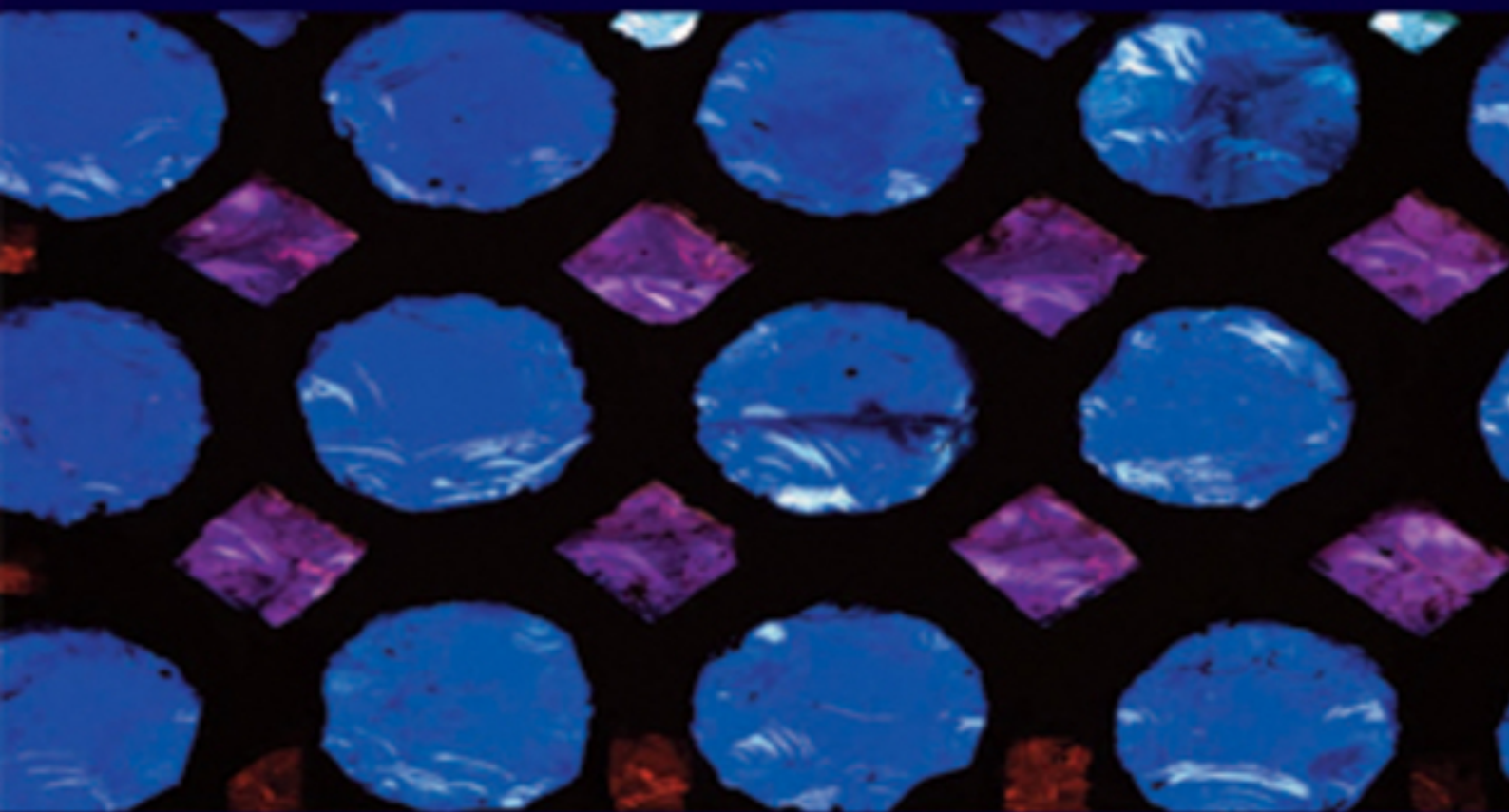


Carbon-based Solids and Materials

Pierre Delhaes



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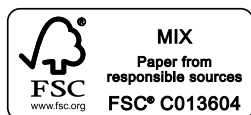


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Introduction

The carbon atom is an essential building block in nature; it is at the origin of life on our planet especially because of the complexity of its chemical bonds. It can also self-assemble in different ways producing numerous solids and materials. Although some have been known for a long time, such as diamond and natural graphite, research in the last 50 years has uncovered other new materials reported as polymorphs. These significant advances constitute an example of the mutually beneficial exchange between science and technology. The rate of knowledge expansion on this topic has sometimes led both researchers and engineers to think that some discoveries were made several times. Hence, we decided to integrate the most recent advances historically, and this was the driving force behind the preparation of this book. To achieve this, the book has been divided into three parts. The first presents five chapters focusing on the allotropic forms of carbon, including their precursors and closely related analogs. The second part focuses on their intrinsic properties, and the third describes the applications of carbon-based materials. The themes and contents are summarized in the table of contents. In the first part (Chapters 1 to 5), we define and describe natural forms of carbon, referring in particular to the allotropes of graphite and diamond, as they are the basis of the newly discovered molecular phases, which include carbynes, fullerenes, and planar or rolled-up graphene sheets. This part is based on thermodynamic and structural characteristics of these phases and is further developed based on concepts borrowed from solid-state physics. Later, the comparison of properties between polymorphic varieties is reported (Chapters 6 to 10) according to a solid-state physics approach. Finally, the last part focuses on materials, introducing the physical chemistry of surfaces and interfaces when exposed to their environment (Chapters 11 to 15). These materials, which are the result of human development, were created to exploit a physical property or specific chemical functionality corresponding directly to the

desired application. We will demonstrate that this area of material science is highly dependent on the evolution of our society and its economy including the current developments of nanosciences and nanotechnologies.

The structure of this section is based on a historical approach that integrates several key references used throughout the whole book. The full list of general references is provided at the end of this introduction; it appears in chronological order commencing with the book by Henry Le Chatelier, which was published more than a century ago and pioneered the description of the different carbon-based phases. The collective manuscript on carbons, published in the 1960s in France has been a benchmark ever since. However, recent developments, in particular the case of the new molecular phases and their properties, have instigated the requirement for new research in order to describe them appropriately. Some theoretical reminders on physics of the solid can be found in various sections, as well as descriptions of the most relevant characterization techniques associated. Thus, in this well of knowledge containing “theory-technique-subject” we have focused on solids and carbon-based materials. It is suggested that the interested reader complement this with a list of less specialized books and websites (see for example Wikipedia online).

In terms of nomenclature we adopted the terminology recommended by IUPAC (E. Fitzer, K.H. Kochling, H.P. Boehm and H. Marsh, publication DKG n° 32, 1998). The main abbreviations and symbols as well as the keywords used are listed in two different indexes. Moreover, in each chapter the most recent and historically significant publications are listed in an effort to highlight the progress in each field of interest. A non-exhaustive and highly subjective approach has been employed in order to establish a classification based on the different varieties of carbon instead of developing each specific property. Finally, we have decided not to highlight the diverse utilizations and industrial applications of these materials (no reference to any patent), which are in constant evolution, but instead to provide an overview of the basic notions used and their evolution with time.

Acknowledgements

This book results from several years of work and its conception and preparation was made possible thanks to the help and cooperation of many colleagues and friends. It has to be considered as the fruit of half a century of research on carbons at the “Centre de recherche Paul Pascal” (Centre National de la Recherche Scientifique et Université de Bordeaux). It is dedicated in memory of the pioneering works on

carbon materials started in the sixties by Adolphe Pacault and André Marchand at Bordeaux. The influence of the scientific community belonging to the French carbon group has also been tremendous with its annual meeting where exchanges and discussions are always intense.

Concerning the manuscript preparation I am deeply grateful to Michel Trinqucoste and Stéphane Reculosa for the illustrations, then to Nicolas Nouvel for the English translation which has been updated and improved, correcting some mistakes present in the French edition. I finally dedicate this book to my wife Christiane Delhaes, our children and grandchildren, who have kindly followed all the steps of this project.

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Below is a list of books that are fundamental references for the work described in this manuscript.

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PART 1

Carbon Phases, Precursors and Parent Compounds

Chapter 1

A Historical Overview

Carbon is a special element in the periodic table; it is not abundant on Earth with only 0.2% of the total mass of our planet being composed of carbon, but its role is nevertheless fundamental. As described by P. Levi [LEV 95], carbon can form bonds with other light elements and with itself, laying the foundation on which chemistry and biology have been developed, and ultimately allowing the miracle of life to happen. We will focus on its ability to bind with itself in different ways, leading to various solids, both natural and artificial. It is worth mentioning that carbon-based materials were and still are the main source of energy utilized by mankind. First, we will consider these materials as the result of human activities, sort of corollary to the evolution the human race, related to each period of time and representative of each successive civilization. In the following presentation, natural carbon-based materials, both from Earth or with a cosmic origin, will be defined and presented. These materials, having been present through the creation of our universe, effectively bridge the gap between astrophysics and geophysics. We will also demonstrate the existence of similarities in both natural and artificial carbon-based materials, as they constitute an important source of information, by showing that there is no real limitation or barrier from one category to the other. Finally, this overview will be completed by the contribution of quantum mechanics over the past hundred years, which opened the way to the current representation of all varieties of known carbons.

1.1. The alchemy of carbon

Coal derived from animal or plants was the first source of carbon utilized by mankind as a result of mastering fire. The word “carbon” comes from the Latin

“*carbo*” meaning coal, which is the natural product obtained from the controlled combustion of vegetal matter. Evidence of its first utilization appears in the parietal art of Cro-Magnon man in the Lascaux caves in Dordogne, France, painted some 15,000 years BC [VAL 00], (see section 1.5.5.4 on C^{14} dating).

During prehistoric times coal was utilized as a source of combustible material as a reducing agent for metals. Approximately 4,000 years BC in the Middle East, ovens capable of melting ores and reducing copper oxide were built using wood coal as the main combustible. Certainly, unexpectedly, a combustion chamber using a reducing atmosphere was built and later controlled. In this context, copper was the first metal to be exploited and utilized, leading to the bronze age.

Starting from this discovery, other metals were isolated. A remarkable case is iron produced during the reduction of iron oxide; this is not straightforward because, unlike copper, metallic iron is not stable and naturally converts into carbides, such as cementite, whose formation control was achieved empirically. Historians have agreed to attribute this invention to the Hittites approximately 1,500 years BC, which presents a millstone for both agriculture and the art of conflict [MOH 90] and was followed by technical progress in metallurgy.

During antiquity, the great civilizations developed applications of metallurgy in various areas, which strongly influenced subsequent developments up to this day. For example, Egyptians used coal prepared from plants as a remedy for gastric problems, relying empirically on its property for great absorbance and natural selectivity, charcoal was utilized as a pigment for make-up (called “*khôl*”) and also for tattoos, but also as the main constituent of bitumen used to prepare mummies [VID 90].

The Chinese have used coal in various mixtures, especially in Chinese ink and for the preparation of the black powder [TEM 00]. The black ink was made of a colloidal suspension of charcoal and has been used since 2,500 years BC for writing, calligraphy, and painting on both paper and silk. The constituents of the black powder are potassium nitrate, sulfur, and coal.

Around 850 AD, Taoist monks developed a formulation of black powder similar to the one used nowadays and developed pyrotechnic applications and its explosive property. From that time onwards, the development of firearms, from rifles to canons, occurred first in Asia then spread to Europe in the Middle Ages (12th and 13th centuries) via the Arabs, changing military techniques worldwide. This invention is a significant outcome of the development of alchemy [BRI 99]; a science developed by the Arab civilization based on the Greek heritage, incorporating the discoveries made in Asia, and later brought to Europe, often through conflict.

1.2. Elemental carbon and its allotropic varieties

The fundamental understanding that preceded the birth of chemistry was the concept of the smallest elemental particles, also called atoms, which was laid out by the Greeks more than 25 centuries ago. The scientific work undertaken in western Europe during the 16th and 17th centuries slowly converged towards the creation of modern chemistry with the definition of atoms described nowadays. This new science evolved from the original work of Antoine Laurent Lavoisier and the publication of his dissertation in 1789 entitled *Traité élémentaire de chimie présenté dans un ordre nouveau et d'après les découvertes modernes* [LAV 89]. In Figure 1.1 we have reproduced the table of simple substances established by Lavoisier where the word “*carbone*” appears in the non-metallic substances in front of its earlier name “*charbon pur*”.

