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2002 J. Phys.: Condens. Matter 14 10449

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Carbon nanostructures under high pressure

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Received 1 June 2002

Published 25 October 2002

Online at stacks.iop.org/JPhysCM/14/10449

Abstract

Results from recent high-pressure experiments in the field of fullerenes are briefly reviewed. In particular, new results on one-, two- and three-dimensional polymerized C_{60} and C_{70} are discussed. Results discussed include the first synthesis of a well defined, one-dimensional polymer based on C_{70} , transformations from two-dimensional (2D) to three-dimensional phases in C_{60} , and doping of 2D C_{60} polymers.

1. Introduction

Many high-pressure studies have been carried out on fullerenes and carbon nanotubes [1–3]. In this paper, some recent developments in this field will be briefly reviewed. Since the field of carbon nanostructures is wide, I will only discuss a small number of selected results including the first synthesis of a well defined, one-dimensional (1D) C_{70} polymer, transformations from 2D to three-dimensional (3D) structures in C_{60} , doping of 2D polymers of C_{60} .

2. A brief overview of C_{60} phases

First I briefly review some structures and phases of C_{60} under pressure [1–3]. High-temperature treatment of C_{60} under high pressure results in the formation of intermolecular bonds, by (2 + 2) cycloaddition [4]. The average number of bonds per molecule increases [1, 3, 5] with increasing pressure p and temperature T . Below 8 GPa and at ‘low’ T dimers or linear chains (1D polymers) are formed. While at higher temperatures 2D phases form. In the low-pressure range the dominant 2D phase has a tetragonal structure but with increasing pressure an increasing fraction of a rhombohedral phase appears [5] in which the polymeric plane is based on the original close-packed (111) plane and each molecule bonds to six nearest neighbours.

Above 8 GPa C_{60} polymerizes rapidly, and 3D structures appear on heating. Several recent papers [6–9] discuss the structures of 3D polymers, but there is still no consensus on which 3D structures can be repeatably produced. At high temperatures the disorder increases and several ‘amorphous’ phases have been reported [2].

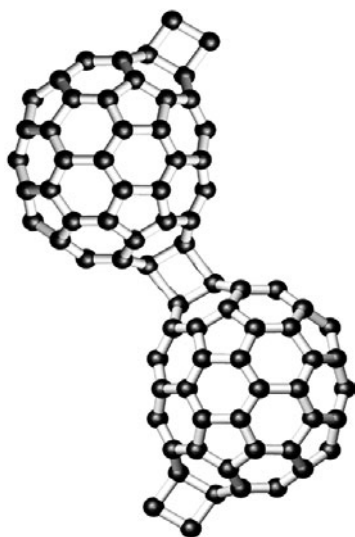


Figure 1. The 'dimer' structural unit of the zigzag chains in 1D polymerized C_{70} .

3. Polymerization of C_{70}

Much less is known about polymerization of C_{70} . Although early studies suggested that C_{70} could not be polymerized by high-pressure treatment, later work shows that several new phases can be created in this way [1, 3, 10–14]. C_{70} does not polymerize as easily as C_{60} , because only the double bonds radiating from the pentagonal polar caps are sufficiently reactive. Most polymers synthesized have been strongly disordered. However, in fcc C_{70} the molecular axes orient along the (111) direction under high pressure, and this molecular orientation under pressure may result in the selective synthesis of only one of several possible $(C_{70})_2$ dimers [13]. This also makes the formation of long-range ordered structures almost impossible, since the trigonal symmetry of the lattice around this direction is incompatible with the pentagonal symmetry of the molecules. However, in hexagonal close-packed (hcp) C_{70} the ABAB stacking makes it possible to create zigzag 'linear' polymer chains. The first structurally well defined C_{70} polymer has recently been produced by Soldatov *et al* treating hcp C_{70} single crystals under hydrostatic conditions at 300 °C above 2 GPa in Umeå [14]. The Raman spectrum shows several new peaks due to the lowering of the symmetry, and NMR data indicate the existence of covalent sp^3 intermolecular bonds. X-ray diffraction shows a zigzag chain structure with a strong molecular deformation (figure 1).

