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2005 J. Phys.: Condens. Matter 17 3221

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Potential super-hard phases and the stability of diamond-like boron–carbon structures

J E Lowther

DST-NRF Centre of Excellence in Strong Materials and School of Physics, University of the Witwatersrand, Johannesburg, South Africa

Received 21 October 2004, in final form 28 February 2005

Published 13 May 2005

Online at stacks.iop.org/JPhysCM/17/3221

Abstract

The properties of some potential super-hard diamond-like boron–carbon phases are examined using *ab initio* computational modelling. Both the bulk and shear modulus show a steady decrease with boron concentration. Two specific phases, namely BC_3 and BC_7 , are singled out and their possible graphitic precursor phases considered. Finally, energies of the graphitic phases are related to the super-hard phases with the same stoichiometry.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

As a point defect, boron is an important impurity in diamond, making the material exhibit p-type behaviour with very nearly shallow defect characteristics [1, 2]. It readily occupies substitutional sites in the diamond lattice about which there is very little lattice relaxation. It is effective in enhancing the hardness of diamond and recently it has been suggested [3] that boron atoms located at the surface of diamond form compressed planar sp^2 bonds with carbon atoms and with a bulk and shear moduli around the surface region increasing over those of the bulk material. Boron itself forms a base for a useful refractory material as is well established by the properties of B_4C and related materials [4–7], although in this material the main building structure relates to boron icosahedra [8, 9] rather than any diamond-related structure.

The maximum concentration of B that can be included into diamond has really not been established to date, although under extreme conditions this content could be significant. Point defect calculations of large concentrations of boron in diamond have indicated that near-neighbour pairing of B atoms is probably unlikely (i.e. the complex is metastable) [10] even though the presence of such near-neighbour defects is suggested from the conductivity of heavily doped boron in diamond [11–13], and even the recent discovery of superconductivity [14] following extreme conditions of high pressure treatment. More recent calculations [15] have suggested that near-neighbour B pairs may be formed in diamond and even act as deep traps for hydrogen. The implication is that large concentrations of boron can indeed be included in diamond, albeit in metastable form. Extreme conditions are apparently

needed for the synthesis of diamond in which superconductivity has been found, again implying some degree of metastability.

Metastable complexes of diamond-structured B–C–N complexes are now established with the recent synthesis of the metastable material BC₂N [16–18]. The precursor to the BC₂N super-hard phase has a graphitic structure with the same stoichiometry [16]. In this case a pressure of around 18 GPa on the graphitic structure was needed to produce the diamond-like BC₂N phase, although the precise structure, i.e. the topological distribution of the B, C or N atoms on the diamond lattice, is not yet established [19, 20]. Claims that such a material is the second hardest material to date have inspired further studies of hard materials having a potential diamond-like structure, and quite recently a B–C phase has been synthesized [21] in which an extreme hardness was also claimed.

It is well known that graphitic structures are the usual precursor phases to super-hard diamond-like structures; graphite leads to diamond, and hexagonal BN leads to cubic BN. Graphitic structures of boron–carbon phases are also known to exist in the stoichiometry BC₃ [22–25] or even BC₅ [24], and nanostructures of BC₃ have also been suggested [26, 27]. A layer hexagonal geometry of BC₃ has been deduced both from experimental [23, 24] and computational [28, 25] studies where the phonon spectra and suggestions of superconductivity in the material were suggested on the basis of this geometry. Thus given the potential that different structures with relatively large concentrations of B can exist in graphitic and other forms, it seems quite reasonable to anticipate that such structures would be precursors to the formation of some kind of advanced hard material under extreme conditions, and perhaps the material would have a diamond structure.

However, there are notable differences regarding the energetics of the graphite–diamond and h-BN to c-BN systems. From computational investigations, the total energy of diamond is very slightly above that of graphite, whereas the reverse is the case for h-BN and BN. This relative ordering of phases indirectly affects the synthesis conditions and possibly related synthesis routes.