By studying this table, where chemical elements lay next to “light” and “calories”, it can be clearly seen how difficult it has been to achieve a rational classification. This essential yet tedious work was accomplished by a large number of chemists in the 19th century with the implementation of symbols to represent chemical reactions. In addition, the attribution of atomic masses associated with these reactions was a key development instigated by J. Dalton in 1808 [DAL 08]. It is only at the end of the century that the periodic table was elaborated by Mendeleev (77 elements were included in 1889) and accepted by the chemist community.

Returning to elemental carbon, it is worth mentioning that the identification of all natural forms was a slow process that took place in the 19th century. Two crystalline allotropes extracted from mines have been known for a long time: graphite (from the Greek *grapho*) and diamond (*adamas*), both of which consist primarily of carbon. Comparing diamond’s extreme hardness and its transparency to the easily cleaved graphite and its shiny black color, the fact that they share a common composition was not obvious. Previously they were compared and sometimes confused with quartz and molybdenite, respectively. The history of diamond as a precious stone seems to start in India during antiquity prior to reaching Europe. It was already mentioned during the 4th century BC in a manuscript written in Sanskrit, and it is interesting to note that the oldest printed book was named *Diamond Sutra*, apparently made in China in the 9th century AD (currently kept at the British museum in London). Much later, Marco Polo described in the documentation of his travels [NEW 50] the use of diamond in China for parures. Finally, the experiment of Sir H. Davy in 1814 is noteworthy, in which he burnt his wife’s diamonds to confirm that the amount of carbon dioxide formed is equivalent to that obtained from coal or graphite [NEW 50]!

	Noms nouveaux.	Noms anciens correspondans.
<i>Substances simples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.</i>	Lumière.....	Lumière. Chaleur. Principe de la chaleur. Fluide igné. Feu. Matière du feu & de la chaleur.
	Calorique.....	Air déphlogistiqué. Air empirical. Air vital. Base de l'air vital. Gaz phlogistiqué.
	Oxygène.....	Mofete. Base de la mofete. Gaz inflammable. Base du gaz inflammable.
	Azote.....	Soufre.
	Hydrogène.....	Phosphore.
	Soufre.....	Charbon pur.
	Phosphore.....	Inconnu.
	Carbone.....	Inconnu.
	Radical muriatique.	Inconnu.
	Radical fluorique.	Inconnu.
<i>Substances simples non métalliques oxidables & acidifiables.</i>	Radical boracique.	Antimoine.
	Antimoine.....	Argent.
	Argent.....	Arsenic.
	Arsenic.....	Bismuth.
	Bismuth.....	Cobalt.
	Cobalt.....	Cuivre.
	Cuivre.....	Etain.
	Etain.....	Fer.
	Fer.....	Manganèse.
	Manganèse.....	Mercure.
<i>Substances simples métalliques oxidables & acidifiables.</i>	Mercure.....	Molybdène.
	Molybdène.....	Nickel.
	Nickel.....	Or.
	Or.....	Platine.
	Platine.....	Plomb.
	Plomb.....	Tungstène.
	Tungstène.....	Zinc.
	Zinc.....	Chaux.
	Chaux.....	Magnésie.
	Magnésie.....	Baryte.
<i>Substances simples salifiables terreuses.</i>	Baryte.....	Alumine.
	Alumine.....	Silice.....
	Silice.....	Terre calcaire, chaux. Magnésie, base du sel d'Epsom. Barote, terre pesante. Argile, terre de l'alun, base de l'alun. Terre siliceuse, terre vitrifiable.

Figure 1.1. Table of simple substances proposed by A.L. Lavoisier in his book entitled *Traité élémentaire de chimie* in 1789 [LAV 89]

During this same century the concept of allotropy (*allos tropos* in Greek), was introduced by Berzelius around 1840 which described the different physical properties that can be obtained from a pure substance. This concept and its corollary describing the structure (polymorphism) seemed to have appeared for the first time in the work of Mitscherlich starting in 1822 [MIS 22], [MIS 23]. An overview of the situation at the beginning of the 20th century is provided by the book of Henry Le Chatelier, *Leçons sur le carbone* (Le Chatelier, 1908). In the second chapter on physical properties we can read the following:

“*Le carbone non combiné se présente sous des formes très curieuses: carbone amorphe, graphite et diamant.*” (pure carbon is present in very curious forms: amorphous carbon, graphite and diamond)

Following the discovery of X-rays by W.H. and W.L. Bragg in 1913 [BRA 13], these authors identified the cubic structure of diamond and, several years later, Hassel and Mark [HAS 24], and simultaneously Bernal [BER 24], discovered the structure of hexagonal graphite. In addition to these crystalline phases, Le Chatelier mentioned an amorphous carbon, which is the general name for all graphite-like carbons, from natural sources (coal mine and other carbon-rich sediments) or synthetic carbons, such as charcoal obtained by a controlled combustion under the influence of temperature. An organic substance is decomposed by the thermal process known as pyrolysis under a controlled atmosphere, by temperature in the range of 500-700°C leading to carbon-based residues or by the carbonization process at higher temperatures (typically going from 700° to 1,500-2,000°C). The study of structure associated with the development of X-ray diffraction of these non-crystalline carbons mainly occurred in the middle of the 20th century ([WAR 41], [FRA 50], [FRA 51]). There are studies of the graphitization process, such as a progressive crystallization into graphite, sometimes an incomplete process, by thermal treatment above 2,000°C (*Les carbones*, Volume 1, Chapter 1, 1963). Consequently, research on the ideal conditions to obtain these non-crystalline forms, their characterizations, and applications as carbon-based materials were a great source of interest in the last century, as the associated developments were strongly related to the successive industrial changes that have shaped our contemporary societies.

1.3. Novel molecular varieties

After World War II, and in the second half of the 20th century, the exponential development in scientific research led to huge advances in the science of carbon with the discovery of new and unexpected structures (presented in Figure 1.2). Focusing on the main events, it is necessary to first mention the unsuccessful

attempts by Von Baeyer in 1885 [BAE 85] to prepare long, linear carbon-chains prior to the work in polymer chemistry. Research on this topic ceased for almost a century and the existence of linear carbon-chains was only later reported in the 1960s by Russian scientists [KUD 93]. They were unfortunately called “carbynes”; currently, they are well-identified structures despite a stability issue. This form of carbon has a white color and is in fact a conjugated polymer described as either of the following two limited structures (alpha and beta forms): poly-yne (alternation of triple and simple bonds) and cumulene (conjugated type structure).

More recently, the discovery of a spherical molecule made of 60 carbon atoms, which was initially called “footballene”, led to great excitement within the chemist community [KRO 85]. This stable icosahedral molecule was not identified in interstellar space, but was prepared in the laboratory by the vaporization of graphite. It is one of the regular polyhedral structures described by Archimedes and Plato in the antiquity, and it follows the criteria described by Euler in the 18th century where 12 pentagons can be surrounded by any number of hexagons, 20 in the present case, to close up completely. Due to the technical development of synthetic methods, especially with the use of electric arcs [KRA 90], large quantities of C₆₀ and other derivatives also members of this new carbon family named “fullerene”, were described in the past years (Dresselhaus, Dresselhaus and Ecklund, 1996).

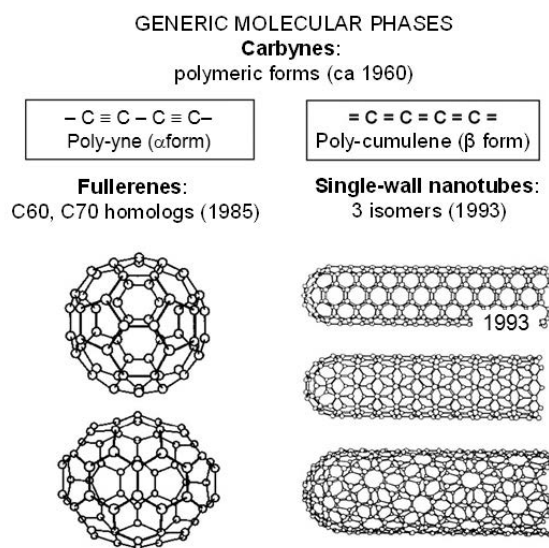


Figure 1.2. Schematic representation of the novel molecular phases of carbon discovered at the end of the 20th century

Finally, the last discovery chronologically, also resulting from the curvature of a graphene sheet describes the formation of single-walled carbon nanotubes often referred to using the abbreviation SWCNTs (see Figure 1.2). Since the very accurate measurements by transmission electron microscopy performed by Iijima and Ichibashi [IJI 93] and the work of Bethune *et al.* [BET 93], the existence of SWCNTs were confirmed in 1993, with diverse cylindrical shapes of an ideal plane of graphene.

It is worth mentioning that filaments with diameters in the nanometer range with several rolled sheets were already known for half a century at that time, as will be discussed later. This new shape is the ultimate molecular version of an atomic structure that, as in the case of fullerenes, raise questions regarding the topology (study of curved atomic surfaces), but also in terms of some fundamental thermodynamic considerations.

These points are presented in the next chapter, associated with the notions of allotropy and polymorphism, with an extension towards possible virtual phases deduced from theoretical calculations of cohesion energies.

1.4. Natural forms

Divided into two families, we will present the natural carbons by briefly describing the wealth of phases that have been discovered and the subsequent benefits uncovered for artificial (man-made or anthropomorphic) carbons.

1.4.1. *Carbon: witness of the evolution of the universe*

Carbon atoms are created by the nuclear fusion reaction that takes place in the heart of stars using light elements. It is generally described as the fusion of three alpha particles (helium nuclei). It is the fourth most abundant element in the solar system after hydrogen, helium, and nitrogen, which also play a role as a carbon source. Similarly to other inorganic species, carbons are identified as part of extraterrestrial objects, such as meteorites, comets, and interstellar dust [ROB 97].

Interstellar matter exists under two very different forms, gas and dust. The former is composed of molecules, atoms, or ions, and constitute 99% of the total interstellar mass. The latter is extremely interesting because of its subdivision into two highly divided dust families, either silicate or carbon based. It is useful to remember that in astrophysics only the emission (or the extinction) of electromagnetic waves can be related to the identification of extraterrestrial matter. That is how molecular models were suggested [LEG 84] to explain the infrared

spectra recorded for polycyclic aromatic hydrocarbons (PAH) without completely solving the problem. Carbon-containing dust can also be characterized by absorption in the ultraviolet (UV) spectra (at 217.5 nm), the origin of which is currently discussed by comparison to model compounds prepared in the laboratory ([PAP 96], [CHO 03]).

The chemistry and isotopic distribution of meteorites or fragments of planet that come from the Moon or Mars, in particular, are collected and analyzed in order to develop a coherent model for the formation of the solar system. This is how several carbon phases were identified, including diamond, which can be found in craters resulting from impacts and the subsequent structural transformations of natural carbon due to a shockwave. In addition to the diamond and graphite phases, carbynes were found in the Ries crater in Bavaria as early as 1968 [ELG 68] and later in other craters such as the Allende crater where nanoparticles of curved graphite resembling the structure of fullerenes or “onion-like” multigonal structures were seen using electron microscopy [HAR 03]. Amongst the inorganic dusts found in chondrites, which are structures that initially appeared in the protosolar nebula, the analysis revealed mostly diamond, a small amount of graphite, and some silicium carbide. These dusts were identified to be more ancient than the solar system and certainly originated from supernovae. Within these carbon chondrites it appears that the formation of diamond nanoparticles is extremely important as a benchmark for various events of interest in astrophysics [HAG 99].

The mechanisms leading to the formation of these molecular species in the interstellar space, especially nuclear reactions using light elements and the subsequent interstellar chemistry that took place producing an immediate isotopic effect, are the cornerstones that led to our current understanding. In particular to get a panoramic view of the extreme diversity of carbon-based materials coming from space, these phases need to be compared to the natural and artificial phases known on Earth.

1.4.2. *Natural carbons from Earth*

The origin of natural carbons is almost essentially related to the mineralization of organic compounds from living matter which occurred under the joint effects of biological degradation, temperature, and pressure; sometimes the catalysis of various carbon-containing products of different compositions (percentage of carbon greater than 50%) are isolated and characterized. They rank amongst fossil combustibles and are very often marine sediments dating from the cold period of the Carboniferous. They are kerogens, insoluble organic matter, dispersed in sedimentary rocks, which are the precursors of oil and other natural derivatives, coals, lignites, and peats, and crystallized carbons (graphite and diamond) [VAN

61]. Therefore, these natural compounds were created under very different conditions, not only in terms of the kinetics involved, but also regarding the diversity of chemical compositions presented by the constitutive plants as introduced as part of the global carbon cycle.

