

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in Physical Review B. Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.

Comment on “Pressure and temperature diagram of polymerized fullerite”

Bertil Sundqvist

Department of Experimental Physics, Umeå University, S-90187 Umeå, Sweden

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Fullerenes such as C_{60} can be polymerized by treatment under high-pressure, high-temperature conditions. I point out that there is a strong correlation between the rotational state of the C_{60} molecules in the initial (pristine) material and the structure of the resulting polymer. [S0163-1829(98)00705-X]

In a recent paper, Marques *et al.*¹ report a very careful and detailed study of the pressure-temperature structural phase diagram of C_{60} in the pressure range between 3.5 and 8 GPa. Several polymerized phases (in which individual molecules are connected by covalent intermolecular bonds) were found. Over most of the range studied a very simple picture emerges, in which the treatment temperature is the dominant parameter determining the crystal structure. Below about 100 °C only a very small amount of polymerization was observed, but between 100 and 400 °C a highly polymerized orthorhombic crystal structure containing linear chains of molecules was observed. Above 400 °C a rhombohedral phase with nominally complete polymerization within the original (111) plane of the cubic crystal was usually observed. However, at the lowest pressures (below 4.5 GPa) this structure was mixed with a large fraction of a tetragonal structure [with bonds forming predominantly along the (110) directions].

Marques *et al.*¹ discuss the polymerization process in some detail, pointing out that the well known photopolymerization process² can only occur in the face-centered-cubic phase of C_{60} where the molecules are able to rotate practically freely. The molecular rotation randomly brings double bonds on adjacent molecules close enough together for the [2+2] cycloaddition reaction² to occur. Since there are no directional constraints on this process the resulting polymer is usually very disordered. In contrast, high-pressure polymerization is often carried out with the material initially in the simple cubic phase where no rapid molecular rotation occurs. Pressure induces a molecular reorientation^{3,4} such that above some pressure near 1–2 GPa a double bond on one molecule faces the center of a hexagon (with three double bonds on its periphery) on the molecular neighbor. With increasing temperature the increase in libration amplitude is then enough to initiate polymerization by bringing the double bonds together. Since the molecules are initially orientationally ordered this process should give a rather well oriented or ordered polymer. This is also

observed for the rhombohedral phase above 4.5 GPa, and, to a lesser extent, the orthorhombic (low-temperature) phase.

In this Comment I wish to point out that the appearance of the tetragonal phase correlates very well with the onset of molecular rotation. In their Fig. 4, Marques *et al.*¹ plot as a dashed line an extrapolation of the phase line for the fcc-to-sc transition occurring near 260 K at zero pressure. This line does not correlate with any other phase boundary in the figure and a possible conclusion is that molecular rotation has no effect on the final structure of the polymer. However, I point out that Marques *et al.* did not use the correct slope for the phase line. They extrapolated the zero-pressure transition temperature 260 K using the slope $dT/dp = 109$ K/GPa obtained by Samara *et al.*⁵ in He gas. Later studies have shown⁶ that He atoms easily diffuse into the intermolecular interstitials of C_{60} , causing significant changes in the physical properties of the material,⁷ and several studies agree^{4,6–8} that the correct phase line slope for pure C_{60} is close to 160 K/GPa. If we use this higher slope we find that the extrapolated transition temperature is about 550 °C at 3.5 GPa and 790 °C at 5 GPa, and the phase line falls exactly on the boundary of the region where the tetragonal phase is observed. This suggests instead that the rotational motion of the molecules is very important in determining the crystal structure of high-pressure, high-temperature polymerized C_{60} . Although material polymerized from the sc phase will form well-oriented polymer structures (orthorhombic or rhombohedral, depending on temperature), material polymerized from the fcc phase will probably contain a very large number of randomly oriented bonds between the densely bonded (111) planes. The tetragonal structure observed might thus be either a well-defined structure arising when a significant number of “random” interplanar bonds are formed during the polymerization process or simply an experimental artifact in which a tetragonal structure is simulated by a large number of random crosslinks in a basically rhombohedral lattice. Whatever the mechanism, the important basic cause is still the fact that molecular rotation is a

very important parameter for determining the structure of the material after polymerization. A large structural disorder resulting from molecular rotation during polymerization is probably also the reason why the structure of the low-

pressure polymerized phase discovered by Bashkin *et al.*⁹ has only recently been clearly identified,¹⁰ since this phase is usually produced at pressures and temperatures well into the stability range of the fcc phase.

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