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Structure of Polymeric Carbon

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Experimental results and model ideas on the structural organisation of different forms of condensed carbon are critically reviewed from the standpoint of polymer science. Stress is laid on the role of chemical bonds between molecules (branching points) and of lamellar and other supermolecular formations in the multi-step process leading to a three-dimensional development of the polymeric carbon structure. Many crystalline forms of carbon (in addition to diamond and graphite) are shown to exist as regular polymers of the carbyne or transitional types. 297 references.

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I. INTRODUCTION

Existing views on the molecular and supermolecular organisation of condensed carbon are not universally held. Different schools of workers apply different treatments to their experimental results, and unfortunately even the terminology varies as between laboratories. Published papers contain a profusion of suggested models of the structure of carbonaceous materials which are often mutually incompatible.

Although the original tentative classifications of solid carbon as a type of polymer were soon followed by extensive articles and monographs, the development of the structural physics of carbon lags at least 25 years behind the present level of polymer science. The structure of the various three-dimensionally cross-linked carbon polymers is still largely unexplained, even in broad terms: even the nature of the interatomic C–C bonds, i.e. the structural chemistry of these materials, is far from clear. Typical of this state of affairs are the various coals, carbynes, and carbon thin films. This is true also of the more highly organised carbonaceous materials such as blacks, cokes, graphites, coals, vitreous carbon, pyrolytic carbon, carbyne, schungite, anthracite, diamond, carbon fibres, microporous adsorbents, composite materials, etc. There is hardly any concept in the materials science of carbon which could not benefit from critical re-examination. Our knowledge is still largely empirical, and much more work is needed before a theoretical understanding can be achieved. The problems lie in many different areas of technology. The present period of detailed studies of the properties of different types of polymeric carbon, aiming to establish a large fund of varied experimental data, must now be followed by a period of constructive thought and generalisation. The most urgent need in the physical chemistry of carbon at present is to generalise and unify the existing information.

All structural methods comprise two basically different aspects: the mathematical formalism, with its system of axioms, and the interpretation needed to apply it to specific problems. The two aspects must be carefully distinguished before the structural method can be successfully applied to structurally indefinite and varied materials such as the different forms of polymeric carbon. Unless this is done we cannot be sure that the conclusions from an experiment stem from the theoretical basis of the method rather than from the far more indeterminate interpretation rules.

In setting up the theoretical basis of a method we should avoid, if possible, terms already loaded with connotations, such as crystallite, phase, graphitisation, interplanar spacing, amorphous carbon, defect, and so on. The mathematical results should preferably be formulated in a neutral language, in order to avoid pre-conceived interpretation. The general theory should be, as far as possible, independent of *a priori* assumptions as to the structure of the unknown system. The initial postulates should be clearly stated, they should have the greatest possible generality, and they should not be biassed towards a specific model of the material under study.

A common mistake in the analysis and interpretation of experimental information is to tackle prematurely the most difficult and interesting question: the selection of a suitable working model. The alternative (and more cautious) approach, adopted in this review, concentrates initially on a pragmatic and inductive study of the model.

II. COORDINATION CHEMISTRY OF CARBON. LENGTH OF C–C BONDS

We have a fairly unambiguous criterion for deciding whether or not a chemical bond exists between two carbon atoms, i.e. whether the two atoms belong to the same molecule: the distance (r) between their nuclei. When an interatomic bond is present, r(C–C) = 120–170 pm.[1–3] Distances shorter than 120 pm between carbon atoms are inadmissible, owing to mutual repulsion. The range 120–170 pm, called the "valence bond" region, is followed by a "forbidden gap", from 170 to 280 pm, beyond which comes another band of allowed carbon–carbon distances: r(C–C) > 280 pm. This is the intermolecular interaction band.

The term molecule applies, in principle, to any sub-assembly of atoms in which each atom is chemically bound to one or more atoms of the same sub-assembly[4]. From this point of view a diamond crystal is a single three-dimensionally cross-linked giant macromolecule. Similarly, an atomic layer in an ideal graphite crystal is a single two-dimensionally cross-linked polymeric macromolecule.

According to the modern structural chemistry of carbon a C atom can be chemically bound to two, three, or four nearest neighbours (not necessarily equidistant from it). Stoichev's rule, well known in the stereochemistry of organic compounds, relates the length of the C–C bond to the number of bonds or atoms attached to this bond:

$$r(\text{C—C}) = 129.9 + 4.0\,n \text{ (pm)}.$$

In this expression $n = 2–6$ is the sum of the coordination numbers of the two carbon atoms forming the bond, less 2:

$$n = z_1 + z_2 - 2\,.$$

Other coordination numbers such as $z = 0$ (clathrate bond), $z = 1$ (end-atom in a radical), and $z > 4$ (e.g. in carborane-like fragments), though possible in principle, are not typical of polymeric carbon.

The coordination chemistry of carbon is still far from being fully developed: the chemical behaviour of a carbon atom is usually described in terms of its valence states (sp, sp^2, sp^3 hybridisation of hydrogen-like wave functions). However, a recent review[3] has shown that the coordination number can be used to reveal new facets of the changes in interatomic C–C distance. Thus, though coordination numbers greater than 4 are not normally considered in the structural chemistry of polymeric carbon[1,2,5,6], it is now well established[3] that in carboranes the C atom can have coordination numbers of 4, 5, and 6, so that

$$r(\text{C—C}) = 107.4 + 5.8\,n \text{ (pm)}; \quad n = 6, 8, 9, 10.$$

The longest C–C bond experimentally found in carboranes[3] is 171 pm.

III. COPOLYMERIC NATURE OF CONDENSED CARBON

The term polymeric has been used[7] exclusively for non-graphitising carbon. However, this usage is terminologically incorrect: it would be more exact to treat the concepts of "condensed" and "polymeric" states of carbon as synonymous.

Polymeric (or, more strictly, copolymeric) carbon is an open lattice or network of atomically cross-linked chains (one-dimensional), tapes (two-dimensional), and diamond-like, polyhedral (carborane) fragments, i.e. three-dimensionally linked rod-like, lamellar, and globular fragments. They form[8] a fairly rigid and oriented three-dimensionally cross-linked structure penetrated from all directions by a system of pores which can be open or closed, in the shape of cylinders or disks, lens-like, needle-like, or spherical. Coal has been likened[9–11] to a conglomerate of linear, branching, and cross-connected amorphous polymers, interlinked by intermolecular interaction forces. It is impossible, in general, to identify individual molecules or pores: this explains the failure of various attempts[12–14] to describe the structure of solid condensed carbons and coals in molecular terms (the "small molecule" theory[15]).

The impossibility of describing solid carbon as a molecular substance (like water, benzene, etc.) is now well recognised[16–21]. Thus, according to Biryukov[22], most of the constituents of natural forms of carbon can be classified as high-molecular compounds (HMC). Coals are mixtures of different HMC, with a three-dimensional heteropolycondensed (hydroaromatic) structure and a low level of polycondensation (2–5 rings). The aromatic rings contain substituents in the form of radicals or aliphatic groups. The number of these substituents decreases as the degree of metamorphism of the coal increases. The rings can be interconnected (cross-linked) by methylene bridges, ether bridges, or bridges of the alicyclic, heterocyclic or biphenyl type.

It has been said[9] that the description of coal as a high-molecular compound with a three-dimensional structure destroys the relevance of studies of its molecular structure, since the concept of "a macromolecule" is now known to be physically meaningless in the chemistry of HMC. Nevertheless a clearer knowledge of the individual molecular constituents (segments, fragments, branches) between the branching or cross-linking points is not useful but essential to a better understanding of the organisation of carbonaceous materials.

IV. THE PACKET AND FRINGE MODEL

The most characteristic X-ray diffraction feature of carbonaceous substances is a set of several more or less diffuse maxima corresponding to the graphite structure superimposed on a continuous background. The most important is the first reflexion, in the region of scattering angles (2θ) between 18 and 32° (for $\lambda = 154$ pm), corresponding to the Bragg periods $d = 280–500$ pm. The reflexion is found in various forms in almost any form of carbon, and it is always the strongest. It is usually ascribed to the presence of small crystallites of graphite[23,24], and the spacing d is interpreted as the distance between plane-parallel layers of carbon atoms or aromatic molecules. It is assumed that carbon atoms have a strong tendency for two-dimensional condensation to give aromatic molecules (graphitisation).

