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Vibrational energies of graphene and hexagonal structured planar B-C complexes

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The high energy vibrations of hexagonal sheets of BC, BC_3, and BC_7 are calculated and compared with graphene. A high energy "*G*" vibration (at 1559 cm^{-1} in graphene) is similar in the B-C structures. Another high energy "*D*" vibration (around 1350 cm^{-1}) is a mode not found in graphene and is attributed to a vibration that is especially sensitive to B concentration.

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Recent interest in hard materials has now been extended to the boron-carbon binary system with the recent suggestions that various B-C-N complexes could have a hardness approaching that of diamond.[1–4] In addition to the hardness aspect of these materials, interest in the B-C materials has further been inspired by the recent observation that high concentrations of B in diamond can induce superconductivity[5] and this could be associated with B atoms introducing other vibration modes.[6,7] The preparation of structures leading to superhard materials is not straightforward and an appropriate precursor phase is the critical feature needed in the synthesis of the material. A B-C hard material is far from exception.

It is well known that graphite leads to diamond and hexagonal BN to the formation of cubic BN—a material with hardness approaching that of diamond[8]—and it is therefore likely that similar graphitic structures will be precursors for possible superhard B-C structures. With the B-C graphitic structures, several investigations have now concluded that stable complexes[9–12] are possible and possibly these could be suitable precursors to the as yet unidentified superhard phases[13] and, in particular, a diamondlike phase.[14,15]

In a single B-C sheet atomic B can be rearranged systematically as symmetric hexagonal structures only for the special stoichiometries BC_3 and BC_7. Here there are both hexagonal C and B rings.[9] With other stoichiometries the exact crystallographic location of B is not as straightforward and possibly a random distribution of B could be the case. The properties of the hexagonal B-C structures have recently received much attention[9,16,17] and there have been a large number of reports of different Raman frequencies.[14,15,18,19] The origin of the two main high energy vibration bands—the so called "*G*" and "*D*" mode Raman peaks—is of speculation and tentatively thought to relate to the ordering of the graphitic sheets in the B-C hexagonal structure and possibly microstructural distortions.[18] The crystallite size in the material has also been considered[18] as being responsible for the different energies of the *G* and *D* modes although the precise nature as to their origin is not understood at a fundamental level.

In the present work we consider the vibrations of planar BC, BC_3, and BC_7 and compare the calculated vibration frequencies with graphene. An *ab initio* calculation as implemented through the VASP (Ref. 20) electronic structure code with PAW pseudopotentials[21] on a (8×8) grid; no symmetry has been used in all cases as was performed earlier for graphene.[22] The local-density functional[23] has been employed with an energy cutoff of 400 eV. All atoms were allowed to fully relax and from the relaxed structure energies of vibrations were obtained. The vacuum between the layers was held at around 10 Å to assure that graphitic sheets do not interact. The calculated electronic structure for the relaxed planar BC_3(g-BC_3) network is shown in Fig. 1

As seen from the figure, there is very strong charge localization between the C atoms in the hexagonal rings clearly indicating that C-C bonding is strongest within the sheet as is expected. However the relatively weak bonding about B also maintains a hexagonal symmetry in BC_3 but with weak bonding to C hexagons. This means that such a system would have hexagonal point symmetry properties similar to that of the simple graphene sheet. In the case of BC_7 the hexagonal structure is also maintained as with BC_3 but here the B atoms are further separated. We have also considered the hypothetical hexagonal BC structure, i.e., equal amounts of B and C in which B atoms replace adjacent C atoms in the graphene sheets; this is also the structure of a BN hexagonal sheet. Full lattice relaxation of all the structures leads to the

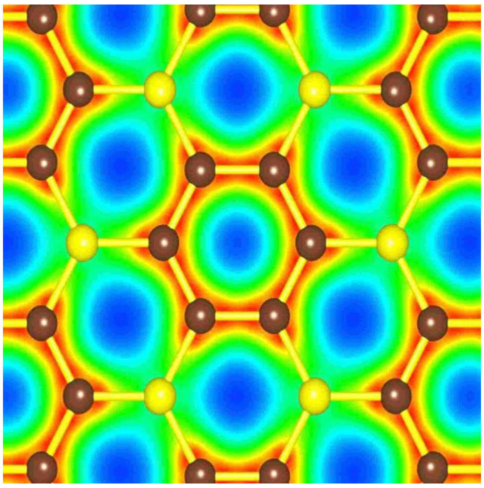

FIG. 1. (Color online) Electronic charge-density distribution of g-BC_3

TABLE I. Calculated hexagonal lattice parameters (Å) and nearest-neighbor interatomic spacing for planar BC_n structure and graphene.

	a (Å)	d(B-C)	d(C-C)
Graphene	2.446		1.412
g-BC_7	2.499	1.484	1.414
g-BC_3	2.563	1.549	1.410
g-BC	2.653	1.532	

results given in Table I where we present the calculated cell parameters for the structures together with interatomic distances. As can be seen the C-C bond length is hardly changed in going from graphene to BC_3 whereas the B-C bond length increases dramatically with B stoichiometry.

