

Graphite and Precursors

Edited by
Pierre Delhaès

World
of
Carbon

Gordon and Breach Science Publishers



GRAPHITE AND PRECURSORS

World of Carbon

Series Editor: Dr Pierre Delhaès, *Centre de recherche Paul Pascal – CNRS, Pessac, France*

Volume 1

Graphite and Precursors

edited by Pierre Delhaès

This book is part of a series. The publisher will accept continuation orders which may be cancelled at any time and which provide for automatic billing and shipping of each title in the series upon publication. Please write for details.

GRAPHITE AND PRECURSORS

Edited by

Pierre Delhaès

*Centre de recherche Paul Pascal – CNRS
Pessac, France*

GORDON AND BREACH SCIENCE PUBLISHERS
Australia • Canada • France • Germany • India • Japan
Luxembourg • Malaysia • The Netherlands • Russia
Singapore • Switzerland

Copyright © 2001 OPA (Overseas Publishers Association) N.V. Published by license under the Gordon and Breach Science Publishers imprint.

All rights reserved.

No part of this book may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and recording, or by any information storage or retrieval system, without permission in writing from the publisher. Printed in Singapore.

Amsteldijk 166
1st Floor
1079 LH Amsterdam
The Netherlands

British Library Cataloguing in Publication Data

Graphite and precursors. – (World of carbon ; v. 1)

1. Graphite 2. Graphite – History

I. Delhaes, Pierre

620.1'98

ISBN: 90-5699-228-7

ISSN: 1560-8557

Cover illustration: Polyedric pores obtained after graphitization at 2800°C
(M. Villey, 1979).

Contents

| | |
|--|------|
| Introduction to the Series | vii |
| Foreword | ix |
| Preface | xi |
| Contributors | xiii |
| 1 Polymorphism of Carbon <i>P. Delhaès</i> | 1 |
| 2 Electronic Band Structure of Graphites <i>M.S. Dresselhaus, G. Dresselhaus and R. Saito</i> | 25 |
| 3 Electronic Conduction <i>J-P. Issi</i> | 45 |
| 4 Magnetic Properties of Graphite and Graphitic Carbons <i>S. Flandrois</i> | 71 |
| 5 Thermal Properties and Nuclear Energy Applications <i>T.D. Burchell</i> | 87 |
| 6 Mechanical Properties <i>B. Rand</i> | 111 |
| 7 Carbon Surface Chemistry <i>H.P. Boehm</i> | 141 |

| | | |
|----|--|-----|
| 8 | Applications of Polycrystalline Graphite <i>M. Inagaki</i> | 179 |
| 9 | Carbonization and Graphitization <i>A. Oberlin and S. Bonnamy</i> | 199 |
| 10 | Preparation and Properties of Mesophase Pitches <i>I. Mochida, Y. Korai, Y.-G. Wang and S-H. Hong</i> | 221 |
| 11 | Amorphous and Non-Crystalline Carbons <i>J. Robertson</i> | 249 |
| 12 | Physical Properties of Pregraphitic Carbons <i>M. Inagaki and Y. Hishiyama</i> | 275 |
| | Index | 295 |

Introduction to the Series

The *World of Carbon* book series aims to propose different approaches to carbon materials which summarize the essential information regarding advances and results accumulated in basic and applied research during this century. Indeed, carbon associated with other atoms is a key element in nature and life. The focus of these books is, however, elemental carbons in a condensed phase, i.e. related to materials science.

Besides the natural forms of carbon, the artificial ones have led to manifold technical applications. They cover areas such as industrial chemistry and metallurgy, terrestrial transport as well as aircraft and aeronautics and environmental protection. These examples are related to the numerous old and new forms of technical carbons that we will present in greater detail below.

The field of research on carbon materials is a beautiful example of the strong interactions between science and technology, where back and forth activity has worked together for a long time. As with other scientific events, an historical approach shows that advances are step by step rather than linear with strong breakthroughs; different strata of knowledge are accumulated but sometimes with a loss of memory of the previous ones. It is crucial for scientific knowledge, as a part of human activity, that a basic synthesis is realized which summarizes the numerous publications appearing every year. The aim of this series is thus to provide short tutorial articles containing a comprehensive summary of the different subjects related to the science of carbon materials. They will be addressed to engineers, scientists and students who are seeking fundamental points without ‘reinventing the wheel.’

World of Carbon will be devoted to specific topics which cover all forms of carbons: the old ones like graphite and diamonds, but also the new ones like fullerenes and nanotubes. Each volume will cover fundamental research in chemistry and physics, as well as current applications and future developments. Such is the case of the first volume, which is devoted to the different forms of graphite and their precursors.

Subsequent volumes will be related to the most important industrial uses of graphitic type carbons: fibers and composites, carbon blacks, foams and aerogels, and insertion and reactivity products. Other polymorphic forms will not be neglected either, such as diamonds

and carbynes but also the molecular curved forms which for example open new avenues in nanotechnology.

We expect to present a collection of the articles at a level and in a style accessible to a large audience that will cover almost all aspects of carbon materials.

Pierre Delhaès
President, French Carbon Group

Foreword

Carbon reigns at the top of a column on the middle of a line of the periodic table, a privileged position, as observed by Primo Levi, who writes in *The Periodic Table* (Shocken Books, NY 1984):

. . . every element says something to someone (something different to each) like the mountain valleys or beaches visited in youth. One must perhaps make an exception for carbon, because it says everything to everyone, that is, it is not specific, in the same way that Adam is not specific as an ancestor . . .

Carbon is, first of all, immune to time. It remained on Earth as stone in the company of oxygen and calcium for millions of years. Plants expelled it along with oxygen, and much later Man used it to construct lime kilns.

Carbon is infinitely variable. It is rarely isolated and has a tendency to join with itself to form multiple constructions. In cubic form, it is called diamond which, when cut, embellishes women and is passed down from generation to generation. It is 'eternal' despite its instability. On the other hand, it is stable when it has a strongly bonded and weakly stacked hexagonal sheet. Much has been written about this very black graphite. These hexagonal planes can thus produce carbon fibers and nanotubes. Carbon, not to be content with these configurations, also likes to constitute long chains of conjugated bonds called carbynes.

Carbon recently exhibited its sensitivity to the mathematization of science by materializing as the Euler relation for polyhedrons in the form of fullerenes. Its solitude in these important structures does not exclude its conviviality with other atoms to create innumerable molecules in which is the majority, though. In addition, numerous hosts can easily penetrate it and therefore create insertion compounds. It is more discrete in the building blocks of living matter which cannot do without its power of hybridization. The carbon atom is thus exceptional. It is for this reason it has been discussed for such a long time (Le Chatelier's course at the Sorbonne in 1908 was called 'Lessons on Carbon') and continues to be so today.

The quest for scientific knowledge has become, since the middle of the twentieth century, a more collective effort rather than an individual one. Those who become interested in this subject by chance have united because of government-led and economic incentives.

