SOLID AND GASEOUS CARBON ALLOTROPES IN ULTRAHIGH VACUUM AT 3 K

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ABSTRACT — In ultrahigh vacuum at 3 K (the ordinary condition of the interstellar matter) carbon can be quench-crystallized in A1-type and A3-type phases and may also become a gas with diatomic $C \equiv C$ molecules, similar to the $N \equiv N$, $O = O$ and $H - H$ molecules of the three other elements that give rise to life.

1 — INTRODUCTION AND GENERAL CONSIDERATIONS

In the temperature and pressure conditions of the earth, carbon, which is the element with the highest melting point, can crystallize in the form of diamond or graphite [1, 2] or be amorphous.

Diamond has a fcc A4-type structure, in which each atom is tetrahedrally bound to four others by single covalent bonds of equal lengths, and all the valence electrons are used in bonding. The result is the formation of a three-dimensional network of strong bonds that confer extreme hardness to the diamond, which is the hardest substance existing in nature. However, the diamond lattice is relatively empty, since the proportion of the available space filled by atoms thought of as hard spheres is only $\pi\sqrt{3}/16$, or about 46 % of the filling factor $\pi\sqrt{2}/6$ for the closest-packed fcc atom disposition, which is the Al-type arrangement.

Graphite has a characteristic hexagonal structure, in which planar layers of atoms composed of benzene-type rings with single σ-bonds and held together by non-localized π-orbital electrons are formed. This structure is strongly anisotropic, because the inter-layer spacing is more than twice as large as the interatomic distance within a layer, and is still emptier than that of diamond, as its filling factor and axis ratio are 0.220 and 2.717, much lower and higher, respectively, than the filling factor $\pi\sqrt{2}/6$ and the axis ratio $\sqrt{8/3}$ for the closest-packed hexagonal atom disposition, which is the A3-type arrangement.

Amorphous carbon has a long-range random glassy structure (with a filling factor of 0.174 - 0.203, even lower than that of graphite) including short-range hexagonal aromatic cell networks, similar to pieces of graphite layers.

The large emptiness of diamond, graphite and amorphous carbon, together with the consideration that carbon belongs to group 4, which comprises three A3-type transition elements (titanium, zirconium and hafnium) and an A1-type non-transition element (lead), led us to try to force carbon to crystallize in closer-packing hexagonal or cubic phases by vapour-quenching in ultrahigh vacuum, at about 3 K, on materials able to promote pseudomorphism. The aim was attained by quench-condensation of carbon vapour, in the form of metastable A3-type or A1-type pseudomorphs, on glass substrates quench-coated with A3-type beryllium films or with double layers consisting of a B1-type LiF base film and a metastable A1-type boron overlay [3]: we have chosen beryllium and boron as they immediately precede carbon in the periodic table of the elements and pseudomorphism needs atom size similarity.

But the most interesting result was not the growth of unusual A3-type and A1-type carbon modifications, which is not a novelty, since we had already vapour-frozen A1-type phases of the three non-transition elements of group 4 immediately following carbon in the periodic table (silicon [4], germanium [4] and tin [5]), but the unexpected composition of the carbon vapour beam reflected from the impinged surfaces, which consists nearly completely of diatomic molecules. This means that in ultrahigh vacuum at about 3 K (which is the normal condition of the intersidereal matter) carbon may exist in the form of gaseous $C \equiv C$ molecules, like the $N \equiv N$, $O = O$ and $H - H$ molecules of the three other elements that give rise to life. Hence we are led to believe that in the interstellar space simple biochemical compounds such as glycine and other amino acids can arise spontaneously from direct synthesis of gaseous carbon, nitrogen, oxygen and hydrogen.

2 — EXPERIMENTAL DETAILS

Prior to the description of the results of the present study let us give some information about the method employed for evaporating carbon, analysing the vapour, growing the metastable A3-type and A1-type pseudomorphic films, and determining their crystal structure, thickness and condensation rate.

Carbon was sublimated from a liquid-nitrogen-cooled boron nitride crucible (suitably covered to avoid emission of solid sparks) by using a 270°-pencil-deflection electron gun. The evaporant consisted of ultrapure microcrystalline graphite granules, obtained by thermal decomposition of tetrachloromethane.

The sublimation took place in a vacuum coating chamber, at pressures from 10^{-10} to 10^{-6} torr, on very smooth, optically polished, square-shaped alkali-zinc borosilicate glass substrates held at 3 K inside a liquid helium-cryostat. Before carbon deposition, the substrates had been degassed by baking in vacuum at 350 °C for 6 hours, cleaned by both ultrasonic agitation at 50 kHz and ionic bombardment using a glow discharge of 5 kV, and quench-coated at 3 K with a single A3-type beryllium film or a double layer consisting of a B1-type LiF base film and a metastable A1-type boron overlay.

