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Electronic structure and magnetism in $g$-C$_4$N$_3$ controlled by strain engineering

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Regulation of magnetism and half-metallicity has attracted much attention because of its potential in spintronics. The magnetic properties and electronic structure of graphitic carbon nitride ($g$-C$_4$N$_3$) with external strain are determined theoretically based on the density function theory and many-body perturbation theory ($G_0W_0$). Asymmetric deformation induced by uniaxial strain not only regulates the magnetic characteristics but also leads to a transformation from half-metallicity to metallicity. However, this transition cannot occur in the structure with symmetric deformation induced by biaxial strain. Our results suggest the use of strain engineering in metal-free spintronics applications. © 2015 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4916814]

Technological advance in information processing is driven by improvement in injecting and manipulating electronic spin.$^1$ With respect to logic and memory devices, materials which filter the current into a single spin channel should be considered and hence, magnetic materials such as metal-DNA complexes, manganese perovskites, diluted magnetic semiconductors, and doped nanostructures have received much attention$^2$–$^{10}$ because they can generate good spin-splitting at the Fermi level in 2D materials. However, this transition cannot occur in the system with symmetric deformation induced by biaxial strain. The understanding of strain-dependent magnetism in $g$-C$_4$N$_3$ is quite limited so far.

In this work, $g$-C$_4$N$_3$ is chosen as the model system to study the relationship between external strain and spin-splitting at the Fermi level. The theoretical derivation discloses that asymmetric deformation induced by uniaxial strain not only regulates the magnetic characteristics but also leads to a transformation from half-metallicity to metallicity. However, this transition cannot occur in the system with symmetric deformation induced by biaxial strain thereby suggesting that strain engineering is an ideal way to control spin polarization.

The theoretical assessment is based on the density functional theory in Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA), using the Vienna $ab$ initio simulation package (VASP) code with projector augmented wave pseudopotentials.$^{19–21}$ The plane-wave energy cutoff of 500 eV is used to expand the Kohn-Sham wave functions and relaxation is carried out until all forces on the free ions converge to 0.03 eV/Å. The vacuum space is at least 15 Å, which is large enough to avoid the interaction between periodic images. The Monkhorst-Pack $k$-points grid is $10 \times 10 \times 1$, which has been tested to be well converged. Spin polarization is included throughout the calculation and to examine the standard calculated results, magnetic calculation is also performed by combining the DFT with many-body perturbation theory in the $G_0W_0$ approximation.$^{22,23}$

The optimized primitive (1 × 1) $g$-C$_4$N$_3$ with the 4.81 Å lattice constant is shown in Fig. 1(a). Substitution of an N atom with a C atom will inject a hole into the nonmagnetic $g$-C$_3$N$_4$ [Fig. 1(d)] consequently altering the electronic structure and magnetic properties. As expected, the magnetic moment becomes $\sim 1.00 \mu_B$ per formula unit in the absence of external strain, and it is evenly distributed among three neighboring nitrogen atoms (Table I showing that each N atom has $\sim 0.33 \mu_B$ magnetic moment). Hence, the spin charge density between spin-up and spin-down ($\rho = \rho_+ - \rho_-$) are...
functionals are frequently used in DFT calculation. For improving the theoretical evaluation of the band gap, hybrid G0W0, respectively. The discrepancy can be attributed to calculated to be 3.35 eV (G0W0), while the result by LDA was 1.32 eV.25 Hence, the results calculated by the PBE and (normal type) are all summarized in Table I. The results without external strain are magnetic moments based on different computational methods

spin polarization is strongly related to structural deformation. These results demonstrate that magnetism induced by deformation induced by biaxial strain (x = y = 10%) cannot completely alter the spin charge density distribution [Fig. 1(e)]. These results demonstrate that magnetism induced by spin polarization is strongly related to structural deformation.

