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Prediction of a nanoporous sp^2-carbon framework structure by combining graph theory with quantum mechanics

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Abstract

A nanoporous carbon framework structure is predicted by combining graph theoretical approaches and density functional calculations. Bond lengths in this polymorph, with all atoms sp^2-hybridised, are in good agreement with typical C–C and C=C bond lengths, bond angles are close to 120°, and it is 0.36 eV/atom less stable than diamond. The electronic structure suggests it is a quasi-one-dimensional metal with anisotropic electronic properties and a spectroscopic signature. The compound has a high bulk modulus of 234(1) GPa but a density similar to that of graphite and amorphous carbon. Changes in the lattice parameters on compression are strongly anisotropic. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The prediction of new materials and their properties is a central topic in condensed matter studies. The theoretical calculation of the properties of hypothetical compounds is especially important if experimental investigations point towards a new structure with unique properties, but not enough material is available for a crystal structure determination. This situation often arises when only thin films of a new compound can be produced. For a systematic search of possible new structures, a fast and reliable approach is needed to provide ‘trial structures’ suitable for testing and optimisation using modern, quantum-mechanical techniques. It would be a significant advantage if the algorithm used to obtain the trial structures could provide a complete enumeration of all possible structures under a given set of constraints. An approach which can potentially fulfill these requirements is based on so-called ‘quotient graphs’ [1]. With this technique, it is possible to exhaustively enumerate classes of three-dimensional nets, find those which can be embedded in Euclidean space and match restrictions imposed by nature on real crystal structures. Here, we use this approach to suggest a new form of carbon.

Polymorphs of crystalline and amorphous carbon have long been at the center of an overwhelming number of experimental and theoretical studies. Of rather recent interest is the synthesis of hard sp^2-bonded carbon modifications, whose properties would be dominated by the extremely strong in-planar bond of graphite [2]. It has been suggested that such

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materials could be synthesised by the laser initiated pulsed cathodic arc method [3]. This technique does not yield enough sample for conventional structure determinations by diffraction methods, but the products of the laser-arc technique can be investigated by electron microscopy and spectroscopic techniques. This allows the confirmation of the predominance of sp^2-bonds [3] and implies a new form of carbonaceous material.

In the light of the above, it is interesting to model sp^2-bonded carbon modifications and compare their properties to those suggested for experimentally produced compounds, so as to establish the structure and other properties. Earlier predictions of possible new sp^2-carbon modifications relied on the tiling of minimal surfaces [4–7]. However, the restriction to structures which can be described by tilings of minimal surfaces is rather severe. Here, we use the graph theoretical approach mentioned above and quantum-mechanical calculations to efficiently search for relatively stable carbon modifications with a framework structure in which all atoms are sp^2-hybridised, and to then predict their properties. The trial structures required for such a search correspond to regular 3-nets, i.e. nets in which each vertex is connected to three neighbours and which can be embedded into Euclidean space. All crystallographically acceptable regular 3-nets with four and six vertices per unit cell have been summarised by Bader et al. [1]. In this case we have chosen the ‘6(3)4-25’-net as a trial structure for the quantum-mechanical calculations. An inspection of the structure shows that it has bond-angles which are all close to 120°. This is a reasonable crystal-chemical constraint when modelling sp^2-hybridised carbon polymorphs.

2. Computational details

The quantum-mechanical computations were performed with both academic and commercial (MSI) versions of the CASTEP code [8,9]. This is a density functional-based total energy code which uses pseudopotentials to describe the electron–ion interaction, a Monkhorst–Pack scheme for the sampling of reciprocal space, and a Broyden–Fletcher–Goldfarb–Shanno-based algorithm [10] for the geometry optimisation. One set of calculations was performed with norm-conserving pseudopotentials at a kinetic energy cut-off of 800 eV and a k-point mesh of 63 k-points in the irreducible part of the Brillouin zone. An additional set of calculations used ultrasoft pseudopotentials [11,12] instead, with a cut-off of 310 eV. The transferability of the norm-conserving pseudopotentials has been established in a previous study [13] and there it was shown that it was preferable to use a generalised gradient approximation [14,15] instead of the local density approximation. Results of the two sets of calculations, using the two different types of pseudopotentials, did not differ significantly.

