-conserving separable pseudopotentials and the valence wave functions expanded in plane waves up to an energy cutoff of 80 rydbergs (1.09 keV) [L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982)]. In our calculations, the XeFe is arranged in an hcp structure with the A and B layers consisting of Xe and Fe, respectively (space group P6m2). We assumed a hexagonal unit cell for both XeFe, and Xe\_Fe, ABC stacking being obtained with, respectively, two layers of Fe and one of Xe or two of Xe and one of Fe (space group P3m1). To find the minimum enthalpies, we used a guasi-Newton method to relax the internal coordinates and the unit-cell shapes of all structures for a given pressure [B. G. Pfrommer, M. Côté, S. G. Louie, M. L. Cohen, J. Comp. Phys. 131, 233 (1997)].
- 22. The ratio of Xe/Fe atomic radii, calculated from the theoretically derived volumes of the unit cells of hcp Xe and hcp Fe at 150 GPa, is 1.288. For comparison; 138 out of 164 experimentally observed Laves phases have a ratio of atomic radii between 1.1 and 1.4 [A. E. Dwight, *Trans. Am. Soc. Met.* 53, 477 (1960)], showing that Xe and Fe are plausible candidates for forming a Laves phase at pressures above 100 GPa. The space group is P6<sub>3</sub>/mmc for the Laves phase.
- See L. V. Woodcock's [*Nature* 385, 141 (1997)] recent analysis emphasizing the importance of entropic stabilization of the fcc relative to the hcp structure for hard-sphere systems.
- 24. A. K. McMahan, Phys. Rev. B 33, 5344 (1986).
- 25 For example, if we assume identical volumes for the fcc and hcp phases  $V_0 = 35 \text{ cm}^3/\text{mol}$  [M. Ross and A. K. McMahan, Phys. Rev. B 21, 1658 (1980)], fitting Birch-Murnaghan equations of state to the experimental data yields  $K_0 = 5.87 (\pm 0.32)$  GPa and  $K_0' = 4.81 (\pm 0.09)$ , and  $K_0 = 5.62 (\pm 0.62)$ GPa and  $K_0' = 4.91 (\pm 0.18)$  for the bulk modulus  $(K_0)$  and pressure derivative  $(K_0')$  of the fcc and hcp phases, respectively [F. Birch, J. Geophys. Res. 83, 1257 (1978); the subscript zero indicates zeropressure conditions and the prime designates a pressure derivative]. In contrast, if we assume identical  $K_0$  and  $K_0'$  for the two phases, a least-squares fit to our data gives the volume  $(V_0)$  of the hcp phase as being 0.3 (±0.5)% larger than that of the fcc phase. Overall, the values of  $V_0$ ,  $K_0$ , and  $K_0'$  for the two phases are within mutual uncertainties and are in close agreement with previous determinations [K. Asaumi, Phys. Rev. B 29, 7026 (1984)].
- 26. Experimentally, we find evidence for a topotactic relation between the two phases, which suggests a martensitic or "military" type transformation [J. W. Christian, *The Theory of Transformations in Metals and Alloys, Part I* (Pergamon, New York, ed. 2, 1975)]. The (111) peak of the fcc phase and the

(002) peak of the hcp phase appear at the same d spacing, which implies identical orientations for the close-packed planes in the two structures [A. F. Schuch, R. L. Mills, D. A. Depatie, *Phys. Rev.* **165**, 1032 (1968)]. A similar geometrical relation explains why three other hcp peaks, (004), (112), and (110), are also coincident with the (222), (311), and (220) fcc peaks. It is possible that the detailed transformation mechanism is sensitive to the presence of even small nonhydrostatic stresses, however, so there is no reason to infer a disagreement between experiment and theory on this point.

 The hcp and bcc phases of Pb also have similar equations of state, a sluggish transformation between phases and a comparable large pressure range in which both phases coexist [H. K. Mao et al., Solid State Commun. 74, 1027 (1990)].

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## The World's Smallest Gas Cylinders?

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Argon gas was trapped at high pressure within hollow carbon tubes grown in vapor that have an outer diameter of between 20 and 150 nanometers. The gas was forced into the tubes by hot isostatically pressing (HIPing) the carbon material for 48 hours at 650°C under an argon pressure of 170 megapascals. Energy dispersive x-ray spectroscopy maps and line scans across the tubes show that the argon is trapped inside the bore and not in the tube walls. The room temperature argon pressure in these tubes was estimated to be about 60 megapascals, which indicates that equilibrium pressure was attained within the tubes at the HIPing temperature. These findings demonstrate the potential for storing gases in such carbon structures.