The nature and proportion of hetero-elements, such as hydrogen, oxygen, nitrogen, or even sulfur, coming from their precursors is an essential part of the geochemical transformation of the sediments, which give rise to various intermediate compounds [DUR 80]. Schematically the main steps leading to the maturation of organic matters are diagenesis (followed usually by a catagenesis stage), which occurs under the influence of external factors both chemical and microbiological, and the metamorphosis, mineral transformation under the influence of external constraints such as temperature, pressure, or even shear forces. These physico-chemical transformations, which occur in the parent rock, initially create molecular gas and liquids, such as natural gas, oil, and heavy oils.

When diagenesis is advanced the heavy compounds left are bitumens or asphaltenes, which are soluble in the common organic solvents associated with some insoluble sediments such as kerogens [MON 97]. In the presence of a more developed metagenesis process different coal ranks, such as anthracites, which are completely fossilized, are obtained with compositions sometimes reaching pure carbon. This evolution of the sediments is linked to their depth of burying and the resulting geothermal gradient, which also depends on events that occurred at geological timescales in the direct surroundings of the parent rocks.

A simple way to classify carbon-based materials and to represent all families of chemical transformations is to build a Van Krevelen diagram [VAN 61], initially used for kerogens [DUR 80] and later expanded to all carbons. On this simplified diagram, presented in Figure 1.3, we have shown each maturation stage as a function of the atomic ratios hydrogen : carbon (H/C) versus oxygen : carbon (O/C). On this chemical base we are able to identify three main types of evolution, initially based on kerogen, which is the most common fossil matter found in the Earth's crust, having a chemical composition very similar to natural carbons [MON 97].

The thermal evolution or maturation of these fossil molecules follows some general rules of evolution, which suggest that the loss of oxygenated compounds occurs first, followed by the loss of hydrogenated compounds. Consequently, it is possible to establish some general structure-properties relationships. Therefore, under the influence of temperature the process of coal formation in nature, coking in the coal industry, or carbonization in laboratories of an organic molecule occurs. These processes are linked to the antagonist effects of hydrogen (an indicator of 2D polymerization) and oxygen (a cross-linker), which are associated with specific structural and physical changes [OBE 80]. This approach highlights a similar behavior

for both natural and artificial carbons and emphasizes the potential of these fossil fuels as materials. Nonetheless, the understanding of the carbonization and graphitization mechanisms, considered as the complete crystallization of amorphous carbons, has led to their utilization as geothermometers in specific conditions [BEY 02].

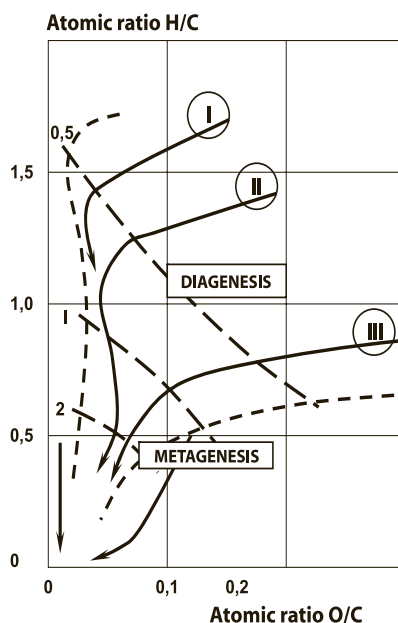


Figure 1.3. Example of a Van Krevelen diagram [VAN 61] representing the thermochemical evolutions of the main kerogen families and of some natural carbons [DUR 80].

(I)= Aliphatic hydrogen-rich sediments from marine sources such as planktons;
(II)= Lacustrine sediments containing hydrogen associated with aromatic molecules and some oxygen; (III)=oxygen-rich sediments from higher land plants

The complete metamorphic evolution, occurring at high temperature and under high pressure, leads to the formation of crystalline phases such as graphite and diamond. We can find natural graphite with a flake-like shape at the interface of all crystalline ground rocks of the crust and often associated with inorganic impurities (mica, quartz, calcite, etc.). The most abundant mines currently in use are those in Sri Lanka, Madagascar, Canada, Russia, and China. To obtain diamonds, it is necessary to produce very high pressure, equivalent to that found 150 km deep in the Earth's crust. To enable the harvesting of these diamonds, there is a need for a volcanic magma to carry them up closer to the surface of the earth. These lava are generally called kimberlite (or lamproites) dating from the Cretaceous period or sometimes even older [CAR 02]. They can be found in the oldest part of the crust, in

South and West Africa (Kimberley region), North America, and Brazil, Russia, India or in Australia. These natural diamonds are classified according to their quality, size, and shape (the commercial unit in use is the carat, corresponding to 0.2 g); their geographical origin is determined by the type of defects and impurities giving specific colors, and linked to the inclusion of inorganic compounds or noble gases [HAG 99].

The quest for diamonds gems has been ongoing since ancient times. More so than gold, it carries a symbolic value as a gemstone, and was considered sacred by some civilizations. This should not hinder its high commercial value and its numerous industrial applications which relate to its remarkable physical properties, transparency when pure, brightness, and hardness. There have been many attempts to increase the production of diamond by the use of synthetic methods since the first experiments of Hannay and Moissan at the end of the 19th century [CAR 02]. They reported the successful preparation of fluor and were apparently able to find some tiny fragments of diamond in the cast iron (Le Chatelier, 1908). Nowadays, there are several processes allowing the preparation of synthetic diamonds, which will be reviewed later.

1.4.3. *Comparison between natural and artificial carbons*

Table 1.1 presents a summary of the different carbon phases known to date that have been prepared under a variety of different conditions, often not well-defined. It is worth mentioning that those that have come from space are created by an abiogenic process and can be very ancient, up to several billions years, whereas those created on Earth have essentially resulted from the mineralization of organic compounds which are several million years old. It seems that the new molecular phases synthesized in the laboratory, fullerenes and nanotubes, exist naturally and are beginning to be detected in the cosmos. The fullerenes are found in trace amount in bitumen from Karelia in northern Russia and are called shungites [ZAI 96] and in planetary nebula. Additionally, very small amounts of carbynes have been detected in products extracted from diamond and graphite mines [CHU 03].

It is important to remember that living matter, especially vegetal, is at the origin of all coals, kerogens, oils, and gaseous compounds that constitute the main source of energy used by mankind [MON 97]. The advance of each civilization can be assessed by following materialistic considerations, looking at the exploitation of energetic compounds, wood and coal, as combustible, then through their valorization as materials [HAL 03]. Hence, charcoal resulting from controlled combustion, has been used as a combustible but also as a filter due to its remarkable absorbency. From this viewpoint the comparison to artificial carbons using pre-established scientific and technological knowledge has been extremely fruitful as

discussed later. Finally, in this context of social and economic development, the environmental aspect and the usage of these resources in terms of supplying more readily renewable fuels, are factors that surfaced recently and that will certainly take a predominant role in the way current research.

Carbon varieties	Sidereal origin	Earth origin
Graphites	Meteorites Carbonaceous chondrites	Graphite mines
Diamonds	Presolar particles Meteorites	Diamond mines (cratons)
Carbynes	Meteorites (chaoites)	Traces in graphite and diamond mines
Fullerenes	Planetary nebula	Shungites
Nanotubes	-	Shungites?
Non-crystalline carbons	Cosmic dust Precursors (PAH)	Kerogens Coals of different rank

Table 1.1. *Summary of natural carbons occurrence*

1.5. Contribution from quantum mechanics

We will discuss the fundamental concepts of quantum mechanics, elaborated at the beginning of the 20th century, which have led to the classification of all carbon phases. Carbon is an element of the second line of the periodic table. The carbon atom has an electron structure composed of six electrons: $1s^2$, $2s^2$ and $2p^2$ quantified on atomic orbitals s and p; it possesses an atomic number (z) of 6, with an atomic mass of 12 for the most common isotope (for other isotopes see section 1.5.4). The sharing of its electrons allows the creation of various types of covalent chemical bonds (C. Kittel, 1970), called simple or multiple, through the hybridization phenomena. This is discussed subsequently and is the foundation for the electronic structures of the different allotropic varieties mentioned previously.

1.5.1. Homonuclear diatomic molecules

The sharing of electrons is based on the linear combination of atomic orbitals (LCAO) to form molecular orbitals [ATK 90]. The core (1s) and valence orbitals (2s and 2p) overlap to give two bonding orbitals and two antibonding orbitals by constructive and destructive interferences of the corresponding wave functions. These homopolar combinations are represented in Figure 1.4 from the classical energetic diagram for C_2 type hydrocarbons:

- part a: s and p_z orbitals are oriented towards the axis of the internuclear bond, creating a molecular orbital type σ with the corresponding symmetry axis;
- part b: p_x and p_y orbitals yield a second type of molecular orbital called π , with a nodal plan of symmetry.

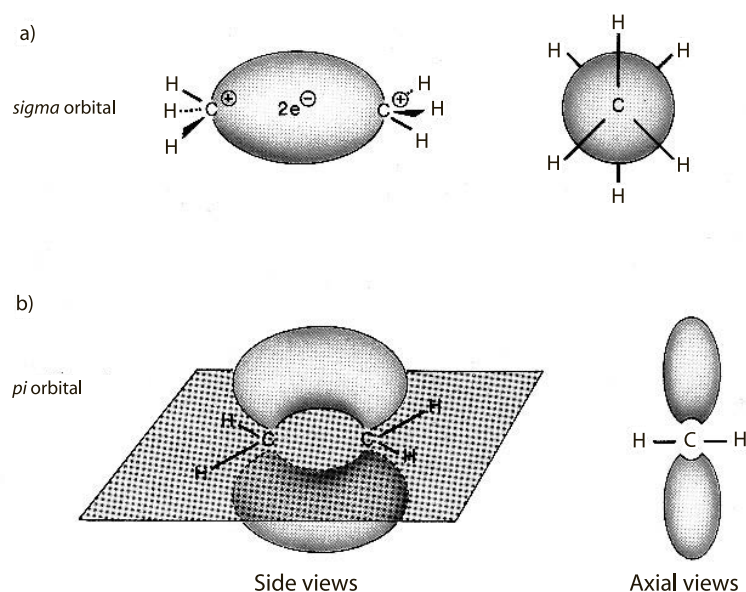


Figure 1.4. Views of sigma and pi orbitals: a) for ethane molecule (C_2H_6); b) for ethylene molecule (C_2H_4)

Through this description we have considered the classical examples representing the molecular orbitals s and p when two and four valence electrons, respectively, are shared between two carbon atoms [ATK 90]. The introduction of a linear combination of all atomic orbitals, displaying the appropriate symmetry, leads to hybridization phenomena allowing for the formation of covalent bonds directed towards and stabilized by the initial overlapping of atomic orbitals. In the case of carbon, the construction of these orbitals leads to three types of bonds classified as follows:

- linear hybridization sp^1 with a bond angle of 180° ($C\equiv C$).
- trigonal planar hybridization sp^2 with a bond angle of 120° ($C=C$).
- tetrahedral hybridization sp^3 with a bond angle of $109^\circ 28'$ ($C-C$).

These different types of hybridizations are associated with the coordination number of the bond and indicate the number of chemically linked adjacent atoms; these define the polymorphic varieties already discussed and are considered to be polyatomic assemblies (C_n).

Historically an important point has been the chemical notion of conjugated molecules; the origin of which can be traced back to Kekule's proposal in the 19th century describing the equilibrium between the mesomeric forms of benzene. Since then, the notion of delocalized electrons has been extended to all molecules, linear or cyclic, bearing π electrons with multiple bonds [SAL 90].

The electronic structure of such polyenes has been studied using quantum mechanics, in particular by using Huckel's rule regarding the chemical stability of neutral aromatic assemblies containing $(4n + 2)$ π electrons [ATK 90]. These assemblies made of benzene rings are the most stable and are called PAHs, as already mentioned. The repartition of an infinite paving of aromatic hexagons defines a nodal plane called graphene, which is at the origin of hexagonal graphite.

This infinite 2D electronic structure can be calculated using monoelectronic approximations also referred to as Huckel's method and generalized Huckel's method, based on the model of molecular orbitals. They provide an explanation for the delocalization of π electrons and the conducting property observed for graphite and other related structures [HOF 88].

