

Electrical and Mechanical Properties of C_{70} Fullerene and Graphite under High Pressures Studied Using Designer Diamond Anvils

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We compare electrical and mechanical properties of C_{70} fullerene with high purity graphite to 48 GPa at room temperature using designer diamond anvils with embedded electrical microprobes. The electrical resistance of C_{70} shows a minimum at 20 GPa with transformation to an amorphous insulating phase complete above 35 GPa, while graphite remains conducting. Nanoindentation shows hardness values 220 times larger for the pressure quenched amorphous phase than for similarly treated graphite. Our studies establish that the amorphous carbon phase produced from C_{70} has unique properties not attainable from graphite.

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The pressure-temperature phase diagrams of fullerenes C_{60} and C_{70} are fascinating because of their richness in terms of polymeric phases and disordered/amorphous carbon phases that can form due to intermolecular interactions between these large molecules in the solid state at high compressions. Most of these new polymeric phases and amorphous carbon phases can be retained at ambient conditions after high-pressure high-temperature synthesis for detailed investigations. The practical and industrial interest in these materials stems from the fact that several of these phases are superhard with hardness sometimes approaching or claimed to be exceeding that of single crystal diamond [1,2]. However, the electrical and mechanical properties after pressure quenching or during the formation of many of these novel phases are poorly understood. Another key issue is a direct comparison between the electrical and mechanical properties of fullerenes and that of ordinary hexagonal graphite under similar conditions. In this Letter we focus on the high-pressure properties of fullerene C_{70} at room temperature. We directly compare its electrical and mechanical properties under extreme compressions in a diamond anvil cell with the properties of graphite.

Earlier room temperature high-pressure studies [3] on C_{70} have documented a gradual amorphization phenomenon beginning at 12 GPa (see Ref. [3] for a summary of previous high-pressure work on C_{60} and C_{70}). Recent x-ray diffraction [4] on C_{70} at high pressures has confirmed that transition to an amorphous phase is completed at 35 GPa and that the amorphous phase has a hardness value of 18 GPa, which is 2–3 times that of work-hardened steel. These results are remarkable because these carbon phases are synthesized at room temperature without any thermal activation. The formation of polymeric phases in C_{70} under high pressures and high temperatures [5] has been studied in the pressure range 0–5 GPa and temperature up to 800 °C. These studies at high pressures have clearly in-

dicated structural changes starting at as low a temperature as 100 °C at 5 GPa. Heating to 800 °C at 5 GPa resulted in the formation of an amorphous phase, which was found to be graphitic type, and electrically conducting. However, mechanical properties of these phases in C_{70} are not known.

We focus on the electrical and mechanical properties of the C_{70} sample at high pressures up to 48 GPa and room temperature. The previous electrical resistance data on C_{70} are limited to the pressure range between 15 and 24 GPa [6]. These data are well below the completion of the transition to the amorphous phase, which is known to occur at 35 GPa. Also, there is no direct comparison between the electrical and mechanical properties of the high-pressure phases of C_{70} and the phases synthesized from ordinary graphite.

The electrical resistance measurements on C_{70} and graphite samples were carried out using designer diamond anvils where tungsten metal probes were patterned using lithographic techniques and encapsulated within a chemical vapor deposited diamond layer. The experimental techniques for homoepitaxial deposition of diamond on top of a diamond anvil to encapsulate electrical microprobes has been described elsewhere [7,8]. In a fully fabricated designer diamond anvil (Fig. 1), electrical probes are exposed only near the center of the diamond for making contact with the sample and elsewhere they are completely insulated within a single crystalline diamond layer. Hence, this designer diamond anvil employed in our high-pressure cell allows us to use metallic gaskets for sample containment and allows for precise four probe electrical resistance measurements. Figure 1 shows the optical micrograph of the designer diamond anvil in reflection showing the eight exposed microprobes near the center, in transmission showing the buried microprobes and with a C_{70} sample in the diamond anvil cell at 44 GPa. Figure 1 also shows that the encapsulated