Using these relaxed structures we then calculated the vibration energies for $k=(0,0,0)$ in the various BC_7 and BC_3 Brillouin zones and the two highest energy modes are given in Table II. From a symmetry analysis, graphene has two atoms in the unit cell and the space group is $P6/mmm$ with vibration modes $A_{2u}+E_{2u}+B_2g+E_{2g}$ of which only E_{2g} is Raman active. With g-BC (and g-BN) on the other hand, the space group is $P\text{-}6m2$ and the mode symmetries are $2A_2''+2E'$ of which E' is Raman active. Thus only one line—commonly labeled the G band—appears in the Raman spectra of both and this is associated with a doubly degenerate E mode. In the case of a single plane of g-BC_3, the unit cell is taken as having eight atoms with a space group $P6/mmm$ and atoms at B (Wyckoff-c) (1/3, 2/3) and C (Wyckoff-l) (1/3, 1/6). The mode symmetries are $A_{1g}+A_{2g}+2B_{2g}+3E_{2g}+E_{1g}+2A_{2u}+B_{2u}+B_{1u}+E_{2u}+3E_{1u}$ of which A_{1g}, E_{2g}, and E_{1g} are Raman active. As A_{2u} and E_{1u} are translational then this would suggest that appearance of up to five lines in the Raman spectra of g-BC_3 of which four would be associated with twofold-degenerate vibrations E_{1g} or E_{2g}. The twofold-degenerate nature of these vibrations is therefore qualitatively similar to that in graphene or g-BN and g-BC. However in BC_3 and BC_7, the hexagonal nature of the B rings apparent in Fig. 1 for g-BC_3 also gives rise to other E modes of vibration. The calculated energy of the two highest energy E modes in the graphene and the various g-BC structures is shown in Table II.

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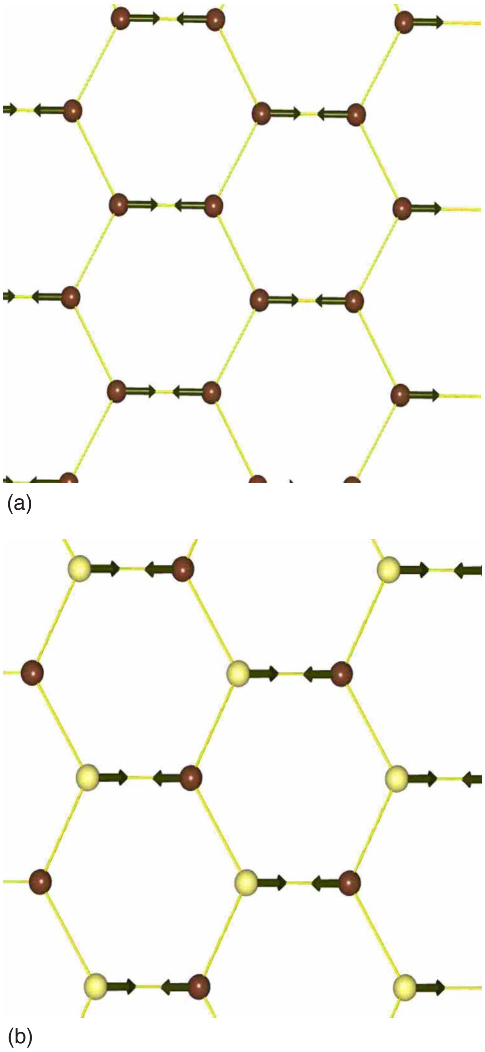
TABLE II. Calculated vibration energies in cm^{-1} at $k=(0,0,0)$. Values in brackets are observed values. For completeness the calculated vibration energy of h-BN is also included calculated using a two-atom unit cell as with g-BC.

	D	G	d(B-C)	d(C-C)
Graphene		1590 (1582–87)		1.412
g-BC7	1366	1554	1.484	1.414
g-BC3	1348	1555	1.549	1.410
g-BC		840	1.532	
h-BN sheet		1382 (1366–70)		



(a)

(b)

FIG. 2. (Color online) G-band vibrations of graphene (top) and g-BC (bottom). Light shaded spheres are B. Arrows represent sense of the atomic displacement—in both cases along the interatomic bond.

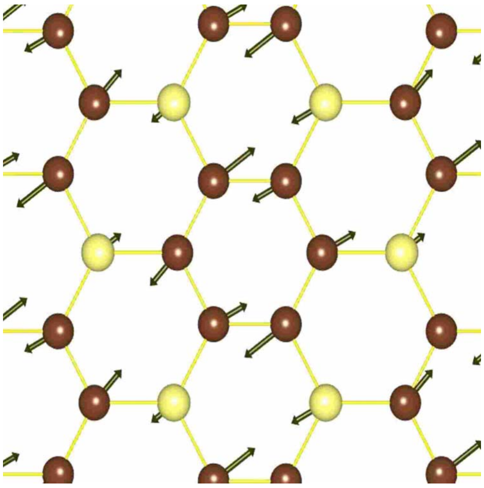


FIG. 3. (Color online) High energy vibration of g-BC_3 calculated at 1550 cm^{-1}. Atomic displacements are slightly away from the interatomic bond unlike graphene.