The presence of 2–4 diffuse reflexions in positions close to those from the (002), (100,101), (004), and (110) graphite planes has been quoted[25] as evidence that the basic structural unit in coals is the graphite network. However, it is now becoming clear that this assertion is misleading, and that the "coincidence" of reflexions from "amorphous" carbons (coal, schungite, vitreous carbon, carbon blacks, etc.) and from crystalline graphite is in many ways fortuitous[26]. Nevertheless, Warren's turbostratic model[23] of two-dimensionally ordered structures has been increasingly applied to amorphous carbons. The size of the graphite blocks (condensed "aromatic macromolecules") and their mutual orientations were inferred from the width of the reflexion and from the approximate "interplanar spacings". The aromatic model was extended to all forms of carbon, including those which yield a different (non-graphitic) diffraction pattern.

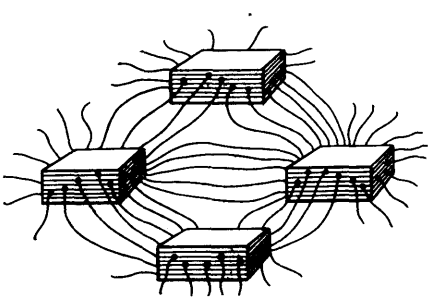


Figure 1. The packet and fringe model of the structure of polymeric carbon.

It is claimed[27] that the presence of graphitic reflexions is direct evidence of the formation of blocks (clusters, packets) of two-dimensional layers of aromatic molecules. On this

evidence the presence of "crystallites" (graphite-like particles, or micelles) having fairly sharp boundaries and immersed in an amorphous matrix has been postulated (Fig.1). In this model the carbonaceous material is treated as a two-phase system (even without allowing for the presence of pores[27]).

All forms of carbon can be arbitrarily classified into two types[16-20,28-34]: 1) organised (ordered, aromatic, nucleated, crystalline, contained in crystallites) and 2) not organised (amorphous, non-aromatic, peripheral, disordered, lying between crystallites in the amorphous matrix).

The position of the reflexions was assumed to be determined by the internal layer structure of the crystallites, and their width by the external dimensions of the crystallites. The crystallite size was treated as the most important of the structural characteristics, and in most cases it was found to be 1–100 nm. The background continuum of the diffraction picture was ascribed to the amorphous matrix. Several structural models of carbon were proposed, all of them based on an aromatic macromolecule (or layer) surrounded by aliphatic, hydroaromatic, and other atomic groups. The basic structural transformation during carbonisation and heat treatment was assumed (*a priori*) to be the growth and ordering of aromatic macromolecules and crystallites as a result of the rearrangement of atomic groupings with bonds of different types. This approach led to the structural model of carbon which we can call the packet (or micelle) and fringe model by analogy with the now superseded fringed micelle model in the structural physics of linear polymers[35,36].

In this model (the "spider" model) the primary structural fragments were thought to be: 1) a two-dimensional aromatic layer in the crystallite, usually assumed to be planar, i.e. absolutely rigid, and 2) a carbon chain with side-groups of hetero-atoms interconnecting the crystallites.

The bundle of chains terminating on any one crystallite is treated as its fringe[37]. The block (or packet, crystallite, micelle, cluster) is a secondary, supermolecular formation in which the distance between the plane parallel carbon layers varies between 335.4 and 344 pm depending on the degree of correlation (three-dimensional order) in the mutual arrangement of these formations. The lower limit was identified with the ideal graphite structure, and the upper limit with the turbostratic structure, i.e. with a fully uncorrelated disposition of the layers[23,24,30]. However, Ruland has shown[38] that even the spacing $d = 344$ pm implies some degree of correlation in the disposition of the layers. Thus one of Franklin's fundamental assumptions[30] appears to be incorrect.

The packet and fringe (micelle and fringe, or crystallite) model of the carbon structure was proposed independently in the early 1950's by Franklin[29-32] and by Kasatochkin[16-19,33], and was subsequently developed by many workers[5,14,20,27,34,38-51]. The model has been used to interpret all types of experimental result[1,2,37]: even a method of determining the fractional amount of aromatic carbon was based on it[52]. Numerous models of the disorder (or partial amorphousness) of polymeric carbon have been proposed[23,24,50-57]: in most cases the amorphousness was ascribed to disordered translation, rotation, and bending of the layers[24,58-68], non-identical valence bonds in some of the atoms (Pauling's quinoid structure[63-65]) or non-identical states of the different surfaces of the same (or of different) two-dimensional aromatic molecules[50,51], or to the presence of two phases in the system (the crystallite packet phase + the amorphous fringe carbon phase). It was suggested[5,20,37] that the amorphous carbon can display every possible level of hybridisation of the states of the four outer electrons in each C atom. In spite of the emphasis on a more or less regular packing of the aromatic layers in the packet (or crystallite), the presence of some regularly packed chain-like fragments was implicitly accepted. No other way of interpreting the mass of experimental facts could be found, especially those derived from X-ray diffraction measurements.

However, the position of the first reflexion often corresponds to $d > 344$ pm,[42-49] and this cannot be explained within the framework of the packet and fringe model[66,67]. Furthermore the intensities of some of the reflexions, in particular the (002) and (004), are often anomalous and do not correspond to the graphite structure[66]. Also, the presence of coherent scattering regions of finite size does not in itself imply that the system must be two-phased, or micro-heterogeneous, as has been recognised in the case of chain (linear) polymers[68,69].

Indeed, high-resolution (~0.3 nm) electron microscopy, interference microscopy (to reveal the periodicity of atomic layers), and phase contrast methods[70] have all been unsuccessful in the search for discrete crystallite particles[67,71-88]. It was found that the size of the bent, twisted, and tangled bundle (micro-fibril), consisting of several tape-like layers (or molecules), can greatly exceed the normal values of L_a and L_c, reaching several micrometres[71-73,81-86]. The finding that not only individual layers (tapes) but also bundles (micro-fibrils) are quite pliable was most unexpected[71-77,87].

The conclusion was that the basic microstructural units include large, distorted graphite layers and long narrow ribbons rather than small three-dimensional crystallites (as suggested by the original X-ray diffraction experiments). Polymeric (rigid, non-graphitising) forms of carbon have been described[7] as a highly distorted form of graphite consisting of tapes rather than layers.

The adherents to the crystallite (micellar fringe) model have now started to describe the crystallite as an assembly of approximately parallel layers without identifiable boundaries between the crystallite and its surroundings, rather than as a normal particle (or micelle)[34,42,66,74-76]. This treatment stems from the belief that the intensity of the reflexion is a measure of defect concentration rather than of the size of the "scattering particle". However, these stipulations amount to admitting the failure of the micellar fringe model of the carbon structure.

V. THE MOLECULAR-TAPE FELT MODEL

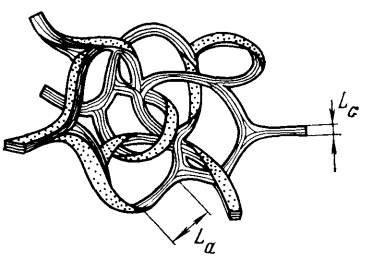


Figure 2. The molecular tape carbon felt model.

The micellar fringe model was followed by the tangled tape model[74,75], in which any carbonaceous substance (from vitreous carbon[72-76] to carbon fibre[7,34,81-88]) is held to consist of a uniform molecular-tape felt without any discrete

supermolecular formations (Fig.2). In this case the difference between vitreous carbon and carbon fibre lies only in the degree of preferred macroscopic (visible) orientation of the ribbon bundles as they diverge, intersect, and come together again[7,44,67].

This model of the structure of carbon was quickly adopted in many published papers and text-books[27,66,89,90]. Nevertheless, in spite of its apparently firm experimental foundations, the model is incompatible with physical reality in two respects. Firstly, by postulating that all the carbon atoms are trigonal (in an exclusively sp^2 hybrid valence state[42]) the felted tape model ignores the possible existence of carbon chains, diamond-like regions with tetrahedral bonds, chemical cross-links, sharp bends, and the intermingling and spiralisation (twisting) of chains, tapes, and layers. Secondly, while rejecting crystallites as real structural elements[73,91], this model also rejects every other discrete structural unit having a higher (supermolecular) level of organisation.

Evidently, in real systems the organisation of the carbon must be less uniform than this model suggests, both from the chemical point of view (interatomic bonds) and from a higher-level standpoint. Recent extensive structural investigations have demonstrated the formation of ordered structures at both the molecular and the supermolecular level not only in crystalline but also in amorphous carbonaceous materials. The formation of these structures is responsible for the loss of three-dimensional homogeneity in carbonaceous materials: it is accompanied by the appearance of interfacial boundaries and localised non-uniformities such as cracks, graphitised regions, and local concentrations of low-molecular compounds.