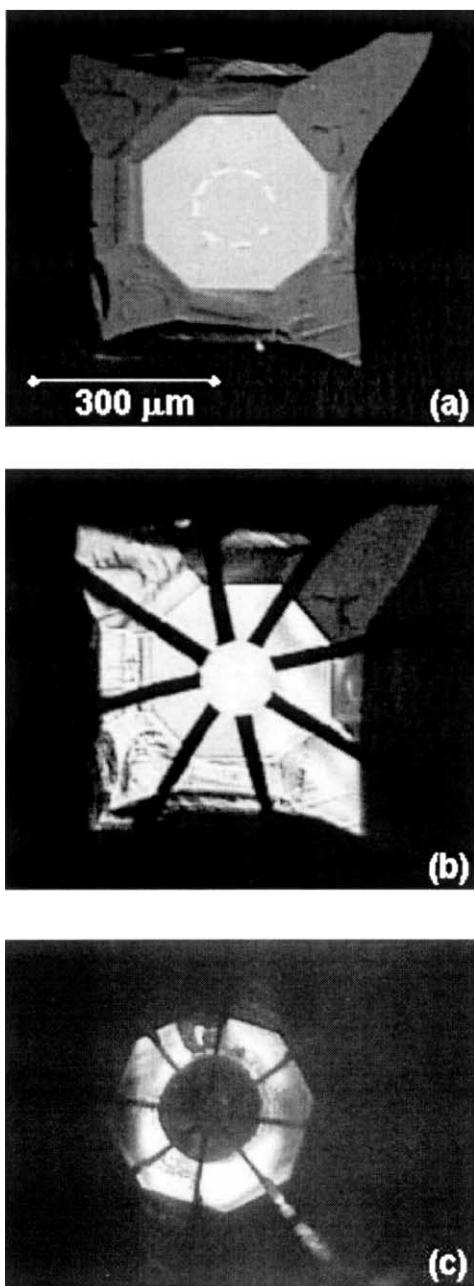


FIG. 1. (a) Optical micrograph of a designer diamond anvil in reflected light. This designer anvil was fabricated using a combination of lithographic and microwave plasma chemical vapor deposition techniques. The central flat area or culet of the diamond anvil is $300\ \mu\text{m}$ in diameter. The eight exposed tungsten metal probes near the center appear reflective in this illumination. (b) Same designer anvil in transmitted light showing tungsten electrical probes buried in the diamond anvil. (c) C_{70} fullerene sample in a metallic gasket hole at a pressure of 44 GPa in reflected light. The electrical measurements indicate an insulating amorphous carbon phase at this pressure.

tungsten microprobes are intact without any deformation at high pressures and can give reliable electrical resistivity data on materials.

C_{70} fullerene of 99% purity and graphite powder of 99.995% purity were purchased from Alfa AESAR. C_{70}

was annealed in an argon atmosphere for 2 h at $400\ ^\circ\text{C}$ to reduce contamination from solvents. Two separate high-pressure experiments were performed to compare electrical properties of C_{70} and graphite. A diamond anvil cell equipped with one standard, flat diamond of culet size $300\ \mu\text{m}$ and one designer anvil containing eight embedded tungsten probes was used in both experiments. Wire was attached to four of the tungsten probes using silver epoxy. Each sample was placed into a $150\text{-}\mu\text{m}$ hole drilled in a spring steel gasket. Ruby was added as a pressure marker. Four probe measurements were taken at each pressure step with a digital multimeter, and ruby fluorescence spectra were collected by a photoluminescence spectrometer. Mechanical properties of the pressure-quenched samples were studied by a nanoindentation technique.

The pure C_{70} sample is semiconducting with a band gap of 1–2 eV. Figure 2 shows the resistance variation of the C_{70} sample for both increasing and decreasing pressures. The starting resistance of the C_{70} sample is around $6 \times 10^6\ \Omega$ (or resistivity of approximately $6 \times 10^4\ \Omega\ \text{cm}$). This is the upper limit of the resistance we could measure with our current setup. On increasing pressure it shows a precipitous drop of 4–5 orders of magnitude with a minimum resistance of about $150\ \Omega$ (resistivity of $1.5\ \Omega\ \text{cm}$) at 20 GPa. Previous high-pressure