3. Results

The orthorhombic trial structure with space group *Immm*, corresponding to one of the quotient graphs embedded into Euclidian space, was relaxed until forces on all atoms were less than 0.1 eV/Å. The relaxed structure is shown in Fig. 1, and the lattice parameters are given in Table 1. We also performed calculations in an orthogonal lattice without symmetry constraints, but to within the accuracy of the calculations the relaxed structure always had space group symmetry *Immm*. Hence, the high symmetry structure corresponds to a local energy minimum of the Born–Oppenheimer hypersurface. Atoms in the new carbon modification are located on Wyckoff positions $4e$ with $x = 0.6029$ and Wyckoff position $8n$ with $x = 0.2780$, $y = 0.2051$. The structure obtained is sensible from a crystal-chemical point of view. It can be described as consisting of zig-zag chains which are joined by C═C groups, where each of the two atoms of the C═C group is bound to two atoms of different chains. Within the chains, the C–C bond distance is 1.406 Å. This is exactly the bond distance which we obtain in calculations of graphite and is within 1% of the experimental value. The bond angles within the chain are 117° and 124°, which are close to the ideal value of 120°. The distance between the carbon atoms in the C═C groups is much shorter (1.33 Å) which is as expected for a double bond, since C═C bond distances between sp^2-hybridised carbon atoms range from 1.32 to 1.36 Å [16]. The bond distance between the atoms

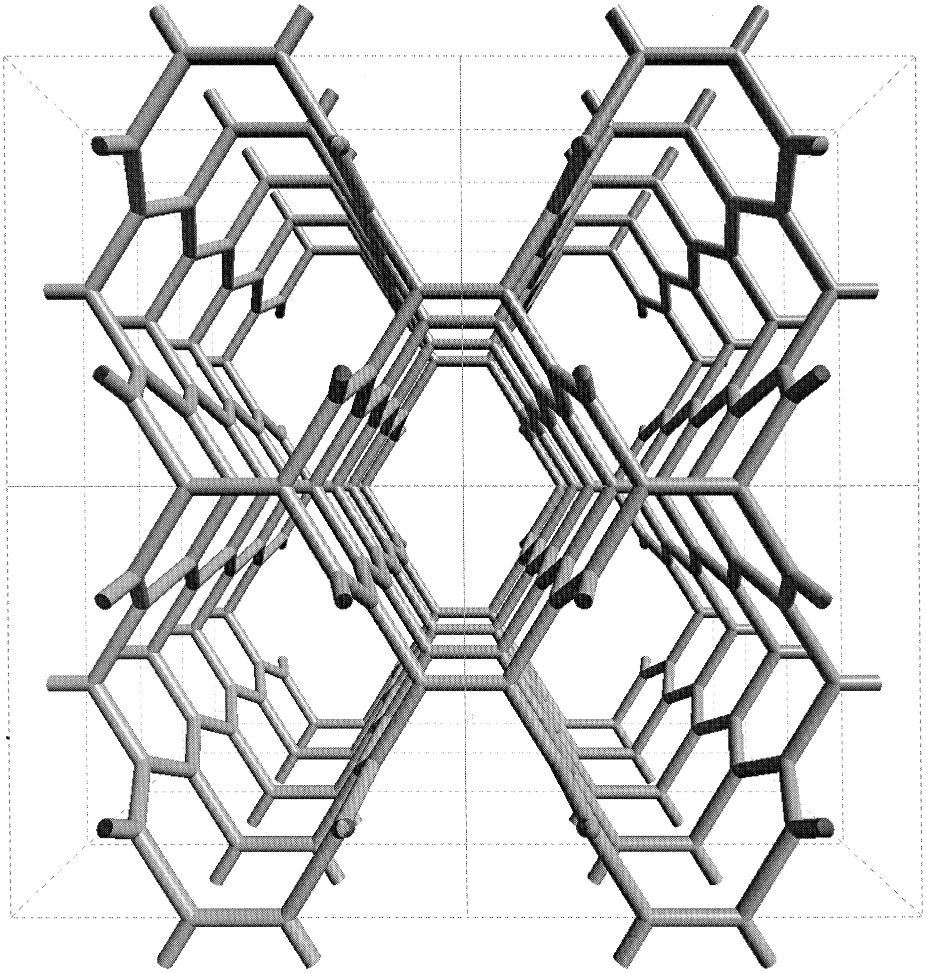

Fig. 1. The structure of the new polymorph. Sixteen unit cells are shown.

belonging to the zig-zag chain and atoms belonging to a C=C group is 1.473 Å which is in very good agreement with distances observed for two sp^2-hybridised carbon atoms, one of which is doubly bonded to a third carbon atom [16]. Difference maps between the valence electron density in the crystal and the superposed valence electron density of non-interacting atoms show that all bonds are covalent, as there is significant charge accumulation between neighbouring atoms. In summary, the bond distances, bond angles and the character of the bonds are very close to typical values observed in other carbon containing compounds. This implies that the structure is rather stable. With respect to the lattice energy the structure is indeed only 0.4 eV/atom less stable than diamond (see Table 1).