Johnson and coworkers[92] have proposed a complex model of the fish-scale structure of a high-molecular carbon fibre (HTT† = 3100 K), including intersecting (even at right angles) and longitudinal bundles of aromatic tapes, pores with sharp angles, regions of imperfect packing of the tapes, sharp bends, and twists in the tapes.

Numerous variants of the two basic structural models (the packet and fringe and the felted molecular tape model) of condensed (copolymeric) carbon are described in recent monographs[7,12,15,20,22,27,66,73,90] and reviews[6,8,40–42,48,51,56,89,93]. In principle they do not contradict, but they complement each other, and therefore all can claim some validity. Each variant focusses attention on certain aspects of the structural hierarchy and of the amorphousness of carbon, while other aspects are ignored. In reality the structure of polymeric carbon is infinitely more rich and varied than even the most complex model suggests.

VI. DIRECT EXPERIMENTAL OBSERVATIONS OF THE NON-UNIFORM MOLECULAR STRUCTURE OF POLYMERIC CARBON.

It is widely assumed that all non-crystalline forms of carbon consist of graphitoids: localised packets of aromatic two-dimensional macromolecules. However, in many cases the shapes of the observed diffraction peaks are not described satisfactorily by this model. For example, even Franklin[31] met this difficulty in a study of the carbonisation products of poly(vinylidene chloride) (PVDC) at 1300 K. From an analysis of the X-ray reflexion profiles [mainly of (110) index] Franklin concluded that 65% of the carbon atoms in this material are accommodated in highly perfect, flat graphitic layers, and 35% in an amorphous phase which gives diffuse scattering. Other workers also reported similar observations[14,40,41].

Kirda and coworkers[57] have shown that the average length of the C–C bonds in anthracite, calculated from the position of the first peak on the atomic radial distribution curves, decreases from 145 to 128 pm if the sample is ground for 20 min in a vibro-mill. They concluded[57] that 66.5% of the carbon in the initial sample exists as flat graphitic layers ~2 nm in diameter, and 33.5% can be classified as amorphous, i.e. not organised in ordered packets. During the grinding operation the relative amount of amorphous carbon in anthracite increases from 33.5 to 43%, and the area of the aromatic layers decreases, but the inter-layer spacing d_{002} remains constant (356 pm). Like the earlier workers[14,29–32,40–41], Kirda and coworkers[57] failed to define the material which they termed amorphous carbon.

An analysis of the atomic radial distribution functions[94,95] has led to the conclusion that regions (or domains) of two types are present in vitreous carbon: graphitic, and tetrahedrally bonded (or diamond-like). Similar views were put forward by other workers[45–49,96–102], though others have doubted the presence of diamond-like regions in vitreous carbon. Ergun and coworkers[45–59] concluded from measurements of hardness and density combined with a determination of the width of the diffraction lines that non-graphitising (rigid) carbons contain different crystalline forms of carbon including a substantial amount of micro-structures in which the atoms are tetrahedrally coordinated.

According to the polyadamantane hypothesis[103,104] different carbon atoms in natural coals have different electronic states and different coordinations: ~50% of the atoms are in structural fragments of the complex cycloalkane (polyadamantane) type, ~10% in alkane chains, and only 26–30% in condensed benzene rings.

Another study of atomic radial distribution functions[105,106] has established that practically no condensed aromatic systems are present in vitrinites from bituminous coals containing 77–90% of carbon. It has also been stated[25] that the structure of the vitrinites from anthracite cannot be described by models based on a condensed aromatic macromolecule. It is assumed that all possible types of carbon bond are found in vitrinites from anthracite (as they are in schungite). At least two methods of carbonising coal are known: those tending towards graphitisation, and those tending towards anthracitation (schungitisation) or, more accurately, carbynisation, i.e. the formation of straight or branching chains, ladders, or tapes of three-dimensionally cross-linked macromolecular fragments.

A combination of physical, physicochemical, and petrological studies[9–11] has shown not only that glubular polymeric structures with linear or branching chains are present in the vitrinite part of coal, especially in natural coals in an intermediate state of metamorphism, but also that linear macromolecular fragments are predominant in these structures.

The view that coals are mainly aliphatic has been put forward by several workers[103,107,108]. Aromatic fragments are thought to be present in small numbers, the coal consisting mainly of linear alkane chains. A study[109] of the acetylation of coals of different levels of metamorphism using the chloro-anhydrides of various aliphatic acids (the Friedel–Crafts reaction) has shown that even in the lean coal stage a three-dimensional network has not yet been formed. The volume of graphitoids in natural coal is estimated[110–112] to be less than 10%: the main bulk consists of linear carbon polymers. A mass spectrometric and gas chromatographic analysis of the products of the oxidation of coals by a 40% aqueous solution of nitric acid at 333 K has shown[113] that up to 38% of the carbon exists as linear alkane chains up to 23 C–C bonds in length.

†HTT is the heat treatment temperature.

Thus, in spite of the lack of quantitative agreement on the carbon chain content of natural coals and anthracites, the presence of such chains is accepted by many workers, including adherents to the micellar fringe model. As was pointed out in Ref.111, the make-up of spatially inhomogeneous, structured natural carbons (coals, semi-cokes, anthracites, carbon blacks, vitreous carbon, carbon fibre, schungite, etc.) is complicated by the enormous number of cross-bonds and branching chains, which make it impossible for the material to soften and be converted into a liquid. Being vitreous, this gelled material can only be converted into a highly elastic state by an increase in temperature.

Whittaker and Tooper[114,115], using electron diffraction, found that most of the fragments in vitreous carbon (with HTT up to 3500 K) give diffuse diffraction patterns containing several rings, but a significant proportion gives only spots and rings or even (in 10% of the cases) a sharp pattern consisting only of spots and corresponding to a single-crystal region in the sample. Unexpectedly, the crystalline fragments between 0.1 and several micrometres in size did not have the graphite structure: in most cases their structure was that of carbyne (chaoite, carbon-VI), diamond, lonsdalite, and other previously unknown forms of carbon. On the other hand, patterns corresponding to crystalline graphite were often twinned (with a rotation of approximately 28.5°), suggesting the presence of two crystalline regions in the same fragment (for example, of the lamellar or platelet type).

From these recent and detailed investigations we may draw the following conclusions.

1. The characteristic size of the uniform regions in vitreous carbon is 10–1000 nm, i.e. much greater than the typical crystallite size calculated from the broadening of the X-ray reflexions (L_a, L_c = 1–20 nm).

2. Though a proportion of the carbon atoms is accommodated in aromatic fragments consisting of 1–3 rings[96], a much larger number of C atoms adopts different types of cooperative arrangement (coordination).

3. The presence of different crystalline forms of carbon causes a broadening of the "graphitic" X-ray lines, additional to the "size" effect, since many of the reflexions for these forms lie close to the characteristic graphite reflexions. This interpretation of the broadening of the (002) band and of the enhanced background near this band was suggested in 1965 by Ruland[116], who tried to analyse the intensity of the band not in terms of the distribution of crystallite sizes L_c but in terms of the distribution of intermolecular distances d. This approach was put forward[116] as an alternative to Franklin's artificial postulate of single atomic layers (macromolecules) and of atomically amorphous carbon, assumed to scatter X-radiation incoherently, in a system as close-packed as polymeric carbon. However, this approach was not developed further, and the broadening of the (002) band is now almost invariably ascribed to the crystallite size L_c.

Early work[12–14,28,117,118] on the structure of natural carbons referred also to the γ-band, corresponding to a structure with a periodicity d = 400–500 pm. Abnormally high values of d_{002} are found in many forms of carbon: for example, the values d_{002} = 360–420 pm are typical of carbon blacks[119], and in carbynes the predominant periodicity is 430–480 pm. On the other hand, for polymeric diamond structures consisting of cross-linked atomic layers the typical intermolecular distances d are much smaller. It has been suggested[12,18,117,118] that the γ-band in coals is determined by the intermolecular distance in a packet ~2 nm in diameter consisting of several small aromatic units (the "bitumen" molecules). The high values of d_{002} in other types of carbon have been ascribed to imperfections (curvature) in the aromatic layers, though the existence of these layers was uncritically accepted. The 430 pm periodicity in carbonised polyacenaphthylene (HTT = 460–570 K) was explained in this way[116].