Currently, there is considerable interest in both C fibers (1-3) and nanotubes (4-6). Apart from efforts to understand the formation process (7), attention has been focused on the encapsulation of elements and compounds, particularly oxides and carbides, inside the tubes, as well as within C nanoparticles (8-11). On the other hand, the encapsulation of gases such as Ar, Kr, or Xe inside C entities like these has received little attention in the literature, although the trapping of  $^{133}\!\mathrm{Xe}$  may improve its uses in medical imaging such as in the case of the lymphatic system (12), where it would be extremely useful to confine the gas physically in some way before injection. Here, we show conclusively how large amounts of Ar can be trapped inside catalytically grown C fibers consisting of multiwalled hollow C tubes with outer and inner diameters ranging from 20 to 150 nm and 10 to 60 nm, respectively.

Hollow C tubes were prepared by catalytic reduction of  $CO_2$  with a modified Vogel process (13). In this method,  $CO_2$ was reacted with Zn to produce CO and ZnO, and the CO was subsequently converted on an Fe catalyst to filamentous graphite (14). One milligram of finely divided Fe catalyst was placed in the end of a closed quartz reaction tube that had previously had a "Zn mirror" deposited on its inner surface. The reaction tube was placed inside a horizontal tube furnace to maintain the Fe catalyst at 600°C and the Zn mirror at 400°C, and the pressure was monitored to determine when the reaction had gone to completion. An Fe carbide bead crystal formed on the catalyst surface, from which the filamentous graphite "grew."

Scanning electron microscopy of the C produced from catalyzed CO<sub>2</sub> decomposition showed it to be composed of many long and winding C fibers with outer diameters of about 20 to 150 nm, which were interwoven and cemented with large pieces of dense material derived from the catalysts. These features are very similar to those observed by other authors (15-21). Backscattered electron imaging indicated that metal was dispersed throughout the fibers and demonstrated that encapsulation had also taken place in the growth mechanism. To investigate the encapsulation of Ar into the various C forms produced catalytically, we hot isostatically pressed (HIPed) the whole sample without any further treatment at 650°C and 170 MPa of Ar for 48 hours. At the end of the HIPing cycle, the gas pressure was reduced from 170 MPa to atmospheric pressure but

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not until a temperature of 100°C was reached. Transmission electron microscopy (TEM) samples were prepared by dispersal of a small amount of the HIPed soot material onto holey C-coated copper grids from a suspension in ethanol. These samples were examined in a JEOL (Tokyo, Japan) 2000 fx scanning TEM with a beryllium window energy dispersive x-ray spectrometer (EDS). Secondary electron images, transmission electron images (TEIs), and x-ray maps showing the distribution of Ar, Fe, and Zn were recorded with this microscope. However, C was not detected because of absorption of low-energy x-rays in the beryllium window. High-resolution images showing nanotube wall structure were recorded with the JEOL 2000 fx operated in TEM mode.

TEM images showed that many of the structures that were tube-like (usually less than 20-nm outer diameter) had many contortions and twists and in some cases a high degree of compartmentalization (22). In addition, many regions within the C structures contained dense material that was determined by EDS to be predominantly composed of Fe. Some closed regions showed the presence of small amounts of trapped Ar. Of greater interest were the C structures that consisted of longer and more uniform hollow tubes (Fig. 1). These hollow tubes were found to be associated with large pieces of Zn- or Fe-derived material, and it was usually very hard to discern the beginning or end of the tube. In several of these tubes, the Ar content was very high, and, furthermore, it appeared to be contained in the cavity of these tubes (Fig. 2).

An x-ray map of an Ar-filled tube (Fig.



**Fig. 1.** A montage of two TEM images that shows two hollow carbon tubes intertwined in dense metallic-based material. The tube on the left was found to contain Ar at high pressure, whereas the tube on the upper right was empty. A montage was needed because the overall length of the tubes was too large for a single image.

2B) clearly shows the association of Ar with the tube. Comparing this image with the TEM image (Fig. 2A) shows that Ar is contained in the hollow cavity of the tube. Also clear from Fig. 2B is the discontinuity halfway along the tube, which indicates that the tube is compartmentalized. TEM and EDS images of this region (Fig. 2, C and D) at higher magnification show both the confinement of the Ar gas and this discontinuity more clearly. The closed region is interesting because it does not seem to be associated with any trapped catalytic material as in bitubes where two tubes grow from the same metal microcrystal (15).