The presence of polyatomic molecules in the carbon vapour beams impinging on the beryllium or boron film and reflected from it was found out by analysing the vapour with a mass spectrometer whose ionizer converts molecules into cations through collisions with electrons extracted from an emission filament by means of a suitable electric field that gives them an energy of about 100 eV, eight times as high as the carbon first-ionization potential, but too low to affect the adsorbed percentages of the impinging molecules: the minimum detectable pressure was lowered by using an electron multiplier, so as to register currents as low as 10^{-17} A, corresponding to pressures of 10^{-13} torr; the angle of impingement was kept large enough to avoid a perceptible mixing of the impinging and reflected beams. The disposition of the carbon atoms according to an A3-type or A1-type arrangement like that of beryllium or boron atoms was deduced from in situ electron-diffraction patterns; the thickness and growth rate of the deposits (which ranged from 100 to 2000 Å and from 1 to 30 Å/sec, respectively) were measured with a piezoelectric quartz-crystal monitor incorporated in the cryostat.

3 — RESULTS, DISCUSSION AND CONCLUSIONS

3.1 — *Sublimation temperature and emitted vapour composition*

Table 1 gives the sublimation temperature of carbon as a function of pressure over the range from 10^{-10} to 10^{-6} torr, together with vapour pressure data quoted by Glang [6]. The temperatures were measured with an accuracy of ± 2 K, by averaging a large number of values, which, excepting some small

TABLE 1 — Sublimation temperature of carbon at various pressures.

Pressure (torr)	Sublimation temperature (K)	
	This work	Glang [6]
10^{-10}	1680	1765
2.10^{-10}	1709	
5.10^{-10}	1752	
10^{-9}	1787	1845
2.10^{-9}	1824	
5.10^{-9}	1878	
10^{-8}	1921	1930
2.10^{-8}	1962	
5.10^{-8}	2022	
10^{-7}	2072	2030
2.10^{-7}	2121	
5.10^{-7}	2184	
10^{-6}	2235	2140

irregularities, were found to be continuously distributed in Gaussian fashion about the mean. A comparison shows that, with increasing pressure, the sublimation temperature rises somewhat more sharply than that of reference [6], and is lower or higher than it according to whether pressure is below or above 2.10^{-8} torr, as results from interpolation.

The composition of the vapour emitted from the crucible is given in the second column of table 2 : the values, which refer to evaporation at 10^{-10} torr from a source at 1680 K, were determined by averaging a large number of data obtained by analysing the beam with a precision of about ± 0.1 %. Note that the vapour consists of single atoms (71.15 %) and polyatomic molecules with an even number of atoms ranging from 2 to 20 with the exception of 8, 12 and 18 (28.85 %).

TABLE 2 — Composition of carbon vapour beams impinging and reflected on beryllium or boron films at 3 K; sticking coefficient.

Molecule	Impinging beam (%)	Reflected beam (%)		Sticking coefficient		Simplest corresponding hydrocarbon
		Be	B	Be	B	
C	71.15	4.25	6.05	0.994	0.991	Methane
C_2	11.85	95.15	92.45	0.193	0.174	Acetylene
C_4	0.60	0.00	0.00	1.000	1.000	Cyclobutadiene
C_6	6.15	0.35	0.90	0.994	0.985	Benzene
C_{10}	3.95	0.20	0.35	0.995	0.991	Naphthalene
C_{14}	3.55	0.05	0.15	0.999	0.996	Anthracene
C_{16}	0.35	0.00	0.00	1.000	1.000	Pyrene
C_{20}	2.40	0.05	0.10	0.998	0.996	Benzopyrene

3.2 — *Deposit crystal structure*

Tables 3 and 4 give crystal structure data of : (1) the vapour-quenched metastable A3-type and A1-type carbon, (2) A3-type and A1-type pseudomorphs with the same lattice constants as the beryllium and boron layers, (3) A3-type and A1-type modifications with the closest-packed filling factor $\pi \sqrt{2}/6$ (corresponding to an A3-type axis ratio $\sqrt{8/3}$), (4) graphite and diamond (which crystallize in hexagonal and A4-type phases with filling factors 0.220 and $\pi\sqrt{3}/16$, respectively) and (5) A3-type (with axis ratio $\sqrt{8/3}$) and A1-type modifications with the same density as graphite and diamond.

TABLE 3 — Lattice constants a and c and unit cell volume V at 3 K, number of atoms per unit cell, n, and density d at 3 K of: A3-type carbon deposits vapour-quenched on A3-type beryllium layers; some hypothetical A3-type carbon phases; and graphite.

