Systematic prediction of crystal structures

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Abstract

A generally applicable and systematic prediction of crystal structures and their properties has been an important goal of crystallography and materials science. Here we present such a general and systematic approach. This approach is based on a combination of graph theory with quantum mechanics. As an application, structures, properties and relative stabilities of small hypothetical carbon polymorphs with up to six atoms per unit cell are presented. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The prediction of new materials and their properties is a central area of research in many fields of the condensed matter sciences. While systematic predictions of possible molecules, such as fullerenes, have long been performed [1–3], predictions for solids are generally based on non-systematic approaches such as simulated annealing techniques, or isomorphic substitution of known structures [4]. The tiling of minimal surfaces, suggested previously as a systematic approach [5–8], is not generally applicable and is inefficient for small structures. Here, we present a general scheme for the systematic prediction of new materials and their properties based on a combination of graph theory and quantum mechanics. Candidate structures are systematically generated [9] and then used as an input to first principles quantum me-

chanical calculations [10]. These yield realistic values for the interatomic distances and properties, such as the relative stability, vibrational spectra, electronic band structure and elastic properties. The approach is demonstrated by the prediction of all possible sp^2-carbon 3D framework structures with up to six atoms in the primitive unit cell.

2. Systematic prediction of crystal structures

In the present scheme, the systematic prediction of structures begins with an enumeration of *nets*, which are infinite, periodic graphs, in which nodes represent atoms and edges represent bonds, giving a graph theoretical description of crystal topologies [11]. The enumeration of all possible nets is achieved by investigating the corresponding finite *labelled quotient graphs* [9]. This is possible, as there is a unique mapping from a labelled quotient graph to a net. A labelled quotient graph is closely related to a crystallographic primitive unit cell, where the labelled edges in the quotient graph

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describe the connectivity of atoms. For a given number of atoms per unit cell all labelled quotient graphs which have a predefined connectivity can be found by combinatorial techniques [9]. The connectivity can be chosen so that in the corresponding structures all atoms, for example, are three-fold coordinated. This method can be extended naturally to cope with any complex coordination in crystal structures. At this stage no information concerning the chemistry is imposed. After a set of quotient graphs describing a set of non-isomorphic nets is found, an attempt is made to embed the nets in Euclidean space. If this is possible while maintaining their connectivity, 3D nets with given space group symmetries are obtained. The vertices in these nets are then decorated with atoms, defining the chemistry of the crystal. These are our candidate structures. As there is no information with respect to the absolute interatomic distances in the nets, a technique is required which allows us to obtain realistic interatomic distances. These can be calculated by modern first principles quantum mechanical methods.

For this, an efficient approach is the density functional based [12,13] plane wave pseudopotential method [14]. If, for any candidate structure, the result of a full geometry optimisation is stable with respect to small strains, the prediction of a stable or metastable polymorph is complete. The effects of temperature can in principle be incorporated by, for example, performing quantum mechanical free energy minimisation or molecular dynamics simulations [15,14]. The procedure is most straightforward for elemental compounds in which nearest neighbours are easy to identify, but can be extended to more complex compounds.

An alternative approach for a systematic enumeration of crystal structures has been developed by Friedrichs et al. [8]. However, our approach is more general and efficient, as quotient graphs can be constructed for any structure and their enumeration is more straightforward than tiling operations. This is especially true if the aim is to construct candidate structures with a small number of atoms per primitive cell or a given connectivity among the atoms.

3. Application to carbon polymorphs

To demonstrate the method, we now present an investigation of all possible sp^2-carbon framework structures with six atoms or fewer per primitive unit cell. The practical aspects of the graph theoretical calculations have been described in detail before [9]. We use the acceptable nets presented there with the same nomenclature, with the exception that for increased clarity we expand the number used for the enumeration to two digits, for example we use 6(3)1–06 instead of 6(3)1–6. We decorate the nodes with carbon atoms. The first principles quantum mechanical full geometry optimisations were performed using both academic and commercial (MSI) versions of the CASTEP code [14,16]. This is a density functional based total-energy code using planewaves to describe the wavefunction and resulting electronic charge densities. Vanderbilt ultrasoft pseudopotentials are used to describe the electron–ion interaction [17,18], the Monkhorst–Pack scheme [19] with a distance of less than 0.04 Å^{-1} between points is used for the sampling of reciprocal space, a BFGS-based algorithm is employed for the geometry optimisation [20] and a generalised gradient approximation is used for the exchange–correlation potential [21,22].

