**Ab initio studies of the possible magnetism by nonmagnetic defects in a BN sheet**

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This study attempts to resolve the following two issues: 1) whether a long-range magnetic order can be established in a material consisting of elements holding only s and p valence electrons, 2) whether the magnetic properties, similar to the electrical properties, can be controlled through defects in the previous systems. Magnetism involving only s- and p-electron elements attracts considerable attention due to the potential for extensive applications as well as the urge to understand its physical origins. Recently, possible ferromagnetism in fullerenes and graphite systems were discovered experimentally while the theoretical studies attempting to find magnetism in some potential nonmagnetic systems were also carried out. However, the origin of ferromagnetism in those systems is still under debate. Through studying different defects concentrations in a 2D system of BN sheet by the first-principles methods, we found that, despite most of the defects doped BN sheet only lead to the formation of local moments, there are systems exhibiting long-range ordered magnetic moment of estimated $T_C \approx 70K$.

BN can form three different bulk structures, i.e. hexagonal, cubic and wurtzite BN. Of these three structures, hexagonal BN ($h$-BN) is the room temperature phase. Similar to graphite, $h$-BN is quasi-2D with weak interaction between layers. Nevertheless, unlike the delocalized $\pi$ electrons in graphite, the different electronegativity of B and N leads to directional binding and thus a wide band gap of at least 4 eV in $h$-BN. The tubular BN has been synthesized experimentally and it was shown that the BN nanotubes rolled up in different ways are all semiconductors. One would therefore expect that the effects of defects in a BN sheet would similarly take place in BN nanotubes.

![FIG 1. 4x4 unit cell for the h-BN sheet. D represents defects created in the system, i.e. impurities of vacancies.](image)
In this work, two types of defects are used to study the possible magnetism in a BN sheet, i.e. vacancies by removing either B or N atoms (denoted by $V_B$ and $V_N$) and impurities of the Be, B, C, N, O, Al and Si atoms substituting for the B or N atom (denoted by, e.g. $C_B$ for C impurities substituting for B atoms) as shown in FIG.1. The calculations are based on density functional theory with the generalized gradient approximation for the exchange-correlation energy functional. The projector augmented-wave method is used to describe the core-valence electron interactions. Supercells composed of $4 \times 4$ primitive unit cells of BN sheet are used to simulate systems with defects. The larger supercells of $8 \times 4$ and $8 \times 8$ were used to study the possible finite magnetic moments induced by defects, as well as the variation of the magnetization energy ($E_M$) and the exchange energy $J$ with respect to the distances between defects ($d_D$), i.e. the defect concentrations.

![Orbital-projected partial DOS for N and B atoms in a BN sheet.](image)

**FIG.2.** Orbital-projected partial DOS for N and B atoms in a BN sheet.

The density of state (DOS) for the BN sheet consists of two valence bands (denoted as VB1 and VB2 hereafter as in FIG.2). The DOS’s are mostly $p_z$-orbital-like near the top of VB2 and the bottom of CB. However, the dominant contribution switches from the $p_z$ orbital on N atoms near the top of VB2 to that on B atoms near the bottom of CB. That is, the electronic excitation in the BN sheet involves displacing the originally $p_z$-orbital electron distribution around the N atoms towards the space around the B atoms.
The effect of defects on DOS is summarized schematically in FIG. 3 which demonstrates the two possible types of formation for the defect bands. For NB, CB, OB, ON and SiB, the bonding abilities of the impurities are stronger than the substituted host atoms (type I) while for BeB, BeN, BN, CN, AlN, and SiN, the weaker bonding ability drives the defect bands (DBs) to the higher-energy region of the original bands. The order in the bonding ability is found to be consistent with the electronegativity order based on the Mulliken scale. The partially occupied defect bands for ON and SiB (BeB and ON) are located at the edge of the original extended CB (VB2) bands which are more likely to be extended in nature and thus lead to larger exchange energies as presented later. Of these studied defect systems, some consist of even numbers of electrons in the supercell, i.e. NB, BN, AlB, and AlN. The even numbers of electrons in the supercell completely fill up the DBs, i.e. no formation of finite moments, and they are therefore excluded from the following discussions. The calculated magnetic moments in BeB and VB were found to vary as $d_D$ increases. However, their magnitudes converge to $1\mu_B$ as $d_D$ increases to 17.37 Å. For the rest defect systems, the calculated magnetic moments are always found to be $1\mu_B$ and independent of $d_D$. 

FIG 3. Schematic diagrams of the effect of defects on DOS. The dashed lines show the possible circumstances in forming metal-like DOS.
To understand how stable these finite moments in the BN sheet are, the magnetization energies, i.e. $E_M$, obtained from the total-energy difference between the systems with and without spin-polarized configuration were calculated (FIG.4). The $E_M$'s of these systems tend to increase as $d_D$ increase which suggests a definite preference for finite magnetic moments for those defect systems with distant nonmagnetic defects. Note that the defect concentrations of 3.125% and 0.78% correspond to a $d_D$ of 10.03 Å and 20.05 Å respectively.
To identify the possible long-range magnetic ordering in these systems, the Heisenberg type of spin coupling is employed to model the interaction \( J \) between the nearest-neighbour magnetic moments due to defects (FIG.5). There are only two systems, i.e. \( \text{O}_N \) and \( \text{V}_B \), which have large enough exchange energies to be identified numerically as magnetically ordered systems. Within the framework of the Heisenberg model, it is possible to estimate the Curie temperature \((T_C)\) while the estimated values \((T_C^{MF})\) from the present treatment are expected as the upper bound. For \( \text{O}_N \) systems with a defect concentration of 3.125\%, the \( T_C^{MF} \) can reach up to 72K. In summary, we have demonstrated that all the studied defect systems with partially filled defect bands exhibited a definite preference for finite magnetic moments. The magnetic properties can depend on the defect concentrations and a long-range magnetic order is likely to occur in the systems of high defect concentration like \( \text{O}_N \) and \( \text{V}_B \) whose defect bands are extended in nature.