However, an alternative explanation is possible, treating the γ-band as an indicator of the existence of carbon in chains and ribbons[25,26]. This treatment assumes not only the existence of distinct chain fragments, but also whole regions of close and partly ordered packing. For example, the diffraction pattern[120] of amorphous poly(vinyl alcohol) ($-CH_2-CHOH-$, $M \cong 40000$), known to be a chain polymer[36], consists of a single broad peak (with d = 437 pm) for different structural and morphological forms of the polymer (powdered, gelatinous, thin-film, fibrous, vitreous, mesomorphic) at 430–480 K. In spite of the difficulty of formulating a fully convincing interpretation[120], this peak must somehow be a measure of the distance between chains, possibly in a state of free or partially hindered rotation (torsional vibrations). The intensity ratio of the bands with d = 350 and 520 pm has been used[121] to calculate the degree of aromatisation (cross-linking of chains) as a function of time during the thermal oxidation of polyacrylonitrile (PAN) fibres.

The period d = 460–480 pm of the broad band observed[7] in the products of the low-temperature carbonisation of phenolic resins (HTT < 1140 K) has been interpreted[7] as the average distance between narrow tapes of aromatic carbon. This period decreased continuously from 480 to 350 pm as the heat-treatment temperature was increased, i.e. as the degree of aromatisation (cross-linking) of the carbon was increased, and as the narrow tapes and chains grew into two-dimensional atomic layers. This process results in the formation of a three-dimensional network structure. ESR spectral results and measurements of the electrical conductivity for carbonised polyacrylonitrile (HTT = 470–1370 K) were successfully interpreted[122] by a two-phase micro-heterogeneous model which describes the semiconductor as a random mixture of a highly conducting (polyconjugated) phase and an insulating (non-cyclised PAN) phase. The size of these regions in relation to one paramagnetic centre (PMC) was estimated to be ~1.5–20 nm.

A specially wide spectrum of molecular structures and supermolecular formations is observed in the condensation (whether homogeneous or heterogeneous) of carbon from its vapour[123–141], from a plasma[142–151], from a molecular-ion beam[151–156], or from solutions[157–161]. The products (in the form of globules, films, whiskers, etc., depending on the rate of the formation process) may contain any of the known (and some previously unknown) forms of crystalline or amorphous carbon: graphitic (two-layer polytype or normal hexagonal graphite), three-layer cubic or rhombohedral graphite, four-layer diamond, and carbyne. The substructure and some properties of evaporated carbon films are discussed in recent review articles[151,162–164].

VII. CARBYNE AND TRANSITIONAL FORMS OF CARBON

The term carbyne denotes a system consisting only of carbon chains held together by van der Waals forces to form a crystal[165–172]. The chains are assumed to be straight, since the electronic state of each C atom is described by *sp* hybrid wave functions (poly-yne $-C\equiv C-$ or polycumulene $=C=C=$ form). In the total absence of chemical intermolecular bonds (or cross-links) between the chains we obtain the originally postulated carbyne structure: an assembly of linear carbon chains without any chemical bonds between them. To confirm the existence of carbyne in this form we

require material as a single crystal of a size sufficient for extensive structural studies: such single crystals are not available at present. Though a liquid consisting of isolated carbon chains can exist, in principle, it has never been prepared.

Evidently, in real samples the carbon chains are chemically cross-linked by bonds showing various periodicities[173]. Whereas in the description of diamond and graphite systems the concept of intermolecular chemical bonds and associated branching systems (three- or four-function branching) is relatively unimportant, this concept becomes vitally important in the description of carbon chain polymers. Though these systems can be formally classified as transitional forms of carbon[5,6,37], we shall apply the concept of a real carbyne form of carbon (as opposed to the ideal carbyne) to a partially cross-linked three-dimensional polymer having a more or less regular (crystalline) structure and predominantly composed of extensive fragments of linearly polymerised carbon.

This wider definition of the carbyne forms of carbon is more general as well as methodologically more accurate. It includes, in addition to two-function (linear chain) lattice positions, the three- and four-function positions associated with branching (chemical cross-linking). From this point of view the graphitic atomic layers (molecules) and the diamond crystals are the limiting cases of network and chain structures respectively, ideally cross-linked by three- and four-function branching points.

Whittaker[174] interprets the graphitic monolayer in exactly this way: as an assembly of ideally cross-linked (in one plane) carbon chains. It has been suggested[175] that a diamond crystal consists of equal numbers of right and left screw axes, i.e. of helically twisted carbon chains.

In the presence of chemical cross-links between chains of linear carbon polymers the relative position of the chains may not be parallel. This is another important new aspect of the treatment of the carbyne structure. We note that the primary structural fragment is now no longer the two-dimensional layer of sp^2 hybridised carbon, but the chain connecting two nearest lattice points (i.e. the cross-link).

In principle the existence of carbon chains cannot be doubted (see, however, Refs.176 and 177). It has been demonstrated by various methods[178–192], including electron and X-ray diffraction[166–171 193–208].

The fundamental maximum of the energy loss spectrum during electron diffraction (in the 20–50 eV range) by evaporated carbon films prepared by various methods is found[187] to lie near 23 eV, i.e. slightly below the value for amorphous carbon and well below the value for graphite and diamond (27 and 34 eV respectively). The position of this maximum is thought[187] to be a characteristic structure parameter of this type of film. In some samples weak peaks were observed at ΔE = 7 and 33 eV. Annealing and storage of the films causes changes in structure (or, more exactly, changes in the energy loss spectrum).

A peak near 23 eV has been observed[186] for carbyne (in reality, a complex mixture of chain, ring, diamond, and other fragments). However, this result was reported only tentatively, and as possibly due to the presence of traces of oxygen. All the carbons examined (graphite, plasma black, carbyne, diamond) gave a broad band near 17 eV. The carbyne spectrum included two sub-bands, at 16 and 17 eV, reminiscent of the sub-bands found in diamond.

The Raman resonance spectra for poly-yne are interpreted[184] as a clear indication of one-dimensional chains with alternating bonds: the chain length is estimated to be 30 ± 20 C≡C bonds.

The Raman spectrum of natural graphite[180,181] consists of one (Stokes) absorption line at 1570–1580 cm^{-1}. In vitreous carbon, coal, pyrolytic carbon, and carbon black[182] two lines are seen (at 1360 and 1580 cm^{-1}), and in evaporated and white carbon (chaoite, carbyne) three lines[180,181]: at 1360, 1580, and 2140 cm^{-1}. The additional broad line at 2140 cm^{-1} in the carbyne spectrum is ascribed to conjugated acetylene bonds, $(-C\equiv C-)_n$.

Thus all the polymeric carbons show a sharp absorption band at 1570–1580 cm^{-1}, corresponding to a system of conjugated C=C bonds. The i.r. spectra of some samples of paracyanogen $(CN)_x$ also show a single, sharp absorption band at 1570 cm^{-1},[209,210] typical of the C=N bond[211], and therefore this band cannot be used to establish the electronic structure of our systems. It has been suggested[210,211], from X-ray diffraction results, that paracyanogen also has a layer lattice of the graphite type, with alternate C atoms replaced by N atoms, and the black colour and high stability of paracyanogen have been ascribed to resonance interactions involving electron transfer. The C–N interatomic distance in paracyanogen (136 pm) and the C–C distance in graphite (142 pm) are not very different: the difference between the interplanar spacings (~450 and 335 pm) is much greater[210,211]. On the other hand the colour of crystalline carbyne particles is white.

Obviously, all possible electronic states in condensed carbon atoms cannot be reduced to three types, with sp, sp^2, and sp^3 hybridisation. For example, s^2p^2 hybridisation is also possible (bivalent carbon model[7,212]), as well as multi-step hybridisation of already hybridised states, etc. Theoretical calculations suggest that the following structures are relatively stable: four-coordinated planar carbon (singlet biradical)[213], diamond-like three-coordinated amorphous carbon[135], pentagonal pyramids (a half-sandwich, positively charged in the cyclopentadienyl ring base of the pyramid[214]), and other electronic states[215,216].

Even the electronic structure of graphite is still being discussed[49,63–65,217], and doubts have been expressed on the dynamic equivalence of the σ-bonds in the layer, on their planarity, and their hexagonal symmetry. An orthorhombic elementary cell has been suggested[49,63,64], with a = 240.9, b = 433.9, c = 670.8 pm: the so-called quinoid structure, in which two-thirds of the C–C bonds are 145.3 pm long and the remaining one-third 135.7 pm, the bond angle being 112, 124, and 124°.