This is how associations were created. The first one was very informal, created in the United States under the energetic impetus of Professor Mrozowski. In France, Professors Letort and Pacault founded the French Group for the Study of Carbon, which was succeeded by cooperative study under a program organized by the Centre National de Recherche Scientifique (CNRS, or National Center for Scientific Research). Among this group's activities, which for that matter continue today, the publication of a collective work should be noted: *Les carbones* (Masson, Paris, 1965). This treatise was followed by a series of monographs edited by Professors Walker and Throwers and published in the United States.

Recently, the discovery of new forms of carbon have opened up new avenues of research, as reported in *Le carbone dans tous ses états* (Gordon and Breach Science Publishers, Amsterdam, 1997, to be published in English under the title *Carbon Molecules and Materials*). In this context of renewal, a collective and international work is necessary to encompass the knowledge that has been acquired and to make it encyclopedic. Such is the goal of this series of books, to which I wish much success.

Professor A. Pacault
Honorary Director of the Centre de Recherches Paul Pascal
Corresponding Member of the French Academy of Sciences

Preface

The natural forms of carbon such as solid, coal or graphite flakes have been known since antiquity. Human activity associated with this substance, what the Romans called *carbonis*, started long ago with chars from firewood used for ritual paintings and in primitive metallurgical processes.

The knowledge of the element carbon in chemistry and its technical applications on a larger scale are, however, a very recent development. The industrial revolution in Europe nearly two centuries ago began exploiting coal mines and resulted in numerous applications of these graphitic forms that are still actively used today.

To illustrate these points, *Graphite and Precursors*, the first volume of the *World of Carbon* book series, is devoted to these graphitic forms after recognizing the other allotropes such as diamond, a second natural form of the carbon element. For this purpose, three main parts have been developed in this book. The first one deals with the basic properties of crystalline graphite, a very peculiar solid that is black, shiny and conducts electricity; it exhibits an anisotropic behavior for all its remarkable physical properties, in particular the electronic ones associated with a two dimensional π electronic gas.

The second part demonstrates how the main applications of graphitic materials are related in connection to their refractory character; some outstanding examples are their use as electrical brushes, electrodes for electric furnaces or nuclear energy applications, for example in fission or fusion reactors.

Carbon precursors are presented in the third and final section with a twofold purpose. The first is to correlate the organic precursors from benzenic and small condensed aromatic derivatives, known as the basal structural units, for nanoscale graphitic organization. The main chemical steps are respectively pyrolysis, carbonization and graphitization processes. The second purpose is to control this chemical evolution to create more elaborate forms for these carbon precursors. Indeed, within the past several decades, new sophisticated production of carbon materials has lead to novel applications. In this volume, the basic concepts and the associated manufacturing processes for the most stable forms of graphitic materials will be described, and the exciting new applications will be presented in the forthcoming volumes of this series.



Taylor & Francis

Taylor & Francis Group

<http://taylorandfrancis.com>

Contributors

H.P. Boehm

Universität München
Munich
Germany

S. Bonnamy

Centre de recherche sur le matière divisée
Orléans
France

T.D. Burchell

Oak Ridge National Laboratory
Oakridge TN
USA

P. Delhaès

Centre de Recherche Paul Pascal
Pessac
France

G. Dresselhaus

MIT
Cambridge MA
USA

M.S. Dresselhaus

MIT
Cambridge MA
USA

S. Flandrois

Centre de Recherche Paul Pascal
Pessac
France

Y. Hishiyama

Musashi Institute of Technology
Tokyo
Japan

S-H. Hong

Kyushu University
Fukuoka
Japan

M. Inagaki

Hokkaido University
Sapporo
Japan

J-P. Issi

Université Catholique de Louvain
Louvain-la-Neuve
Belgium

Y. Korai

Kyushu University
Fukuoka
Japan

I. Mochida

Kyushu University

Fukuoka

Japan

A. Oberlin

Saint Martin de Londres

France

B. Rand

University of Leeds

Leeds

UK

J. Robertson

Cambridge University

Cambridge

UK

R. Saito

University of Electro-Communications

Tokyo

Japan

Y-G. Wang

Kyushu University

Fukuoka

Japan

1. Polymorphism of Carbon

P. DELHAËS

*Centre de recherche Paul Pascal, CNRS, Université Bordeaux I, avenue Albert Schweitzer,
33600 PESSAC, France*

1.1 INTRODUCTION

Carbon, the lightest of the group IV elements of the periodic table, is certainly the most versatile and interesting with respect to materials properties because of its various forms and phases.

Different solid state varieties of carbon are existing naturally, either on earth or extraterrestrially but there are also artificial forms. For more than one century, starting with EDISON's experiment on hot incandescent carbonaceous filament many forms of carbon have been prepared or even discovered in laboratory. Currently, these old and new classes of carbon are respectively graphite (the most stable phase) and diamond on one hand, carbynes and fullerenes on the other. In this review, we will include recent breakthroughs due to these new molecular forms of carbons, such as C_{60} and its analogs as well as nanotubes, which are described as curved atomic surfaces (Dresselhaus *et al.*, 1995).

The review begins by summarizing our knowledge of the thermodynamically stable and metastable phases of elemental carbon over a wide range of pressure, temperature and, eventually, reaction conditions. In a second section, we will define the critical parameters that allow us to explain and classify carbon's rich polymorphism (Delhaës, 1997). Recent experimental and theoretical works have established and predicted new metastable crystalline phases. These points will be summarized in the third part of this general presentation. We will examine the influence of heteroatoms which are usually hydrogen, oxygen or nitrogen on non-crystalline precursor forms of graphitic or diamond like carbon. A general description and classification of these carbon materials will

TABLE 1. Schematic classification of different forms of carbons.

| Physical dimensionality and coordination number (z) | Typical chemical bonding | | | Solid state phases |
|--|--------------------------|---------------|------------------------------------|------------------------------|
| | hybridization | length (Å) | energy (eV·mole ⁻¹) | |
| 3D (tetrahedral structures, $z = 4$) | sp^3 - sp^3 | 1.54 | 15 | diamonds |
| 2D (lamellar structures, $z = 3$) | aro-aro | 1.40 | 25 | graphites (plane surfaces) |
| | sp^2 - sp^2 | 1.33 | 26.5 | fullerenes (curved surfaces) |
| 1D (chains or rings, $z = 2$) | sp^1 - sp^1 | 1.21 | 35 | carbynes |

be given. A complementary approach will be the influence of the neighbouring atoms in the Mandeleev table of elements, boron and nitrogen, which lead to doped carbon and solid solutions exhibiting a similar polymorphism with modified physical properties. Finally, without giving any detail on the interesting properties of these materials we sketch they are mainly divided in two broad classes, those with thermo-mechanical properties including hardness and those with functional properties associated with electronic attractive characteristics.

1.2 POLYMORPHISM OF CRYSTALLINE CARBONS

1.2.1 Basic Concepts

The nature of the chemical bonding between neighbouring carbon atoms is of prime interest. Its electronic hybridization ($1s^2$, $2s^2$, $2p^2$) leads to several types of covalent bonding.* As can be demonstrated with a quantum chemistry treatment on the hypothetical diatomic C_2 molecule, the linear combination of atomic orbitals (LCAO) leads to two-kinds of molecular orbitals (Atkins P.W., 1990): the σ -type orbital with a cylindrical symmetry about the internuclear axis, and the π -type orbital with nodal plane including the molecular axis. This orbital hybridization allows us to introduce two essential parameters for classifying the different forms of crystalline carbons (Table 1).

