Predicting Ground-State Configurations and electronic properties of monolayer hexagonal C-B-N alloys: Cluster Expansion Method

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Graphene-like C-B-N layered alloys constitute intriguing class of materials exhibiting short and even long-range order and ranging from B- and/or N-doped graphene, through mixtures of graphene and hexagonal boron nitride (h-BN) domains, to C-doped h-BN systems. Despite of considerable scientific interest and numerous experimental and theoretical studies, overall understanding of the equilibrium morphology, stability, phase diagrams, and electronic structure of such two-dimensional ternary alloys is far of being complete. Our previous Monte Carlo studies within valence force field (VFF) scheme with Tersoff's reactive potential have revealed that C-B-N ternary alloys deviate strongly from random alloys, exhibit short-range ordering, and have tendency to form graphene and h-BN domains [1]. We have also found out on the basis of tight-binding (TB) calculations that the energy band gap in C-B-N alloys decreases very quickly with the growing concentration of carbon [2]. In the combined VFF-TB studies, it has been necessary to consider systems with thousands of atoms and search through a huge configuration space, which is not accessible in any direct *ab initio* approach.

In the present study, we aim at providing the predictions for ternary C-B-N alloys on the level of the density functional theory calculations, which would allow us to assess the accuracy of our previous results based on the VFF scheme. The method of choice is the *cluster expansion* (CE) approach that has been employed in numerous studies of alloys [3]. In the CE method the alloy Hamiltonian is mapped on the Heisenberg-like lattice model with pair, triplet, and quadruplet interactions and the constants of these interactions are established from a series of *ab initio* calculations for carefully chosen set of clusters. However, in typical CE calculations this expansion is arbitrarily truncated neglecting higher order interactions, and the estimation of the resulting error in total energies gets impossible. In the present studies, taking advantage of the VFF calculations, we are able to determine the required order in the cluster expansion, just comparing the CE calculations with a given degree of clusters with the full total energy calculations for the alloy system, just consistently employing the Tersoff's potential in both types of calculations. Having determined the required degree of the CE, we are now in position to calculate the energies of all required clusters employing the DFT calculations and further employ Monte Carlo sampling method for the effective Hamiltonian to find the energetically most favorable configurations of C-B-N alloys.

In the present study, we employ CELL package [3] for derivation of cluster expansion model for C-B-N monolayer alloys and *ab initio* all-electron package *exciting!* [4] to calculate cluster's energies. The employed procedure delivers the most accurate up to now results for the C-B-N alloys in the whole range of concentrations, which generally exhibit qualitative agreement with predictions based on VFF model.

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