4. Results

Attempts were made to relax all 14 candidate structures obtained from the graph theoretical investigation. A structure was considered to have been relaxed when the remaining forces on all atoms were less than 0.1 eV/Å and the remaining stress less than 0.08 GPa. This was achieved for all candidate structures. The relaxed structures were then subjected to a further geometry optimisation in which only the translational symmetry was maintained. These relaxations led to the same result as the symmetry constrained relaxations for all but three of the structures, namely 6(3)1–06, 6(3)1–11 and 6(3)2–27. From the symmetry-constrained calculations it was known that these are the least energetically stable structures with six atoms per unit cell. The quantum mechanical
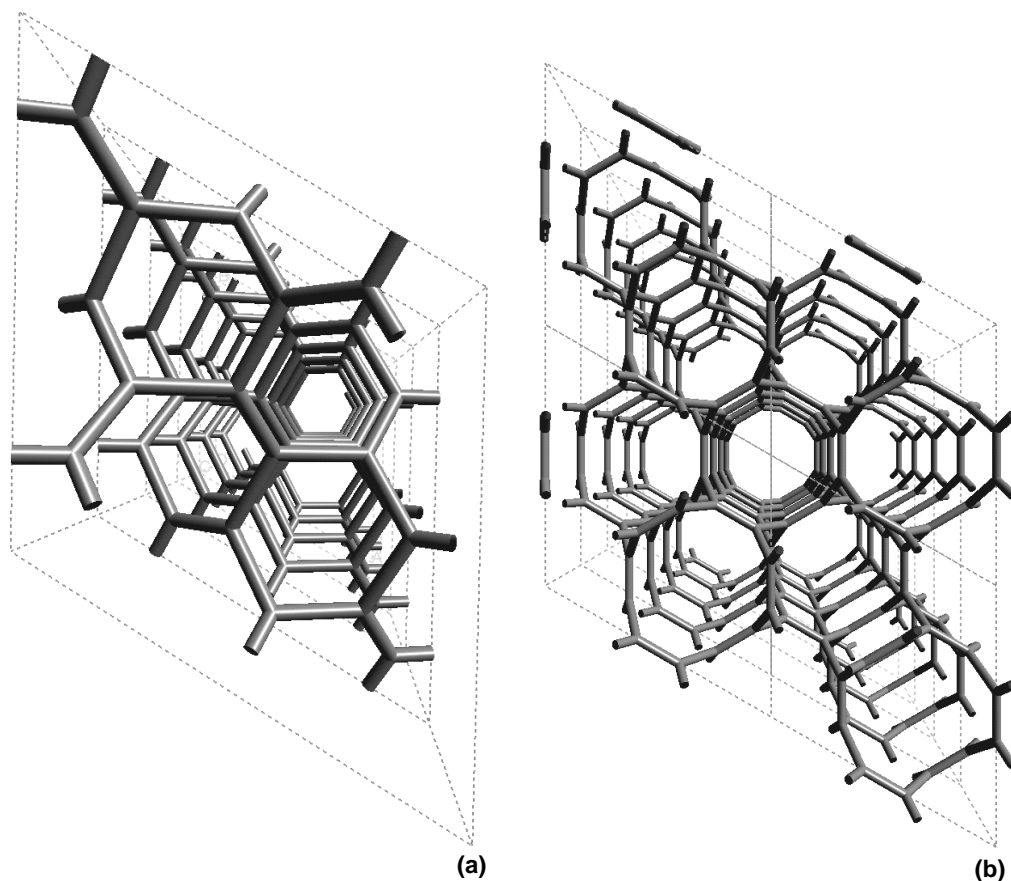
Fig. 1. A selection of geometry-optimised structures of hypothetical carbon polymorphs. The structures were derived from (a) the 6(3)1–10 net, (b) the 6(3)2–22 net, (c) the 6(3)3–26 net, and (d) the 6(3)4–25 net. Structural parameters are given in Table 1.

calculations therefore show that these three candidate structures are unstable with respect to small distortions. Hence, they are rejected as hypothetical metastable carbon polymorphs within the constraints of six atoms per unit cell imposed initially.