- (i) The coordination number of a given carbon atom ($z = 4, 3$ or 2) in the solid state:
 - A carbon atom is bound to four equidistant nearest neighbours in a tetrahedral arrangement as in cubic diamond (Figure 1). This is simple σ -type bonding associated with sp^3 orbital hybridization.
 - A carbon atom is bound to three equidistant nearest neighbours 120° apart in a given plane as in hexagonal graphite (Figure 1). A double bond with both σ and π -types are present, inducing a shorter bond length than in the first situation (sp^2 hybridization in a planar symmetry).
 - A carbon atom is bound to two neighbours in a linear chain where it can form a single and a triple bond (sp^1 hybridization). This situation is encountered in polymeric forms of carbon called carbynes (see part 1.3.1).

*Three carbon isotopes are known ^{12}C , ^{13}C , ^{14}C that we do not detail in this general presentation.

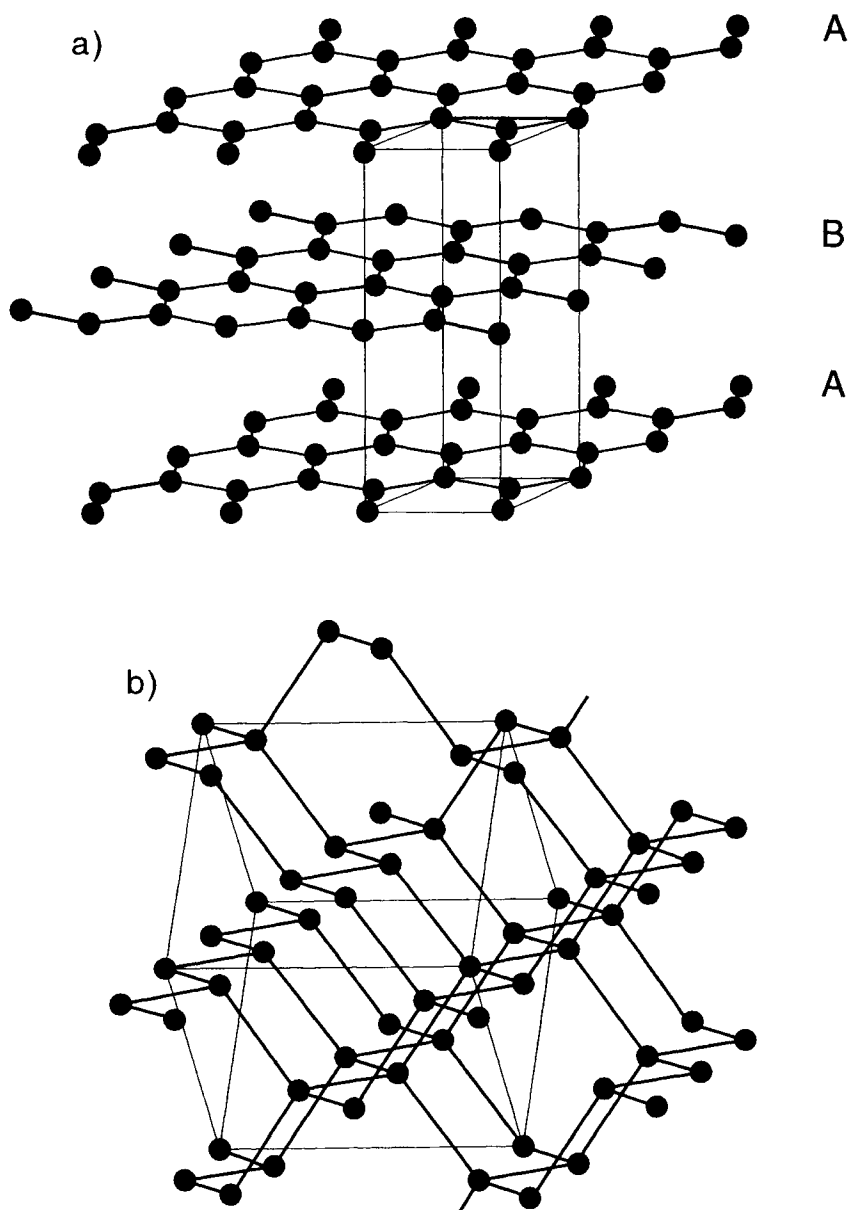


FIGURE 1. Crystallographic structures of the two most representative carbon allotrops: (a) hexagonal graphite with the layering sequence ABAB... (b) cubic face centered diamond.

- (ii) The lattice dimensionality and the associated topological approach, in particular by defining the number of carbon atoms in polycyclic forms.

Indeed in classical euclidian geometry there is a direct relationship between the lattice dimensionality (1D, 2D or 3D) and together the coordination number and the hybridization orbitals. This is due to the invariance of translation and rotation symmetries associated with usual atomic and molecular crystallographic structures.

In the case of topological changes such as the number of bonds in a given ring it has been shown that the surface curvature as found in fullerenes opens the way to new allotropic forms (Kroto *et al.*, 1985). One interesting point, because of the surface curvature is the onset of a rehybridization process inducing a certain amount of σ character in a π type orbital which modifies its aromatic character (Haddon, 1992).

To summarize this part (see Table 1) we observe that the type of chemical bonding is a convenient way to classify the physical properties which are dependent on the type of bonding and its energy. A simple σ -type bonding is sufficient to characterize the structural thermal and mechanical properties whereas the presence of π orbitals will be crucial for electronic and magnetic properties (Delhaès, 1997).

1.2.2 Thermodynamic Stability and Associated Phase Diagram

A stable thermodynamic state is associated with the absolute minimum of Gibbs free energy expressed as a function of P and T , but the existence of local minima will induce the possibility of metastable states. The probability of a phase transformation is determined by the Gibbs free energy difference ΔG , between the two considered states and the possible thermodynamic paths between them (Figure 2). Two main points are relevant:

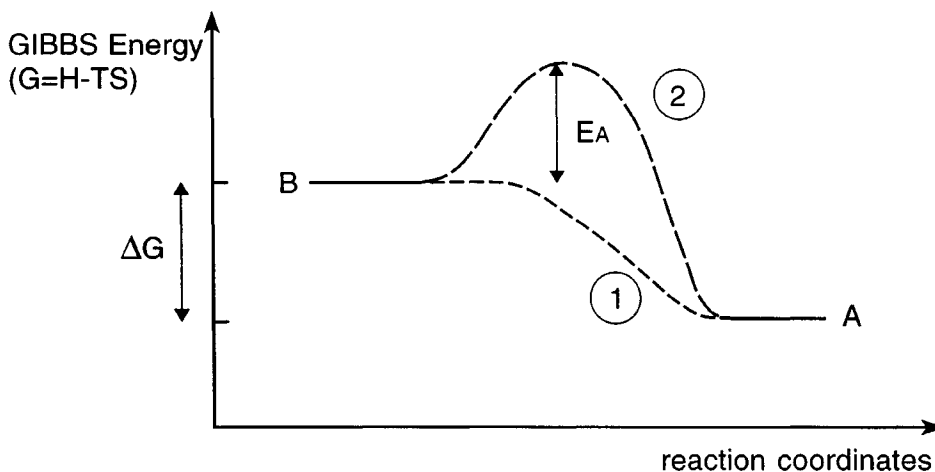


FIGURE 2. Schematic representation of the GIBBS energy change $|\Delta G|$ between a thermodynamically stable state (A) and unstable or metastable one (B). If the path is of type 1 the state B will be always unstable, but if the path has a large energy barrier, E_A , compared to the thermal energy, as path 2, a metastable state B will be obtained and stabilized.

