

Structural stability of the B_{80} fullerene against defect formation

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Using a systematic search algorithm we identify several types of point defects in the boron fullerene with 80 atoms. All these point defect leave the cage structure intact. In addition the cage structure is also very stable with respect to elastic deformations and addition or removal of atoms.

Since boron is a neighbor of carbon in the periodic table, they share a lot of similarities. The sp^2 hybridization of the valence electrons, the electron deficiency, large coordination numbers and short covalent radius allow boron to form strong directed chemical bonds and give rise to rich variety of possible nanostructures. Boron nanostructures share some common basic units following the so-called "Aufbau principle" [1]. Various kinds of boron nanostructures, such as boron nanotubes [2, 3], boron fullerenes [4, 5] and boron sheets [2] have been studied both experimentally and theoretically. The B_{80} fullerene has recently been identified in density functional calculations as an energetically very favorable structure [6]. Like the carbon fullerenes boron based fullerenes might thus play an important role [7] if one succeeds in synthesizing them. In contrast to other fullerenes where defects have been studied in detail, the defects in B_{80} have not yet been studied. Since materials are never perfect in reality, it is important to have information about the structure and energetics of their defects. In this article we study the defects of B_{80} . Whereas in previous studies of defects in various materials educated guesses were made to identify defects, we use a systematic search algorithm [10] to find them. As a consequence we find not only one type of defect but several of them. All the defects we found leave the cage structure intact. This stability should make their synthesis easier. If in an initial stage of the synthesis an imperfect structure is generated, it forms nevertheless a cage structure and it can later anneal into the perfect cage structure.

In the first publication on the B_{80} fullerene a perfect icosahedral structure was proposed [6]. In a subsequent publication [7] a distorted icosahedron was presented as the ground state if the PBE [8] density functional is used. Our calculations confirm that the distorted cage is the ground state within PBE. However the distortion is marginal and atoms are displaced by less than 0.035 Bohr with respect to the ideal structure as shown in Fig 1. The energy differences are also small and as a matter of fact a LDA functional [9] favors the perfect icosahedral structure by about the same amount of energy (Table I). Because the deviations from the icosahedral structure are so small we will call in the following both the perfect and the slightly distorted icosahedral

states just icosahedral.

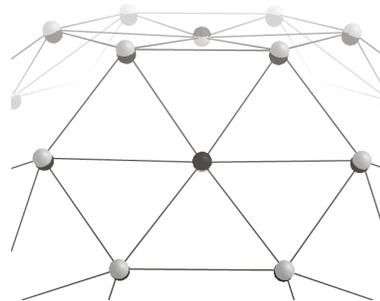


FIG. 1: A section of the B_{80} fullerene that illustrates the differences in the ground state geometries of the LDA ground state (grey spheres) and the PBE ground state (black spheres). In the LDA geometry the hexagon centered atoms are exactly in the plane of the hexagon, in the PBE geometry they move slightly inside.

In order to search in a systematic way for defect structures we used the minima hopping algorithm [10] together with the BigDFT electronic structure program [11] from the ABINIT package [12]. The BigDFT electronic structure program uses a wavelet basis set. This is a systematic basis set and the number of basis functions was chosen such that energies are accurate to within better than 1 mHa. Pseudopotentials were used to eliminate the core electrons [13]. Minima hopping is an algorithm to find the global minimum as well as other low energy structures. It is entirely unbiased and applicable to any system. After exploring some 20 configurations with the minima hopping algorithm we could not find any configurations where the cage structure was destroyed. The configurations we found in this way were combinations of several of the basic defect structures that we will discuss below. Combining these basic defects can give rise to a large number of defective cage structures all of which are very close in energy to the ground state.

A B_{80} fullerene can be obtained from the C_{60} fullerene structure by adding 20 atoms in the center of the 20 hexagons of the C_{60} fullerene structure. The B_{80} fullerene exhibits however a larger variety of defect struc-

tures than the C_{60} fullerene. There are defects where a pentagon is destroyed and a distorted hexagon or heptagon is created. We will in the following call this new class of defects hexagon/heptagon defects. Once a defect has been created it can be shifted to different places on the surface of the cage. This is shown in Fig. 2. The barriers for the displacements of the hexagons are low. For the process leading from the perfect structure (top structure in Fig. 2) to the first defect structure (below perfect structure in Fig. 2) the barrier height is .073 Ha (2.0 eV) in LDA and .067 Ha (1.8 eV) in PBE. Displacements of defects are thus expected to give rise to some plastic deformation behavior of the B_{80} fullerene.

Hexagon defects can also be created by shifting a group of atoms as shown in Fig. 3. In contrast to the previous hexagon defect shown in panel D of Fig. 2, where the hexagon is neighbor to a pentagon, the hexagon is isolated from the pentagons in this case. The fullerene cage is also relatively strongly distorted for this defect. We will call this defect type 4 defect.

It is not too surprising that the B_{80} fullerene inherits also the Stone-Wales type of defect [14]. If one adds to a C_{60} with a Stone-Wales defect again 20 atoms into the hexagons one obtains the B_{80} with a Stone-Wales defect shown in Fig. 4. The number of pentagons is 12 as in the perfect structure, but two pentagons became now neighbors. More pathways exist however in B_{80} than in C_{60} to create a Stone-Wales defect. One can for instance transform the defect in Fig. 3 into a Stone-Wales defect by moving one atom which is part of the hexagon and closest to the next pentagon towards the center of the hexagon.