It has also been shown that the specific heat $C = f(T)$ curves of different polymeric carbons lie in the following (increasing) sequence: diamond, graphite, anthracite (and schungite), carbyne, and heat treated polyfurfural (HTT = 790 K, a mainly linear polymer)[178,179]: the heat of combustion of carbyne, Q = 84.54–88.80 kcal $mole^{-1}$, is significantly lower than those of graphite (94.05 kcal $mole^{-1}$) and of diamond[173]. The conclusion is that carbon in chains is thermodynamically more stable than graphite or diamond[173].

The specific heat of these materials at very low temperatures (0.44–4.5 K) has been found[218], surprisingly, to obey the law $C = \alpha T^3 + \gamma T$. The linear term almost certainly denotes the presence of a one-dimensional phonon spectrum. After neutron irradiation the coefficient γ increases, and α decreases (in parallel with degradation of the vitreous carbon)[219].

X-Ray and electron diffraction studies[220–226] of natural or artificial graphites had shown (even in the 1930's and 1940's) anomalous reflexions which could not be assigned to known crystalline modifications of carbon. In order to account for these reflexions various graphitic superstructures had to be postulated, though they could not be independently confirmed.

The observation[102] in the electron diffraction patterns from similar vacuum-evaporated films (of density 2.4 g cm^{-3}) of eleven diffuse haloes could only be explained by assuming that the intensity maxima were neither from graphite nor from diamond structures.

An electron diffraction camera (ER-100) has been used[227-230] also to study carbon films evaporated by an electron beam under the following conditions: vacuum ~5 × 10^{-7} mmHg, substrate NaCl or $BaCl_2$, T = 310–340 K, angle of incidence of the electron beam on the substrate 60°, rate of condensation 0.2–0.3 nm s^{-1}, film thickness δ = 10 or 80 nm. The electron diffraction patterns showed six haloes, the strongest being for d = 455 pm with δ = 10 nm and d = 485 pm with δ = 80 nm. The authors conventionally assumed that these large "interlayer spacings" are due to the insertion of carbon atoms between the graphite nets, giving distorted and highly supersaturated interstitial solid solutions of carbon in carbon. The regions of coherent electron scattering for which L_a = 1.2 nm and L_c = 0.8 nm were identified with strongly distorted graphite crystals in which the regularity of the mutual orientation of neighbouring graphite nets had been lost.

The atoms in evaporated films are often assumed to be grouped in diamond-like and graphite-like fragments[102,133,163,231]. In recent years it has become clear that thin carbon films (usually graphite-like[162-164,232,233]) can be in a polycrystalline cubic (diamond) phase completely free from graphite impurities when prepared under special conditions[143-159,234], the individual diamond crystallites reaching 5 μm dimensions[152-156]. However, the possible carbon structures in evaporated films are not limited to graphite and cubic diamond[187,235]. Fragments of lonsdalite and other unidentified ("intermediate") phases have been detected[149,236] in substantial amounts in carbon deposits, together with the cubic diamond phase. These phases were believed to be chaoite (α-carbyne). Cubic graphite also has been observed in condensed deposits[237,238]. But in most cases the investigators were "forced to discover" new crystalline forms of carbon[170,171,194-208,237-246].

Thus Aust and Drickamer[237] reported preliminary data on the synthesis of a new crystalline (high-pressure) carbon phase, formed by compressing a single crystal of graphite to 150 kbar. They described the crystal as cubic (a = 554.5 pm), with n = 24 atoms in the elementary cell and a density ρ = 2.80 g cm^{-3}. Later work, however, showed that these results were erroneous.

There are reports[241,242] that the condensation of a carbon plasma in a vacuum on a freshly cleaved KCl single crystal gives, in addition to a finely divided diamond-like deposit of particle size 1–2 nm (giving diffuse electron diffraction rings corresponding to d = 209, 115, 74, and 59 pm), also a scattering of faceted microcrystallites between 10 and 300 μm in size, giving electron diffraction patterns of the monocrystalline and the polycrystalline type. These crystals were indexed in the body-centred cubic lattice: a = 427.9 pm, n = 16, ρ = 4.1 g cm^{-3}. This new crystalline carbon phase, with a density 15% higher than that of diamond, is thought[241,242] to consist of close-packed slightly distorted tetrahedra.

The carbyne family continues to grow. At least six varieties of carbyne (polytypes) are known at present[169-171,194-201,207,208]: according to Whittaker[174] there may be eight.

A recent paper describes the synthesis of chaoite[247] ("a new hexagonal allotropic form of carbon") from vitreous carbon wafers compressed by a shock wave to 100 GPa. The structure was identified by electron diffraction (a = 893.7 ± 4.0 pm). The possibility of homogeneous nucleation and selective growth of diamond and other forms of carbon had been suggested[129-133], including carbyne phases, if conditions in the gas phase are optimised for a particular form: for example, laser irradiation of liquid hydrocarbons was found to favour the formation of microscopic diamond and carbyne granules.

Crystalline carbon in the carbyne form has been detected in thin lamellar streaks and in graphitic deposits[248]. As Whittaker points out[248], carbynes are not a rare form of carbon: their natural distribution is relatively wide.

We should stress that carbynes are not necessarily always crystalline. Their degree of order (or crystallinity) can be arbitrary.

The "rediscovery" of carbon has continued, at an increasing rate, during the past few years. We can expect, as a result, new and truly "polymeric" concepts to be developed in the structural physics of carbon. Thus, it has been established[245] in principle that carbon can exist in new crystalline structures showing sp^2 hybridisation of the atomic orbitals and topologically different from known modifications (diamond, graphite, and carbyne). These structures can arise through the formation of covalent bonds (regular cross-links) between helical carbon chains. Though the formation of these carbon polymers is kinetically hindered, the chains are thermodynamically stable owing to the presence of high energy barriers which prevent the conversion of the system into graphite or diamond.

Further new and surprising properties of carbon in thin films has been observed. For example, the colour of vacuum-evaporated films previously heat treated at 550 K slowly changes (at ~1 mm min^{-1}) from black to grey after a localised pin-prick has been applied[249]. The thicker the film, the faster is the motion of the colour-change front (within the range δ = 15–200 nm). Simultaneously with the colour change, the electrical conductivity increases by an order or more. Heat treatment has a similar effect. After this structural change the carbon films become amorphous, or are converted into a mixture of interpenetrating fine particles of graphite and diamond phases.

The instability of the electron distribution (for example, in a fixed configuration of the nuclei) occasionally manifests itself as the reversible memory switching effect shown by many disordered oxide and glass systems[250] in evaporated carbon deposits[251], in vitreous carbon[252], etc. The electrical resistance of these systems suddenly falls, following the application of a voltage above some threshold value (2–10 V), by several orders of magnitude (for example, from 450 to 1.8 kOhm). Both states (high-resistance and low-resistance) are metastable, and can be "remembered" for several days[250-253]. This means that the electronic subsystem of the material can be in one of several metastable states (energy levels), i.e. the material shows non-equivalence of the C atoms (in particular, a variable degree of ionicity), alternation of the interatomic bonds, and changes in the type of localisation and distribution of the electrons surrounding the atomic cores. It is suggested[252] that in the presence of an electric field thin needle-like conducting channels are formed in the film, as in the development of low-temperature trans-polarisation in ferroelectric materials[254]. (The same explanation has been applied to the switching effect in filamentary Sb_2S_3 single crystals[255].) However, the nature of the low-resistance state is still under discussion[250,256].

The ESR absorption of different forms of carbon is due to the presence of at least two types of PMC, differing in geometric configuration and in internal structure. The narrow ESR signal is assigned[257] to unpaired, delocalised electrons, located in the aromatic regions of cyclically polymerised carbon, whereas the origin of the broad signal is thought to be a set of PMC localised in the "amorphous" phase of the system: small oxygen-containing or (more probably) carbon radicals with planar or linear π-conjugation. Samples of vitrinite from Donets gas carbon[258] previously heat treated

for 30 min at 900 K (i.e. having a maximum concentration of PMC) give a vacuum ESR signal (at 10^{-4} mmHg) whose intensity varies steeply and reversibly with the measurement temperature: it falls about 10-fold when the sample is cooled to 290 K, and returns to its initial value when the sample is re-heated *in vacuo* within the resonator of the spectrometer. As the intensity of the broad signal increases, a narrow ESR signal appears, and grows. On the other hand, if the heating and cooling cycles in the cavity are carried out under ordinary conditions (rather than in a vacuum) the intensity of the ESR signal becomes a maximum at 470–570 K. The increased intensity of the ESR absorption of heat treated vitrinite samples on cooling has been explained[258] not by the formation of free radicals or by irreversible rearrangements of the molecular structure, but by changes in the collective state of the electronic subsystem (possibly, of π-associations) under the influence of temperature.