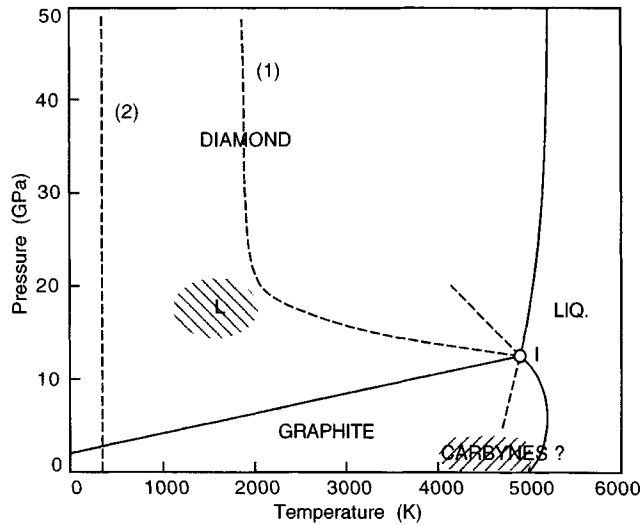


FIGURE 3. Phase diagram of carbon (Bundy *et al.*, 1996). Solid lines represent equilibrium phase boundaries and the associated triple point *I*; dotted lines 1 and 2 represent respectively the threshold of fast P/T cycles that convert graphite or hexagonal diamond (called *L* in the phase diagram) into cubic diamond, and the path along which an hexagonal graphite compressed at room temperature is transformed. Note that the question mark following carbynes indicate the possible existence region.

- (i) The phase transformation between two thermodynamic states is governed by the existence or absence of an activation energy (E_A). If $E_A \sim 0$, then only an unstable state will exist. On the other hand if $E_A \gg kT$ (the thermal energy) the energy barrier will create a local minimum on the energy surface leading to the presence of a quenched kinetic state.
- (ii) This second situation is favoured in such as the presence of large bonding energy (see Table 1) and high associated cohesion energy is found in carbon materials. When the carbon atoms are locked into a given phase configuration, a large amount of activation energy is required to produce a different stable phase. Therefore high temperatures and high pressures are necessary to initiate spontaneous phase transitions.

Following this general picture, a classical thermodynamic phase diagram has been established after several decades of experimental work (Bundy *et al.*, 1996). The (P , T) phase diagram for atomic carbon is presented in Figure 3. Its salient features are the following:

- The transition line between the stable graphite and diamond stable regions runs from 1.7 GPa/OK to the graphite-diamond-liquid triple point *I* (12 GPa/5000 K) (Berman and Simon, 1995). It should be mentioned that with thermal treatment under inert atmosphere diamond is completely transformed into graphite at about 1800°C.

- The melting line of graphite is extended from the triple point down to 0.011 GPa/5000 K (for the lower pressure region the vapor phase is present).
- The melting line of diamond runs to higher P and T above the triple point with a positive slope (Bundy *et al.*, 1996).

Beyond this general presentation several points which remain controversial are noteworthy:

- A hexagonal diamond structure called Lonsdaleite is known to be stable at high T and P (see dotted line in Figure 3).
- The carbyne phase could exist at high temperatures below the melting line of graphite.
- The liquid phase region could be divided in two parts, one would be an insulator and the other an electrical conductor (Van Theil and Ree, 1993).

To finish this phase diagram presentation, it is useful to point out the following points. These phase transformations are considered as theoretically reversible. For example, this means that we can observe a change between graphite and diamond and the transition enthalpy is under characteristic of a first order transition. Out of equilibrium conditions, such as shock waves, strong local pressures, or catalytic phase transformations are also realized but not represented on Figure 3 (Bundy *et al.*, 1996). Furthermore one step further can exist if some irreversible chemical reaction is occurring and we get a new defined compound associated with a reaction diagram. We assume that this situation is occurring in the new fullerene type phases which are molecular solids (C_n) as compared with the classical extended solids just described above (C_∞). These new phases will be described in part 1.3.2.

1.2.3 Theoretical Approaches and New Predicted Phases

The synthesis of cubic diamond thanks to different techniques which afford an excess of input energy (shock waves, high pressure or plasma chemistry) (Demazeau, 1997), has opened the way to unknown compounds. These experimental approaches are based upon theoretical calculations which predict non-existent forms of carbon and related compounds (Cohen, 1994). In the classical models a calculation of the excess cohesion energy at zero Kelvin compared to the stable thermodynamic phase is carried out, neglecting the entropic term of the Gibbs energy (see Figure 2). This approach has been developed by some authors (Cohen, 1994; Hoffmann *et al.*, 1983). Several models considered, based on quantum mechanical calculations for periodic solids having itinerant electrons. Concerning static properties, such as hardness, an equation of state (for instance Birch-Murnaghan's equation) is widely used where the cohesion energy is calculated as a function of the volume. The essential parameter is the bulk modulus B_0 at zero Kelvin and its pressure derivative for the equilibrium volume. A semi empirical expression for B_0 has been proposed as a useful starting point for calculations:

$$B_0 = -V_0 \left(\frac{dP}{dT} \right)_{T \Rightarrow 0} = \frac{\langle N_c \rangle}{4} (1972 - 220\lambda) d^{-3.5}$$

where $\langle N_c \rangle$ is the average coordination number for the compound considered and λ is an empirical ionicity factor which is zero for pure carbon solids. It is clear from this relation that short bond lengths with a large bond energy are best for getting a large B_0 . Indeed the highest density of strong covalent bonds will lead to superhard compounds associated to a very low compressibility factor. The presence of single (σ -type) or multiple bonds ($\sigma + \pi$ -types) in the carbon network will also be essential for the understanding of electronic properties (Dresselhaus *et al.*, 1998).

1.3 REAL AND VIRTUAL FORMS OF CARBONS

Considering the large number of carbon polymorphs these solid phases will be classified based on their coordination number but not from the type of hybridization that was previously introduced. For each class of crystalline structure with a fixed coordination number we will present the different real or virtual (i.e. predicted but not found experimentally) allotropic forms with different polytypes. The unavoidable presence of covalent chemical bonds in four, three or two directions induce a physical dimensionality for all the properties. This topological approach will be pursued by analyzing the new forms of carbon described on curved surfaces (fullerene type). In the last section we will examine the more exotic structures which have been predicted based on mixed coordination numbers.