To verify the reliability of the calculation, the calculated magnetic moments based on different computational methods are summarized in Table I. The results without external strain (normal type) are all ~1.0 \( \mu_B \), which are independent of the computational methods. The magnetic moments with \( x = 10\% \) strain (boldface type) decrease to 0 \( \mu_B \) [local-density approximation (LDA) and GGA] and 0.3 \( \mu_B \) (PBE and G0W0), respectively. The discrepancy can be attributed to differences in the methods but does not affect the conclusion. It is well known that DFT generally underestimates the band gap because the independent-electron picture breaks down as a result of the strong Coulombic interactions.24 In order to improve the theoretical evaluation of the band gap, hybrid functionals are frequently used in DFT calculation. For example, a hybrid-DFT band gap of the \( g-C_3N_4 \) structure was calculated to be 3.35 eV (G0W0), while the result by LDA was 1.32 eV.25 Hence, the results calculated by the PBE and G0W0 methods are adopted and described in this work because they are more exact.18 In the \( g-C_3N_4 \) structure, the injected hole from the C4 atom can make the original atomic population (1.09 in \( g-C_3N_4 \)) and charge transfer (0.41 eV in \( g-C_3N_4 \)) of C1-N1 bond decreases to 1.02 and 0.34 eV, respectively. The redistributed electron wave function makes the generation of spin splitting at the \( p_z \) orbit of the N atoms and therefore 1.0 \( \mu_B \) magnetic moments appear at all three N atoms. In the presence of uniaxial strain, overlapping of the electron wave function at C1-N1 bonds is enhanced (atomic population becoming 1.05) and asymmetric deformation makes the spin density to deviate from the N atoms to N-C bond vicinity [Figs. 1(c) and 1(f)]. The electronic structure changes makes the original spin splitting small and the total magnetic moment diminishes to 0.30 \( \mu_B \). This process is more clearly illustrated in the band structure transformation.

In the absence of external strain, the calculated band structure [along high symmetry points as shown in the inset in Fig. 4(d)] and the spin-resolved total density of state (DOS) of \((1 \times 1)\) \( g-C_3N_4 \) is displayed in Figs. 2(a) and 2(b). The detailed band structure analysis shows that the spin-up (marked by up) bands cross the Femi energy, whereas the spin-down (marked by dn) ones show a very large band gap (~2.2 eV). Therefore, only the spin-up electron can be transported in this system and the current flow should be fully spin-polarized, i.e., half-metallicity. DOS splitting shows that the spin-up bands are fully occupied while the spin-down bands are partially filled, resulting in a 1.0 \( \mu_B \) magnetic moment. When the uniaxial strain of 10% is applied along the \( x \) direction (\( x = 10\% \)) as shown in Figs. 2(c) and 2(d), the lower spin splitting energy makes spin-down bands to increase to the Femi level (green line) and restriction to spin-down electron transport is abrogated. The valence band maxima of spin-up and spin-down all exceed the Fermi level and this system exhibits good metallicity. Meanwhile, the DOS splitting between the spin-up and spin-down states is reduced and the magnetic moment also decreases to 0.30 \( \mu_B \). Owing to these magnetic transformations in the \( g-C_3N_4 \) structure, the spin filtering characteristics fail and all the electrons (spin-down and spin-up) can be transported freely thereby greatly impacting the performance in spintronics applications.

### Table I. Calculated magnetic moments of \((1 \times 1)\) \( g-C_3N_4 \) with 0% (normal type) and 10% (boldface type) uniaxial strains along the \( x \) direction by different computational methods.

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>N1</th>
<th>N2</th>
<th>N3</th>
<th>Total</th>
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<tr>
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<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.30</td>
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<td>0.00</td>
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<tr>
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<td>-0.01</td>
<td>-0.01</td>
<td>-0.01</td>
<td>1.00</td>
</tr>
<tr>
<td>G0W0</td>
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<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.32</td>
</tr>
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</table>

- FIG. 1. Optimized \((1 \times 1)\) \( g-C_3N_4 \) (a) and \( g-C_3N_4 \) (d) structure. Calculated spin densities of \((1 \times 1)\) \( g-C_3N_4 \) with 0% (b) and 10% (c) biaxial strain.
- Calculated spin densities of \((1 \times 1)\) \( g-C_3N_4 \) with 10% uniaxial strain along \( x \) (f) and \( y \) (c) directions. Silver gray and brown balls stand for N and C atoms, respectively.