More recent work[122,257–261] has tended to rely on improved methods of analysing the ESR spectra, using the entire spectrum rather than the shape of a single line, and allowing for complex, polymodal spectra, in order to extract information on the size of the structure fragments (radicals) of various types. The concept of clustering of paramagnetic centres has been firmly established in a recent paper[261].

Whittaker and Kintner[197] showed that the high-temperature emission (sublimation) of carbon at $T = 2800–4000$ K occurs mainly as graphite and carbyne particles, giving a visible Tyndall effect. In all types of carbon examined (graphite, coke, and carbon black compositions with spectroscopic carbon, pyrolytic carbon, or vitreous carbon as a binder) the weight of sample lost through the emission of particles was 60–90% of the total weight loss. Particle size varied from molecular (1–100 nm) to 60 μm.

Cypres and coworkers[262] have reported a thermogravimetric study of the hydrogenation kinetics ($C \rightarrow CH_4$) of high-purity (nuclear) graphite, i.e. of the gasification of graphite at atmospheric pressure in a stream of pure hydrogen at 1220 K in the presence of finely divided metallic iron as a catalyst. The rate of gasification was directly proportional to the concentration of iron in the sample. Graphite and α-iron were detected in partially gasified samples by X-ray diffraction. The diffraction patterns included three anomalous lines which could not be assigned to any known carbide. By using electron diffraction the following structural periods d_{hkl} (in pm) were observed for the new phases in different orientations:

214.0; 123.9; 106.3; 75.4; 70.0; 348.7; 238.9; 118.0; 79.4; 461.5; 261.5; 174.3; 152.8; 132.6; 98.1; 88.0.

The periods corresponding to the strongest reflexions are underlined. No attempt was made to discuss the nature of these new phases, though the correlation between some of the periods and those given by Whittaker and Wolten[198] for carbon-VI (carbyne) is striking ($a = 924$ pm, $c = 1224$ pm). Carbyne forms of carbon, more stable towards hydrogen, may be formed from graphite in the H–C–Fe system.

Carbynes are only beginning to gain general acceptance. They have tended to be ignored in the technical as well as in the scientific literature because of the reluctance to accept the exaggerated concept of an artificially graphitised polymeric carbon[16–20,23–25,28–34] (highly dispersed, turbostratic, defective, fine-, crypto-, or paracrystalline, etc.).

In spite of these difficulties approximately 100 papers on the structure, synthesis, properties, and even possible applications of carbyne have already been published, including several reviews[166–168,172,263,264]. Nevertheless carbyne remains a chemical curiosity: so far no atomic structure calculations have been carried out for any of its many modifications, nor have electron distribution calculations been attempted. The history of the discovery and of the gradual acceptance of carbyne (from the scientific and the practical point of view) is itself a fascinating study. By now the preparation of carbyne and the problems arising from its structure and properties have been integrated into the general problem of elemental (polymeric) carbon.

VIII. CONDENSATION OF CARBON AND LAMELLAR FORMATIONS

In general, graphite, carbon black, diamond, and carbyne can be formed from the gas phase (including plasmas and ionic–molecular beams). Evidently, the type of carbon formed is determined by kinetic rather than by thermodynamic factors: the intensity of the flow of carbon atoms being deposited, their energy, the degree of clustering (cooperation) in the flow, the structure and temperature of the substrate, the pressure and composition of the gaseous medium, etc.

In a d.c. arc carbon whiskers up to 3 cm long and ~10 μm in diameter can be formed[53]. According to recent evidence a whisker is a scroll of coaxial, helical carbon layers oriented normally to the substrate, i.e. parallel to the growth direction (axis) of the whisker. Surprisingly, a thin "leader", ~20 nm in diameter, grows first, and is subsequently thickened[265].

Characteristic spirals have been observed in synthetic and in natural graphites[266]. It was suggested[267] that graphite crystals grow by the addition of atoms or atomic groups to the edges of crystal faces. Though several crystallisation centres are thereby buried, some growth steps ~10 nm high are also formed. These spirals are easily seen in an electron microscope: they point to the pyramidal growth of layers in artificial graphite single crystals[268,269]. Conical graphite crystals consisting of thin packets of graphite layers successively wrapped round the c axis have also been observed. Their formation is interpreted as evidence of a spiral growth mechanism of the crystal.

Growth from acetylene-containing gases[124,141] on molybdenum disks heated by radiation from an LG-25 laser has yielded hollow carbon whiskers having a "bamboo" morphology, i.e. with a longitudinal periodicity. Straight, bent, or helically shaped whiskers have been obtained. According to diffraction measurements the graphite basal planes are stretched along the growth direction of the whiskers, which explains their high tensile strength. Electron diffraction measurements showed that the whiskerisation of carbon filaments 6 μm in diameter produces, in addition to graphite, also carbyne and other unidentified carbon phases having periods $d = 455$, 390, 340, 283, 262, 247, 213, 158, 147, and 123 pm.

The formation of hollow carbon whiskers with cylindrical internal cavities 2–50 nm in diameter has been reported also from other laboratories[270]. The filament body consists of two coaxial parts. One, adjacent to the axial cavity, is composed of long carbon layers extending along the axis, which apparently grew during the early stages of the process. The second (external) part of the filament is probably formed by pyrolytic deposition of "amorphous" carbon during a subsequent stage.

The graphitoid model of the growth mechanism and of the inner structure of carbon whiskers is probably far from correct. Thus, filamentary diamond crystals can also be grown from a vapour–gas mixture containing carbon[124,271,272]. In general the initial stages of the heterogeneous condensation (polymerisation) of carbon and the inner structure and morphology of the resulting product (carbon black, diamond,

graphite, carbyne, and "hybrid" forms) have not yet been studied systematically.

In this respect it is interesting to note[273] that the "hexagonal planar nets" in carbon deposits obtained by the decomposition of *p*-xylene in a glow discharge are rotated by 90° and oriented with their plane at right angles to the deposition surface. Growth from the gas phase of graphite scales with their basal plane normal to the deposition surface has also been reported[140].

High-resolution electron microscopy has been used to study partially graphitised film[70]. The films were found to contain vertically oriented one-, two-, and three-layer "graphite platelets", with their *c* axis perpendicular to the primary electron beam. The micrographs of the two- and three-layer graphite platelets showed that the inter-layer spacing in these very thin crystallites is significantly greater than in larger crystals. Convincing evidence was obtained that this observation is not a photographic artefact, but is genuinely due to a weakening of the van der Waals forces between layers in very thin crystals.

Similar features have been observed[274] in the growth of diamond-like films from the gas phase. The films were either fully microcrystalline, with randomly oriented grains, or well textured, with the (110) texture axis perpendicular to the substrate (consisting of the (111) face of a natural diamond crystal). However, deposition from ionic beams on polycrystalline substrates gave mainly diamond crystals with a (111) orientation[152-153].

Samples prepared by static compression of powdered graphite were recently found[275] to contain ~70% of lonsdalite, up to 20% of diamond, and up to 10% of graphite. One-dimensional disorder effects in the disposition of the (001) basal planes of lonsdalite have been detected. The powders were found (by transmission electron microscopy) to consist of flat particles, reflecting the platelet structure of the initial graphite. The textures observed on the electron diffraction patterns indicated (111) diamond planes and (001) lonsdalite planes perpendicular to the surface of the particle (which before the phase transition consisted of a (001) graphite plane). The observed orientations could have been caused by a martensitic transformation of the graphite by the mechanism known as longitudinal layer bending. During the graphite → lonsdalite transition equivalent systems of (100) graphite planes are transformed into (001) lonsdalite planes, and the [001] direction in graphite becomes the [100] direction in lonsdalite.

The block size of the lonsdalite, revealed by dark-field electron microscopy in the (103) reflexion, was about 4 nm, and that of the diamond in the (111) reflexion was 10–15 nm. The lattice parameters were: $a_l = 251.6 \pm 0.5$ pm, $c_l = 418 \pm 2$ pm, $a_d = 355.8 \pm 0.5$ pm. The latter value is substantially lower than the corresponding value for perfect, large diamond crystals ($a = 356.70 \pm 0.01$ pm).