1.3.1 Structures With a Fixed Coordination Number

1.3.1.1 Carbynes

The linear arrangement of elemental carbon as in other conjugated polymers (see polyacetylenes or polydiacetylenes for example) has been mentioned in the literature (Kudryautsev *et al.*, 1997). Basically, this polymeric form can be derived either from a chain with alternating single and triple bonds (polyynes) with alternate bond lengths of 1.20 Å and 1.58 Å or alternatively from double bonds (polycumulene) with a uniform bond length: 1.28 Å (see Table 2).

The first polyyne configuration appears to be the most stable because of the stabilization caused by the opening of a gap at the Fermi level for the π electronic gas. This is referred to as the Peierls distortion effect (Kastner *et al.*, 1995).

However the existence of pure carbyne forms as the so called α and β forms is still controversial. A complete X-ray diffraction analysis of any linear species is not yet available due to the lack of a suitably sized carbyne single crystal, but several structures have been announced. There are continuing reports on its synthesis (Kudryavtsev *et al.*, 1997) and its natural occurrence. Firstly, natural carbynes have been reported in exotic environments such as interstellar space, meteorites and meteoritic craters (Heimann *et al.*, 1984). Secondly, several attempts have been carried to synthesize long chains. It has been shown that species up to 30–300 atoms could be prepared (Kavan, 1998) using different synthetic routes or physical methods. For example, thermally stable acetylenic carbon species capped with inert groups present a chain length of more than 300 atoms (Lagow *et al.*, 1995). Another example is the “carbolite” compound, prepared by quenching of the carbon vapours from

TABLE 2. Experimental and calculated symmetries and bond lengths, bulk moduli, and excess cohesion energy, at zero Kelvin and under atmospheric pressure, calculated from the Birch-Murnaghan equation of state (Yin and Cohen, 1983; Spear *et al.*, 1990).

| Phases | Crystal symmetry and C-C bond length $d(\text{\AA})$ | Specific mass (g/cm^3) | Bulk modulus (GPa) | Difference of cohesion energy ΔE_c ($\text{eV}\cdot\text{atom}^{-1}$) |
|------------------------------|--|-----------------------------------|--------------------|---|
| (1) Tricoordinated graphite | hexagonal ($d = 1.42$) | 2.26 | 280 | 0 |
| | rhomboedral ($d = 1.42$) | | – | (small) |
| bct-4 | tetragonal ($d = 1.44$) | 2.96 | 360 | +1.1 |
| H-6 | hexagonal ($d = 1.46$) | 3.16 | 370 | +1.7 |
| (2) Tetracoordinated diamond | cubic ($d = 1.54$) | 3.51 | 440 | +0.30 |
| | hexagonal ($d = 1.54$) | 3.51 | 440 | +0.33 |
| BC-8 | cubic (centered) | 4.0 | 410 | +1.0 |

arc discharge, which consists of a parallel array of carbon chains (Palnichenko and Tanuma, 1996). It appears that the structural and physical properties of this high temperature carbon allotrop are progressively emerging thanks to the improvement of new synthesis techniques for stabilizing these so-called “white” forms of carbon.

1.3.1.2 Graphites

This basic form of carbon is constituted with sp^2 type aromatic bonds which form condensed hexagonal cycles. This planar, and supposed by infinite, atomic sheet is called graphene (see Table 2). The bulk forms of graphite type allotrops are formed by the stacking of the graphene layers. Except for the possibility of the hypothetical carbon six-rings stacked with the identity period of 1 (1H-polytype) (Heimann *et al.*, 1984) the low temperature and low pressure forms are the well known hexagonal and rhombohedral unit cells. The lattice structure of a single crystal of graphite is hexagonal (space group $P6_3/mmc$ and polytype 2H): the graphene layers are stacked in translational ...ABAB... sequence with an in-plane nearest neighbor distance of 1.421 Å and perpendicular interplane distance of 3.354 Å at room temperature (Figure 1) (Bacon, 1948). A second possibility is a stacking periodicity ...ABCABC... as discovered in a rhombohedral phase. The hexagonal phase is thermodynamically stable but in particular thanks to grinding processes a large percentage of rhombohedral form can be obtained (Boehm and Hoffmann, 1955).

More generally, weak disorder can result from stacking faults. These departures from the ideal translation give rise to a small increase of the graphite interlayer distance. The graphene layers become both uncorrelated with their neighbour and possess a mean finite size, in which case they are called turbostratic carbons or graphites (see in the following part 1.4).

The electronic structure of these two dimensional graphene structures is a zero gap semiconductor (contact point between the valence and conduction π bands) which are transformed for an ideal hexagonal graphite, to a semi-metal with a small π band overlap (Dresselhauss *et al.*, 1998).

New metastable phases have been proposed which consist entirely of threefold coordinated carbon in a rigid three dimensional lattice, as in a diamond type phase (Hoffmann *et al.*, 1983). The proposed goal is to combine the electronic properties of graphite with the structural ones of diamond. Two series of theoretical analysis on hypothetical crystalline phases have been carried out consisting of layers of polyene chains joined by bonds parallel to the *c* axis. The orientation of the chains rotates about the *c*-axis either by 60° (H-6 structure) (Tamor and Hass, 1990) or by 90° (bct-4 structure) (Liu and Cohen, 1992) (see Figure 4).

From theoretical calculations it appears that the excess cohesive energy for this metastable phases, which could be low-compressive metals with an hardness comparable to diamond, is not prohibitive for expecting some metastable phase (see Table 2). It should be mentioned nevertheless that no experimental approach has been reported so far.

1.3.1.3 Diamonds

In the ideal diamond structure every carbon atom is surrounded by four other carbon atoms at the corner of a regular tetrahedron forming strong covalent sp^3 bonds. The crystal structure is cubic face centered (Fd3m space group) (Figure 1). An hexagonal form of diamond called Lonsdaleite exists (Bundy and Kasper, 1967) with the same crystal symmetry as hexagonal graphite but with different site locations and a smaller interplanar separation. It also should be mentioned that in artificial diamonds a series of polytypes analogous to those well known in silicon polytypes can be described through their vibrational spectra (Spear *et al.*, 1990). Two other metastable phases have been quoted by Russian workers but not yet confirmed. They used very energetic techniques thanks to ionic discharges. They report a new cubic centered form with a calculated density exceeding by 15% the density of cubic diamond (Matyushenko *et al.*, 1979) and on the other hand a new f.c.c. structure with a monoatomic unit cell of a lower density ($d = 1.59 \text{ g.cm}^{-3}$). This so called γ -carbon could be metallic but quite instable because of longer bond lengths compared to those in diamond (Palatnik *et al.*, 1985).

Besides the esthetic appearance, the cubic diamond phase is characterized by its unique hardness and its stability under high pressure. Since experimentalists are attempting to reach very large pressures, it becomes important to investigate theoretically the possible phase transformations under very high pressure. Indeed it has been calculated that as a function of the unit cell volume five different phases of tetracoordinated carbons could be expected (Yin and Cohen, 1983). The only phases which could be obtained under high hydrostatic pressure are a simple cubic one and a body-centered cubic structure (BC8). It is interesting to note that a parent to BC8, a superdense carbon called supercubane (Figure 5) was proposed independently (Johnston and Hoffmann, 1989) to explain the polycrystalline material found experimentally with a plasma technique (Matyushenko *et al.*, 1979).

