

## Gap Reduction and the Collapse of Solid C<sub>60</sub> to a New Phase of Carbon under Pressure

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We have studied solid C<sub>60</sub>, measuring the shift of the optical absorption edge with pressure to 35 GPa. In the range of 0–17 GPa, extrapolation of the absorption edge indicates that metallization should occur by 33 GPa. However, from 17 to 25 GPa an irreversible transition to a “transparent phase” occurs. Raman scattering of the depressurized sample shows no trace of C<sub>60</sub>, diamond, or graphite, indicating that the transition involves the collapse of the C<sub>60</sub> molecules into a new structure of carbon.

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Recently there have been a number of fascinating results on the properties of fullerite (solid C<sub>60</sub>) at ambient conditions and at high pressure. These include observations of high- $T_c$  superconductivity [1] in doped fullerite and speculations that compressed fullerite might be harder than diamond [2]. In this work we intended to study the insulator-metal (IM) transition in pure fullerite and its ultrahigh pressure compressibility, as a material which hardens with increasing pressure might have important technological implications. We pressurized fullerite to 35 GPa in a diamond-anvil cell (DAC) and studied its optical absorption spectrum and Raman scattering cross section. Initially, with increasing pressure, the optical absorption threshold energy (ATE) shifts to lower energy, implying that fullerite should metallize in the 30–40 GPa pressure range. However, in the range 17–25 GPa the fullerite undergoes a sluggish irreversible transformation to a phase with reduced optical density; the transition is accelerated by raising the pressure to 35 GPa. Upon reducing the pressure to zero the sample does not revert to the low-pressure fullerite phase. Raman scattering measurements showed no trace of the C<sub>60</sub> molecules so we conclude that the C<sub>60</sub> molecules have collapsed. Furthermore, the Raman spectra of the collapsed fullerite (CF) phase cannot be identified with that of diamond or graphite, so we conclude that the CF phase is a new phase of carbon existing at zero pressure.

High-purity C<sub>60</sub> (less than 1% C<sub>70</sub> content) was vacuum evaporated onto a diamond culet to form a rather uniform homogeneous film with a thickness of 2.5  $\mu\text{m}$ , as measured by optical interference techniques. A few grains of ruby were scattered on the sample for pressure determination. A T301 stainless-steel gasket with a 100- $\mu\text{m}$ -diam hole was placed over the sample and mounted in the DAC. We used xenon as a quasihydrostatic pressure medium; this was loaded cryogenically [3]. Measurements presented in this Letter were made at room temperature (295 K). Raman scattering was carried out using the 5145- $\text{\AA}$  argon ion laser line and a Spex Triplemate monochromator with a Tracor Northern diode array. Laser power fluence was restricted to below 300  $\text{W}/\text{cm}^2$  to prevent overheating and burning or thermal

deformation of the samples. Absorption spectroscopy was carried out in the visible; spectra were normalized to the transmission of a suitable pinhole. Pressure was measured using the ruby fluorescence scale [4] and was quasihydrostatic: both ruby  $R$  lines were always well resolved and we estimated the pressure variation across the sample to be less than 0.3 GPa in the worst case.

Fullerite has the fcc structure [5] at ambient pressure and temperature. Duclos *et al.* showed that this remained the stable phase to about 20 GPa and determined the equation of state (EOS) to this pressure [6]. They also found that under nonhydrostatic pressure conditions a new phase appeared in the 16–20-GPa pressure region. Earlier optical absorption spectra have been measured at ambient conditions to find the ATE to be 15 748  $\text{cm}^{-1}$  [7]. Zero-pressure optical properties calculated from electronic band-structure theory by Ching *et al.* [8] are in reasonable agreement with our observations. Xu, Huang, and Ching [9] have studied the effect of pressure on the band gap and find that it is reduced with increasing pressure. We note that the smallest valence-conduction band gap, usually referred to as the band gap, is direct and is an optically forbidden transition. When this gap closes the insulator becomes a metal. The next larger band gap in fullerite is direct and allowed, resulting in an optical absorption threshold. Assuming that the lowest two gaps do not cross, a determination of the pressure at which the ATE goes to zero will set an upper bound on the pressure for the IM transition in fullerite. We determined the ATE by the zero crossing of a linear extrapolation of the absorption edge (this gives a slightly different value of the ATE than was determined in Ref. [7]).