The pressure-induced structural changes are highly anisotropic. While the short c-lattice parameter decreases upon compression by 1% at 9 GPa, the a lattice constant decreases by 2.7%, while the b lattice parameter increases slightly at small compressions and then remains approximately constant. The pressure dependence of the unit cell volume can be described equally well by a second- or third-order Birch–Murnaghan equation of state as for the latter case the pressure derivative of the bulk modulus is $B' = \partial B/\partial P = 4(1)$. In both cases the computed bulk modulus is $B = 234(1)$ GPa.

Table 1
Theoretical data for crystalline carbon polymorphs

	a (Å)	b (Å)	c (Å)	Density (g/cm^3)	Energy [a] (eV/atom)
Diamond (theo.)	3.5303	–	–	3.6	0
Diamond (exp.) [b]	3.5670	–	–	3.56	
Lonsdaleite (theo.)	2.4830	–	4.1347	3.6	0.026
Lonsdaleite (exp.) [c]	2.52	–	4.12	3.56	
Polybenzene [d]	6.014	–	–	2.2	0.07
C_{60}	–	–	–	–	0.3 [e]
New polymorph	**6.517**	**6.093**	**2.483**	**2.4**	**0.36**
Supercubane [f]	4.8164	–	–	2.9	0.64
BC8	4.4316	–	–	3.7	0.724
10^3-Structure [g]	4.0709	–	–	2.4	1.169

[a] Relative to diamond.
[b] Exp. values from Ref. [27].
[c] Exp. values from Ref. [27].
[d] Ref. [7], recomputed here.
[e] Computed using results of Ref. [7]; see text.
[f] Ref. [13].
[g] Ref. [7], recomputed here.

The stability of the new polymorph can be compared to that of other hypothetical carbon polymorphs and to that of the fullerenes. We recomputed the energy of some of the low energy sp^2-carbon structures suggested by Ref. [7] and used their results to compare the stability of the new polymorph to C_{60}. The energy difference between polybenzene and the 10^3-structure computed in the present study is similar to that obtained by Ref. [7]. This allows us to use the energy difference computed by Ref. [7] between polybenzene and C_{60} to estimate the relative stability of the new polymorph. As Table 1 shows, the new polymorph is only slightly less stable than C_{60}. The new polymorph is significantly more stable than hypothetical sp^3-carbon framework structures, such as supercubane [13] and BC8-carbon [17–20]. The results we obtained for BC8 carbon are also given in Table 1. The internal parameter of the relaxed structure is 0.09345, which results in bond lengths of 1.615 and 1.434 Å. The computed structural parameters and the relative energy difference between diamond and BC8 carbon are similar to those obtained elsewhere [17–20].

The new carbon modification presented here is a nanoporous framework structure, where the smallest diameter of the channels running parallel to the c-axis is 4.4 Å. The band structure shown in Fig. 2 implies that although the new polymorph has a three-dimensional framework structure it is a quasi-one-dimensional metal with strongly anisotropic electronic properties. This is similar to theoretical [21–23] and experimental [24,25] findings for nanotubes, which can be, depending on the helicity of the tube lattice and their diameter, strongly one-dimensional conductors. This is consistent with a description of the structure of the new polymorph as a dense packing of compressed nanotubes, with shared walls. The conductivity of nanotubes can be understood in terms of the dependence of the band structure on a vector describing the chirality and the fiber diameter [22–25]. While the structure of the new polymorph can also be described as consisting of interpenetrating carbon spirals, where one turn of the spiral is equal to twice the c-lattice parameter, an elegant analysis such as in the case of nanotubes does not immediately present itself. The combination of the metallic character of the structure and the large diameter of the channels implies that it should be rather straightforward to intercalate Li atoms.