1.5.2. *Curved surfaces: the rehybridization phenomena*

The discovery of fullerenes and carbon nanotubes has led to the reconsideration of sp^2 hybridization, initially defined in the case of planar symmetry. Moreover, the curved plan of graphene implies the loss of the 100% pure sp^2 character: this is the process of rehybridization described by Haddon [HAD 92] who has demonstrated that a sp^3 character is reintroduced in the π orbital as a function of the local distortion when the symmetry of the nodal plan is not respected anymore. The result obtained from quantum mechanics calculations is presented in Figure 1.5 for C_{60} and the larger fullerenes known; hence, the chemical bond can have as much as 10% of sp^3 character. Associated with carbon-based five-membered rings, the structure can be curved implying a deficit in π electrons, which affects the electronic properties of fullerenes and, to a lesser extent, those of other carbons with curved surfaces, such as nanotubes.

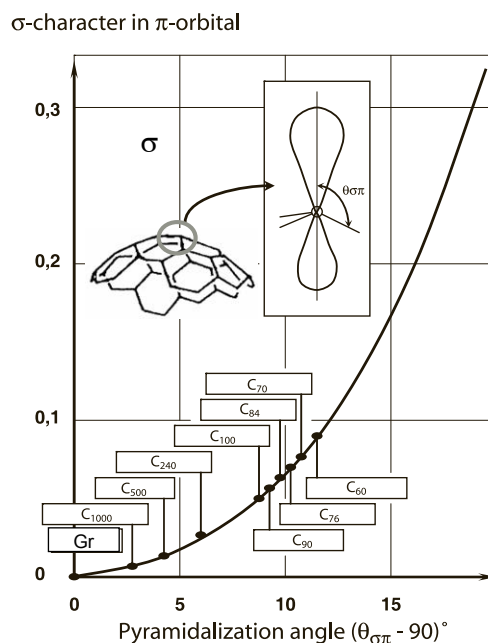


Figure 1.5. Rehybridization as a function of the pyramidalization angle for different fullerenes indicating the percentage of induced sigma character (adapted from [HAD 92])

1.5.3. Presentation of the crystalline forms

The quantum mechanics of these structures elucidates the correlation between the microscopic description and the macroscopic classification of carbon-based solids as defined previously (see Table 1.1). Also, there is a relation between the type of bonding, simple or multiple, and the 3D structural arrangement. As mentioned previously, the type of bond is related to the number of close neighbors or coordination number, and is associated with a structural dimensionality. An empirical rule, proposed by Joffe and Riegel in 1960 [DEL 97], gave the coordination number (z) as being equal to the full dimensionality (D) plus 1.

In Table 1.2, according to a previously mentioned proposition [HEI 97], we have classified the main structural characteristics of the carbon phases based on the respective types of orbital hybridizations (only the case of carbynes remains unique, see Figure 1.2). The first important piece of information concerns the bond length, which gets shorter when the quantity of valence electrons shared increases, exhibiting higher binding energies. This fact leads to high cohesion energies and

very stable thermodynamic phases (see Chapter 2). Another point is the classification of the different polymorphic varieties as a function of their inherent structural dimensionality, in agreement with the empirical rule of Joffe and Riegel, for the case of classic phases, but inapplicable to curved atomic surfaces, characterized by a non-integer value for their hybridization (fractional parameter ϵ is related to the rehybridization phenomena). The most important point is the influence on the anisotropy of the physical properties, which are associated with the type of bonding present, and which produces their fundamental characteristics. For example, in Figure 1.6, the structures of cubic diamond ($D = 3$), which has a 3D structure and is an insulating material with almost isotropic properties, and hexagonal graphite, which has a near 2D structure ($D = 2$), is lamellar, and is a conducting material which illustrates the presence of essentially anisotropic properties.

Carbynes, monoatomic polymers, are electronically monodimensional, which is similar to the case of single-walled carbon nanotubes (SWCNTs). We will see the influence of specific atomic arrangements on their relationships, but also the intrinsic differences between these polymorphic varieties in the following chapters. In all graphitic structures there are Van Der Waals interactions in addition to the covalent bonds described. These weak interactions take place predominantly between two graphene sheets, inside a batch of single-walled carbon nanotubes or in fullerenes stacks [GIR 02]. They are significant interactions leading to intercalation or insertion properties, which can provide new materials and a succinct description of this will be given later.

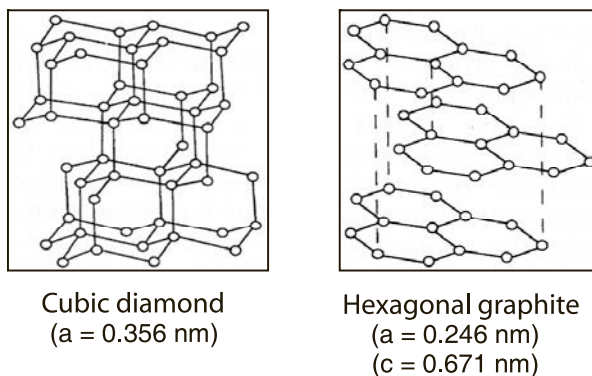


Figure 1.6. Crystallographic structures observed at room temperature under atmospheric pressure for cubic diamond and hexagonal graphite (stacking ABA type of graphene planes with a distance $c/2 = 0.3354$ nm)

C ($1s^2, 2s^2, 2p^2$)				
Hybridization types	$s p^3$	$s p^2$	$s p^1$	$s p^{2+\epsilon}$
Crystalline forms	Diamonds	Graphites	Carbynes β^*	Fullerenes/ nanotubes
Coordination number, z	4	3	2	3
Physical dimension, D	3	2	1	0.1
Length, d (Å)	1.54	1.40	1.21	1.33/1.40
Bond energy (eV/mol)	15	25	35	> 25

* Carbynes α : alternant simple and triple bonds

Table 1.2. *Fundamental physical characteristics of main carbon phases
(values obtained at room temperature under atmospheric pressure)*

1.5.4. The isotopes of the carbon atom

Stable and unstable isotopes of carbon exist; hence, aside from the common isotope with an atomic number equal 12 (six protons and six neutrons), there are the stable isotope 13 with a natural abundance of 1.11%, and the unstable isotope 14 in trace amount (average abundance around 10^{-12}), which is central to radio-chronology.

Isotope 13 presents a nuclear spin (I) of 1/2 in contrast to isotope 12, which gives it a very important role not only for nuclear magnetic resonance (NMR) studies but also for other physical properties related to atomic vibrations, such as thermal conductivity. It is also a useful tool for problems related to the dating of meteorites, or in kerogens [DUR 80] due to modern separation techniques.

Isotope 14 has a natural radioactivity, which enables its use for archeological dating covering prehistoric times and antiquity [AIT 90]. This method is simple in principle (reminder in Box 1.1) but difficult in practice, due to obvious risks of contamination. There are calibration issues related to changes in the concentration of C^{14} over time and in different geographical zones. However, these changes have led to modern paleoclimatology, highlighting major changes that occurred during Earth's history. The dating range afforded by this technique is between 500 and 50,000 years with an accuracy of a few percents compared with other physical methods that have been developed.

This technique has been predominantly used to date all carbon-based pigments used by mankind as described at the beginning of this chapter, especially those used in prehistoric cave with wall paintings [VAL 00].

Box 1.1. Principle of radiochronology

Natural radioactivity is the emission of particles or electromagnetic radiation by an unstable nucleus whose disintegration speed is directly dependent on the nature of the nucleus itself. In general this “parent” nucleus gives rise to a stable “daughter” nucleus. The fundamental relationship of radioactivity gives the number of unstable “parent” nuclei, $P(t)$, as a function of the initial number, P_0 :

$$P(t) = P_0 \exp(-\lambda t) \quad [1.1]$$

with λ being the decay constant of the corresponding nucleus.

If P_0 is known and if $P(t)$ is measurable, the age of the system is determined by the following equation:

$$t = 1/\lambda \cdot \ln(P_0/P(t)) \quad [1.2]$$

In general nuclear physicists define half-life (T) as the time necessary for half of the initial number of nuclei to decay, such as $T = 0.693/\lambda$.

From these equations, it is possible to calculate the age of a closed system for which there has been no addition or subtraction of nuclei from the environment.

This method is the principal of the dating technique used for carbon 14, also called radiocarbon, as initially reported by Libby in 1952, who also determined its half-life, $T = 5,568 \pm 30$ years [LIB 52].

Moreover, C^{14} is the result of a nuclear reaction between a neutron and a nitrogen nuclei after the loss of a proton. It decays by emitting a β particle (electron) and yielding a nitrogen nucleus (N^{14}). Hence, 1% of C^{14} atoms are disintegrated after 83 years.

An equilibrium has been reached between the production of C^{14} by cosmic irradiation and its natural decay. Hence, all living organisms exhibit the same isotopic distribution than Earth's atmosphere and oceanic carbonates. When a living system dies, exchange with the environment stops and the inflow of carbon from the outside is interrupted. From this moment onwards, the quantity of C^{14} declines according to the radioactive decay law. By using modern titration methods, based on mass spectroscopy and β irradiation detectors, the half-life currently accepted is $T = 5,730 \pm 40$ years, taking the year 1950 of our era as the reference point [LAN 92].

1.6. Conclusion

In this first chapter we have shown that carbon is one of the most important elements in astrochemistry, in part due to its nucleosynthesis in stars and subsequent presence throughout the universe, but also as a fundamental building block for life on Earth. The various carbon-based structures act as irreplaceable geological benchmarks of Earth's history. They have been closely related to human activity since the early hours of our species and correlate with the development of various civilizations, illustrated by the traditional fabrication of charcoal (Figure 1.7). Both natural and artificial carbons have many similarities in terms of properties, which are important to recent industrial applications in which they are used as energy sources or for the fabrication of various materials. A chronological review of the main applications since the 19th century, showing the strong link with fundamental research, was described by Derbyshire et al. [DER 95] and modern applications have been summarized by Marsh [MAR 97]. This huge wealth of knowledge is particularly highlighted by the presentation and the classification of all polymorphic varieties of carbon known to date. The discovery of new molecular phases has led to a renewal of interest for material sciences with the current developments in nanotechnologies. This organization will be presented at the structural level first, and subsequently, in relation to physical and chemical properties with an emphasis on the comparison between different polymorphic varieties.



Figure 1.7. Postcard of a charcoal fire taken about one century ago nearby Dax, in the southwest of France

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Chapter 2

Polymorphism of Crystalline Phases

A set of atoms or molecules that constitute a macroscopically homogenous system physically defined in space is called a phase, according to the usual thermodynamic definition. In general, we identify a phase as solid, liquid, or gas, and two questions have to be addressed. Firstly, in the case of condensed phases, how atoms or molecules hold together in a more or less ordered structure in relation to the chemical bonds that have formed and subject to the corresponding resulting gain in energy. Secondly, what is the process by which temperature and pressure can drive the change from one phase to another: what are the rules associated with a phase transition? These two aspects are part of phenomenological thermodynamics [BOC 68], which describes stable phases encountered for a given pure substance, in particular in the solid state when several crystalline forms exist. As mentioned in Chapter 1, carbon atoms can form different types of covalent bonds and therefore exist as allotropes or polymorphs depending on the diversity of morphologies observed. Note that the description of the mechanisms involved will be described later (see Chapters 3 and 5).

2.1. Thermodynamic stability and phase diagram

Following a phenomenological approach, we will define within a phase diagram the area of stability for the solid phases of carbon mentioned in Chapter 1. Furthermore, the conditions required to go from one allotropic variety to another will be examined from the stable phase of reference, which is hexagonal graphite. Hence, in Box 2.1 the criteria of thermodynamic stability are outlined prior to

discussing any metastable or unstable state. The analysis of the phase diagram of carbon affords a wealth of information and raises many questions, especially in relation to the new molecular phases. This is naturally followed by the definition of the associated equations of state and cohesive energy (E_c); the latter being determined as the energy necessary to bring together atoms that are initially infinitely far from each other at 0 K. As a result of the enormous development of computational power, it is now possible to compare the cohesion energies of atomic or molecular assemblies based on the concept of crystalline symmetry and the principle of optimal stacking, initially developed by Kitaigorodskii [KIT 73]. This step has enabled theoretical forecasts on new and not yet experimentally identified phases. In a second part, we will present these virtual phases and compare them with known real phases by evaluating the resulting physical properties, for example comparing ultra-hard virtual phases with cubic diamond.