The purpose of this paper is to consider possible structures and properties of B–C diamond structures and relate these to similar graphitic structures that could potentially be precursor phases. The approach employed is an *ab initio* pseudopotential density functional approach which is now commonly used in analysing systems similar to the one specified here. In the theoretical analysis we use two forms of the density functional, namely local density approximation (LDA) and a generalized gradient approximation (GGA), as a way of treating the electron exchange and correlation. In the case of graphitic structures we bear in mind earlier results [29, 30] that the GGA can severely underestimate properties of graphitic structures.

2. Computational details and results

The computational approach employed uses projector augmented wave (PAW) pseudopotentials [31] within the LDA as parameterized by Perdew and Zunger [32] and implemented through a variable-cell option of the VASP electronic structure code [33] and employing a plane waves basis calculated on an $8 \times 8 \times 8$ Monkhorst–Pack grid [34]. In the case of carbon-based materials, LDA usually gives a better description of the cohesive properties as well as the elastic constants. However, as we find the energy differences between phases are relatively small, we have also employed a GGA functional [35] to clarify the results. In all cases a full geometry optimization has been performed on each of the systems.

Given that we are considering the metastability of B–C structures, we define their relative stability as follows:

$$E_f = E_{\text{tot}}[\text{B}_m\text{C}_n] - m\mu_{\text{B}} - n\mu_{\text{C}}$$

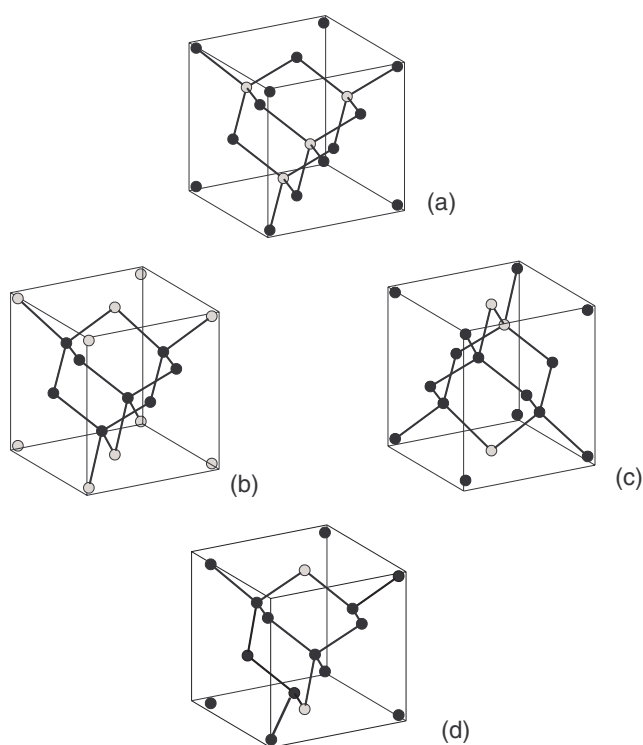


Figure 1. Crystal geometry of BC₇ 8-atom diamond-like B₄C₄ (a), BC₃a—tetragonal (b), BC₃b—trigonal (c) and BC₇ (d). Dark spheres represent C.

where E_{tot} is the total energy of the supercell and μ are atomic enthalpies. The latter depend upon the chemical environment, and here we have taken μ_{C} appropriate to diamond and μ_{B} from a calculation of a suitable form of boron. In the present case we have used the tetragonal structure of B₅₀ that has also been considered before [36].

2.1. Diamond-like structures

A potential diamond-related phase can be considered as being formed from a simple 8-atom unit cell of the diamond lattice with B or C atoms placed at the various lattice points according to the nominal lattice stoichiometry. In the case of the structure BC₃ there are only two possibilities corresponding to either tetragonal or trigonal locations (with B–B) bonds for the two B atoms in the 8-atom unit cell, whereas for BC (i.e. B₄C₄ in the 8-atom cell) or BC₇ there is only one structure if we omit any B–B bonds. Figure 1 schematically shows the structures that have been considered.