The Raman spectrum of fullerite has been extensively studied by Bethune *et al.* [10] under ambient pressure conditions and is rich in vibrational transitions. Recently Duclos *et al.* [11] have shown that when a pure sample of fullerite is left in air for times of order 1 h, the Raman spectrum is slightly perturbed due to an oxygen impurity; our sample suffers from this. We do not believe that this significantly affects our results and conclusions as the perturbation is small and this is evidently present in most fullerite that has been studied to date, including samples

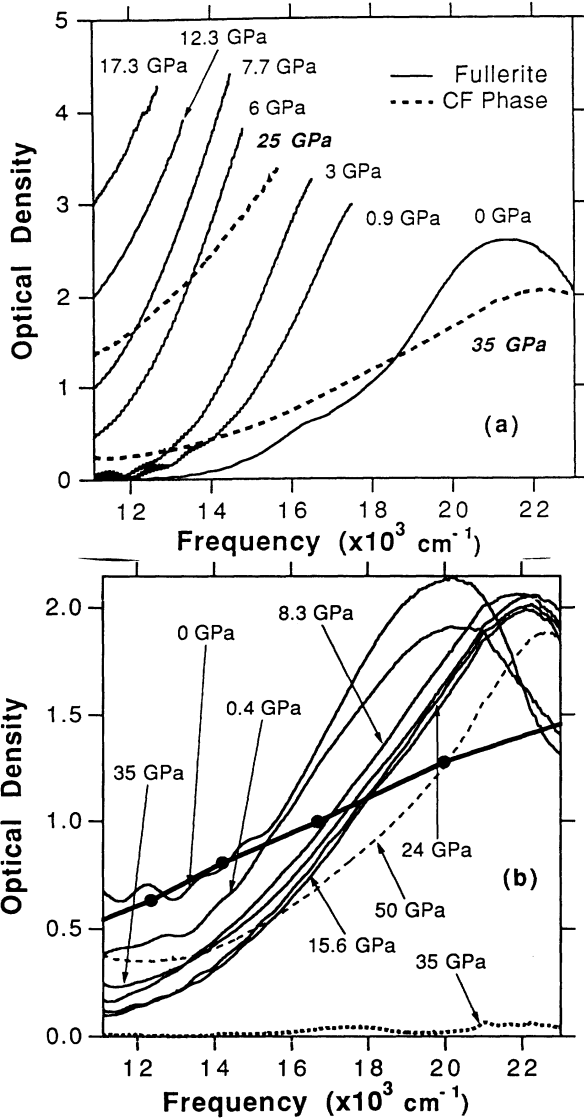


FIG. 1. The optical density of pressurized fullerite as a function of frequency for (a) increasing pressure and (b) decreasing pressure. The heavy line with points is the optical density of zero pressure  $\alpha$ -C, for a thickness equivalent to a tenth that of our film sample; the dotted line is the optical density of a 6-mm-thick sample of type-I diamond.

studied for structural and orientational order determinations.

In Fig. 1 we show the absorption spectra for our sample (the fringes on the absorption spectra are due to interference within the  $\text{C}_{60}$ -xenon-diamond cavity). Our ambient pressure results agree with earlier reports [7]. With increasing pressure the ATE shifted to the infrared until at a pressure of about 17 GPa our sample was so optically dense in the visible that light leakage from cracks in the sample no longer allowed a threshold to be accurately determined, and under these conditions our measurements were no longer sensitive to small changes in the optical properties. We then slowly increased the pres-

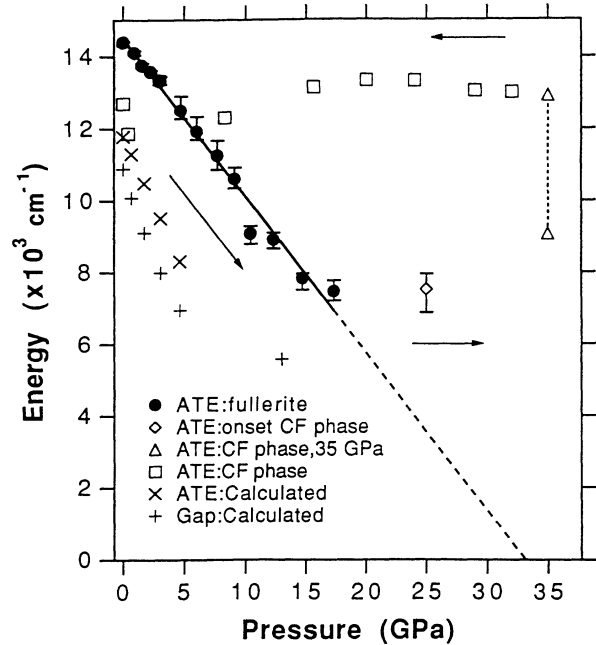


FIG. 2. The optical absorption threshold energy as a function of pressure. The arrows indicate the pressure path. The error bars represent the uncertainty in the ATE due to spatial variations in the sample. The open symbols indicate the behavior of the ATE after the phase transition. The triangles at 35 GPa indicate the range of spatial variations of the ATE in the sample. The open squares represent the ATE in the most transparent region. Theoretical predictions are also shown for comparison.