Four of the geometry-optimised structures are shown in Fig. 1, and the structural parameters of all of the hypothetical polymorphs are given in Table 1. After the relaxation, the carbon–carbon bonds had, with one exception, values of 1.34–1.48 Å, which are consistent with the experimentally observed distances between singly and doubly bonded sp^2-hybridised carbon atoms. The one exception was the result of the relaxation of the trial structure derived from the 6(3)5–09 net, which had C–C

distances of about 1.55 Å. Closer analysis shows that each atom is coordinated by four nearly equidistant neighbours. While the bond lengths in this polymorph are very close to those in diamond, the tetrahedral angles ($\approx 94°$) deviate significantly from the ideal tetrahedral angle. This is consistent with the computed lattice energy, which indicates that this structure is rather unstable. These results are a further demonstration that quantum mechanical methods must be used for the geometry optimisation, as force-field (empirical) models will generally not be flexible enough so as to allow a change of coordination during the relaxation. All structures are predicted to be less dense than diamond. The most stable structures have bond angles close to 120° and often exhibit conjugated π-chains.
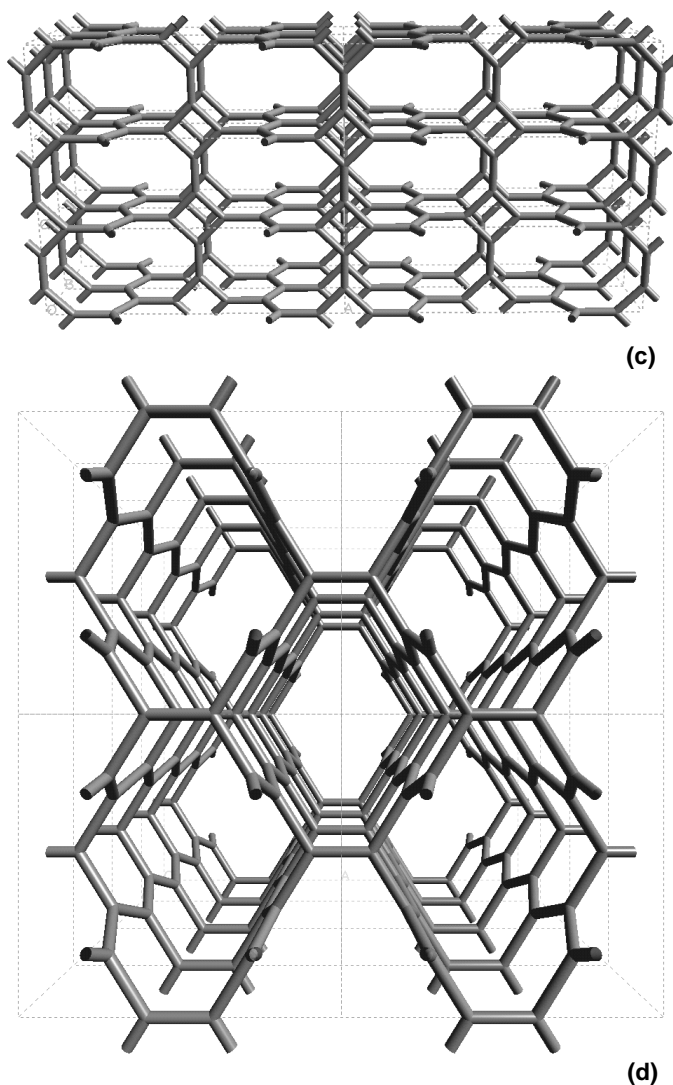
(c)

(d)

Fig. 1. (Continued).