Table 1 gives the results deduced for these structures and also the calculated bulk modulus as obtained from a least squares fit to the Birch equation of state [37] and a shear modulus (C_{44}) as obtained from a similar fits to a simple quadratic function. With the BC₃ structures the departure from cubic symmetry is very small, with the tetragonal structure emerging as that with the lowest energy. When calculating a shear (C_{44}) modulus for these slightly tetragonal or trigonal structures, we have used a lattice distortion in a similar way to that used for the cubic system but shearing lattice sides with the smaller cell constants. The value so deduced must therefore be treated with some caution, and is justified only because the trigonal or tetragonal deformation is really quite small.

Table 1. Cell structure, total energy, relative stability and some elastic properties of 8-atom diamond-like B_nC_m structures. Experimental values are in brackets. Energies are quoted to meV/atom; the estimated error of uncertainty is about 10 meV/atom.

		a (Å)	c (Å)	E_{tot} (eV/atom)	E_f (eV)	B (GPa)	B'	C_{44} (GPa)
BC	[LDA]	3.745	3.745	-8.346	0.395	301	3.57	281
	[GGA]	3.790	3.790	-7.467	0.368	279	3.63	128
BC ₃ (a)	[LDA]	3.509	3.876	-9.265	0.168	379	3.59	398
	[GGA]	3.553	3.913	-8.307	0.160	352	3.65	285
BC ₃ (b)	[LDA]	3.642	3.611	-9.239	0.194	378	2.94	448
	[GGA]	3.685	3.685	-8.281	0.181	337	3.53	362
BC ₇	[LDA]	3.581	3.581	-9.642	0.137	418	3.62	545
	[GGA]	3.621	3.621	-8.643	0.133	387	3.69	421
Diamond	[LDA]	3.536		-10.125		465	4.01	609
	[GGA]	3.574		-9.089		432	3.69	572
		(3.567) ^a				(433–442) ^b		(576) ^c
B ₅₀	[LDA]	8.728	4.906	-7.357		220	3.40	
	[GGA]	8.834	4.965	-6.583				
		(8.74) ^d	(5.08) ^d					
		(8.750) ^f	(5.091) ^f			(199–213) ^e		

^a Reference [38].

^b Reference [39, 40].

^c Reference [41, 20].

^d Reference [42].

^e Reference [5].

^f Reference [36].

We note a steady decrease of both the bulk and the shear modulus with B concentration, but more importantly all structures are seen to be metastable, at least relative to diamond and boron. The calculated properties of these chosen reference structures are also given in table 1. There is also an increasing metastability with increasing B concentration, a conclusion reached irrespective of whether we employ LDA or GGA functionals.

In figure 2 we now show the electronic band structure of the various systems and as obtained from the LDA calculations. For the system BC₇ the top of the valence band is partially occupied, following the well-known acceptor properties of the B defect in diamond. In the systems BC₃ and diamond-like BC, however, the Fermi energy lies among occupied states, and whilst there are energy gaps lying above these states it is likely that these systems may have some metallic character. Again we bear in mind that for the BC₃ systems there is very small distortion from cubic symmetry when plotting these band structures.

2.2. Graphitic structures

There has been extensive work on the inclusion of B in the graphite structure, but in the present case we have only considered graphitic structures for the concentrations BC₃ and BC₇. Graphite BC₃ has received extensive attention recently [43, 44, 28], following its synthesis [22, 23]. Here the B atoms are contained as hexagonal units within the graphitic plane, as shown in figure 3(a), and with several possible orderings of these planes. It is likely that there is no preferential ordering of the planes, as calculations indicate that the planes lie very close together energetically [28].