4. Transformations between polymeric phases of C_{60}

Early studies suggested that the 1D low-pressure linear chain phase had an orthorhombic structure and an $Immm$ symmetry [15]. The 2D phases, can then in principle be produced by bonding the chains together side by side by cycloaddition. However, later structural studies showed [16] that the chains in the orthorhombic phase are actually slightly rotated around their axes such that this model might not work.

Transformations from 2D phases into 3D phases are also possible, and recent calculations have suggested that such transformations can result from uniaxial compression of 2D phases [6, 7]. Okada *et al* [6] suggested that uniaxial compression of the tetragonal phase

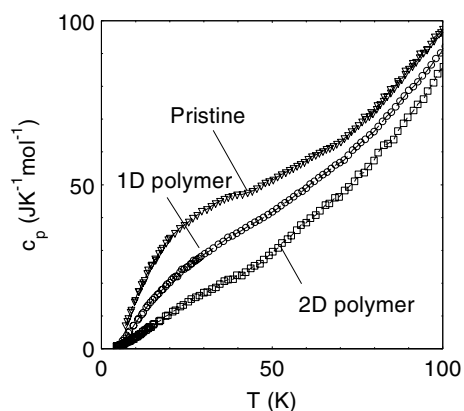


Figure 2. The low- T specific heat capacity of pristine C_{60} and 1D and 2D polymers.

to 20 GPa could result in the formation of a metallic 3D phase, possibly a superconductor with a critical temperature close to room temperature. We have therefore synthesized tetragonal C_{60} and subjected this to very high pressures. *In situ* Raman studies under pressure show that a structural transformation does indeed occur near 20 GPa [17]. The tetragonal phase disappears near 15 GPa and new Raman lines appear above 20 GPa. The new phase is marginally metastable at ambient conditions [18]; samples can be brought back to atmospheric pressure intact, but disintegrate explosively after a few hours or days.

5. Properties of 2D C_{60}

The creation of covalent intermolecular bonds in C_{60} leads to changes in the physical properties. Some are obvious: replacement of the weak van der Waals interactions by covalent bonds should increase the strength of the material and modify the phonon spectrum. The latter effect has been verified by inelastic neutron scattering studies [19]. This is reflected also in the specific heat capacity, where the low-temperature ‘Debye’ contribution is shifted to higher temperatures after polymerization [20], as shown in figure 2. The increased bond strength is also reflected in a decrease in the thermal expansion coefficient [21].

The decrease in intermolecular distance on polymerization also leads to a larger overlap of the electron bands. Calculations show that all 2D phases should be semiconductors. This is contradicted by a recent study on rhombohedral C_{60} [22], which shows a metallic behaviour in the polymeric planes and an extreme anisotropy with a ratio of $1:10^8$ between the resistivity in the plane and that along the axis. It is not yet known whether this very large value, is ‘intrinsic’ to the crystal structure or a result of orientational disorder between planes. The resistivity along the axis shows a ‘non-metallic’ dependence on temperature, while the slope of the in-plane resistivity versus temperature is positive at high T . The in-plane resistivity shows a minimum at some intermediate temperature indicating weak localization [22]. This assumption is supported by results from magnetoresistance studies. Finally, a recent magnetic study [23] of this phase has shown that ferromagnetism may occur after high- T treatment in a narrow range of T , a most unexpected discovery meriting further attention.

6. Doping of 2D C₆₀

Like graphite fullerenes can be doped into a metallic state. The obvious similarity between graphite and 2D polymeric C₆₀ raises the question whether the latter materials can also be doped (intercalated). Under atmospheric conditions, the only known layered intercalation fullerene compound is Na₄C₆₀, which forms a body-centred monoclinic structure in which the C₆₀ molecules form polymerized sheets. Attempts to intercalate 2D polymeric C₆₀ at atmospheric pressure have not been successful, but there are reports that heavy alkali metals can be inserted into rhombohedral C₆₀ under high-pressure conditions [24]. Treatment of C₆₀ in the presence of liquid K under pressure–temperature conditions similar to those used to synthesize tetragonal C₆₀ also results in the formation of materials with as yet unknown structures and Raman spectra similar to that of tetragonal C₆₀ [25]. However, these spectra also show a strong broadening of the H_g modes, indicating the presence of a strong interaction between phonons and band electrons.

Acknowledgment

This work was financially supported by the Swedish Research Council (VR).

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