Some other crystal chemical results are more surprising. For example, we found that a four membered ring does not necessarily imply that a structure is particularly unstable. Of course, carbon four membered rings are known to exist in cubane and related compounds [23,24], but have not been experimentally found in crystals. The total energy calculations can be used to estimate the relative stability of the predicted polymorphs. It is our experience that DFT-GGA calculations of graphite (with the interlayer binding having a significant van

der Waals contribution) are inaccurate, and hence, since the van der Waals contribution to the bonding of our framework structures is insignificant, we prefer to compare the computed lattice energies to that of diamond (Table 1).

Fig. 2 shows the total density of states of two of the more stable polymorphs, 6(3)1–10 and 6(3)2–22. 6(3)2–22 is found to be a semiconductor with a GGA band-gap of around 1.9 eV, while 6(3)1–10 is a semimetal with its density of states approaching zero at the Fermi energy, not unlike

Table 1
Structures, lattice energies relative to diamond (ΔE), and densities of the hypothetical carbon polymorphs[A]

Net	Space group	Lattice parameters and cell angles			Atom positions			ΔE	Density
					x/a	y/b	z/c	(eV/atom)	(g/cm^3)
Four atoms per primitive unit cell									
4(3)1	$I4_132$	4.0861	4.0861	4.0861	0.1250	0.1250	0.1250	1.166	2.33
4(3)2[d]	$I4_1/amd$	2.5161	2.5161	8.5655	0.0000	0.0000	0.0863	0.448	2.94
Six atoms per primitive unit cell									
6(3)1–06[a]	$P6_222$	4.0512	4.0512	2.4681	0.3208	0.0000	0.0000	1.448	3.41
6(3)1–10	$R\bar{3}m$	6.8001	6.8001	3.5963	0.8798	0.1202	0.0586	0.358	2.49
6(3)1–1[a]	$I\bar{4}m2$	4.7295	4.7295	4.9157	0.5000	0.0000	0.0957	1.132	2.18
					0.2197	0.0000	0.0075		
6(3)2–21	$P6_222$	3.9026	3.9026	3.7496	0.3980	0.7960	0.0000	0.624	2.42
6(3)2–22[b]	$R\bar{3}m$	7.0934	7.0934	3.5658	0.4056	0.0000	0.0000	0.397	2.31
6(3)2–27[a]	$R32$	7.8949	7.8949	3.7669	0.1020	0.0000	0.0000	1.097	1.77
					0.2830	0.0000	0.0000		
6(3)3–26	$Cmmm$	11.2452	2.5164	3.4056	0.0906	0.0000	0.0000	0.556	2.48
					0.0000	0.0000	0.2976		
					0.2202	0.0000	0.0000		
6(3)3–27	$Imm2$	2.5923	3.7825	10.8878	0.0000	0.0000	0.8698	0.675	2.24
					0.0000	0.0000	0.0058		
					0.5000	0.0000	0.0649		
					0.5000	0.0000	0.1973		
					0.5000	0.1841	0.3067		
6(3)4–25[e]	$Immm$	6.5208	6.1194	2.4911	0.6029	0.0000	0.0000	0.381	2.41
					0.2781	0.2051	0.0000		
6(3)5–09	$P1$	3.8132	3.8124	3.8121	−0.0999	−0.1287	−0.0751	1.062	3.10
		100.41	100.42	129.67	0.4722	0.2481	0.1201		
					−0.1512	0.4297	−0.0752		
					0.8489	0.8202	0.3153		
					0.7221	−0.0019	0.6202		
					0.2903	0.8712	0.3152		
6(3)6–09[c]	$P6_222$	2.6223	2.6223	6.3024	0.5000	0.0000	0.1141	0.793	3.19
6(3)6–11	$P1$	3.7465	3.8758	3.9124	−0.0913	0.0878	−0.1527	0.615	2.42
		60.62	89.99	90.03	0.5756	0.0886	0.0417		
					0.9087	−0.1144	0.6401		
					0.5757	0.8853	0.4457		
					0.2434	0.6905	0.6401		
					0.2434	0.2830	−0.1522		
Diamond (theo)	$Fd\bar{3}m$	3.5368	3.5368	3.5368	0.0000	0.0000	0.0000	0.0	3.61
Diamond (exp.)	$Fd\bar{3}m$	3.5670	3.5670	3.5670	0.0000	0.0000	0.0000	–	3.52