sure to see if the sample would show any visual changes. At a pressure of about 25 GPa it became more transparent, as demonstrated by the spectrum shown in Fig. 1(a). The sample transparency increased dramatically when the pressure was increased to 35 GPa. The pressure was held constant but the transparency continued to increase over a 2- to 3-d period.

Although the sample appeared optically uniform at zero pressure, as the pressure increased, the 100- $\mu\text{m}$ -diam sample which we examined with a 3-9- $\mu\text{m}$ -diam window became slightly nonuniform in its visible transmission. We attribute the nonuniformity to partial release of the sample from the diamond surface. Since diamond is not very compressible, the sections which are attached undergo a more uniaxial stress, while the released sections will be subjected to a quasihydrostatic pressure. The nonuniformity increased substantially above the transition pressure. At this time we have not determined which parts of the sample released, but this is under analysis.

In Fig. 1(b) we show the absorption in the most transparent part of the sample as the pressure was reduced to zero. Over most of the range it is almost unchanged; only at the lowest pressures is there a substantial shift of the spectrum. In Fig. 2 we show the ATE as a function of pressure, with the arrows indicating the pressure path

which was taken. We also show the theoretical results of Xu, Huang, and Ching [9] for the gap and ATE. If we linearly extrapolate data points for the fullerite phase, we predict an upper bound of 33 GPa for the IM transition, whereas a linear extrapolation of the ATE with density (derived from the EOS of Ref. [6]) gives 58 GPa. The theoretical work does not extend to sufficient densities to predict gap closure or metallization; however, it is noted that at pressures of the order of 20 GPa covalent bonding between adjacent atoms in neighboring  $C_{60}$  molecular units must be considered.

In an attempt to identify the new phase we opened the DAC in a nitrogen atmosphere and measured the Raman spectra of the sample, as well as that of residual fullerite on the edges of the diamond culet region, which was never subjected to high pressures; these are shown Fig. 3. The new phase has a broad unstructured Raman line in the region where sharp Raman lines due to covalently bonded carbon-carbon vibrations are normally found. If the sample had transformed to a disordered or different phase of  $C_{60}$ , we would still expect to see strong Raman lines due to internal vibrational modes of the molecule. From the spectra we conclude that the  $C_{60}$  was destroyed at the high pressure transition and the sample has transformed to a different form of carbon [12], probably amorphous as inferred from the broad Raman spectrum. This is the "collapsed fullerite" phase, which probably prefers  $sp^3$ - $sp^2$  covalent bonding for carbon.

It would be useful if the new phase could be identified from its Raman spectrum. Hexagonal graphite has a strong Raman phonon line at  $1581\text{ cm}^{-1}$  [11]. Amorphitized graphite and other graphite forms (activated charcoal, soot) have additional lines in this region [13]. We studied this frequency region and found no evidence of these lines. The Raman intensity which shows up in the spectra is that of the diamond phonon and a broad unstructured line. Since the sharp line may have come from the anvil itself, we carefully removed a piece of the CF phase and studied its Raman spectrum, finding no diamond phonon line. Thus, the new phase at zero pressure is not cubic diamond; nor is it graphite or amorphous graphite. A particular form of amorphous carbon called  $a$ -C has a Raman spectrum similar to the one we observe for CF [14]. However, the Raman spectrum, by itself, of amorphous carbon structures may be inadequate for structural determination [15]. Hauser [16] has measured the optical absorption coefficient of  $a$ -C and we show his optical density divided by 10 in Fig. 1(b) (solid curve with points). Clearly  $a$ -C has much stronger absorption, monotonically increasing with frequency, whereas CF peaks at about  $20000\text{ cm}^{-1}$  and then falls off. We conclude that CF is not  $a$ -C and must be a new amorphous phase of carbon.