The last point relative to some new predicted phases is the transformation into higher-coordinated structures at very large pressure. A theoretical simulation has shown that under terapascal pressures diamond could collapse into a metallic sixfold coordinated structure, named SC4, despite large activation barriers (Scandolo *et al.*, 1996). To conclude, it appears that the search for new hard phases is an exciting novel subject which needs sophisticated experimental approaches.

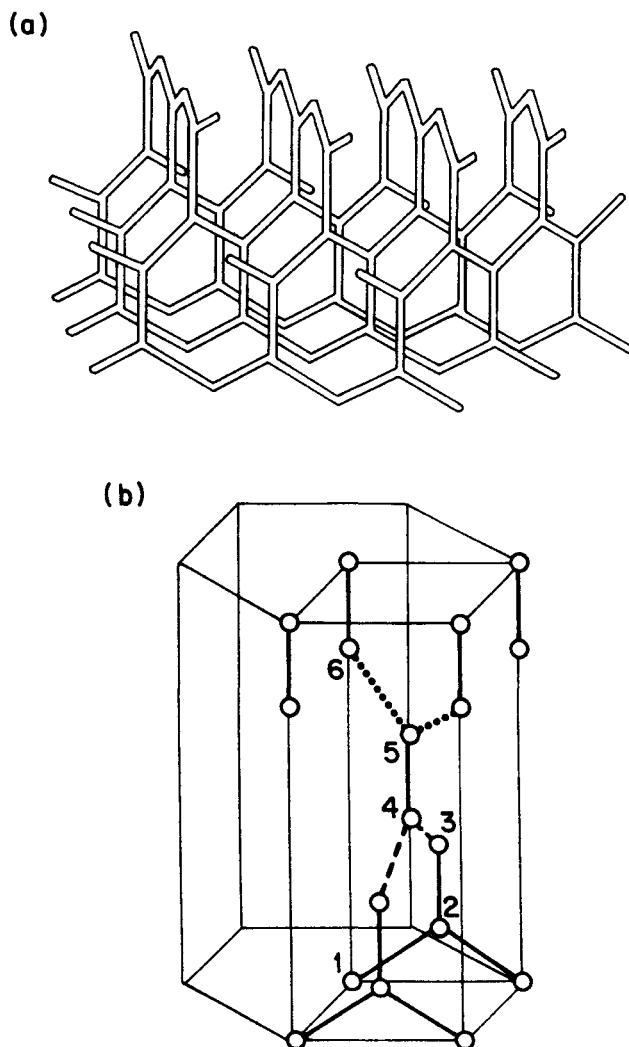


FIGURE 4. Perspective view (a) and unit cell (b) of the H-6 structure showing only the bonds between nearest neighbour atoms (from Tamor and Hass, 1990).

1.3.2 Structures on Curved Surfaces

1.3.2.1 Historical Outline

A new chemistry of carbon materials started a few years ago with the possible synthesis of a molecular-cage arrangement consisting of sixty carbon atoms with the form of a soccer ball (Kroto *et al.*, 1985). This new perspective has been confirmed by the chemical isolation of

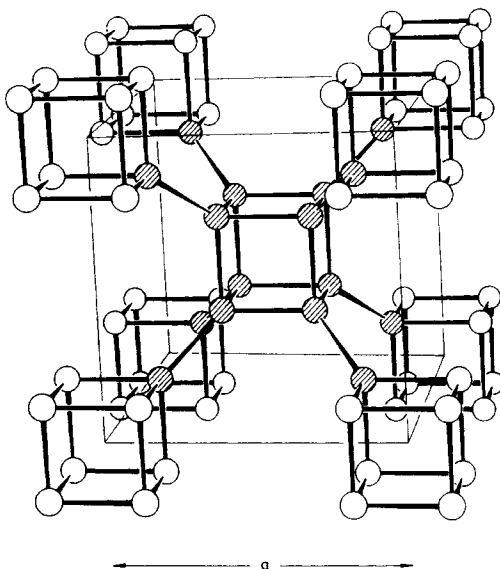


FIGURE 5. Proposed supercubane structure with a cubic unit cell of length a (shaded atoms) (from Johnston and Hoffmann, 1989).

C_{60} thanks to a plasma generated in a simple arc discharge and its structural characterization (Krätchmer *et al.*, 1990). Indeed the nearly spherical molecule C_{60} , as predicted by Euler's rule (see Figure 6), and the so called related fullerenes have attracted a great deal of interest in the recent years. Hollow cage structures with different numbers of atoms have been observed but also a new tubular form called nanotubes, are formed upon the addition of catalysts inside the carbon electrodes (Ijima, 1991). It appears immediately that the cylindrical portions of the tubules consist of rolled graphene sheets which can be either capped or not depending on the diameter and the experimental conditions. The fundamental point associated with these new forms is that the graphene type sheets are very flexible, as has also been found for other lamellar compounds such as BN or some chalcogenides. It appears that the trigonal carbon network can form new molecular carbon species. This general mechanism may be driven by the energetic gain involved in the competition between the elimination of dangling bonds and the plane curvature, but the details of the growth processes are not fully elucidated.

During their formation not only hexagons, but also pentagons (or eventually heptagons or octagons) are formed which induce a curvature of the graphene sheets (Ebbesen, 1994). It appears, therefore, that for this peculiar class of surface allotrops, a general topological classification is useful.

1.3.2.2 Topological classification

It is necessary to apply non-euclidian geometry for curved surfaces (Schwarz, 1890). Two basic parameters are useful to define these fullerene type structures, the mean curvature H