To obtain an estimate of the Ar pressure in these tubes, we used a JEOL 2000 fx II TEM equipped with an ultrathin window (UTW) EDS. This UTW allowed detection of x-rays from C in the nanotube walls as well as detection of x-rays from heavier elements that were present in the sample. The EDS sensitivity to Ar x-rays relative to C x-rays was determined by examination of  $Ar_1C_{60}$  (23), in which the atomic ratio Ar:C is 1:60. EDS spectra were collected from an Ar-filled tube with the electron beam focused so that it only covered the central part of the tube. The atomic ratio of Ar:C was calculated to be  $9(\pm 2):91(\pm 2)$ . It was assumed that the

**Table 1.** Tubes observed by TEM in the 20- to 150-nm range that were found to be empty or to contain Ar in high quantities. The possible nature of the two ends of the tube is given by two of the following abbreviations: s, sealed; o, open; and c, obstructed by catalyst. The number of tubes observed with this configuration is given after the abbreviations.

Tube size (nm)	Number of tubes	Ar-filled tubes		Empty tubes	
		Number	Ends of tube	Number	Ends of tube
20 to 50	9	4	s, c 3 c, c 1	5	s, c 1 o, s 1
50 to 100	17	5	s, s 2 s, c 2 c, c 1	12	c, c 3 o, s 2 o, c 4 s, c 2
100 to 150	4	2	c, c 1 s, c 1	2	c, c 2 s, s 2 o, c 1 o, s 1



Fig. 2. TEM images and x-ray maps of a typical Ar-filled tube that winds its way through dense solid material. The C tube is clearly seen to be hollow and has an outer diameter of 140 nm and an inner bore diameter of 60 nm. (A), (C), and (E) show TEM images, whereas (B), (D), and (F) display the corresponding x-ray map images. In the latter panels, the K $\alpha$  x-ray emissions from Ar, Fe, and Zn are shown in red, green, and blue, respectively, A discontinuity in the tube is indicated in the images by the arrows. The scale bars on (A), (C), and (E) represent 100 nm.

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measured tube region approximated a sandwich of an Ar layer of a thickness equal to the inner diameter of the tube (60 nm) between two graphitic layers of thicknesses equal to the wall thickness of the tube (40 nm). The density of the C walls was assumed to be that of graphite (2.26 g  $cm^{-3}$ ). Working from these assumptions we found the number of Ar atoms per liter to be 1.5  $\pm 0.4 \times 10^{25}$ . We then equated this number to a gas pressure of  $60 \pm 15$ MPa using the ideal gas law. The observed variation for the given tube is quite understandable given the approximate nature of the calculation. The main errors arise from the nonuniformity of the tube and the positioning of the electron beam on the tube. The measured room temperature tube pressure indicates that the time scale for the tubes to reach the HIPed pressure is less than the time scale for sealing the tubes at the temperature of 650°C, because a pressure of 170 MPa at 650°C translates to a pressure of  $\sim$ 55 MPa at room temperature for an ideal gas.

Line scans across the tube conclusively showed the Ar to be trapped inside the cavity (Fig. 3). The transmitted electron



Fig. 3. (A) The TEM image of the C tube in Fig. 1 with black arrows indicating where the line scans shown in (B) and (C) were taken across the tube. The line scans are before (B) and after (C) a high dose of electron irradiation. The section of the tube in this figure is also seen in Fig. 1.





(Fig. 3, B and C, respectively) that there is no Ar in the tube walls before electron irradiation.

Studies of other tubes showed that they either contained Ar in large amounts or not at all. It was found that the concentration of Ar could be uniform over long sections of a tube with no visible breaks, which indicates little compartmentalization. Some tubes, which had large regions unobstructed by dense material, allowed study of the wall structure (Fig. 4A). The outside wall of the tube appears to have been damaged, producing an amorphized crust similar to that seen on spherical C onions formed by C ion implantation into copper (24). Beneath this crust, high-resolution TEM images indicate that the undamaged wall of the tube is a graphitic multilayered structure. This structure could be composed of many concentric tubes that have grown on top of each other or, alternatively, a single sheet of graphite that has been "rolled-up" during growth. In contrast, the walls from C tubes that have not undergone HIPing do not show such an amorphous C layer (Fig. 4B). We conclude that the amorphization is a result of the elevated temperature used for HIPing.