[A] All hypothetical structures are less stable and less dense than diamond. [a] indicates a structure which is only stable when the symmetry is constrained to the given space group, i.e., it is not stable with respect to small lattice distortions. The following structures have been studied previously: [b] tight-binding calculations [28]; [c] tight-binding [4] and DFT [29] calculations; [d] extended Hückel [30] and DFT [31] calculations; [e] DFT calculations [25].

graphite. Other polymorphs such as the one derived from the 6(3)4–25 net are found to be metallic [25]. This variety of electronic structure in a single series of polymorphs is intriguing and could have practical implications.

Further analysis of the electronic structure of the polymorphs reveals a possible means of their identification in situations where only small quantities may have been synthesised. For example, in samples produced by chemical vapour de-
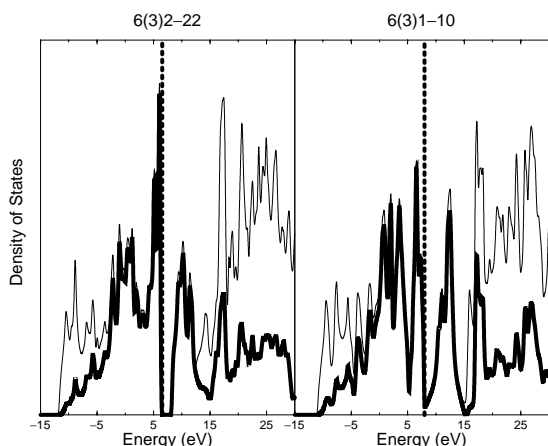
Fig. 2. The total density of states (thin lines) and the p-projected density of states (heavy lines) of two hypothetical carbon polymorphs, derived from the 6(3)2–22 and 6(3)1–10 nets.

position, unknown sp^2-bonded structures are often encountered [26]. Different phases in such samples could be identified by measuring their electron energy loss spectra using a Scanning Transmission Electron Microscope fitted with a magnetic prism for energy analysis of the transmitted beam [27]. This spectrum can be correlated to the p-projected density of states which we can also obtain from our calculations. Fig. 2 shows such p-projected densities of states for the 6(3)1–10 and 6(3)2–22 polymorphs.

5. Conclusion

We have demonstrated here the fertility of combining graph theory and quantum mechanical calculations to systematically predict crystal structures and their properties. Of course, the calculations do not provide any information about how these structures may be synthesised. However, the lattice energies of some of the structures are comparable to those of the fullerenes, and we believe that their structural simplicity increases the likelihood of their synthesis. Some of the structures presented here are derived from nets presented by Wells [11] and have been investigated previously [4,28,25]. Here, however, a complete enumeration of all possible sp^2-carbon framework structures with not more than six atoms per primitive unit cell is presented. In addition, the state-of-the-art quantum mechanical calculations performed here provide more reliable property predictions than earlier tight-binding calculations. Hence, the spectroscopic signatures of these structures can be computed, which may help to understand spectra from novel carbon polymorphs, where insufficient sample is available for structural studies. The extension of the graph theoretical approach to larger unit cells is in principle straightforward, but computationally demanding. As the two stages of the structure prediction are independent of each other, progress in quantum mechanical calculations or in available computing power can immediately be employed. The quantum mechanical part is currently limited to the prediction of ideal 3D periodic crystals. The graph theoretical approach, however, can be extended to a description based on super space groups. While the main purpose of this paper has been to demonstrate a systematic approach to the prediction of new materials, our results on metastable carbon polymorphs show that even if only very small structures are considered, materials with a very wide range of appealing electronic, structural and mechanical properties are waiting to be synthesised.

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