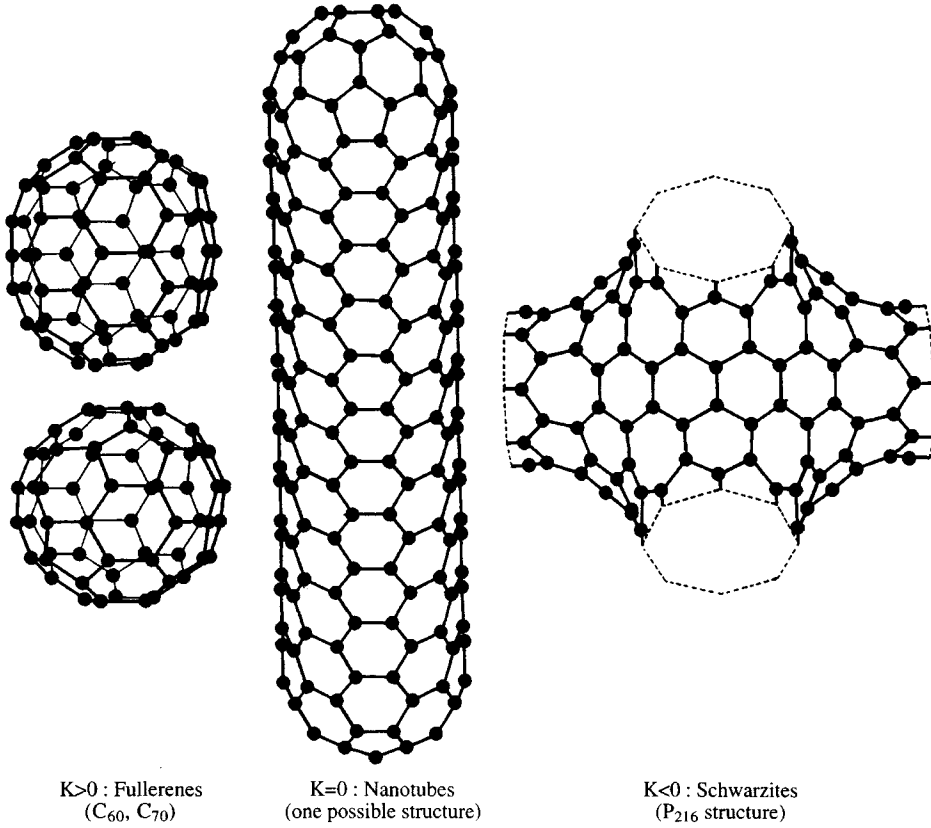


FIGURE 6. Examples of curved graphene varieties classified through their Gaussian curvature K (from Delhaës, 1997).

and the Gaussian curvature K :

$$H = \frac{K_1 + K_2}{2}, \quad K = K_1 \cdot K_2$$

where K_1 and K_2 are two local curvatures at a given point on the surface. The gaussian curvature, homogeneous to a surface inverse, allows us to classify the following geometrical shapes (Terrones and Mackay, 1992):

- $K > 0$ (sphere): fullerenes C_{60} and homologs
- $K = 0$ (plane or cylinder if $H \neq 0$): nanotubes
- $K < 0$ (saddle): Schwarzites (see in the following)

- The Fullerenes

The 60 carbon atoms are known to form a truncated icosahedron where all carbon sites are equivalent. This truncated icosahedron one of the perfect polyhedres described by Platon, has 20 hexagons and 12 isolated pentagons consistent with Euler's theorem. It crystallizes at room temperature in a cubic face centered system. Because of this high molecular symmetry C_{60} has attracted a lot of interest in physics and chemistry. However the synthesis of larger molecular weight fullerenes by arc discharge techniques is also noteworthy. The next fullerenes beyond C_{60} that satisfy the isolated pentagon rule are C_{70} and C_{76} . Currently significant or small quantities of C_{70} , C_{76} , C_{78} , C_{82} , C_{84} and C_{86} have been isolated (for C_{78} and higher compounds, several isomers are expected). The structure and properties of these higher mass fullerenes are now under study. It should be mentioned that larger carbon aggregates up to the range C_{600} – C_{700} have been observed in mass spectra along with small onion-like particles (Dresselhaus *et al.*, 1995). Finally, a C_{36} molecule has also been detected experimentally which shows that new molecular forms of carbon have yet to be discovered (Piskoti *et al.*, 1998).

- The Nanotubes

The synthesis of hollow tubes consisting of concentric cylindrical sheets proceed in different ways. The first one was by using d.c. electric discharge at high temperature (locally around 3600°C) which furnish a mixture of different types of carbon. The second way has been the catalytic decomposition of hydrocarbons with transition metal catalysts (Fe, Co, Ni) at low temperatures (below 1000°C) as already developed for microfibers (Baker and Harris, 1978). More recently a laser ablation technique has been proposed which leads to better defined nanotubes (Thess *et al.*, 1996). Indeed typical carbon nanotubes are 1–25 nm across with a length up to 10 μm . They consist of 1–50 graphene cylinders wrapped around each other along a common long axis.

The experimental evolution has been to synthesize at the beginning multiwalled and then single wall nanotubes, which are formed by the laser method for which a very narrow diameter distribution is detected. As shown by transmission electron microscopy (TEM) these nanotubes with different diameters can be either capped or open. For the thinner ones ($\varnothing = 7 \text{ \AA}$) a half-fullerene C_{60} capping can exist (Figure 6) or for larger sizes, and sometimes after heat treatment a conical shape is observed. Indeed there is currently a large variety of nanotubes and the main pending problem is to prepare a homogeneous batch. The purification of single wall nanotubes, which form in aligned bundles, is a necessary technical improvement. Nevertheless, the structural and physical properties (electronic and mechanical characteristics) are under study for these defect free single wall nanotubes which offer different folding symmetry including arm-chair, zig-zag, chiral nanotubes (Dresselhaus *et al.*, 1995). Indeed the understanding of gas phase growth mechanisms and the associated topological and atomic defects are of prime interest for defining different morphologies. Nanoparticles are also formed under these experimental conditions as nanocones (Sattler, 1995) helix shape tubules and microfibers (Ihara and Itoh, 1995) or even onions (Ugarte, 1995). Currently a large development is occurring relative to the potential nanotechnologies. There is currently much interest in using nanotubes to develop potential nanotechnologies.

- The Schwarzites

It has been also suggested that graphene type structures with a negative gaussian curvature may be possible by introducing seven- or eight-membered rings in addition to the usual six-membered rings (Terrones and Mackay, 1992; Lenosky *et al.*, 1992). In fact these negatively curved carbon networks belong to the class of periodic minimal surfaces (Schwarz, 1890) and it has been suggested that these novel tridimensional carbon structures be called "Schwarzites".

Several models of periodic graphite-like surfaces have been investigated theoretically; These models consist of different kinds of periodic surfaces (P,D,G types) with big unit cells containing from 24 to 216 atoms (see one example called P.216 on Figure 6). Following the general principles outlined in paragraph 2.3 calculations of the cohesive energy and bulk modulus have been carried out for these extended systems. It has been shown that the cohesive energy appears to be greater than in C_{60} . This means that these forms could exist as a metastable state. One interesting case is the polybenzene model with only 24 carbon atoms in a simple cubic unit cell (Huang *et al.*, 1993). Nevertheless in spite of different attempts no clear experimental evidence for their existence has been presented so far.

1.3.2.3 Physical properties and phase stability

A few remarks relative to the physical properties of these surface allotropes should be made. The surface curvature induces a bond distortion because of the presence of a local strain which produces a rehybridization of the molecular orbitals (Haddon, 1992). Indeed the hybridization is no longer a π -orbital of sp^2 type, but there is a mixing with the σ -orbital which is significant for C_{60} , C_{70} and small radius nanotubes. This effect will modify the electronic properties and the chemical reactivity of the smallest molecular compounds and will become less and less important for more extended systems.

The π -type electronic dimensionality of these forms complements their structures (Dresselhaus *et al.*, 1998). C_{60} and its homologues can be considered zero dimensional, the nanotubes are one dimensional, a graphene sheet is two dimensional, and the predicted Schwarzites would be rather three dimensional. The physical properties of fullerenes and the many nanotubes isomers can be associated with quantum size effects, which is one of the reason why there is such excitement for probing and manipulating these nanoscale materials (Odom *et al.*, 1998; Issi, 1998).