Lastly, there are many reports[168-170,198,207,208,248] of individual crystalline carbyne particles with well developed facets and a platelet shape (lamellar or scale-like). It is thought that the partially cross-linked carbon chains are oriented at right angles (or at an angle which can vary by discrete amounts) to the basal face of the lamella. It follows that, as in the crystallisation of organic macromolecular chains (for example, polyethylene), the fundamental and simplest morphological unit in polymeric carbon is a thin, transparent particle (lamella) ~10 nm thick. The size of the lamella in the two other dimensions (i.e. in the direction of the basal plane) can be much greater: up to several tens or even hundreds of micrometres. The surface of these faces is fairly even, flat, and smooth, without any visible steps. The lamella as a whole can be sharply bent, folded, and twisted (Fig.3). Several lamellae stacked together produce piles, pyramids, and aggregates of the fan and bundle type (Fig.4). In general carbyne particles are conglomerates of separate lamellae, showing varying degrees of complexity.



Figure 3. Lamellar particle of α-carbyne (×20000).

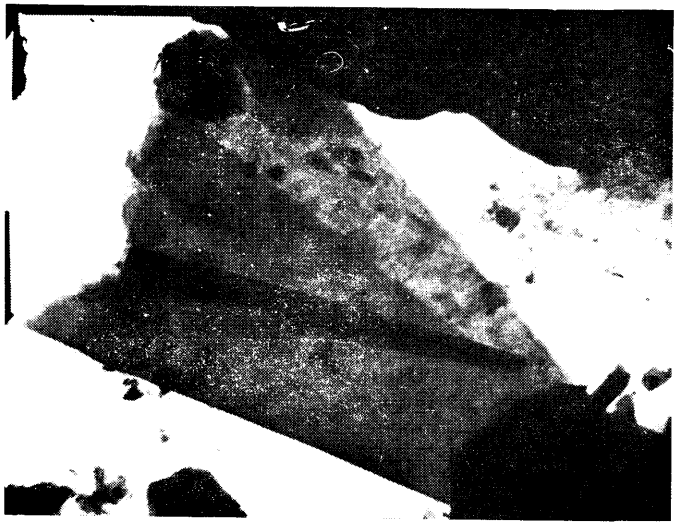


Figure 4. Aggregate of lamellar carbyne particles (×10000).

If carbon vapour is condensed on a cold substrate sufficiently slowly the product consists mainly of carbyne forms of carbon. The deposit is an assembly of fragment, mostly platelet-like. The thicker particles (stacks of lamellae,

Fig. 5) break up into several thinner particles, like schungite, when fractured by compression[276]. This observation convincingly demonstrates that large carbyne particles have a layered inner structure.



Figure 5. Layer structure of a condensed carbon particle (×2000).



Figure 6. Typical electron diffraction pattern of a carbyne lamella (with Au reference rings).

It has also been observed that under the influence of the electron beam an initially sharp diffraction pattern (spots and rings, Fig.6) often becomes gradually more diffuse, and after some time (~1 min) disappears. Amorphisation by electrons has been observed also in organic chain polymers[35], but not in diamond or graphite crystals. After irradiation the basal surface of the lamella develops pits ("sores") of various shapes. Similar fibrillar "vacuoles" have been observed by other workers[198,274]: the former were produced by radiation, but the latter were present in the sample as deposited from the gas phase, and they had almost invariably a regular conical shape.

Filamentary particles are occasionally detected in the scanning electron microscope[207]. This has led to the suggestion that individual carbon chains (molecules) become associated into a bundle of uniform composition[173,263]: a kind of primitive fibril. In this case dense particles are formed by the combination of submicroscopic filamentary particles[207]. Obviously these are the fragments which can be observed experimentally (to a varying extent) in all forms of condensed carbon, and they are the main structural units at the second (supermolecular) organisation level.

By combining dark-field contrast techniques with scanning electron microscopy in the transmission mode (which can sample a region only 0.24 nm in diameter) Isaacson and coworkers[277] have studied the structure of carbon films 0.68 nm thick condensed from the vapour phase, i.e. consisting of only 2–4 atomic layers. Both stepped and smooth regions over 3 nm in diameter were observed.

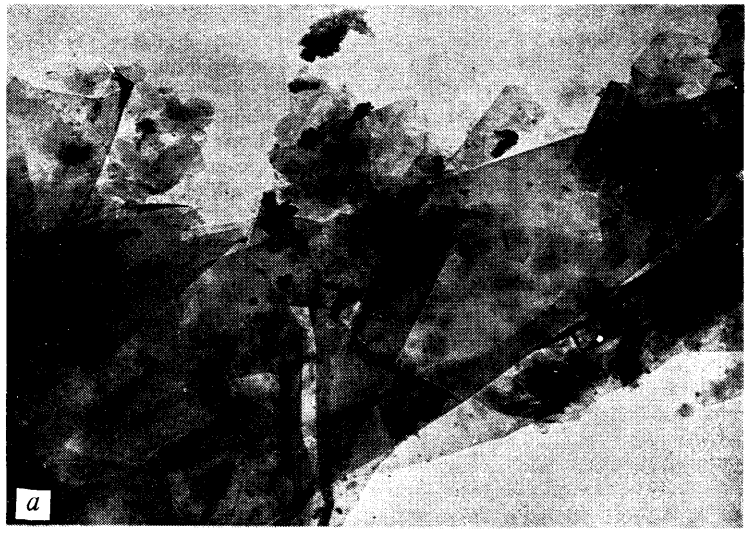




Figure 7. Lamellar microstructure of heat treated anthracite (HTT 3200 K): *a*) electron micrograph (×25000), *b*) electron diffraction pattern.

Carbon particles obtained by reducing polytetrafluoroethylene with sodium amalgam[278] consist of lamellae reminiscent of those found in polytetrafluoroethylene spherulites, a few tens of nanometres thick.

In anthracites the layer structure can be observed at all levels[111,112], from the optical (platelet shaped deposits) to the molecular. An electron micrograph and the corresponding selected-area diffraction pattern of thermo-graphite particles[279] prepared at 3100 K are shown in Fig.7. Platelets 10–30 nm thick are clearly visible. The individual lamellae consist of a parallel stack of aromatic layers parallel to the large faces. On the other hand the chains in the carbyne lamellae are oriented (apparently) at right angles to these faces, since most of the selected-area electron diffraction patterns have hexagonal symmetry.

A very unusual structure has been observed[280,281] in pitch cokes: ultrasonic dispersion can split off platelets (lamellae) thin enough to be transparent to the electron beam. The boundaries of the lamellae are clearly visible because the optical density is uniform within a single stack but it changes in discrete steps over the micrograph as a whole. Selected-area electron diffraction patterns from lamellar particles of unheated petroleum coke have shown[282] (002) and (004) reflexions from planes oriented almost normal to the planes responsible for the (110) and (100) reflexions, as in the case of mesophase particles. Hence the electron beam was aligned almost parallel to the atomic layers. These results were interpreted by assuming an oblique exposure, with the particles oriented preferentially at right angles to the substrate.

It has been shown[283] that irradiation of a thin carbon film with an Ar ion beam of 1.2 MeV energy produces surface corrugations, revealed by the appearance in the electron diffraction pattern of "three-dimensional" reflexions of the (112) and (002) type in addition to the basal ($hk0$) reflexions. It was also noted[284] that graphite single crystals are degraded in discrete steps rather than continuously when irradiated with neutrons: polygonisation into smaller crystals is the most likely mechanism.

Local electron diffraction patterns from lamellar particles in a single crystal of carbyne (Fig.8) can show a large number of weak but quite sharp rings corresponding to basal reflexions from graphite (probably deposited epitaxially on the large faces of the carbyne lamellae). In this case the system is evidently two-phased: carbyne, and a thin but extensive layer of relatively well ordered graphite. We should note that even Franklin[31] often observed one or two sharp lines corresponding to the periods d = 342.6 and 336 pm against the background of a diffuse (002) line in non-graphitising forms of carbon (from poly(vinylidene chloride) or sugar charcoal, 83.1% C, HTT = 2300–3300 K). A sharp peak against a diffuse (002) background is clearly visible also in heat treated wood charcoal[285], and in neutron-irradiated graphite[286,287]. Two-phase graphitisation is examined in depth in Refs.288 and 289.