Box 2.1. Reminder of the definition and criteria for thermodynamic phase stability

The thermodynamic equilibrium of a phase is characterized by a set of extensive parameters, which are associated with intensive parameters in an energy representation: usually these are the temperature (T), the pressure (P) and the chemical potential (μ) in the case of several components reacting together. In the absence of a chemical reaction, the variables T and P make it possible to define the state of a system in agreement with Gibbs phase rule [MAR 95]. The associated function of state is then the free enthalpy (or Gibbs energy) $G(P, T)$ given as:

$$G = H - TS \quad [2.1]$$

where H is the enthalpy and S the entropy of the system and both being also functions of state. If the only intensive variable is temperature the corresponding state function is free energy F ($F = U - TS$, U being the internal energy).

In thermodynamics, as in mechanics, the steady state of a system is determined by state function extrema with stability conditions, and through analysis of the derivative: these are the Gibbs-Duhem criteria of stability [BOC 68]. In the absence of any chemical reaction, a thermodynamically stable state corresponds to an absolute minimum of this state function. Thus, when under the action of temperature or pressure the value of the free enthalpy of a second phase becomes lower than the current one, there is a first-order phase transition of

structural origin between two solid phases. This type of phase transition, presumably reversible, is governed by the Clapeyron equation with a specific enthalpy variation at the transition (ΔH):

$$dP/dT = (1/T) \Delta H/\Delta V \quad [2.2]$$

where ΔH is the difference of the molar enthalpy of the two phases and ΔV is the difference between their respective molar volumes.

Moreover, a homogenous and stable phase is characterized by an equation of state, an expression that connects the thermodynamic variables already defined and makes it possible to describe its physical state. In the case of a solid there is not a single equation but a general formulation has been proposed $P = F(V, T)$, which is called the Debye-Gruneisen equation (Mr. Gerl and J.P. Issi, 1997). In this kind of expression a relevant thermodynamic parameter is the coefficient of compressibility or its reverse the modulus of rigidity taken at the absolute zero:

$$B_0 = -V_0 (dP/dV) \quad [2.3]$$

where V_0 is the volume of the solid phase at the equilibrium. This equation of state makes it possible to express the minimum of the free enthalpy (or free energy) according to experimental thermodynamic parameters.

2.1.1. *Stable and metastable phases*

The thermodynamic stability of a phase corresponds to an absolute minimum of the state function considered, in general, the free enthalpy, but other local minima can occur, which will be at the origin of unstable or metastable states. The occurrence of a phase transformation will be determined by the difference in free enthalpy ΔG , between the two states and by the possible thermodynamic pathway between them. Figure 2.1 is a schematic representation of two typical evolutions of the free energy according to the reaction coordinate:

a) between the two thermodynamic states A and B there is no energy barrier; the necessary energy of activation (E_a) is close to zero and state B is then unstable. We need a quenching phenomenon, with a sharp variation of an intensive variable such as T or P, to obtain often this type of non-crystallized frozen state;

b) between these two states, to go from B towards A, there is a strong energy barrier such as $E_a > kT$ (thermal energy). There is then a local minimum of energy and the possibility of obtaining a metastable state with a lifetime that is either long

enough or infinitely long for an observer. It is called a kinetic state: under particular conditions it can evolve, even very slowly, to the thermodynamically stable state. This type of situation is favored by strong chemical bonding energy as in the case of carbon-based solids (see Table 1.2), which will involve high cohesion energy.

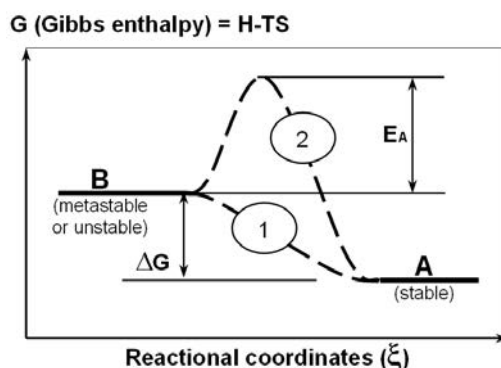


Figure 2.1. Schematic representation of the free enthalpy evolution during a state change: evolution of state B towards state A according to two possible reaction pathways 1 and 2

Moreover, in the presence of a catalyst it will be possible to decrease the energy barrier involved by modifying the reaction process and the associated pathway, thus the kinetic aspect of the transformation. It is then possible to arrive at the same final state A, starting from B, even if several metastable intermediate states were possible. This remark shows the importance of the experimental conditions, which will be discussed later.

2.1.2. The phase diagram of carbon

Many reports, in particular those of Whittaker [WHI 78] and Bundy *et al.* [BUN 89], have led the way to the current phase diagram of carbon, which is established assuming that each phase is composed of an infinite number of atoms (C_∞). This diagram, shown in Figure 2.2, is unique amongst pure substances; it is a summary of a large number of publications on specific points [BUN 96] that will be described.

Previous studies [ROS 38], based on the comparison of the heat of combustion for graphite and diamond, have shown that graphite is the most stable phase under normal conditions. The direct consequence of this thermodynamic stability is that all other metastable phases can be transformed into graphite under the influence of temperature if a thermal treatment is applied under inert atmosphere. This diagram presents three solid phases, graphite, diamond, and carbyne with their respective

domain of stability and a first triple point (T^1) where diamond, graphite, and liquid all coexist. In addition, liquid and gas phases exist at very high temperatures, with a classical second triple point (T). These two triple points are presented in Figure 2.3 where the area of low pressure is detailed with the localization of the zone of partial stability for carbynes.

A mechanism for the transformation of graphite into carbyne by the opening of chemical bonds around 2,600°C has been described [WHI 78]. It has the advantage of allowing visualization of the structural transformation by suggesting two different types of transformation (see section 2.1.4 and Figure 2.6).

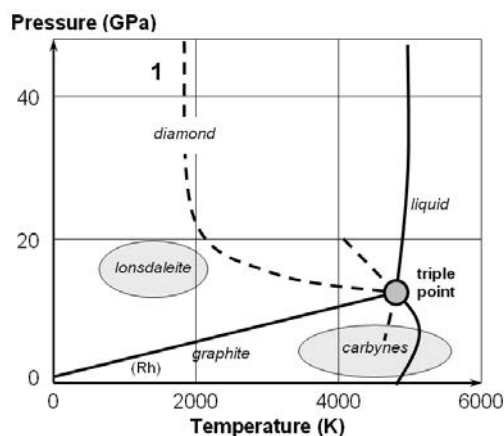


Figure 2.2. Thermodynamic phase diagram (P , T) of carbon (adapted from [BUN 96])

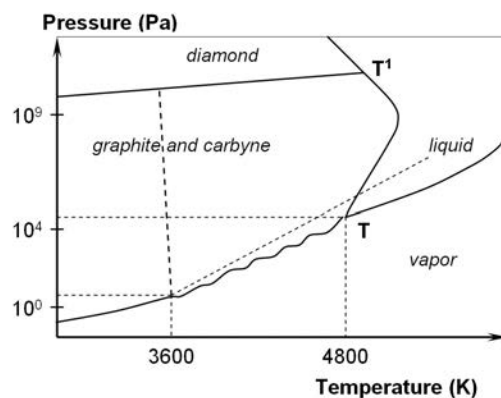


Figure 2.3. Part of the phase diagram of elemental carbon under low pressure and high temperature (adapted from [WHI 78])

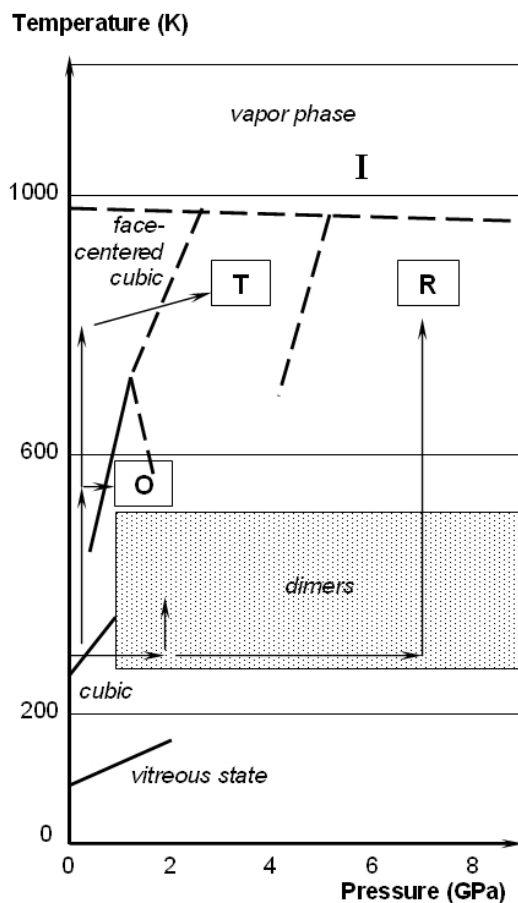


Figure 2.4. Diagram of transformation of fullerene C_{60} as a function of P and T ; the arrows show paths used for the synthesis of different (O, T, R) crystalline phases (adapted from [DAV 00])

We will now explicitly describe the essential characteristics of this diagram.

2.1.2.1. Transition lines between graphite and diamond

An important point is that structural studies on specific samples have shown that the graphite and diamond phases are not unique. There are lamellar polytypes that have a sequential stacking of graphene that is different to hexagonal graphite (see crystallographic stacking Figure 2.4), giving rise to a metastable variety, rhombohedral graphite [BOE 55], which has not yet been isolated as a pure material.

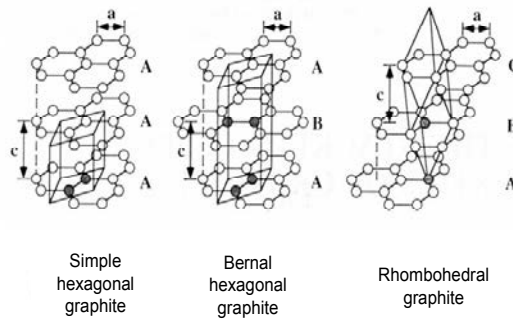


Figure 2.5. *Presentation of graphitic structures with different types of stacking and unit cells*

Diamond also has a hexagonal variety, discovered in 1960 and called Lonsdaleite [BUN 67]; it is stable in a small area of the phase diagram (indicated in the L zone of Figure 2.2). Between these two main phases there is a transition indicated by a solid line. Established by the work of Simon and Bernard [BER 55], its domain goes from low temperature, with the point at 7 GPa/0 K all the way to the triple point graphite-diamond-liquid located at 12 GPa/5,000 K. This transition line confirms that graphite is the most thermodynamically stable phase under standard conditions, whereas diamond is only a metastable phase. The phase transition that is taking place is of the first order with a strong enthalpy because it is associated with a change of the coordination number (z) of carbon. The mechanism of this so-called reconstructive transition has been the subject of many theoretical studies; two key reports were authored by Kertesz and Hoffmann [KER 84] and Sandré and Cyrot-Lackmann [SAN 97] who suggested that the rhombohedral graphite phase acts as an intermediate polytype in the structural transformation of diamond. From an experimental point of view, in addition to the thermal transformation by heating at 1,500°C two main types of kinetic approaches have been successful: the utilization of a catalyst, often a transition metal solvated under strong static pressure, and a shockwave-based method resulting from a large deflagration and a sudden decompression, occasionally with the help of a catalyst [DEM 97]. According to Bundy *et al.* [BUN 96], there is a kinetic transformation (represented by a dash line in Figure 2.2) implying that under the effect of fast T-P cycles hexagonal graphite and lonsdaleite can be converted into cubic diamond [BOV 59]. This curve delimits the effective zone of metastability of graphite, demonstrating that when a large pressure is applied the cubic diamond phase is systematically obtained.

2.1.2.2. *Fusion lines and properties in the liquid state*

Fusion temperatures are located around 4,000-5,000 K because they require high transition enthalpy. A recent review [SAV 05], looked back at the pioneering work of Pirani in 1930, and reported an extensive study of this phenomenon with a special focus on the results obtained by intense laser pulses. This study led to the heat of fusion for graphite (120 kJ/mol), which is much lower than the heat of vaporization (730 kJ/mol), and indicated that the liquid phase should have a molecular nature. The fusion line on the top right of the triple point should present an azeotropic point (corresponding to a vertical tangent on the transition line of Figure 2.2), which led some authors to speculate on the possible existence of two distinct liquid phases [VAN 05]. There could be a transition between insulating and conducting liquid phases [WU 02] depending solely on the coordination number associated with each carbon atom, initially they would be tetra-coordinated, but could be simply tri- and bi-coordinated when placed under lower pressure. However, it seems extremely difficult to experimentally identify this type of phase transition.

