Magnetism in doped two-dimensional honeycomb structures of III-V binary compounds.

Krzysztof Zberecki

Faculty of Physics, Warsaw University of Technology, ul. Koszykowa 75, 00-662 Warsaw, Poland

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Using first-principles plane-wave calculations systematic study of magnetic properties of doped two-dimensional honeycomb structures of III-V binary compounds have been conducted, either for magnetic or nonmagnetic dopants. Calculations show, that all cases where magnetic moment is non-zero are energetically more favorable. For such cases band structure and (partial) density of states were calculated and analyzed in detail. The possible applications of these structures were also discussed.

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I. INTRODUCTION

Since its discovery in 2004 graphene [1] draws much attention because of unique features of this two-dimensional system. Graphene is composed of a sp²-bonded carbon atoms forming honeycomb structure. It has very interesting electronic structure with characteristic, linear energy dispersion near K point of Brillouin zone. Summary of the subject can be found for example in [2]. Shortly after, experimental techniques allowed fabrication of other new two-dimensional materials, like BN and MoS₂ honeycomb structures [2] or ZnO monolayers [3]. The discovery of such stable two-dimensional material like graphene triggered search for similar structures made from different compounds. Up to now many of these hypothetical structures constructed from silanene (2D Si) and germanane (2D Ge) [4, 5], III-V compounds [6], SiC [7] or ZnO [8] have been studied theoretically. On the other hand graphene and other nano-scale materials are recognized as future building blocks of new electronics technologies [10], including spintronics (e.g. [11]). In the case of low (one- and two-) dimensional structures problem arises because of famous Mermin-Wagner theorem [12], which prevents ferro- or antiferromagnetic order to occur in finite temperatures, which is essential for spintronics and other modern applications. This started the theoretical and experimental search for magnetism in graphene and other structures. One of the most promising directions is emergence of magnetism in such structures as an effect of presence of local defects [13]. According to works of Palacios et al. [14] and, independently, of Yazev [15] single-atom defects can induce ferromagnetism in graphene based materials. In both cases, the magnetic order arises as an effect of presence of single-atom defects in combination with a sublattice discriminating mechanism, in agreement with Lieb’s theorem [16]. Based on these findings several theoretical studies have been conducted in search for magnetism in low-dimensional structures either for graphene and BN [18] or other (hypothetical) structures like SiC [7].

II. COMPUTATIONAL DETAILS

To investigate magnetic properties of GaN, AlN and InN honeycomb structures a series of ab-initio calculations have been conducted with use of DFT VASP code [19, 20] with PAW potentials [21]. For both spin-unpolarized and spin-polarized cases exchange-correlation potential has been approximated by generalized gradient approximation (GGA) using PW91 functional [22]. Kinetic energy cutoff of 500 eV for plane-wave basis set has been used. Supercells of size 4x4x1 have been checked to be large enough to prevent defects interact with its periodic image. For both spin-unpolarized and spin-polarized cases exchange-correlation potential has been approximated by generalized gradient approximation (GGA) using PW91 functional [22]. Kinetic energy cutoff of 500 eV for plane-wave basis set has been used. Supercells of size 4x4x1 have been checked to be large enough to prevent defects interact with its periodic image. In all cases for self-consistent structure optimizations, the Brillouin zone (BZ) was sampled by 20x20x1 special k points. All structures have been optimized for both, spin-unpolarized and spin-polarized cases unless Feynman-Hellman forces acting on each atom become smaller than 10⁻⁴ eV/Å. A vacuum spacing of 12 Å was applied to hinder the interactions between monolayers in adjacent supercells. Calculated lattice constants are in agreement with [8].
III. RESULTS

As mentioned, non-magnetic honeycomb sheets can attain spin polarized states due to presence of local defects. In this work two kinds of defects have been analysed - vacancies and substitutions.

For all three compounds a vacancy was generated first by removing a single atom, Al, Ga, In or N from each supercell, then the atomic structure was optimized. In all cases structures with single N vacancy are non-magnetic, while Al, Ga or In vacancies induce non-zero magnetic moment, equal to 3.00 μB. This is in disagreement with Lieb’s theorem, which states that magnetic moment should be equal to 1.00 μB when one of sublattices has exactly one atom more/less than the other (e.g. NAl - NN = ± 1). This discrepancy can be addressed to charge transfer from Al(Ga,In) to N. Fig. 1 shows density of states (DoS) for spin-polarized Al-vacant AlN, on which difference between majority spin (up) and minority spin (dn) in the vicinity of Fermi level (horizontal line) can be observed which is the main source of non-zero magnetic moment. Analysis of calculated partial magnetisation shows that almost all magnetic moment is situated on p-states of N atoms located in the area of vacancy. This is in full agreement with previous studies of vacancies in SiC [7].

![DoS AlN-Al 2D](image)

FIG. 1: Density of states of Al-vacant AlN.