We have considered two possible stacking configurations—shown in figures 3(a) and (b)—with a 16-atom unit cell representing the structure in both cases. The results are given in table 2. As mentioned earlier, this model has proven successful in several computational

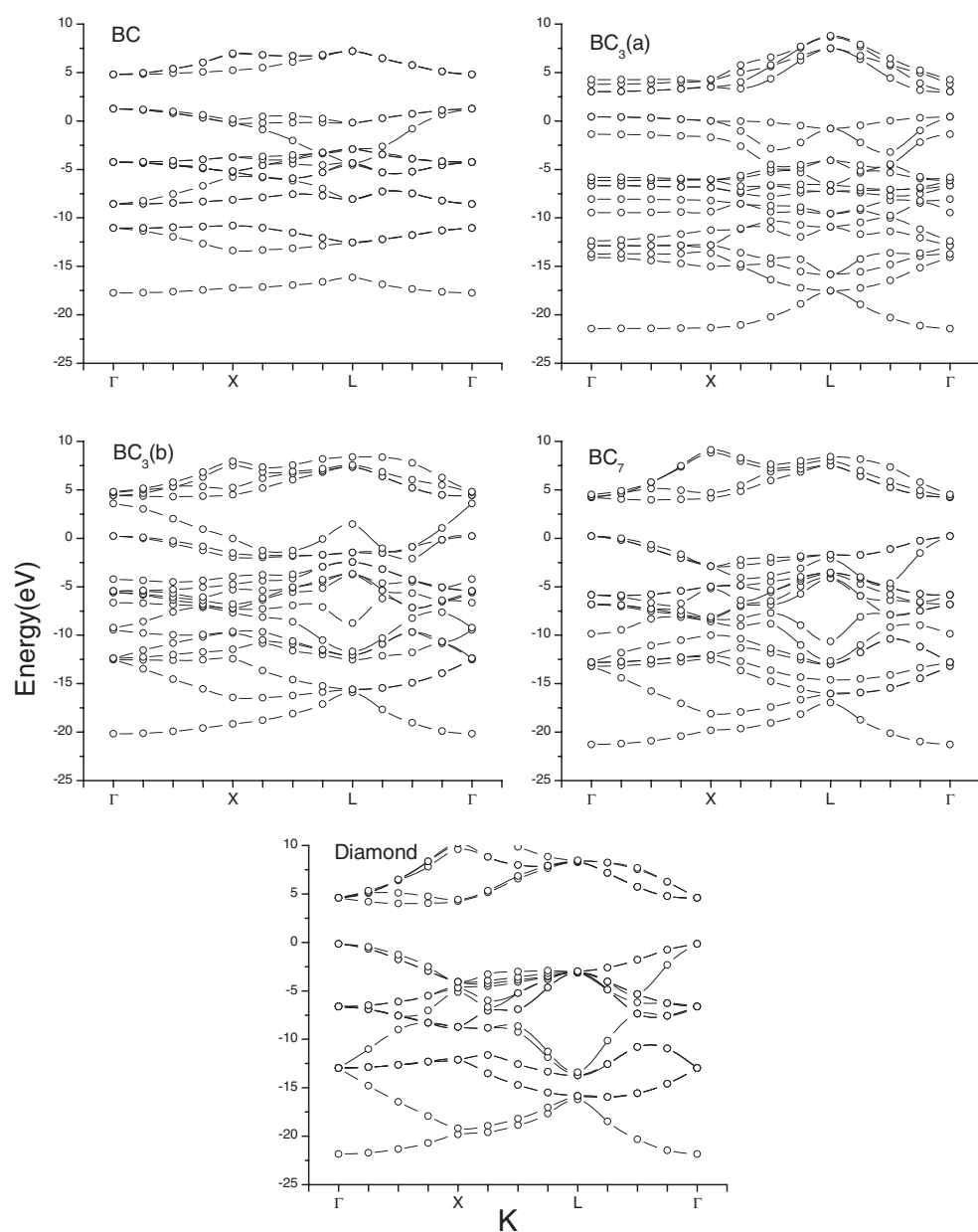


Figure 2. Energy band structure of diamond and different B-C compositions within an 8-atom unit cell. The energy is measured from the calculated Fermi energy.