Finally, it is important to mention that at high pressure, beyond the triple point T, the fusion of diamond has a slope dP/dT positive, determined with different specific techniques [DEM 97] and possible other highly symmetrical phases of high density which can be found (see section 2.3).

2.1.2.3. *Vaporization and characteristics of the gas phase*

At high temperature and under low pressure, after the area of the classical triple point T allocated at 0.2 GPa and around 4,800 K, by following the gas-liquid transition line (the critical point does not seem to be clearly defined), it becomes possible to vaporize graphite by the Joule effect or by using power lasers [SAV 05]. Thus, the heat of evaporation necessary (as listed above) is equivalent to the cohesive energy of the solid. The gas phase is composed of carbon atoms but also some unstable molecules such as C_2 , C_3 and some small linear polyatomic chains [THO 02] certainly being the recollection of a carbyne phase existing at lower temperature (see Figure 2.3). These molecules are at the source of the very rich chemistry of the gas phase, in particular in the case of the formation of molecular carbons at high temperature [KRA 90].

2.1.3. *Case of the molecular phases*

These newly discovered phases have not yet been added to the thermodynamic diagram of the carbon element shown in Figure 2.2. Hence, this new class of molecular phases with curved atomic surfaces can be considered as being made of a finite number of carbon atoms; this is the case of fullerenes (especially C_{60} and C_{70}) and carbon nanotubes in their ideal structures, which are single-walled graphene

tubes closed at both ends. This contrasts the case of classic carbon-based solids and their infinite number of carbon atoms, which implies that adding more atoms at the border does not affect the thermodynamic phase in place, which is already supposed as infinite. Moreover, in a diagram at thermodynamic equilibrium a phase transformation must be reversible [MAR 95] under conditions in which an intensive parameter is modified (see Box 2.1); this is not the case for either fullerenes or carbon nanotubes, where a cycle of chemical transformations appears to be compulsory. These considerations have led various authors to consider that these structures are independent pure substances with their own phase diagram, in particular in the case of the original fullerene of formula C_{60} , the only phase that has been fully studied in this regard [VAU 97].

At ambient temperatures C_{60} is a solid with a face centered cubic structure based on quasi-spherical molecules; they are icosahedra of molecular symmetry I_h , which turn on themselves independently from one another. Below 255 K these molecules lose part of their freedom of rotation, the C_{60} molecules are not equivalent anymore and the structure becomes simple cubic [HEI 91]. This is a first-order phase transition as demonstrated by structural and thermal studies [GRI 93]. The higher homolog C_{70} of lower molecular symmetry (symmetry D_{5h}) presents a more complex behavior, a solvent-sensitive crystallization process, and several structural transformations. Starting from a frozen monoclinic structure below 276 K, the crystal becomes compact hexagonal with two successive varieties, then rhombohedral and finally face centered cubic when the temperature increases [VAN 92]. These are typical behaviors for plastic crystals that exhibit a long-distance translational order with an orientational disorder depending on temperature and pressure [VAU 97].

At high temperature fullerenes do not seem to present a liquid phase, which contradicts the result of theoretical calculations, based on molecular dynamics [BRO 97]. In the case of C_{60} there is sublimation above 700 K which has a high value of the standard enthalpy of sublimation ($\Delta H = 181$ kJ/mol) [PIA 95]. Under the influence of pressure this molecule is not stable: placed under high pressure ($P = 15$ GPa) around $1,500^\circ\text{C}$ it transforms into diamond. By adjusting the variable P and T the Van der Waals intermolecular interactions become more reactive and lead to the formation of oligomers with mostly dimers and trimers [MAR 96]. This transformation diagram [DAV 00] is presented in Figure 2.5 where, at atmospheric pressure, by following the temperature axis, we can find the phase diagram of molecular C_{60} . As a function of pressure three domains exist: below 350 K pressure only affects the orientation of the molecules without changing the molecular structure; between 350 and 900 K there are chemical reactions by cyclo-addition and the formation of dimeric, trimeric, and polymeric phases; finally beyond 900 K the molecular structure collapses and yields new molecular phases that are currently being identified ([BLA 99], [MOR 04]). A multitude of new phases, of increased

dimensionality have been discovered: orthorhombic (1D), rhombohedral and tetragonal (2D), and finally, cubic (3D), whose domains of existence are represented in Figure 2.5. They display interesting physical properties compared with those of classic phases, which will be described later.

Crystalline phase	Crystallographic structure	Space group	Cell parameters (nm)	Specific mass (g/cm ³)	References
Graphites					
Hexagonal	Hexagonal	P63-mmc	a = 0.246 c = 0.671	2.26	Lipson and Stokes [LIP 42]
Rhombohedral	Rhombohedral	R3m	a = 0.246 c = 1.006	2.26	
Diamonds					
Cubic	Face centered cubic	Fd3m	a = 1.40	3.51	Vaughan [VAU 97]
Hexagonal	Hexagonal	P63-mmc	a = 0.252 c = 0.412	3.51	
Carbynes (*)					
Phase α	Hexagonal	P31,2	a = 8.92 c = 15.36	2.68	Heimann <i>et al.</i> [HEI 84]
Phase β	Hexagonal	P31,2	a = 8.24 c = 7.68	3.13	
Fullerenes					
C ₆₀	Face centered cubic	Fm3m	a = 1.416	1.68	Vaughan [VAU 97]
C ₇₀	Rhombohedral	R3m	a = 1.013 c = 2.785	1.69	

* Crystalline phases that are not fully identified.

Table 2.1. Main crystalline phases of carbon at ambient temperature (300 K) and under atmospheric pressure

2.1.4. Crystallographic presentation of usual phases

To summarize this first section, we have defined the main known and identified phases of carbon, prior to discussing all the different phases suggested from theoretical calculations. We have classified all the known crystallographic structures

in Table 2.1, which were obtained by either X-ray crystallography or electron microdiffraction.

The rules applying to more or less compact packing, already mentioned in the beginning of this chapter [KIT 73], lead to highly symmetric phases but bearing very different specific masses, which is maximal for diamond-type phases. These are always lower than the theoretical maximum expected for ideal compact stacking [VAU 97] allowing for the possible existence of phases with even greater density. Diamond in its cubic phase has eight carbon atoms per unit cell, linked by a single type of covalent bond to four neighbors. As mentioned previously, there is an extremely similar hexagonal phase, which differs only by the type of coordination to the third neighbor; its physical properties are quasi-identical to those of the usual cubic phase. Indeed shockwave experiments indicate the presence of a novel phase called BC_8 [KNU 08] (see Figure 2.8)

The standard structure of graphite is hexagonal with four atoms per unit cell. Its structure is characterized by planar sheets also called graphene, which can present different types of stacking characterized by their polytype shown in Figure 2.4. Hence, several sequences are possible, first a stacking without any translational effect of the type AAA, which is not observed here because this type of compact stacking requires all atoms to overlay perfectly. A translation of half a crystallographic period (length of translation $a/\sqrt{3}$), is possible implying that half of the carbon atoms are located in the middle of the hexagons of the neighboring planes: this is the classical ABABA stacking of the hexagonal structure. There are also ABCABC type stackings with a periodicity on the c axis that corresponds to a shift of three consecutive planes: this is the rhombohedral phase with *a priori* the same distance between graphene sheets and the same specific mass (Table 3.1) [LIP 42]. Other sequences should be possible without any privileged order or with an ABCD polytype or even with random translations. Such stacking faults would lead to structures called turbostratic, discussed in many studies related to non-crystalline graphitic carbons (see *Les carbones*, Volume 1, Chapter 1, 1963).

Carbynes, linear chains similar to cumulenes ($=C=C=$)_n in the case of the ideal alpha form, or alternated poly-ynes ($-C\equiv C-$)_n in the case of the ideal beta form, do not proceed to form stable and well-crystallized phases as presented in Figure 2.6 from a truncated section of graphene [KNU 08]. Thus, their hexagonal crystallographic structures has not yet been fully characterized and the unit cells reported in Table 2.1 are the subject of controversy; this is partly due to contamination effects and chemical modifications with defaults in the main chains leading to several related 1D polytypes, such as the natural phase chaoite (see Figure 2.6).

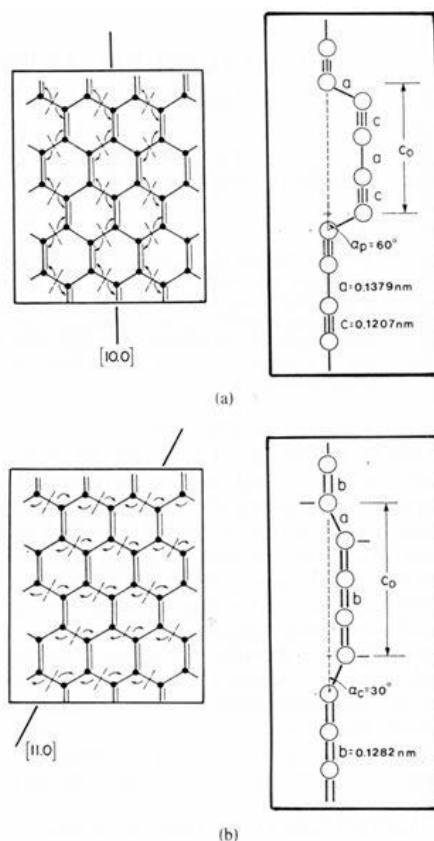


Figure 2.6. Illustration of the formation of carbyne chains from the directed ideal breaking of chemical bonds in a graphene plane (adapted from [HEI 84])

Stable at normal temperature and pressure, the molecular phases of C_{60} and C_{70} are a function of the molecular symmetry with different and shorter intramolecular than intermolecular bonds. These represent Van der Waals interactions in all three directions. It is the analog of the Van der Waals gap between graphene sheets or between carbyne chains introduced in the first chapter; it is important to remember that this is a fundamental characteristic regarding the insertion of atoms or molecules within these structures. Finally, a last point concerns single-walled carbon nanotubes (SWCNTs) and their assembly into organized bundles. Hence, such 2D triangular structures of nanotubes have been observed by electron diffraction showing a structure similar to those of crystallized polymers [JOU 97].

Finally, the transformations under pressure or as a function of temperature for these different phases have been studied as polymerized fullerene phases (see Figure 2.5 for example). Alternatively a shockwave, created by an explosion, is an efficient experimental way to prepare allotropic varieties of diamond. The experimental research for these new 3D phases, which could be extremely hard, will be discussed at the end of this chapter.

However, if a thermal treatment is applied under an inert atmosphere (in order to avoid oxidation) to any of the polymorphic varieties known, the phase obtained is always hexagonal graphite. Hence, the undesirable rhombohedral phase is fully converted into hexagonal graphite by thermal treatment around 1,500°C [GAS 67] and slow heating of diamond to 1,800°C leads to complete transformation of its structure into hexagonal graphite [EVA 64]. The case of C_{60} is quite unique, by avoiding sublimation, around 800°C its face-centered cubic structure is destroyed and around 1,300°C graphite-like sheets are detected by X-ray diffraction [MOC 97]. Finally, SWCNTs are transformed into multiwalled carbon nanotubes (MWCNTs) at 2,200°C, which in turn give rise to stacks of graphene planes around 2,800°C [LOP 02]. These temperatures of transformation are qualitatively representative of the involved activation energies (as defined in Figure 2.1) for the trajectories associated with the state change, clearly highlighting their metastable character in comparison to hexagonal graphite.

2.2. Classical forms of carbon

For each family we will look at experimentally identified compounds and others that have been predicted theoretically. We will specifically examine the variety of virtual phases modeled using computers but which are rarely observed experimentally. In this regard, we will use the coordination number (z) as the main classification parameter, as defined previously (see Table 1.2), without considering any hybridization state of the associated bonds. In order to compare all the different phases, we will need to return to the thermodynamics of solids, which will enable a comparison of the different polymorphs.

