

Berseneva, Krasheninnikov, and Nieminen Reply: In the preceding Comment [1], Huang and Wei (HW) raised several questions on the validity of the results presented in our recently published Letter [2]. In particular, based on simple electron counting arguments and band structure calculations within the framework of density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) [3] functional for exchange and correlations, HW argued that some of the substitutional defects in *h*-BN cannot have high charge states. They concluded that the formation energies of charged C impurities and the corresponding defect transition energy levels presented in [2] are wrong. In what follows, we show that, even if HW's arguments on the thermodynamic instability of high charge states are correct, they will give rise to minor changes in the formation energies of the defects and will not affect any of the conclusions drawn in Ref. [2].

Although the DFT-PBE approach is not the best one for calculations of the electronic structure of ideal semiconductors and those with defects, we agree that it gives the qualitatively correct picture for substitutional C impurities in *h*-BN sheets and that high charge states (beyond -1 , 0 , and $+1$) of single impurities may not exist in the real physical system. As evident from Fig. 2 in [2], the $(-1, 0, +1)$ formation energies of single-atom impurities calculated for the 200-atom supercell as functions of electron chemical potential μ_e are indeed lower than those corresponding to higher charge states, except for values of μ_e just at the conduction band minimum (CBM). The crossing of the lines standing for 0 , -1 , and -2 states very close to CBM (hardly noticeable in Fig. 2) stems from the finite size of our system and the accuracy of our calculations (0.2 eV with the account for finite-size corrections [4,5]). We checked that the crossing can completely be eliminated if CBM is computed more accurately. Thus, for the infinite system, single impurities with high charge states have higher total energies than those with low charge states.

Figure 3 in [2] presents the lowest formation energies of single C impurities in B and N positions (C_B and C_N , respectively) and 4C complexes ($4C_{1B3N}$ and $4C_{3B1N}$) in the 32-atom system as calculated using DFT with the PBE [3] and Heyd-Scuseria-Ernzerhof (HSE) [6] functionals. The main idea behind this figure was to demonstrate a good agreement between the PBE and a more accurate HSE method, and finite-size corrections were not taken into account here, as HSE calculations are computationally too expensive to perform calculations for larger systems required for scaling. We agree that the lines corresponding to the charge state “ -3 ” are misleading,

as it should not be present in the infinite system. This changes defect formation energies at values of the electron chemical potential μ_e very close to CBM only, making in fact our conclusions even stronger: the formation energy of defects with preferential B substitution grows up with μ_e , while the formation energy of defects with preferential N substitution decreases, thus increasing the probability for preferential substitutional doping when the system is charged.

We stress that, for more complicated substitutional defects composed from 4–80 C atoms, charge states higher than ± 1 can be realized, so that one of the most important results of our Letter, negative formation energies of positively charged defects with preferential B substitution [Fig. 2(f)], is not affected by HW's remarks.

Finally, we would like to emphasize that our simulations describe the post-synthesis substitutional doping under electron irradiation in a transmission electron microscope [7]. The nanoscale samples, especially poor electrical conductors loosely connected to the environment, are not in equilibrium and can acquire electric charge, making HW's last remark that our analysis is not applicable to equilibrium growth conditions irrelevant.

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