Further analysis of the electronic structure reveals a possible means of identification of this new polymorph in situations where only small quantities may have been synthesised. A projection of the density of

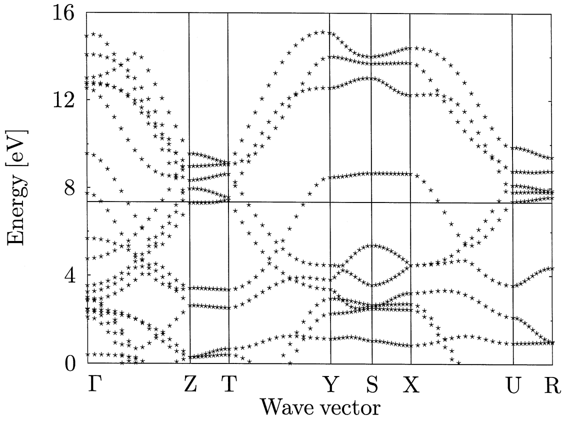

Fig. 2. The band structure of the new polymorph. The labelling of points in the Brillouin zone is: $\Gamma = 0,0,0$; $Z = 0,0,\frac{1}{2}$; $T = \frac{1}{2},0,\frac{1}{2}$; $Y = \frac{1}{2},0,0$; $S = \frac{1}{2},\frac{1}{2},0$; $X = 0,\frac{1}{2},0$; $U = 0,\frac{1}{2},\frac{1}{2}$; $R = \frac{1}{2},\frac{1}{2},\frac{1}{2}$. Directions $\Gamma \rightarrow Z$, $Y \rightarrow T$, $X \rightarrow U$ are parallel to the channel, while $T \rightarrow Z$, $Y \rightarrow S$, $S \rightarrow X$, and $U \rightarrow R$ are perpendicular to the channels. The Fermi level is indicated by the horizontal line.

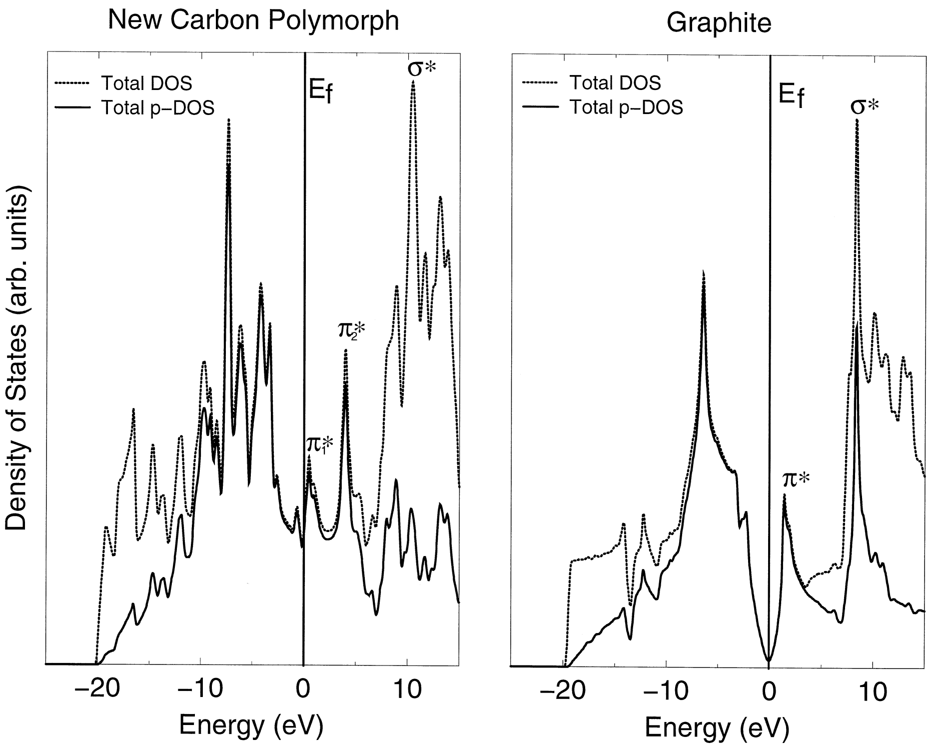

Fig. 3. The total density of states (dashed lines) and the p-projected density of states (solid lines) for the new sp^2-bonded carbon polymorph (left panel) and graphite (right panel). The π_2^* peak is due to the atoms in the zig-zag chains, while the π_1^* peak is due to the remaining atoms.

states onto the atomic 2p wavefunction of carbon (see Fig. 3) clearly reveals a split in the π^* peak, in contrast to the situation in graphite. Resolving the projected density of states further into contributions from the individual atomic sites indicates that the π_2^* peak derives from the carbon atoms in the chains, and the π_1^* peak from the remaining sites. The relative intensities of these π^* peaks may be explained by the relative frequency of the two sites, namely 2:1. Such a p-projected density of states is just what could be measured using a scanning transmission electron microscope (STEM) fitted with an electron energy loss (EEL) spectrometer (ignoring effects of orientation, weakly energy dependent matrix elements, and a presumably weak core-hole effect) [26]. The carbon K-edge (at about 285 eV) is the result of excitations from the 1s core electron, through the dipole operator, into states of p-symmetry in the conduction band. The focussed electron beam of the STEM can take measurements from very small samples (sub-nanometer probes are becoming common). Similar spectral features might be expected in X-ray absorption spectroscopy, but larger samples would be required.