2.2.1. Cohesive energy and equation of state for solids

We have seen previously that the cohesive energy of a solid (E_c) is defined as the difference between the energy of the crystalline phase formed and the total energy of each of its atomic or molecular constituents supposedly located infinitely far from one another. The energy gain is related to the formation of chemical bonds and the subsequent sharing of valence electrons (M. Gerl and J. P. Issi, 1997). In order to obtain a value for any cohesive energy it is necessary to choose an equation of state

(see Box 2.1) and a model, in general based on quantum mechanics, for the type of interactions between particles. There is no absolute calculation but a choice in function of the family of compounds studied, because this calculation is dependant on the reference state used, which in our case will be hexagonal graphite or sometimes cubic diamond. In addition, these calculations are made at absolute zero, which in the expression of the energy or enthalpy of the system corresponding to a negligible value for the entropy. In fact, it is supposedly nonexistent at absolute zero and very small at the P and T considered, which is not necessarily true due to a possible structural disorder [MAR 95], as discussed in Chapter 3.

An interesting situation in the case of covalent and isotropic solids is to start from the Birch [BIR 52] and Murnaghan [MUR 44] equation of state that is based on the expression of the rigid modulus, which is related to the elasticity constant of the solid. It allows the evaluation of structural properties, such as hardness, for the considered solid [COH 94].

The overall energy of the solid is expressed as a function of volume:

$$E(V) = B_0 V / B'_0 \left[(B'_0 + 1)^{-1} \left(V_0 / V \right)^{B'_0} + 1 \right] + \text{constant} \quad [2.4]$$

with B_0 the modulus of rigidity (see Box 2.1) and B'_0 its derivative, which is assumed to be constant, related to pressure for the volume at the equilibrium V_0 .

For a given crystalline symmetry and with a model taking into account electronic interactions terms, determined empirically or calculated based on approximations (in particular those issued from quantum mechanics), it is possible to calculate the system's energy as a function of the occupied volume [YIN 82]. Minimization of this function leads to the volume at the equilibrium V_0 related to unit cell parameters and the modulus B_0 and B'_0 ; thus B_0 is proportional to the second derivative of internal energy related to volume.

This value corresponds, without the constant related to the energy of infinitely distant atoms or molecules, to the cohesive energy of the systems, E_c . Relative variations are often taken into account because they represent small differences between large numbers, hence the cohesion energy for graphite is estimated to be around 7.4 eV/atom or 170.5 J/atom, which corresponds to the sublimation energy already defined. They allow the comparison between various metastable states related to a reference state by calculating the difference [STA 87]:

$$\Delta E_c = E_c(\text{phase}) - E_c(\text{reference}) \quad [2.5]$$

As B_0 is related to the type of chemical bonding and affects characteristics such as hardness, Cohen [COH 94] developed a semi-empirical approach to correlate

these parameters. In the case of covalent and isotropic solids, the modulus of rigidity depends on the bond length (d) and on the degree of ionicity (λ):

$$B_T = 1\,971 - 220 \lambda/d^{3.5} [(z)/4] \quad [2.6]$$

with B_T the modulus of rigidity at a given temperature (T), expressed using pressure units (GPa), d in Angstroms, and λ a measurement of the degree of ionicity. Finally, z is the average coordination number, equal to 4 in principle. In the case of homopolar carbon-carbon bonds (see Chapter 1) the degree of ionicity is equal to zero, which implies that the modulus of rigidity is at a maximum. Moreover, the reduction of bond lengths is an important parameter, which is why light elements are used as well as pressure to increase atomic density and therefore yielding phases potentially harder than diamond which have relatively long bond lengths. Hence, an ideal experimental parameter is the modulus of rigidity, associated with the excess value calculated for the cohesive energy (see Table 2.2). One of the first calculations of this kind, based on a simple extended Hückel model [STA 87], has provided confirmation for the excess energy of diamond phases, approximately 0.3 eV corresponding to 10-times thermal agitation at ambient temperature, and especially those of the carbyne phases, alpha and beta, which have a large excess ΔE_c greater than 1 eV, which indicates their instability when assembled into infinitely long chains. More recently the development of calculation methods utilizing more sophisticated techniques, such as LDA (local density approximation; [COH 94; FAH 87]) have led to predictions regarding new phases displaying interesting physical properties with an excess of cohesive energy similar to those of known polymorphic varieties: this is the subject discussed in the next sections.

2.2.2. Structures with a fixed coordination number

2.2.2.1. Carbynes ($z = 2$)

As mentioned previously, carbynes belong to the carbon family with linear and elongated structures similar to those of hydrogenated polymers such as polyacetylene or polydiacetylene, which can be considered as precursors [BUN 94]. For a long time their existence was the subject of controversy, but it is now accepted even without a satisfactory harvest of crystals to date [HEI 99]. Several structures have been proposed based on the two ideal phases introduced earlier (see Figure 1.2 and Table 2.1). An ideal mechanism for their formation starting from a graphene sheet was proposed by Whittaker [WHI 79] affording the establishment of structure types mentioned previously (Figure 2.6): the alpha structure presents a poly-yne structure with two types of chemical bonds, simple and triple, with lengths of approximately 1.20 and 1.38 Å, respectively, and a beta-type structure similar to cumulene, which is a resonance structure of the first variety with an homogenous bond length of 1.28 Å.

Different strategies have been created in order to prepare carbynes and they can be divided into two categories. The first is a physical approach starting from molten or vaporized phases related to the use of a large amount of heat [HEI 99]. This approach is in agreement with the thermodynamic diagram (Figure 2.3) and the presence in the vapor phase of small conjugated atomic chains that are most stable when the number of atoms does not exceed 10 [PAI 93]. The alternative to the simple formation of oligomers is a chemical methodology that has been greatly developed in recent years to produce true polymers by reducing precursors while maintaining an unchanged backbone [KAV 94] or by controlling the polymerization [HEI 99]. There have been reports of polyacetylene with up to 300 carbon atoms prepared using the method of functional side chain protection [LAG 95]. These structures present faults of linearity called *kinks* (see Figure 2.6) and other structural defects or contaminations that have to date undermined all attempts to prepare good single crystals. Research on new phases called carbenoids have led to the sketching of novel molecular architectures based on acetylenic units by exploiting the immense potential of organic chemistry [DIE 94]. Hence, reports of 1D phases such as carbolytes [TAN 95] or related structures [MEL 85] have been enthusiastically received but have not yet been confirmed.

2.2.2.2. Graphites ($z = 3$)

We have already mentioned the existence of different types of stacking within these lamellar structures; graphene sheets can simply stack (AAA) according to a compact hexagonal stacking or shifted by half a period (ABA), therefore, leading to the hexagonal phase described by Bernal (see Table 2.1), or even with a (ABCA) sequence from the rhombohedral phase detected in small proportion (Figure 2.4). A theoretical approach of these different polytypes, based on calculations of the cohesive energies and the associated electronic structures obtained by applying an *ab initio* method issued from quantum mechanics [CHA 94], led to the demonstration that with a small excess of cohesive energy ΔE_c for the rhombohedral variety the presence of an (AAA) stacking is very unlikely in the current case (this type of stacking exists for hexagonal boron nitride as shown in Chapter 4). These calculations also indicate the homogeneity of delocalized π electrons on 2D systems, which are fundamental to the electronic properties found for these solids.

This observation led several researchers to speculate how best to conciliate the planar trigonal configuration of sp^2 carbon atoms with 3D structures such as diamond. Hence, rotation around a C-C bond axis, in order to rationally fill space was a theoretical challenge, by analyzing the excess of cohesive energy of each system and trying to deduce the kind of structural properties that could result. This idea was initially suggested by Hoffmann *et al.* [HOF 83] who proposed a 90° rotation of a layer of benzene cycles over the next one starting from a model system composed of chains. It is then possible to build a tetragonal unit cell corresponding

to structure called “bct4” or “hoffmanene”. A second hypothesis [TAM 90] was formulated by suggesting a rotation of only 60° between layers leading to a new hexagonal phase “H-6” (see Figure 2.7).

Later, other structures capable of rationally filling the Euclidian space were also proposed. This the case of the so-called cubic graphite conceived from poly-p-paraphenylene with a controlled rotation of benzene rings to produce a structure with cubic symmetry [BAU 93b]. We can also mention polybenzene (named “6.8 ~ 2D”) based on benzene cycles coordinated to one another [OKE 92] or another polymorph with an orthorhombic unit cell yielding channel-like structures [WIN 99]. Theoretical calculations on the characteristics of these structures (see Table 2.2) indicate that these phases have a modulus of rigidity comparable to cubic diamond with an excess of cohesive energy similar to the one calculated for carbyne phases [STA 87]. Such provisional results suggest that these phases could produce a phase where both a conducting property and extreme hardness could probably coexist in a metastable state. It would be possible to prepare such phases if an adequate fabrication process could be developed.

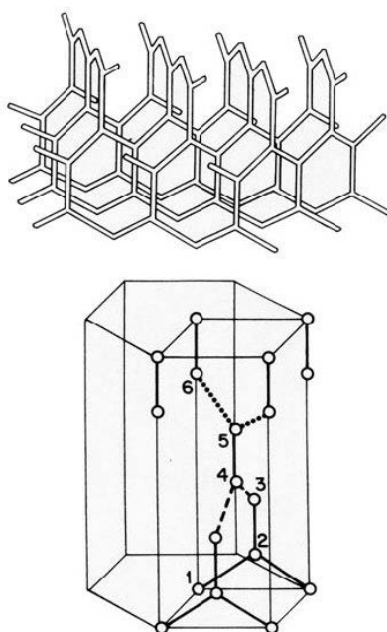


Figure 2.7. 3D representation of the structure of the hypothetical structure “H-6” and drawing of the associated unit cell (adapted from [BAU 93b])

Phase	Crystalline system	Specific mass (g/cm ³)	Compressibility coefficient B ₀ (GPa)	Excess of cohesive energy $\Delta E_c(E_v/\text{atom})$	References
Z = 3: tri-coordinated systems					
Graphite	Hexagonal	2.26	30	0	Hoffman <i>et al.</i> [HOF 83]
Bct-4	Tetragonal	2.96	360	1.1	Tamor and Hass
H-6	Hexagonal	3.16	370	1.7	
Polybenzene	Quadratic	2.19		0.07*	[TAM 90]
New polymorph	Orthorhombic	2.40	234	0.36*	O'Keefe <i>et al.</i> [OKE 92] Winkler <i>et al.</i> [WIN 99]
Z = 4: tetra-coordinated systems					
Diamond	CFC	3.51	440	0.30	Fahy and Louis [FAH 87]
	Hexagonal	3.51	440	0.33	
BC ₈	CFC	4.0	410	1.0	

* ΔE_c calculated by comparison to the cubic diamond phase

Table 2.2. Structural and physical characteristics, calculated from a Birch-Murnaghan equation of state and a theoretical model of energy ([FAH 87], [YIN 93]), for different real and virtual phases

2.2.2.3. Diamonds ($z = 4$)

In a similar fashion the diamond phase is also characterized by polytypes, which are well-described and present new possibilities for analogous structures from the two known varieties [SPE 90]. However, other possibilities have been taken into account from a theoretical viewpoint; whilst the tetra-coordinated character of the atom remains, more than half a dozen have been considered [STA 87; YIN 93]. The initial work on superdense carbon phases was once again undertaken by Hoffmann's group [JOH 89], which suggested a supercubane by analogy to an analog of silicium (Figure 2.8). A variation of this phase, called BC₈, has been intensively studied because of the existence of an accessible metastable state (see Table 2.2). Thus, Baughman *et al.* have also proposed a so-called rectangular phase, which theoretically changes into graphite at ambient temperature [BAU 97]. Theoretical calculations [FAH 87] have shown that the various possible cubic phases have free enthalpy minima that change with the pressure applied to the system. Hence, a BC₈-type cubic phase appears by applying a shockwave technique [KNU 08].

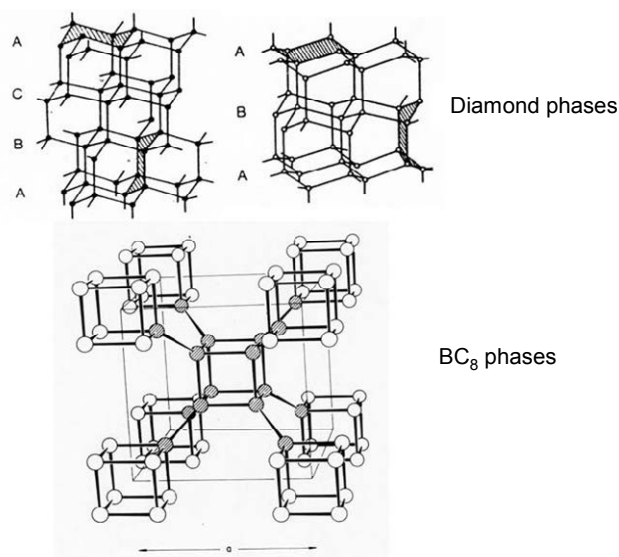


Figure 2.8. Real diamond structures under cubic and hexagonal forms (differentiable by the presence of boat or chair forms) and the proposed form of the cubic phase BC_8 (from [YIN 93])

To complete this presentation of virtual structures, it is important to mention the possibility of a higher coordination number, for example, 6, which was considered some time ago [LIB 63]. A structure (called SC4) with metallic properties could be obtained under extreme pressure [SCA 96].

