2D $B_xC_yN_z$ layers as predicted by the cluster-expansion approach

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Statement of problem

• Two-dimensional single layer materials are of special importance since they are usually parent structures of one-dimensional nanotubes and zero-dimensional nanocages

• A numerous of experimental and theoretical studies have been devoted to the investigation of the structure and properties of graphene doped with B or N as well as 2D $B_xC_yN_z$ alloys

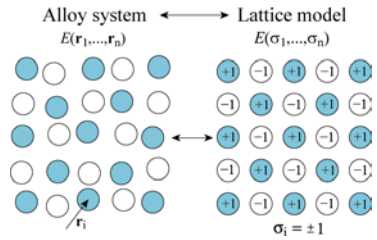
• Question: how the B and N atoms are arranged in the honeycomb lattice at a given "impurity" concentration?

Computational details

• The first principles DFT calculations are done using the Quantum ESPRESSO package; the projected augmented wave (PAW) method and the PBE exchange-correlation functional are used

• The cluster-expansion computations are done using the Alloy-Theoretic Automated Toolkit (ATAT)

The cluster-expansion formalism



$$E(\sigma_1,...,\sigma_n) = \sum_{\{i\}} J_{ij}\,\sigma_i\sigma_j + \sum_{\{i,j,k\}} J_{ijk}\,\sigma_i\sigma_j\sigma_k + ... = \sum_{\alpha} J_\alpha\,\sigma_\alpha$$

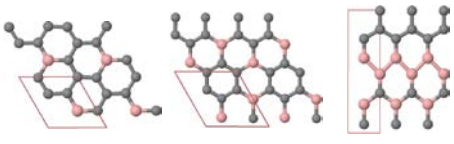
• The cluster-expansion technique is a method to calculate alloy properties *only* based on the alloy *configuration*, i.e., the distribution of the alloy constituents on the crystal lattice

• The ATAT package uses the *ab-initio* total energies and tries to find the best cluster expansion for the given set of structures and energies available at any step of the calculation; also proposes new structures to be calculated in order to improve the cluster expansion

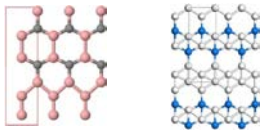
The predicted 2D structures

Some of the 2D structures predicted by the cluster-expansion technic

B_xC_{1-x}

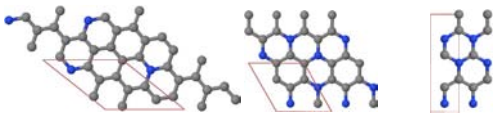


(17%) (25%) (38%)

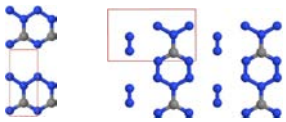


(75%) X. Luo *et al.*

$C_{1-x}N_x$



(10%) (25%) (38%)



(75%) (88%)

Important facts

• With this approach, we are able to predict low energy 2D structures for concentrations *x* up to ~50%

• For small concentrations of B or N, the impurity atoms tend to be as distant as possible in the graphene network

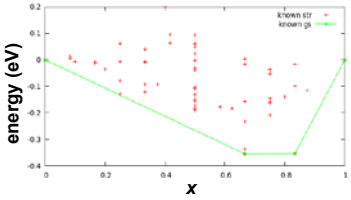
• For larger concentration of B, the boron atoms segregate and form 2D clusters with a triangular network of atoms.

Results

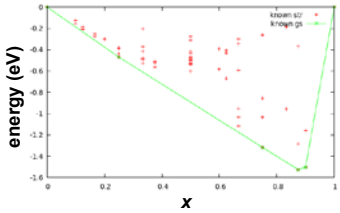
• The formation energies predicted from the cluster-expansion are larger for structures doped with N than those doped with B

• Except from some "magic" configurations (like BC_3) all 2D structures are metallic

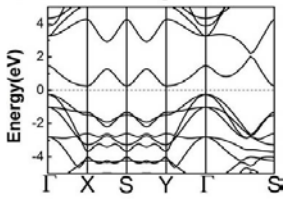
B_xC_{1-x}



$C_{1-x}N_x$



BC_3



Conclusions

• We predict that higher concentrations of N than B dopants can be incorporated into the graphene network without destroying it

• Most of the predicted 2D structures are metallic

References

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X. Luo *et al.*, J. Am. Chem. Soc. **133**, 16285 (2011).
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