In the case of substitution the procedure was as follows. For all three compounds various single foreign atoms have been substituted, then structure has been optimized. In the case of AlN and GaN, Al or Ga has been substituted by atoms from 4-th period of periodic table from K to Zn, including Na and Mg for AlN. In the case of InN, In has been substituted by atoms from 5-th period of periodic table from Rb to Cd, excluding Tc. In all three compounds, N has been substituted by C, B and P atoms. Table I shows calculated magnetic moments and differences between total energy of spin-unpolarized and spin-polarized states, \( \Delta E = E_{\text{osp}} - E_{\text{usp}} \), i.e. positive value of \( \Delta E \) means that spin-polarized state is more energetically favored. This is the case for all compounds with non-zero magnetic moment - the largest energy differences (up to 1.25 eV) are for instances with highest values of magnetic moment. For AlN highest values of induced magnetic moment are in case of Mn, Co (4.00 μB) and for Fe (4.26 μB). Similar situation can be observed for GaN doped with Mn, Co and Fe. With decreasing number of d-shell electrons value of magnetic moment drops as well as for the case of Zn which has d-shell closed. In the case of InN this tendency holds although values of magnetic moments are much smaller, being the highest for Ru and Rh. Figs. 2 and 3 show mechanism of generation of magnetic moment in the case of GaN doped with Ni. Left plot of Fig. 2 shows bandstructure of Ni-doped GaN vs. undoped one (which is a semiconductor with bandgap equal to 2.30 eV, calculated within GGA) in spin-unpolarized case. One can see the formation of doping bands in the vicinity of Fermi level. The top right plot shows bandstructure of GaN+Ni in the spin-polarized case, where can be observed quite large splitting of these bands between spin up and down bands.

Top plots of Fig. 3 show density of states for spin polarized case. Right one shows total DoS vs. DoS of spin up and down. Fermi energy is almost exactly in the middle of splitted up and down DoS. Left plot shows vicinity of Fermi energy more closely, where large splitting of up and down DoS can be observed. Since almost all electrons occupying vicinity of Fermi level are d-shell electrons, which can be read from partial density of states (bottom left plot) the mechanism of magnetic moment emergence becomes clear. Calculations show that this mechanism is universal for all structures having non-zero magnetic moment doped with transition metal elements. In case of doping with alkali metal elements and alkaline earth metal elements only in Na- and K-doped AlN calculations show non-zero magnetic moment (1.88 and 1.70 μB, respectively for Na and K). Mechanism of formation of magnetic moment is similar to the case of vacant structures (since Na and K have only one valence electron). Fig. 2 shows DoS for spin-polarized Na-doped AlN, on which difference between spin up and spin down in the vicinity of Fermi level can be observed.

![DoS AlN+Na 2D](image)

FIG. 2: Density of states of Na-doped AlN.

This is similar to situation depicted on Fig. 1 although in the case of Na-doped structure splitting is smaller. In case of substitution of N atom by C, B and P, only C-doped structures had non-zero magnetic moment, which...
was equal to 1.00 $\mu_B$ in all compounds. Magnetic states in all cases are lower by about 0.1 eV than nonmagnetic states.

IV. CONCLUSIONS

Ab-initio calculations have been conducted for vacancy and substitution defects in honeycomb AlN, GaN and InN compounds. Calculations show that in all three compounds vacancy of Al, Ga or In respectively gives magnetic moment of 3.00 $\mu_B$, which is interesting conclusion from application point of view. On the other hand substitution of Al or Ga by transition metal elements (Mn, Fe, Co) can give even higher value of magnetic moment (4.00 $\mu_B$). Since technique of implantation of metal atoms into 2D surface has been recently reported, it is also very promising direction. On the other hand substitution by non-metallic atoms or substitution of nitrogen atoms by IV or V group atoms does not give significant magnetic moment. These results may give a hint for experimentalists seeking for two-dimensional magnetic materials.

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FIG. 3: Bandstructure of Ni-doped GaN. Details in text.

FIG. 4: Density of states for Ni-doped GaN. Details in text.
|          | Na  | Mg  | K   | Ca  | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\mu(\mu_B)$ |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| AlN      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| GaN      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| InN      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

**TABLE I:** Magnetic moments and total energy differences between spin up and spin down states for different transition metal elements dopants.

|          | K   | Ca  | Sc  | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\mu(\mu_B)$ |     |     |     |     |     |     |     |     |     |     |     |     |     |     |
| AlN      | 1.88| 1.70| 0.96| 0.90| 1.72| 2.90| 3.99| 4.26| 3.96| 2.98| 1.85|      |     |     |
| GaN      | 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00| 0.00|
| InN      |     |     |     |     |     |     |     |     |     |     |     |     |     |     |

**TABLE II:** Magnetic moments and total energy differences between spin up and spin down states for different dopants.

|          | B   | C   | P   |
|----------|-----|-----|-----|
| AlN      |     |     |     |
| $\mu(\mu_B)$ | 0.00| 1.00| 0.00|
| $\Delta E\ (eV)$ | 0.00| 0.14| 0.00|
| GaN      |     |     |     |
| $\mu(\mu_B)$ | 0.00| 1.00| 0.00|
| $\Delta E\ (eV)$ | 0.00| 0.11| 0.00|
| InN      |     |     |     |
| $\mu(\mu_B)$ | 0.00| 1.00| 0.00|
| $\Delta E\ (eV)$ | 0.00| 0.10| 0.00|