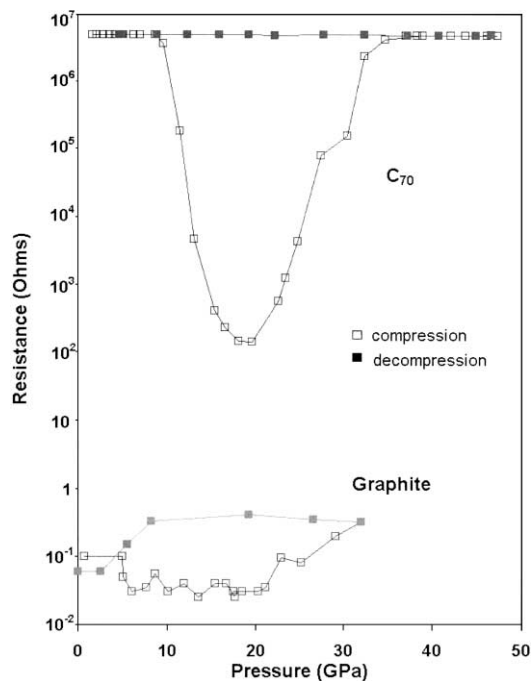


FIG. 2. Electrical resistance of the C_{70} fullerene sample and a high purity graphite sample to high pressures of 48 GPa plotted on the same scale. The C_{70} sample shows a sharp drop in resistance followed by a sharp increase with a minimum in resistance at 20 GPa. The insulating state of the C_{70} sample attained at 48 GPa is irreversible and is retained on decreasing pressure to ambient conditions. The graphite sample shows a much smaller increase in resistance just above 20 GPa and the change is completely reversible with decreasing pressure.

high-temperature studies have fitted a three-dimensional variable range hopping conductivity model to this decrease in resistance with pressure where structural defects give rise to the localized electronic states in the energy gap [6]. The variation in the electrical resistance with pressure is then attributed to a rapid increase in the electronic density of states at the Fermi level, $N(E_f)$, which increases with pressure. After 20 GPa, the electrical resistance of C_{70} rises rapidly and reaches $10^6 \Omega$ value by 35 GPa. It should be noted that the actual resistance of the C_{70} sample after 35 GPa might be greater than $10^6 \Omega$, the highest value which could be recorded in our setup. We attribute this rise in electrical resistance to the formation of an insulating amorphous carbon phase with the collapse of the C_{70} cage. This collapse of the cage is noted to be gradual, taking place in the 20–35 GPa range, even in experiments with alcohol as a pressure medium. However, additional high-pressure experiments in a helium medium are necessary to explore further the pressure range of collapse under hydrostatic compression. This insulating amorphous carbon phase has some fraction of sp^3 bonded carbon as revealed by Raman spectroscopy and transition to this phase is completed by 35 GPa [4]. This sp^3 carbon component in the amorphous carbon presumably arises from the collapse of the surface of the C_{70} molecules, which can be regarded as a topologically distorted graphite plane due to its high share of fivefold rings. Therefore the minimum in resistance at 20 GPa is due to the competing decrease in the semiconducting phase and the increase due to amorphization. On decompression of this sample from 48 GPa, the insulating high-pressure amorphous carbon phase is irreversibly retained to the ambient condition (Fig. 2). In contrast, the graphite sample shows metallic behavior throughout this pressure range with resistance in the range of 0.05 to 0.5 Ω . It should be added that we document an increase in resistance in the graphite sample starting just above 20 GPa, but this increase is much smaller than C_{70} and the graphite sample remains conducting throughout our pressure range. This resistance increase in graphite has been previously documented [9] and is generally ascribed to a phase transition [10] that is reversible below 10 GPa. The reversibility of the graphite transition was confirmed by optical absorption, as the sample is known to become opaque again after release of pressure. Our graphite results are consistent with earlier results as the resistance drops back close to the ambient pressure value on decreasing pressure.

We have also investigated the mechanical properties of pressure-quenched C_{70} and pressure-quenched graphite by nanoindentation hardness measurements. This was done by indenting our samples with a Berkovich diamond indenter with a tip radius of 50 nm. The pressure-quenched samples are estimated to be 10–20 μm in thickness. The hardness (H) of the sample was calculated with the simple relation $H = L/A$, where L is the applied load to the in-

dentor and A is the projected area of contact under the load. Nanoindentation techniques with a continuous stiffness method [11] allow for the measurement of hardness continuously at various depths into the sample and the optical micrograph of the nine indentations on the sample is shown in Fig. 3. The hardness data for the quenched C_{70} sample are compared with graphite at various depths into the sample. The average hardness value obtained at a 1000-nm depth from the nine indentations for the C_{70} sample is 30 ± 6 GPa, while for graphite at the same depth it is 0.14 ± 0.07 GPa. It should be added that the previous hardness value of 18 GPa in earlier experiments [4] was an understatement due to the use of a blunt diamond indenter tip caused by indenting diamondlike materials. The present hardness value of 30 ± 6 GPa was confirmed by using a new, sharp tip and carefully calibrating the tip before and after the indentation using a silica standard. We also show the hardness value of a single crystal diamond, 100 GPa, for comparison in Fig. 4. Thus, the hardness of the pressure-quenched C_{70} sample is about one-third of that of the single crystal diamond and a factor of 220 higher than the hardness value for hexagonal graphite under similar conditions.