	LDA	PBE
perfect Icosahedron	0.	0.
distorted Icosahedron	.020	-.020
defect type 1	.053	.027
defect type 2	.062	.035
defect type 3	.027	.066
defect type 4	.061	.040
Stone Wales type defect	.050	.026

TABLE I: The energies of various configurations with respect to the highest symmetry icosahedral fullerene as calculated with the LDA [9] and PBE [8] density functionals in unit of Ha. All the energies are the energies of relaxed structures with the exception of perfect icosahedron in PBE and the distorted icosahedron in LDA.

In addition to being stable against defect formation, the B_{80} fullerene is also highly stable against elastic deformations. We enforced for instance several strong deformations onto the cage such as a sharp edge together with flat regions shown in Fig. 5. Such a structure could serve as a nucleation site for a more compact cluster structure. We found however that the fullerene always

relaxed back to the open icosahedral structure during a geometry optimization.

The B_{80} fullerene is also stable against the removal or addition of a single atom. If one removes a boron atom from the center of a hexagon to obtain B_{79} or if one adds a boron atom in the center of a pentagon to obtain B_{81} one obtains structures whose cohesive energy per atom differs by less than .5 mHa from the values of the icosahedral B_{80} . Consecutive hexagons can be filled until one obtains the B_{92} fullerene. The cohesive energies per atom changes hardly when going from B_{80} to B_{92} . The cohesive energy for B_{92} that we calculated is only 1 mHa less than the one for B_{80} . Our number is exactly in between the two numbers given in reference [6].

In summary, we have shown that several different types of point defects exist in the B_{80} fullerene and that the cage like structure is stable against all these point defects as well as against strong deformations and changes in the number of atoms. Since other boron nanostructures are built up according to the same basic construction principles, it is to be expected that the same or very similar defects can be found in other boron nanostructures.

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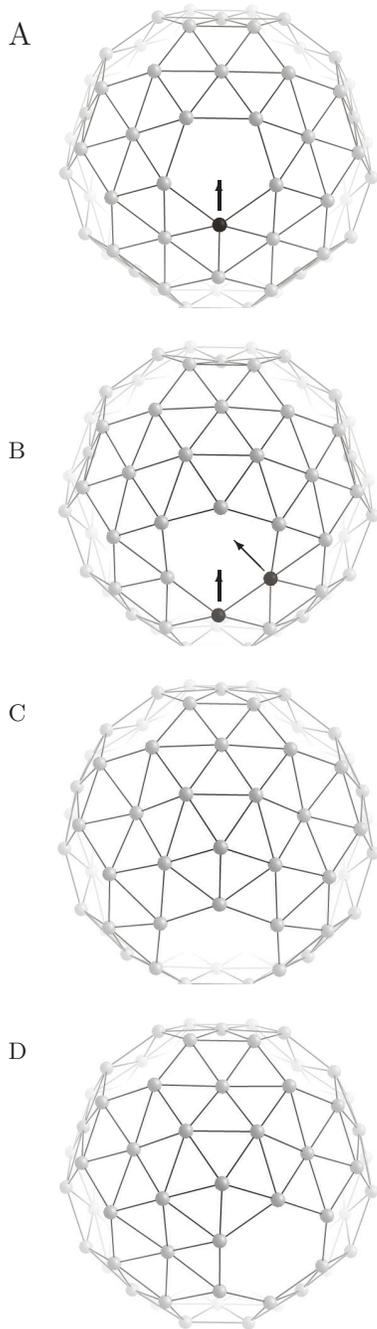


FIG. 2: Illustration of the hexagon and heptagon defects. To get from the icosahedral ground state configuration (top panel A) to the hexagon defect structure (panel below) one has to shift the black atom in the uppermost panel upward as indicated by the arrow. The hexagon defect in the second lowest panel B can then be shifted to the positions in the second lowest and lowest panel C and D by moving upwards or upwards to the left either of the two black atoms in the second uppermost panel as indicated by the two arrows. In panel B and D the defect is a hexagon, in panel C a heptagon. The defects in panels B,C and D will be denoted in Table I as type 1,2 and 3.

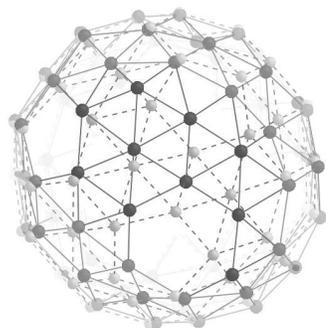


FIG. 3: The picture shows the most distorted part of a type 4 defect in B_{80} . The lighter atoms and dotted bonds show the positions of atoms in perfect structure and the dark atoms with solid bonds shows the B_{80} with the defect.

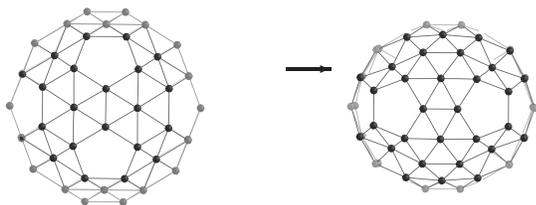


FIG. 4: A perfect B_{80} (on the left) and a Stone-Wales type defect in B_{80} .

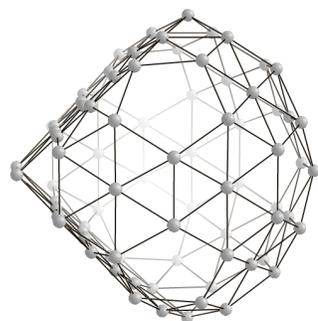


FIG. 5: A B_{80} fullerene that was deformed such that it has a sharp edge and two flat surfaces. This strongly deformed structure relaxes back to the icosahedral structure.