2.3. Molecular and exotic forms

In the specific case of tri-coordinated curved surfaces we will now introduce another topological variable describing the number of carbon atoms in a cycle ($n \neq 6$), allowing for further classification. Finally in this section, we will mention compounds with various coordination numbers leading to different exotic varieties. For this presentation we will once again use the notions of cohesive energy and metastability as defined in the section 2.2.1.

2.3.1. Tri-coordinated structures on curved surfaces

We will summarize the required geometrical notions prior to presenting the main families, with their typical structures based on curved graphene sheets. The crystallographic structures associated with a crystalline solid are based on the

invariance of symmetry operations such as translations and rotations associated with the construction of regular polyhedrons inside a Euclidian space. These structures are not practical if there is a conflict between long- and short-range orders, corresponding to a situation where the symmetry of molecular elements does not correspond to the symmetry of the overall spatial arrangement. A solution for the interaction of these elements is therefore to position them on a curved surface [VON 87]. Hence, for such a system that intrinsically implies the formation of crystalline and non-crystalline defaults, the possibility to be in an ideal state, without geometrical aggravation or fault, is described as being part of a 3D non-Euclidian space. Therefore, a general concept can be deduced regarding the adaptation of chemical structures to find their collective order by regarding them in a curved space minimizing both free energy and free enthalpy of the system. This is the case for molecular assemblies such as liquid crystals, thermotropic or lyotropic (fluctuant amphiphilic films) [CHA 85], or more generally, in various domains of condensed matter, by exploiting different arrangements and methods to share space [HYD 77].

Topological models related to these curved surfaces have captivated mathematicians since the end of the 19th century, by reference to the work of Schwartz [SCH 90]. These surfaces can be classified according to two different local curvatures:

– the average curvature:

$$H = \frac{1}{2}(K_1 + K_2) \quad [2.7]$$

where K_1 and K_2 are the inverse curvatures of perpendicular radii on a given point;

– the Gaussian curvature:

$$K = K_1 \cdot K_2 \quad [2.8]$$

This curvature is proportional to the inverse of a surface and allows for the following classifications:

- if $K > 0$ it is a sphere;
- if $K = 0$, a plane or a cylinder (it is necessary to use the average curvature to identify which one it is, $H = 0$ for a plane);
- if $K < 0$ for a saddle shape.

The combined utilization of these curvatures permits the study of infinite periodical surfaces of minimal energy presenting negative Gaussian curvatures. There are different structures showing a rich polymorphism, called “schwarzites” type F, P, G, etc., according to their symmetry elements; several authors have mentioned them and have tried to demonstrate their existence.

As previously mentioned, the pertinent chemical parameter is the number of carbon atoms in the cycle, which will be equal to 5, 7, or 8, being integrated into the main frame of hexagonal cycles. A curved plane of graphene must form except in one case: a hexagon-pentagon pair, corresponding to azulene, could allow for planar graphene to form with a small excess of cohesive energy to potentially yield structures called “haeckelite”, which should conduct electricity [ROC 04]. In general the energetic cost of curving a plan of graphene is largely compensated by the energetic gain of closing all available bonds. Hence, the presence of unquenched chemical bonds always has a high energetic cost. The result is a quasi-infinite number of structures. This observation relies on mathematical rules established by Euler in the 18th century, to define classes of polyhedrons in a 3D space [FOW 95]. We will use these geometrical arguments to present the three subcategories already mentioned and to compare them with real systems.

2.3.1.1. *Fullerenes*

The discovery of this family has been the topic of several presentations (see M. Dresselhaus, G. Dresselhaus and P. Eklund, 1997), and we have already introduced the two most representative molecules C_{60} and C_{70} . The most important factor regarding the formation of fullerene cages is the Euler postulate which describes the necessity of incorporating isolated pentagons. From Euler's relation [FOW 95] it is then possible to define them as polyhedrons with 12 pentagons and n hexagons. Hence, after the discovery of C_{60} molecules and their icosahedral structure (12 pentagons and 20 hexagons), many different compounds with remarkable molecular symmetry and energies of formation have been isolated or at least identified [COU 87]. After the discovery of C_{70} with the shape of a rugby ball, molecules C_{76} , C_{78} (with three isomers), C_{82} , C_{84} (two isomers), and other fullerenes of larger molecular weights, have been discovered in spite of considerable difficulties for both preparation and separation of all individual molecular species.

The stability of fullerenes containing less than 60 carbon atoms have been investigated, especially the cases of C_{24} , C_{28} , C_{32} , C_{34} , and C_{50} [KRO 87] but their individual purification and identification is still problematic. The smallest member of this family is supposedly a dodecahedron of formula C_{20} , formed by pentagons with a phenomenon of full rehybridization, which is expected to be very unstable due to large constraints applied to each of the chemical bonds [ZEG 93]. Another theoretically predicted structure is that of the molecule C_{24} , which is composed of hexagons and heptagons and resembles C_{60} : this is presented in Table 2.3.

In the context of this presentation of fullerenes it is noteworthy to consider the important role of organic synthesis in the development of these molecules and related species. Excluding the internal reorganization with the so-called Stone-Wales transformation, their chemical reactivity is considerable, with inter-conversion

between pentagons and hexagons enabling many different addition reactions to take place [MAC 91] yielding a variety of new compounds. As mentioned previously, under the influence of pressure or other parameters, the cyclo-addition of C_{60} leads to the formation of dimers, trimers (see section 2.1.3), and to several other related entities, but also to the formation of complexes by encapsulation or charge transfer [HIR 94].

2.3.1.2. Nanotubes

In this section we focus on SWCNTs as previously described in Chapter 1. These are molecular objects resulting from the winding of a graphene nanosheet (Figure 2.9), a fundamental component of all rod-like structures that will be presented later. The essential parameters of SWCNTs are diameter and helicity, associated with the possibility to present open or closed extremities [DRE 95]. A carbon cylinder can be described by the winding of a graphene sheet allowing the overlapping of two extremities O and A by a network vector $\vec{C}$ such as:

$$\vec{C} = n\vec{a}_1 + m\vec{a}_2 \quad [2.9]$$

This vector, called “chiral”, bridges two equivalent sites of a carbon nanotubes with unit vectors $\vec{a}_1$ and $\vec{a}_2$ of the unit cell containing two carbon atoms, are equal to $\sqrt{3} d(C-C) = 0.246$ nm, with n and m two random integers. This couple of positive numbers (n, m) , characteristic of the chiral vector, defines the circumference of a nanotube.

Hence, a nanotubes is defined by its diameter D_t and its chiral angle θ that determine the length of vector $\vec{C}$ and its orientation (Figure 2.9a). The diameter D_t and the chiral angle θ can be expressed as a function of the indices n and m :

$$D_t = \sqrt{(m^2 + mn + n^2)} \times a/\pi \quad [2.10]$$

and:

$$\theta = \arctan(\sqrt{m/(2n+m)}) \quad [2.11]$$

Due to the hexagonal symmetry of the graphene plan all nanotubes can be classified according to the pair of indices (n, m) such as $0 < m < n$. In general all nanotubes are chiral ($0 < m < n$) with a random value for the angle θ , an exception is made for the cases of “armchair” ($n = m$) with $\theta = 30^\circ$, and “zigzag” ($m = 0$) with $\theta = 0$. Examples of each of these three nanotubes configurations closed by semi-fullerenes are shown in Figure 2.9b where we can see that in the “armchair” configuration, carbon-based hexagonal cycles are placed parallel to the tube axis, whereas this arrangement is perpendicular in the “zigzag” configuration, and is

random for standard chiral nanotubes. Their electronic and vibrational structures are highly dependent on their diameter and chiral angle [SAM 03]; this will be discussed in more detail later. It is noteworthy that the preparation of a specific isomer or the separation between all different chiral species with very similar cohesive energies, is a key problem that is not yet fully resolved.

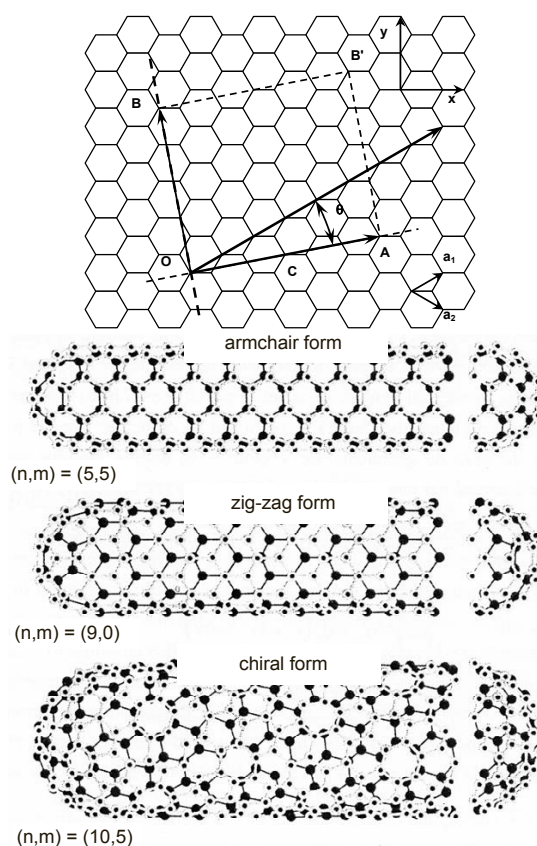


Figure 2.9. a) Graphene sheet, with the definition of the chiral vector $\vec{c}$; and b) examples of three series of SWCNTs (adapted from [SAM 03])

To conclude this presentation it is important to indicate that SWCNTs are not found as isolated and pure entities; they are almost always present as a mixture of configurations aggregated into bundle structures [JOU 97], quite often with a narrow distribution of diameters but with large variations of the chiral angle. Hence, to provide a set of indicative values, a standard SWCNT will have a diameter of

1.4 nm and a length of several microns, possibly closed by half a C_{60} at both extremities.

The observed bundles are due to the Van der Waals interactions taking place between nanotubes, this aggregation also allows a further decrease of their free energy; hence the concentric rolling of several nanotubes is indeed favorable [CHA 93] leading to carbon nanotubes with double walls (DWCNT) [COL 03], but also to MWCNTs with variable diameters.

2.3.1.3. *Schwarzites*

As stated previously, infinite triperiodic structures with a negative Gaussian curvature and an average curvature equal zero can exist when built on seven to eight-membered rings. Several authors [LEN 93; TOW 92] have suggested the existence of complex structures as presented in Figure 2.10; they have large unit cells and therefore each of them contain a large number of atoms. Hence, calculations of cohesive energies and modulus of rigidity have shed light on the possible existence of over 15 phases more or less metastable [HUA 93]: two examples are provided in Table 2.3 through a comparison with fullerenes and analogs. Two conclusions are therefore formulated:

- the excess of cohesive energy, relative to hexagonal graphite and for the calculation conditions, is low for both types of schwarzites compared to C_{60} ; they would be *a priori* in a less metastable state without any assumptions regarding the activation energy applied in a possible fabrication process;
- the modulus of rigidity calculated is smaller than that found for adamantane and is associated with a lower density; therefore, it can be assumed that these phases will not have remarkable hardness.

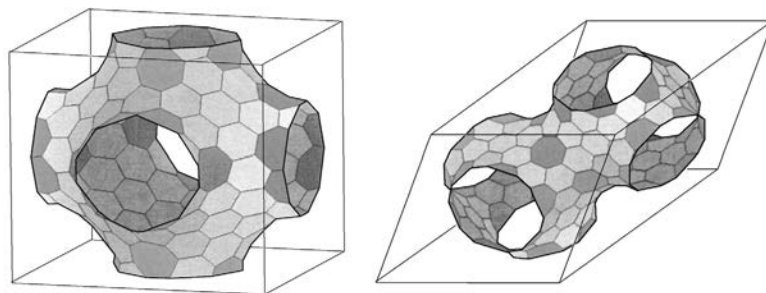


Figure 2.10. Examples of schwarzites crystallographic structures (from [HUA 93])