In conclusion, we have shown the unique electrical and mechanical properties of a C_{70} sample on compression

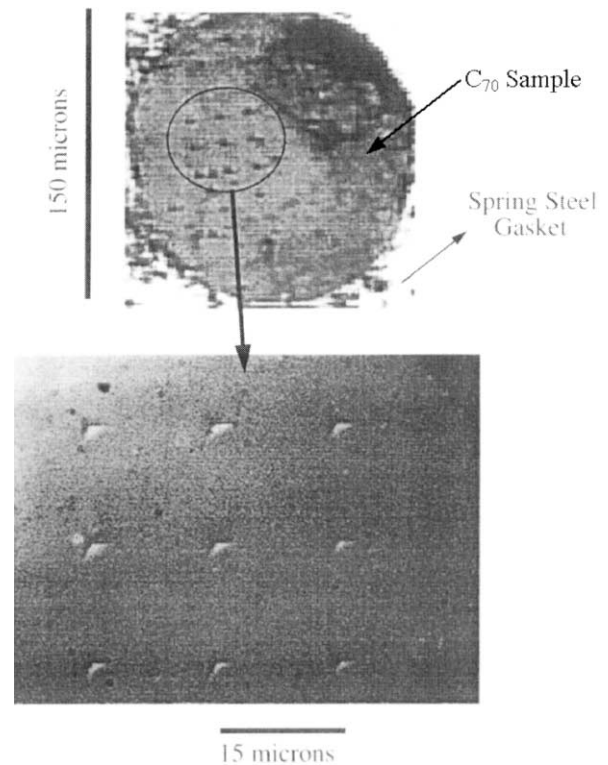


FIG. 3. Nanoindentation of the pressure quenched amorphous phase produced from C_{70} . The sample size is 150 μm in diameter and the upper panel shows the nine indentations made with a force of 500 mN during the hardness measurements. The lower panel shows the close-up look of the indentations. The size of these indentations is small indicating a very hard material.

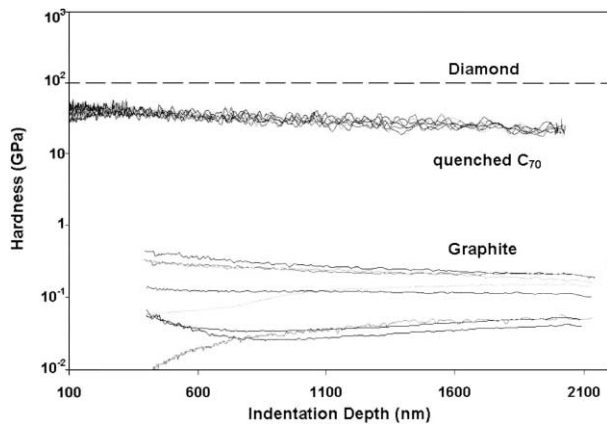


FIG. 4. Hardness values for the pressure quenched C_{70} sample and graphite sample as a function of the penetration depth into the sample. For both samples we show the results of nine indentations. Surface asperities affect the measurements at lower depths, but the measurements attain steady state values at a depth of 600 nm. At a depth of 1000 nm, the pressure quenched C_{70} phase has a mean hardness value of 30 ± 6 GPa and pressure quenched graphite has a mean hardness value of 0.14 ± 0.07 GPa. We also show for comparison the hardness value of 100 GPa for a single crystal diamond.

at room temperature and compared it with the properties of graphite under identical conditions. The C_{70} sample shows semiconducting to insulating transition at 20 GPa and this insulating phase transition is completed by 35 GPa. Graphite on the other hand shows only a modest increase in resistance and remains conducting throughout this pressure range. Our hardness measurement shows that pressure-quenched graphite is “soft” while the amorphous carbon phase quenched from C_{70} is “hard” with values of hardness of about one-third of that of a single crystal diamond. Considering that these measurements were done

at room temperature, further exploitation of the temperature variable might result in novel carbon materials with superior electrical and mechanical properties.

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