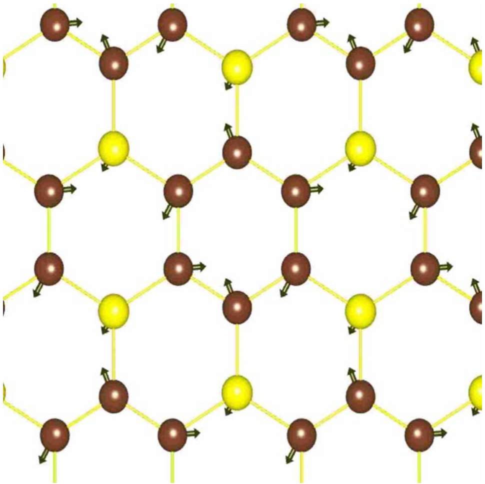


FIG. 4. (Color online) Energy second highest energy vibration of the g-BC$_3$ vibration structure calculated at 1347 cm^{-1}.

to obtain the relative atomic displacement of the vibration modes. In Fig. 2 we show the modes associated with the higher G energy modes observed in graphene and also the speculative g-BC. Figure 3 shows the vibration of the highest energy E mode of g-BC$_3$.

As expected there is a similarity between graphene and g-BC where alternating movement of atoms giving a lateral "z appearance" of distortion directed exactly along two adjacent C bonds. This continues somewhat to BC$_3$ where the z appearance is present both in the distortion of the C atoms and also the B atoms. However the mode is subtly modified from that of graphene or the g-BC due to B affecting the direction of motion of the C atoms and in turn this affects the energy of the vibration. In the case of the hexagonal C rings, the direction of the vibration occurring exactly along the C-C bond in graphene has been subtly distorted by the presence of B to take place slightly away from interatomic bond direction. This results in a slight change in the vibration frequency of the G modes that is associated with the C hexagons.

The influence of B also introduces other modes. The next lowest energy mode we find also associated with E vibrations is observed as the D band in the Raman spectra that has been observed in several B-C hexagonal structures. The nature of this mode is now shown in Fig. 4.

As seen there is no similarity at all with the earlier G modes. The z appearance of the atom vibrations in the hexagonal rings is not present at all and movement of the C atoms is well away from direction of the interatomic bonds in an almost rotational motion. As the direction of atomic movement in the vibration lies further from the interatomic bond this mode is far sensitive to, for example, the presence of B. Indeed as shown in Table II, the calculated vibration energies of the mode are quite sensitive to the B stoichiometry. We add that the D mode vibration has often been associated with K- or M-point vibrations in the Brillouin zone of graphene. The nature of the vibration in Fig. 4 above is quite similar to that calculated for the K or M points of graphene[24] and is thus not inconsistent with the argument[24] that the D modes are related to the K and M points in graphene. Indeed such k points would map onto the Γ point of a similar Brillouin zone to that used here for BC$_3$, etc. Figure 5 finally shows a comparison of the present calculations with recent reports of energies of the G and D modes and various B-C graphitic structures. As can be seen, in general, agreement is quite good.

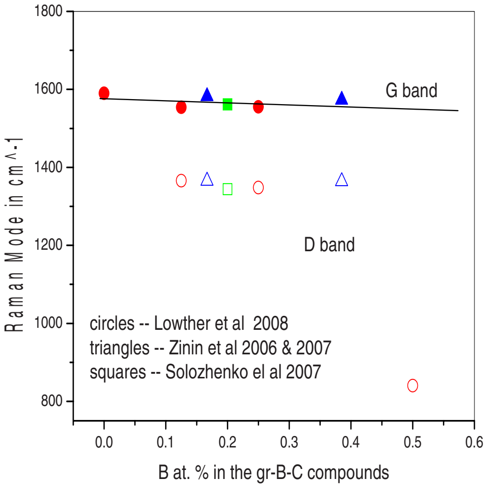


FIG. 5. (Color online) Comparison of vibrational energies of the G and D Raman bands in various B-C graphitic structures. Circles are the present calculations, triangles from Zinin and co-workers (Refs. 14 and 15), and squares from Solozhenko *et al.* (Ref. 25).

In conclusion calculations presented here on various B-C graphitic structures have indicated that hexagonal structures of C-C bonds remains close to that found in graphene apart from slight deformation due to the presence of B away from the hexagonal units. This vibration is associated with the highest energy vibration—the G band—and shows little dependence on B. The next highest energy band—the D band—relates to highly asymmetric modes and is far more dependent on B stoichiometry. We add that all calculations have been performed on exactly flat hexagonal sheets containing no defects. The role played by sheet buckling and defects remains for further investigation.

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