Material	a (Å)	c (Å)	c / a	V (Å^3)	n	d (g / cm^3)
A3 deposit	2.297	3.682	1.6030	50.473	6	2.3709
A3 pseudomorph	2.278	3.572	1.5680	48.158	6	2.4849
A3 close-packed phase	1.5444	2.5220	1.6330	15.628	6	7.6571
Graphite	2.4605	6.6841	2.7166	105.133	12	2.2765
A3 phase as dense as graphite	2.3140	3.7787	1.6330	52.567	6	2.2765

TABLE 4 — Lattice constant a and unit cell volume V at 3 K, number of atoms per unit cell, n, and density d at 3 K of: A1-type carbon deposits vapour-quenched on A1-type boron layers; some hypothetical A1-type carbon phases; and diamond.

Material	a (Å)	V (Å^3)	n	d (g/cm^3)
A1 deposit	2.755	20.911	4	3.8151
A1 pseudomorph	2.669	19.013	4	4.1960
A1 close-packed phase	2.1841	10.419	4	7.6571
Diamond	3.5666	45.369	8	3.5169
A1 phase as dense as diamond	2.8308	22.684	4	3.5169

The values of the lattice constants of (1) and (2) are means of those of a large number of samples whose lattice constants were determined with an accuracy of approximately ± 0.1 %; those of (3) were found by calculations; those of (4) were obtained from the values at room temperature by taking into account thermal contraction; those of (5) were deduced from (4); all values of the unit cell volume and density were calculated from the lattice constants.

A glance shows that the A3-type and A1-type deposits are less dense than would be expected for no-lattice-misfit pseudomorphic growth, much less dense than ideal closest-packed phases (where the atoms, thought of as hard spheres, are arranged so as to fill the maximum proportion of the available volume), and only 1.041 and 1.085 times as dense as graphite and diamond, respectively; whereas the theoretical closest-packing A3-to-graphite and A1-to-diamond structure filling-factor ratios are 3.364 and 2.177.

These results are not surprising, since, in spite of the constraint imposed on the overlay lattice by the beryllium-carbon or boron-carbon interatomic bonds due to van der Waals forces, the overlay and base-film lattices cannot fit, as the distance between carbon atoms must be larger than those between beryllium or boron atoms, because beryllium, boron and carbon are consecutive elements with 4, 5 and 6 electrons, respectively, and the atom size increases with the number of electrons. Owing to the opposition of the electron shell repulsion to the above constraint, the lattice constants of the A3-type and A1-type carbon layers are only almost midway between those of a no-lattice-misfit pseudomorph and those of an ideal A3-type or A1-type modification with the same density as graphite or diamond.

A comparison of the data of table 4 with those given in references [4] and [5] shows that the A1-to-A4 phase density ratio of carbon (1.085) is much less than that of silicon (1.98), germanium (2.05) and tin (1.82 to 2.08, depending on the material of the base film), which are near the closest-packed theoretical value (2.177). As to the lattice misfit, let us point out that the base-film/overlay lattice-constant difference of carbon is negative, as that of tin, whereas those of silicon and germanium are positive.

3.3 — *Reflected vapour composition*

The film growth process may be envisaged as a vapour-to-solid transformation arising from the van der Waals attraction of the impinging vapour molecules to the substrate or growing-film surface, due to the interaction of their fluctuating dipole and quadrupole moments (associated with the instantaneous position of the electrons in the atoms) with those induced in the surface atoms, or vice versa. As a result, the vapour molecules lose their velocity component orthogonal to the surface and are physically adsorbed, but may or may not be completely thermally equilibrated. In the latter case they move over the surface by jumping from one potential well to another till they interact with other adsorbed molecules to create stable solid clusters (whose growth and coalescence are the birth stages of the film), with release of the condensation heat; or the molecules recover, because of thermal agitation, a velocity component normal to the surface and desorb into the vapour phase. The probability that an impinging molecule will be incorporated into the film is given by the sticking coefficient, which corresponds to the ratio of the amount of material condensed on the surface to the total amount impinged [7].

The composition of the vapour desorbed from the carbon overlays growing on beryllium or boron base films is given in the third and fourth columns of table 2; the corresponding sticking coefficients, found out by calculation, are given in the fifth and sixth columns. As may be seen, the impinging molecules are completely (C_4 and C_{16}) or nearly completely (C, C_6, C_{10}, C_{14} and C_{20}) incorporated into the film, with the exception of the diatomic molecules, which are reflected in the proportion of 80.7 % (beryllium base layer) or 82.6 % (boron base layer).

These data show that in ultrahigh vacuum at about 3 K the $C \equiv C$ molecule is stabler in the gaseous than in the solid phase, so that in the interstellar space there should be anywhere $C \equiv C$, $N \equiv N$, $O = 0$ and $H - H$ gaseous molecules. These may react to produce glycine, other amino acids and biochemical compounds associated with life; hence the conjecture that life may originate from intersidereal matter, and therefore be distributed throughout the whole universe.

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