To confirm our results we prepared a second sample by a different technique. Powdered  $C_{60}$  was heated to  $250^\circ\text{C}$  in a vacuum to minimize oxygen impurity problems. This was packed into a gasket and compressed

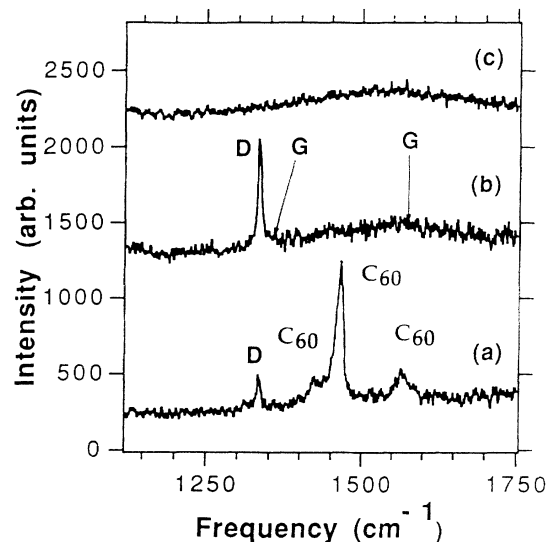


FIG. 3. The Raman scattering spectra of (a) fullerite, (b) the film of the collapsed fullerite phase, and (c) the second sample of collapsed fullerite. The peaks at  $1332\text{ cm}^{-1}$  ( $D$ ) arise from the diamond-anvil substrate. The symbol  $G$  indicates the expected frequency of graphite Raman transitions and  $C_{60}$  identifies the known peaks of fullerite.

without a compression fluid. The sample was disk shaped with an initial thickness of  $62\text{ }\mu\text{m}$ . The sample was raised to a high pressure (50 GPa at the center and 32 GPa on the edges) and visually monitored. The black nontransmitting fullerite became a grainy transparent sample, yellow in transmitted light. It is evidently very hard, as in releasing the load the central region supported a pressure of 23 GPa while the edges were at about 2.5 GPa. The Raman spectrum was identical to that of the first sample and is shown in Fig. 3. The absorption spectrum is shown in Fig. 1(b). For further comparison we show the optical density of a 6-mm-thick sample of type-I diamond under load; although one cannot make an absolute identification from an absorption spectrum over a limited frequency range, there seems to be little overlap of CF with diamond.

We believe that part of the attenuation of light in the CF samples was due to scattering from nonuniformities in the samples. The second sample is substantially thicker than the film, yet is about equally transparent. This may imply that the transition to CF did not go to completion by 35 GPa in the film. At zero pressure both samples became darker. We believe that this is in part due to increased scattering as the sample decompactifies.

The sluggishness of the transition observed in both samples might be understood from a large volume difference between the fullerite and the CF phases. If the  $C_{60}$  molecules collapse, this will reduce the local volume required for the carbon atoms, reducing the local pressure and stopping further transformation until the total sample volume is further reduced by increasing the external load.

Recently Yoo and Nellis [17] have shock compressed fullerite up to 100 GPa, observing a transition at about 18 GPa (shock time of order 50 ns). The Raman spectra of recovered samples showed vibrational lines characteristic of graphite. We suspect that the differences from our results are due to the substantially higher temperatures that their samples reach in the shock. Núñez Regueiro *et al.* [18] report a change in the electrical conductivity of fullerite at 15–20 GPa, which we suspect is due to the same transition we have observed. The CF phase is most likely the phase observed by Duclos *et al.* in the same pressure range [6]. A transition to a new phase with increased electrical resistivity has been observed in compressed graphite in this pressure regime; however, its zero-pressure stability is unclear [19].

We conclude by observing that the predicted high-pressure superhard property of fullerite as well as the metallization of pure fullerite are inaccessible states of matter due to the transition to the CF phase at a lower pressure. The CF phase appears to be a new amorphous structure of carbon.

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*Note added.*—Subsequent to the submission of this Letter reports of work by other groups have come to our attention. M. Núñez Regueiro, P. Monceau, and J. L. Hodeau, *Nature (London)* **355**, 237 (1992), reported an irreversible pressure-induced transformation of fullerite to a sample that contained small crystallites of diamond. The Raman spectrum of this sample [M. Núñez-Regueiro (private communication)] differs from ours. Y. S. Raptis, D. W. Snoke, K. Syassen, S. Roth, P. Bernier, and A. Zahab (to be published) have reported the irreversible pressure-induced transformation of a mixture of C<sub>60</sub>-C<sub>70</sub> to amorphous graphite.

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- [12] We cannot exclude the possibility that C<sub>60</sub> molecules irreversibly covalently bond, without the destruction of the molecular units, resulting in severely broadened Raman spectra. However, we consider this to be highly unlikely.
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