The temperature and pressure stabilities and the phase transformations of C_{60} are a key point of interest when considering the C_{60} molecule as an independent molecular species that could be transformed under T or P to another surface or volume allotropes. This reaction diagram (Figure 7) has been investigated by different authors (Nunez-Regueiro *et al.*, 1995; Blank *et al.*, 1997) and the main features are the following:

- At moderate temperature under hydrostatic pressure several oligomeric and polymeric phases of C_{60} have been isolated and characterized (see orthorhombic and rhomboedral phases).
- With increased temperature an irreversible chemical transformation to a graphitic phase is observed.

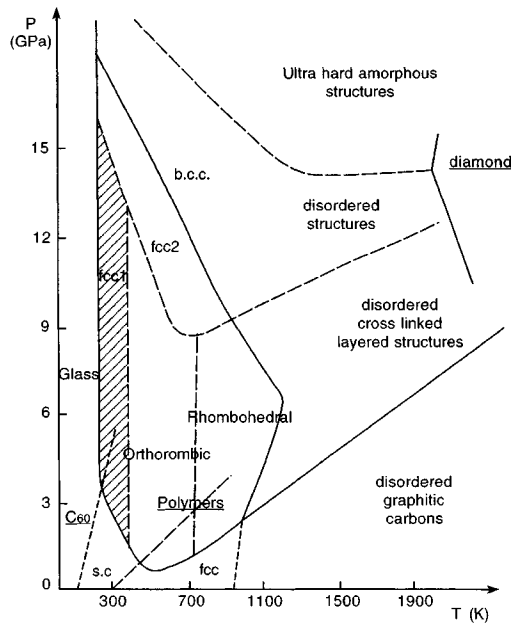


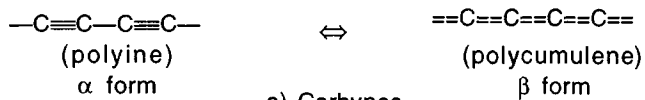
FIGURE 7. Sketch of the pressure-temperature reaction diagram showing the various phases of C_{60} created under different experimental constraints (from respectively Blank *et al.*, 1998 and Nunez-Regueiro *et al.*, 1996).

- At very high pressures (up to 20 GPa) a diamond phase is formed along with other ultrahard phases which are not yet completely characterized.

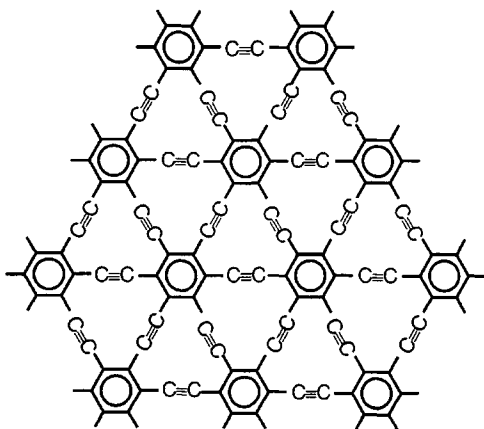
Indeed, a quite large number of more or less crystalline materials have been discovered which are not fully characterized (see Figure 7), but these experiments open the way to a new field of investigation.

1.3.3 Exotic Structures with Variable Coordination Numbers

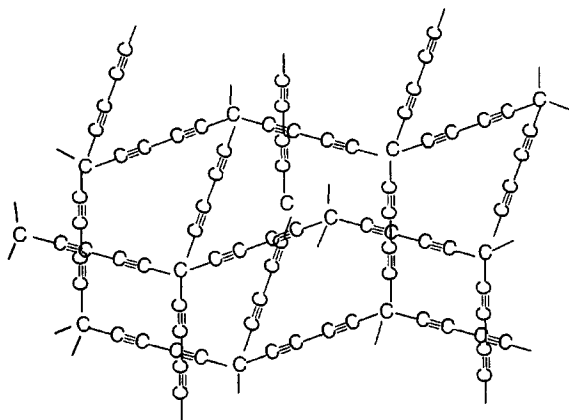
An alternative is to predict new forms of carbon with mixed coordination numbers i.e. with $z = 2$ and 3 or $z = 3$ and 4 . The pursued goal is to combine the physical properties of the classical allotropes such as hexagonal graphite and cubic diamond, with rational space filling structures. These topological approaches are based on Wells's seminal work on the structure of two and three dimensional nets and polyedra forms (Wells, 1977). It must be noticed, however, that almost none of these theoretical predictions have been experimentally confirmed which is why they are called "exotic".



a) Carbynes



b) Graphyne



c) poly-"tetraethylmethane"

FIGURE 8. Examples of proposed acetylenic polymeric carbons with different space fillings: (a) 1D: linear polyynes "carbynes"; (b) 2D: layer of graphyne (from Baughman *et al.*, 1987); (c) 3D: possible superdiamondoid network (from Diederich, 1994).

1.3.3.1 (2-3) Connected carbon nets

These systems would present an intermediary between carbynes and graphene as conjugated polymers with an average of more than one π electron per carbon atom. Different types of molecular organisations, linear or layered, can be envisaged with carbons in both sp^2 (or sp^3) and sp states.

The first of these interconnected chains, to that reinforce the thermostability and mechanical properties of poly-*p*-phenylene or poly(-*p*-phenylene) xlylidene, to form a crystalline cubic state (Baughman and Lui, 1993). Conjugated enediynes also have examined because a 3D organization could be obtained (Figure 8) there are serious synthetic problems to get ordered polymers (Gleiter and Kratz, 1993; Diederich, 1994).

Secondly, the prediction of structure and properties for planar structures appears more attractive with a reasonably low formation energy. This proposal is based on molecular sheets with the same planar symmetry as graphene, which can be formally viewed as resulting from the replacement of one third of the aromatic carbon-carbon bonds by $-C\equiv C-$ linkages (Baughman *et al.*, 1987). This material called graphyne should behave as a quite large bandgap semiconductor (see Figure 8).

1.3.3.2 (4-3) Connected carbon nets

The goal is to propose new compounds with an intermediate valency between graphite and diamond, i.e. less than one p electron per carbon atom. Planar systems with a variable number of carbon atoms inside a ring (four or ten-numbered rings for example) are selected. They form a 2D plane nets which can be interconnected by tetracoordinated carbons to obtain a 3D lattice (Merz *et al.*, 1987).

More recently a 3–4 connected net containing trigonal and tetrahedral atoms in a 2:1 ratio, built upon the 1-4 cyclohexadienne motif, has been proposed (Bucknum and Hoffmann, 1994). An hypothetical tetragonal form based on a spiroconjugation (Figure 9) could give rise to a new conducting and dense form of carbon (“Glitter model”). All these predicted forms will need the control of specific synthetic chemistry to be effectively realized in the future.

1.4 NON-CRYSTALLINE AND DOPED CARBONS

Up to now we have presented real or virtual crystals, but non-crystalline or doped forms of carbon exist when some positional disorder is present in homogeneous or inhomogeneous solids. The different types of disorder which have been recognized (Delhaes and Carmona, 1981) are the following:

- mixtures of chemical bondings in pure carbon (tetracoordinated and tricoordinated atoms),
- lattice defects associated with the loss of a long range order with two main types of local organization (glasses or microcristallites),
- presence of linked heteroatoms (H,H,N,O,...) or so-called impurities in insertional or in substitutional positions (as for example B or N).