From a comparison of the measured electron loss spectrum with the calculated p-density of states we can conclude that the new carbonaceous material synthesised by Ref. [3] does not have the structure of the polymorph presented here. The prediction of the structure and some properties of a new polymorph of carbon with unusual structural features and physical properties is nevertheless a convincing demonstration of the fertility of the combination of graph theory and quantum mechanics, which we are currently extending by calculating the ground state properties of all possible carbon polymorphs which can be represented by regular 3-nets with less than six vertices per unit cell. The extension to incorporate more sophisticated crystal chemical constraints in the search for more complex crystal structures is in principle straightforward and can be automated to a significant extent.

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References

[1] M. Bader, W.E. Klee, G. Thimm, Zeitsch. Kristallogr. 212 (1997) 553.

[2] M.M.J. Treacy, T.W. Ebbesen, J.M. Gibson, Nature 381 (1996) 678.

[3] I. Alexandrou, H.-J. Scheibe, C.J. Kiely, A.J. Papworth, G.A.J. Amaratunga, B. Schultrich, Condensed-Matter preprint server 9905130 (unpublished).

[4] A.L. Mackay, H. Terrones, Nature 352 (1991) 762.

[5] D. Vanderbilt, J. Tersoff, Phys. Rev. Lett. 68 (1992) 511.

[6] T. Lenosky, X. Gonze, M. Teter, V. Elser, Nature 355 (1992) 333.

[7] M. O’Keefe, G.B. Adams, O.F. Sankey, Phys. Rev. Lett. 68 (1992) 2325.

[8] M.C. Payne, M.P. Teter, D.C. Allan, T.A. Arias, J.D. Johannopoulos, Rev. Mod. Phys. 64 (1992) 1045.

[9] Cerius^2 Users Guide, Molecular Simulations, San Diego, CA, 1997.

[10] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, Numerical Recipies in C, Cambridge University Press, 1992.

[11] D. Vanderbilt, Phys. Rev. B41 (1990) 7892.

[12] G. Kresse, J. Hafner, J. Phys.: Condensed Matter 6 (1994) 8245.

[13] B. Winkler, V. Milman, Chem. Phys. Lett. 293 (1998) 284.

[14] J.P. Perdew et al., Phys. Rev. B46 (1992) 6671.

[15] J.A. White, D.M. Bird, Phys. Rev. B50 (1994) 4954.

[16] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, R. Taylor, in: A.J.C. Wilson (Ed.), International Tables for Crystallography, The International Union of Crystallography, vol. C: Mathematical, Physical and Chemical Tables, Kluwer Academic, Dordrecht, 1992, pp. 685–706.

[17] J. Furthmüller, J. Hafner, G. Kresse, Phys. Rev. B 50 (1994) 15606.

[18] J. Crain, S.J. Clark, G.J. Ackland, M.C. Payne, V. Milman, P.D. Hatton, B.J. Reid, Phys. Rev. B 49 (1994) 5329.

[19] S. Fahy, G. Louie, Phys. Rev. B 36 (1987) 3373.

[20] R. Biswas, R.M. Martin, R.J. Needs, O.H. Nielsen, Phys. Rev. B 35 (1987) 9559.

[21] J.W. Mintmire, B.I. Dunalp, C.T. White, Phys. Rev. Lett. 68 (1992) 631.

[22] R. Saito, M. Fujita, G. Dresselhaus, M.S. Dresselhaus, Appl. Phys. Lett. 60 (1992) 2204.

[23] N. Hamada, S.-I. Sawada, A. Oshiyama, Phys. Rev. Lett. 68 (1992) 1579.

[24] T. W Odom, J.-L. Huang, P. Kim, C.M. Lieber, Nature 391 (1998) 62.

[25] J.W.G. Wildöer, L.C. Venema, A.G. Rinzler, R.E. Smalley, C. Dekker, Nature 391 (1998) 59.

[26] D.A. Muller, Y. Tzou, R. Raj, J. Silcox, Nature 366 (1993) 725.

[27] P. Eckerlin H. Kandler, in: K.A. Hellwege, A.M. Hellwege (Eds.), Strukturdaten der Elemente und Intermetallischen Phasen, vol. III, New Series, Springer, Berlin, 1971.