In Fig. 4, A and B, the graphitic layers appearing in the cross section are not parallel to the outer wall of the carbon tube. The angle of the planes to the direction of the tube is estimated to be  $\sim 9^{\circ}$  in both cases. This could be a reflection of the growth mechanism, and several explanations are possible. For example, the C sheet may form a scroll structure, or the tube may consist of individual cones of single C layers with their centers missing. Tibbetts et al. (25) have prepared, using an Fe catalyst to decompose methane, tubes grown in vapor that are similar in structure to the ones we have prepared and that have a similar range in size (50- to 100-nm outer diameter). The graphitic planes were inclined at  $\sim 12^{\circ}$  to the tube axis, which compares favorably with the  $\sim$ 9° value found in our study. The idea of individual cones of single graphitic layers is very plausible in light of the accepted structure of certain solid C filaments (26-28) where the stacked cone structure is clearly seen.

Fig. 4. High-resolution TEM images of the walls of (A) HIPed and (B) un-HIPed tubes. The presence of an amorphous crust is evident in (A). The graphitic layers are at an angle of  $9^{\circ}$  to the outer surface of the tube wall, as indicated by the line.



The nature of the tube wall resulting from the staggered graphitic layers of either a scroll or a cone structure would provide a continuous path between the layers through which Ar may diffuse into the cavity. Nolan et al. (26) have pointed out that cone type tubes and fibers would have unsaturated valences at their edges. Mordkovich et al. (29) have also proposed a model for K intercalation into multiwalled nanotubes in which the nanotubes are assumed to have a scroll structure. allowing the K atoms to pass inward by attack of the helicoid on the outside edge of the scroll. In our case, amorphization as a result of the HIPing process may be responsible for sealing the gas within the tube. If a tube contains Ar, its ends must be effectively sealed. The HIPing temperature was too low to melt any of the Fe- or Zn-based materials (assuming no Zn metal was present after reaction with  $CO_2$ ), which suggests that the ends of the Arcontaining tubes were sealed before HIPing. If this requirement is not met, Ar will not be retained in the tube. A similar HIPing experiment performed at the lower temperature of 400°C showed no evidence of tubes with Ar trapped in them, nor was any amorphization of the outer wall observed under these conditions. Brunaer-Emmett-Teller measurements on tubes of this type by Tibbetts et al. (25) gave a value of 9.91 m<sup>2</sup> for nitrogen gas absorption at room temperature. This is about half the actual physical value calculated geometrically and indicates that the tubes have little porosity. The Ar-filled tubes imply that the porosity must increase greatly at higher temperatures, that gas is more freely able to pass between the slanting graphitic layers and the inside of the tube, and that at the higher temperature, the amorphous crust formation prevents the gas from leaving.

A second C sample containing catalytically grown tubes prepared by the same synthesis route was HIPed under the same conditions as before to confirm our results. A further TEM study was carried out on the second HIPed sample, and we indiscriminately selected 30 tubes with an outer diameter in the range of 20 to 150 nm (Table 1). We found that a total of 11 tubes had Ar trapped in them at high pressures. In the majority of these filled tubes, we were able to find at least one of the ends of the tube, which was, as expected, sealed. We also found that out of the 19 empty tubes, 9 clearly had an open end. A couple of the tubes appeared to be sealed at both ends but contained no gas. It appears that the number of filled tubes is dictated largely by how many tubes have both ends sealed; there is no indication

that tube diameter is an important factor in the diameter range studied.

The filled tubes were found to retain their Ar content with little change over several months at room temperature. Carbon tubes of the structure shown in this paper and those of other authors (25) thus show possibilities for gas storage. It is clear that if the tubes have a scroll structure (29) and are sealed at both ends, then it should also be possible to fill nanotubes of smaller dimensions with gases, whereas conventional nanotubes with a parallel wall structure may need to be filled through an open end before the end is sealed.

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## Asymmetric Catalysis with Water: Efficient Kinetic Resolution of Terminal Epoxides by Means of Catalytic Hydrolysis

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Epoxides are versatile building blocks for organic synthesis. However, terminal epoxides are arguably the most important subclass of these compounds, and no general and practical method exists for their production in enantiomerically pure form. Terminal epoxides are available very inexpensively as racemic mixtures, and kinetic resolution is an attractive strategy for the production of optically active epoxides, given an economical and operationally simple method. Readily accessible synthetic catalysts (chiral cobalt-based salen complexes) have been used for the efficient asymmetric hydrolysis of terminal epoxides. This process uses water as the only reagent, no added solvent, and low loadings of a recyclable catalyst (<0.5 mole percent), and it affords highly valuable terminal epoxides and 1,2-diols in high yield with high enantiomeric enrichment.

Asymmetric catalysis provides access to optically active epoxides either by oxygenatom transfer to alkenes (1) or by carbene

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addition to carbonyl compounds (2). Both strategies have been developed to varying degrees, but significant gaps still exist in the scope of these methodologies. For example, there are still no effective enantioselective epoxidation methods known for the synthe-

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