investigations of the properties of BC_3 . The structures shown in figures 3(a) and (b) are the lower energy structures as deduced from these earlier calculations. In agreement with the earlier calculations [28] the two possible ways of stacking are indeed quite close in energy. Similarly, we have considered a 16-atom unit cell to represent stacking of a BC_7 graphite system, again with two possible ways of stacking the planes, as shown in figures 4(a) and (b). The two ways of stacking the planes have nearly the same energy difference as that found for

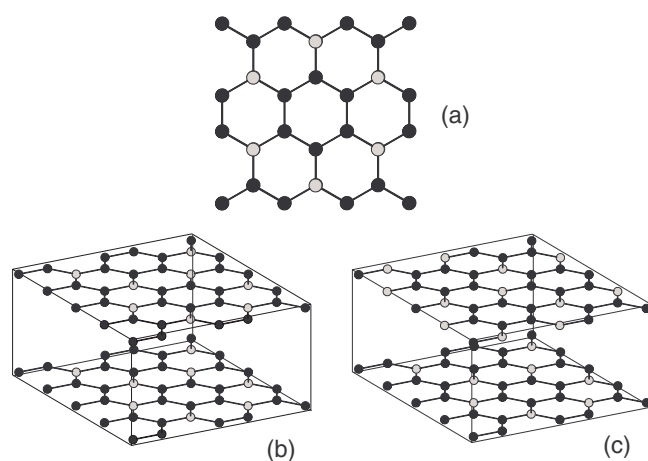


Figure 3. Crystal geometry of BC_3 graphitic structures. In (a) the relative location of B in a hexagonal sheet is shown, and (b) and (c) indicate AA and AB stacking of the planes.

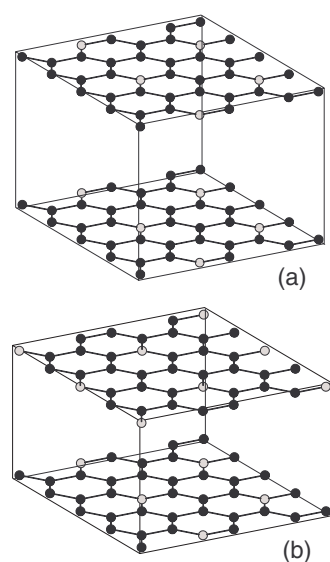


Figure 4. Crystal geometry of BC_7 graphitic structures. (a) and (b) indicate AA and AB stacking of the planes.

BC_3 . We also add that the closely spaced energy of the stacking sequences is like that exhibited in h-BN [30].

Unlike results for the diamond structures, there are marked deviations between the LDA and GGA calculations. The GGA calculations vastly overestimate the crystal structure, especially the c -axis. This was also found to be the case for BN [29, 30], and thus suggest that conclusions based on GGA are to be treated with some caution for the present structures.

2.3. Relative energies

For all structures we can finally estimate an energy difference between the lowest energy diamond-like phase and the stoichiometrically similar graphite phase, and this value is now

Table 2. Cell structure, total energy and relative stability of some graphitic B_nC_m structures. Experimental values are in brackets.