This phenomenon clearly suggests the presence of relatively extensive crystalline regions ("islands") within the main, more amorphous material, and has been interpreted as heterogeneous graphitisation of the carbon vy evaporation and condensation on crystallisation centres, by transport of the carbon in the form of volatile compounds with hetero-atoms, and by other mechanisms[27,31,37,290–292]. However, an alternative agency leading to "heterogeneous graphitisation" is the presence of internal surfaces, and in particular the large faces of lamellar formations. By analogy with organic polymers we may assume that the lamellar structure in carbon is relatively labile, and easily destroyed. In a styrene–isoprene copolymer the largest period (60 nm) begins to increase quite rapidly[293] at temperatures as low as ~470 K, reaching 120 nm at 520 K: at the same time the number of low-angle reflexions decreases from 10 to 3. Above 520 K the low-angle diffraction pattern disappears completely. This behaviour suggests that the lamellar structure is not re-established when the molten polymer is cooled.

Brief (10–20 s) heating of oriented polyethylene samples 4.5 K above the melting point was also found[294] to cause a substantial increase in the large period: from 32 to 90 nm.

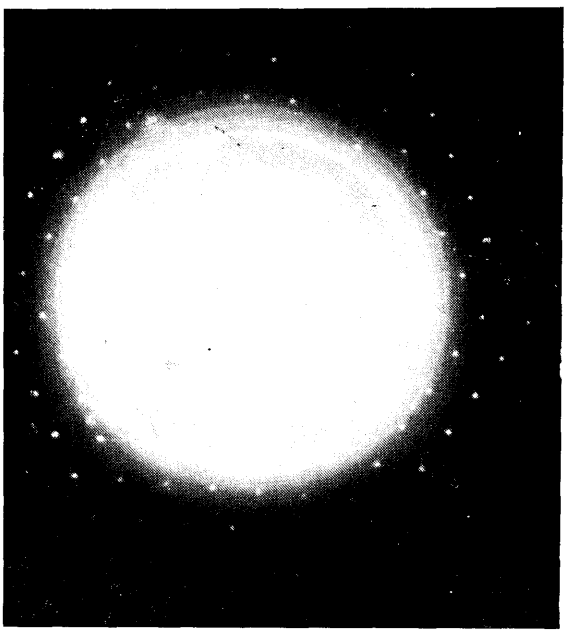


Figure 8. Selected-area electron diffraction pattern of a lamellar particle of deposited α-carbyne.

Experiments on the "pure" condensation (polymerisation) of elemental carbon under fully controlled conditions so far reported are few. Nevertheless the following conclusions are legitimate.

1. White carbyne deposits are obtained, apparently, under the milder condensation conditions: fairly high vacuum, low flux and energy of the atoms or groups of atoms (or ions) impinging on the substrate, low rate of deposition. The chains appear to grow normally to the surface without developing cross-links. Univalent hetero-atoms (e.g. hydrogen) in the surrounding medium may stabilise the chain and prevent cross-linking. These conditions occur during laser irradiation (in a vacuum) of pyrolytic graphite platelets, followed by condensation of the vapour on another platelet[204,207] or near the rim of the resulting crater[180–183,199,200]. They also occur during the normal evaporation (emission) of carbon from the hotter parts of the surface and condensation on the cooler parts[198], during the evaporation of spectroscopically pure carbon in an electric arc in a vacuum evaporator, followed by free crystallisation of the vapour on a freshly cleaved rocksalt crystal[208], during the synthesis of carbyne from organic compounds in a glow discharge[244], in a low-temperature plasma[142,241,242], etc.

2. Diamond (lonsdalite), on the other hand, is obtained under less mild condensation conditions: high energy of the impinging atoms or ions (which thus penetrate deep into the already deposited film and perturb its structure, "mingling"

the carbon atoms and favouring chemical cross-linking). The substrate in this case plays only a minor role. This probably explains the fact that diamond rather than carbyne films are almost invariable obtained from molecular (or ion) beams in a vacuum[143-156]. It is also found[295] that the bombardment of thin graphite films partially ordered (in three dimensions) with Ar^+, N^+, He^+, and Ne^+ ions of average energy 50–80 keV converts the sample into a new modification of carbon which has a low electrical conductivity, a high hardness, and a face-centred cubic lattice of period a = 369 pm (as compared with a = 356.70 pm for diamond). A chemically active surrounding atmosphere and a high pressure also favour the cross-linking of carbon atoms and chains into diamond forms of carbon[236]: this is probably the mechanism of the synthesis of diamond from the gas phase by Deryagin and Fedoseev's method[124-133,136-139]. Pressures (under shock tube conditions) up to 120 GPa have also been shown to convert graphite into diamond, and diamond into a metallic carbon phase[296,297]. Vitreous carbon under shock compression is converted into an ordered state (probably a diamond phase[296]).

3. Under ordinary (moderate) conditions, with a fairly high concentration of gas-phase atoms of not too high energy, layer polymers of carbon are formed: pyrolytic graphite, carbon black, and pyrolytic carbon, with a high or a low concentration of inter-chain and inter-layer chemical bonds (cross-links) in a regular arrangement.

IX. CONCLUSIONS

Solid carbonaceous materials had traditionally been classified into three categories: diamond (lonsdalite), crystalline graphite, and amorphous carbons.

According to well established classical views substances such as blacks, coals, cokes, schungite, pyrolytic carbon, evaporated layers, etc. are systems consisting of small graphite fragments (crystallites) embedded in random orientations in the amorphous material. The basic component of all forms of carbon (except diamond and lonsdalite) was thought to be the aromatic two-dimensional layer (or macromolecule). The difference between different substances was purely quantitative, depending on the difference in size and shape of these layers, as well as on their degree of perfection (flatness) and the order of their mutual orientation. Obviously, diamond and lonsdalite are an exception to the general rule. The diamond type of lattice forms a special subgroup among the symmetry space groups defined in crystallography and in crystal chemistry.

The temptation to fit all the multitude of non-diamond polymeric forms of carbon into the Procrustean bed of graphite is still strong. The discovery of long tape-like aromatic fragments and diamond-like inclusions, the amorphous fringe concept (i.e. carbon chains and extensive layers (macromolecules) connecting different graphite crystallites), the concept of coexisting atoms of different types (with sp, sp^2, or sp^3 hybridisation of the atomic orbitals) in the so-called transitional forms of carbon, even the discovery of new crystalline (carbyne) forms of carbon have rocked the foundations of the graphitoid conception of the artificial graphitisation of polymeric carbon but have failed to destroy it. The sharpest criticism of this conception arose from studies of the nature of coals, in which linear carbon polymers were suggested as an alternative to the graphitons (or aromatic layers).

In this review we have tried to demonstrate the limitations of the graphitoid ideas as applied not only to coals but to all forms of carbon by analysing experimental data and theoretical models. Crystalline graphites and diamonds (in two, three, or many layers) are only a few of the forms in which polymeric carbon can exist: they may be the commonest, but not necessarily the most stable. This conclusion is no longer in doubt. Crystalline carbyne, which contains carbon chains between branching points, has as much physical reality as graphites and diamonds. Whereas in the traditional approach the very suggestion of transitional forms of carbon in a crystalline state (regular type) appears absurd, experiment shows the opposite, namely that an immeasurably large number of crystalline forms of carbon can exist. This phenomenon is yet another illustration of the many unique aspects of carbon as an element: it is not surprising that life on earth should have developed through the biochemistry of its compounds.

The electronic subsystem of a cooperative system of carbon atoms is very labile. It is characterised by a large number of metastable states: transitions between these states are possible, giving switching effects, even for a given (fixed) configuration of the atomic nuclei. Equally numerous are the possible types of electronic state of the atomic "loggias". The coordination (cooperation) between atoms can differ, the coordination number z usually varying between 2 and 4, though other values are possible. In this sense a one-component substance consisting of single carbon atoms should more correctly be treated as consisting of atoms of different types, since the atoms are not identical. The possible combinations of even three kinds of carbon atom (in reality, far more than three) are very numerous and varied. They amount to a set of systems of indeterminate composition and both regular and non-regular structure.

Some crystalline forms of carbon may have very unusual electrophysical, magnetic, or mechanical properties: they can be superconductors, conductors, semiconductors, or insulators. The strategic objectives of current carbon research include the development of a systematic approach to a unified scientific description of cooperative phenomena in elemental carbon, the controlled synthesis of carbon crystals having prescribed properties, and the study of the structure and properties of these crystals.

Diamond has long been used as a super-hard material, and graphite also has found widespread practical applications. Carbyne is now beginning to establish itself. Polymeric carbon, in its enormous variety of forms and modifications, will undoubtedly become a leading technological material. The strong tendency of carbon towards localised cooperation (polymerisation), increasing with temperature, gives it an advantage over all other polymers, which are degraded by heat.

The general progress in carbon science and the developments in the carbon industry have created new prospects for the application of different types of carbon in electronics, the aircraft industry, space technology, medicine, constructional materials, etc.

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