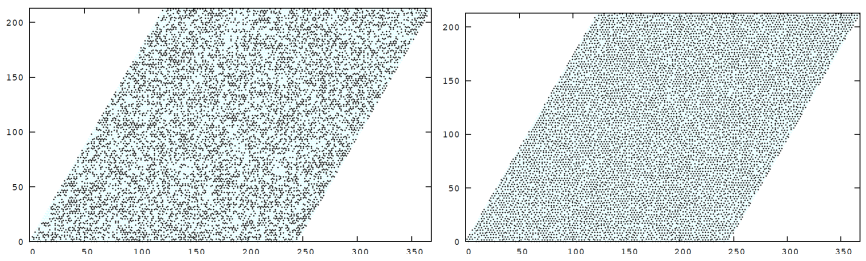
Ordering in binary B_xC_{1-x}, N_xC_{1-x} and ternary $B_{0.25}N_{0.25}C_{0.5}$ honeycomb graphene-like alloys

Agnieszka Jamróz and Jacek A. Majewski

Faculty of Physics, University of Warsaw, ul. L. Pasteura 5, 02-093 Warszawa, Poland

Boron and Nitrogen doped graphene layers constitute very important class of materials, mostly because B and N are natural dopants for carbon systems (*p*- and *n*-type, respectively). At higher concentration of dopants one should consider such systems as binary or ternary alloys. A fundamental issue for any alloy is the degree of ordering among its constituent atoms and to quantify the alloy position between its extreme phases (completely random alloy or perfectly ordered crystal). In these studies, we determine the degree of structural ordering in binary B_xC_{1-x} and N_xC_{1-x} alloys for the x ranging from 0 to 0.5, and also in the ternary $B_{0.25}N_{0.25}C_{0.5}$ alloys with fixed concentrations of constituents. We analyze short-range and long-range ordering, as quantified by the Warren-Cowley short-range order and the Bragg-Williams long-range order parameter, respectively, employing the formalism successfully applied for nitride ternary and quaternary alloys [1]. This comprehensive analysis covers relevant range temperatures and is based on Monte Carlo (MC) calculations within the NVT ensemble employing Metropolis algorithm and Valence Force Field (VFF) approach to calculate the total energies of the of the system. We use Tersoff like potentials for C, N, and B atoms as parametrized by Matsunaga [2]. We perform also density functional theory based calculations (employing the *SIESTA* and sometimes *VASP* code) to test the predictions of VFF potential.

The employed computational scheme allows one to find the equilibrium distribution of dopants over the graphene lattice for the whole range B and N concentrations as a function of temperature. Further, we determine ordering effects in in the studied alloys. To get reasonable statistics, we perform many Monte Carlo runs (with up to $2x10^5$ MC steps) starting from the random distribution of constituents over the lattice. The exemplary MC run is depicted for NC alloy with N concentration of 40% in the figure below.



Left panel – the initial distribution of N and C atoms over 240x240 lattice sites
Right panel – the distribution of atoms after 100000 MC steps

The main points of our simulations for the studied binary alloys can be summarized as follows: (i) there exists short range order in Nitrogen and Boron doped graphene, (ii) no long range order has been discovered, and (iii) the mixed C-N and B-N bonds are favorable for all dopant concentrations up to 50%, whereas B-B and particularly N-N bonds are unfavorable. For the $B_{0.25}N_{0.25}C_{0.5}$ honeycomb alloy we find out that the random alloy is not stable and relaxes to structures exhibiting short-range order. We have also found a metastable ordered phase of this alloy with the barrier exceeding 1500K.

This work has been supported by the European Funds for Regional Development within the SICMAT Project (Contact No. UDA-POIG.01.03.01-14-155/09).

[1] M. Łopuszyński and J. A. Majewski, *Phys. Rev. B* **85**, 035211 (2012).
[2] N. Matsunaga *et al*., *Jpn. J. Appl. Phys.* **39**, 48 (2000).