Structure		a (Å)	c (Å)	E_{tot} (eV/atom)	E_f (eV)
BC ₃ (AA)	[LDA]	2.56	3.36	−9.176	0.168
BC ₃ (AA)	[GGA]	2.59	4.12	−8.386	0.072
BC ₃ (AB)	[LDA]	2.56	3.12	−9.207	0.194
BC ₃ (AB)	[GGA]	2.58	3.58	−8.386	0.077
BC ₃		(2.46) ^a	(3.34) ^a		
BC ₇ (AA)	[LDA]	2.50	3.20	−9.612	0.166
BC ₇ (AA)	[GGA]	2.50	3.20	−8.742	0.034
BC ₇ (AB)	[LDA]	2.50	3.24	−9.605	0.174
BC ₇ (AB)	[GGA]	2.50	3.24	−8.386	0.390
B _{0.17} C _{0.83}			(3.305) ^b		
Graphite	[LDA]	2.448	3.314	−10.126	
Graphite	[GGA]	2.469	3.884	−9.216	
Graphite		(2.47) ^c	(3.36) ^c		

^a Reference [22].^b Reference [24].^c Reference [42].**Table 3.** Relative stability of some graphitic B_nC_m structures (eV/atom); a negative value indicates that the diamond-like phase is below the equivalent graphitic phase.

Structure	AA stacking	AB stacking	AA stacking	AB stacking
	[LDA]	[LDA]	[GGA]	[GGA]
BC ₃ a	−0.079	−0.058	0.087	0.083
BC ₃ b	−0.054	−0.032	0.108	0.104
BC ₇	−0.029	−0.037	0.099	−0.257

given in table 3. All the LDA results strikingly follow the same trend, indicating that the energy of the graphitic structure is *below* that of the equivalent diamond-like phase. The GGA results sometimes suggest an alternative ordering but no consistency of trend. But we have discussed earlier that GGA is not able to predict reasonable crystal graphitic structures for other systems, and thus the GGA results in table 3 must be treated with considerable scepticism.

3. Discussion

It is anticipated that heavy concentrations of B in diamond will lead to complexes that are metastable relative to diamond and boron under ambient conditions. As such these materials will require extreme conditions to be synthesized; it may then be possible to stabilize these materials at ambient conditions. The calculations presented here quantify energy aspects of the metastability, and have also predicted properties of such materials should a successful route be attainable. Notably it was found that, in a diamond-like structure, there are large values of the bulk modulus and the C_{44} component of the shear constant is high, suggesting that such structures would be potentially new hard materials. Whilst not being as hard as diamond, the overall electronic character indicates different features to that of diamond. The larger the concentration of boron, the less hard the material would be, and, additionally, incorporation of large amounts of boron affects the conducting character. We have specifically focused on boron complexes with a nominal stoichiometry BC₃ or BC₇ because of increasing evidence

that in a graphitic form such complexes may actually be stable. Such complexes may also be the precursor route toward the synthesis of the hard diamond-like form.

This graphitic precursor route has been the approach followed recently [21], and where graphitic B-containing structures were used as precursors for a high pressure synthesis of potential ultra-hard phases. After the synthesis the lattice parameter of boron-doped diamond was found to be 3.5773 Å, somewhat larger than that of pure diamond (3.5667 Å). We note that this value is quite near the (LDA) predicted here for the BC₇ structure which was calculated here to be 3.581 Å. Hence it is very likely that the material synthesized corresponds to a boron-doped material with the diamond structure, and moreover if this is the case the material would certainly exhibit hard characteristics.

The situation regarding the stability of the diamond phases with respect to the nominal graphitic structures is not as clear. As with diamond and BN, the energy differences between the diamond-like and various graphitic phases is quite small. From the fundamental point of view the magnitude of such energy differences depends on whether the LDA or GGA approximation is applied, even though there is similarity in trend predicted from the different functionals for the crystal structure and elastic moduli of the diamond-like phases. At this point though we bear in mind the shortcomings of the GGA regarding the energetics of h-BN relative to c-BN, and as such we place more reliability on the LDA results than GGA. Then the energy of the hexagonal structures lies very slightly above that of the diamond-like structures. This is similar to the case of BN, but differs from the graphite to diamond system, where kinetic factors are mainly significant [45, 46] for synthesis. In many respects therefore the synthesis conditions of boron-doped diamond may be more similar to those for BN than diamond.

Acknowledgment

This work has been supported by the NRF (SA).

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