*FIG. 2. Calculated band structure and spin-resolved total DOS for \((1 \times 1)\) \( g-C_3N_4 \) shown in Figs. 2(a) and 2(b).*
To display the magnetism changes in detail, the magnetic moment values of \((1 \times 1)\) \(g\)-C\(_4\)N\(_3\) as functions of external strain are calculated and shown in Fig. 3(a). In the presence of uniaxial strain along the \(x\) or \(y\) direction, the magnetic moment (1.00 \(\mu_B\)) first decreases to 0.30 (\(x = 10\%)\) and 0.83 \(\mu_B\) (\(y = 11\%\)), and then increases slowly to 0.56 and 0.98 \(\mu_B\) at 16\% uniaxial strain, which can be attributed to asymmetric deformation. For example, the C1-N1 bond can be stretched monotonically from 1.336 (\(x = 0\%\)) to 1.478 Å (\(x = 16\%\)), whereas the C3-N3 bond is first compressed to 1.305 Å (\(x = 10\%\)) and then stretched to 1.336 Å (\(x = 16\%\)) slowly. The changes in the C3-N3 bond are consistent with the magnetism changes, because stronger orbital overlapping depends only on the compression of C3-N3 bond and has nothing to do with the tensile C1-N1 bond. Therefore, symmetric tensile deformation induced by biaxial strain cannot lead to the magnetism changes. To clearly display the transformation from half-metallicity to metallicity, the energy difference \((E - E_f)\) between the valence band maximum \((E_f)\) at \(\Gamma\) point and Fermi level \((E_f)\) are shown in Fig. 3(b). When \(x = 4\%\) and \(y = 6\%, E - E_f\) of spin-up and spin-down becomes positive (this system beginning to show metallicity). On the contrary, this system with biaxial strain has half-metallicity because the energy differences of spin-down are always negative. To compare the structural stability, the formation energy in this system can be expressed as \(E = E_r - E_a\), where \(E_r\) and \(E_a\) stand for the relaxed and unrelaxed energy. The formation energies as functions of external strain are calculated and shown in Fig. 3(c). The structure with uniaxial strain has a smaller formation energy than that of biaxial strain, indicating that the structures with uniaxial strain are more stable. To further explore the structural stability, the \((1 \times 1)\) \(g\)-C\(_4\)N\(_3\) structure with \(x = 10\%\) strain is calculated by spin-polarized \(ab\) \(initio\) molecular dynamics simulation with a Nose-Hoover thermostat at 300 K. Fig. 3(d) shows the fluctuation in the temperature as a function of simulation time at 300 K. After 30 ps, no structure destruction occurs in this system. The band structure and magnetic values also do not change (\(\sim 0.30 \mu_B\)). This can be understood by that the binding energies of the C-N and C-C bonds are much larger than the thermal energy corresponding to room temperature.

To explore the magnetic ground of \(g\)-C\(_4\)N\(_3\), the ferromagnetic (FM) and antiferromagnetic (AFM) configurations are considered by using the \((2 \times 2)\) supercell. Based on the nearest-neighbor Heisenberg model,\(^{26}\) the energy difference between the FM and AFM configurations can be calculated as

\[
\Delta E_{AFM-FM} = E_{AFM} - E_{FM} = \sum_{i,j} J_{ij} S_i S_j,
\]

where \(J_{ij}\) is the nearest-neighbor magnetic coupling strength and \(S_i\) and \(S_j\) are the net spin of each primitive \((1 \times 1)\) \(g\)-C\(_4\)N\(_3\). Fig. 4(a) discloses that the FM state is the most energetically stable (the values being all positive) and the structure with uniaxial strain along the \(x\) direction has the lowest energy compared to the other two cases. This can be understood by that uniaxial strain can effectively decrease the energy of the FM configuration making it approach that of the AFM configuration due to the magnetism changes [Fig. 3(a)]. The magnetic coupling strengths as functions of external strain are calculated and shown in Fig. 4(b). In the presence of uniaxial strain along the \(x\) or \(y\) direction, the changes in the magnetic coupling strength are similar to those of the magnetic changes as shown in Fig. 3(a). This is because that weaker magnetic moments lead to weaker magnetic coupling strength and smaller \(\Delta E_{AFM-FM}\), as shown by Fig. 4(d). It is important to note that the \((2 \times 2)\) \(g\)-C\(_4\)N\(_3\) structure reconstructs into a slightly distorted structure during geometric optimization in the FM and AFM configurations. This can be used to explain the nonlinear changes of \(\Delta E_{AFM-FM}\) and \(J\) of \((2 \times 2)\) in the \(g\)-C\(_4\)N\(_3\) structure with biaxial strain. To understand the physical origin of magnetism, a detailed analysis of the orbital-resolved magnetic moments in the \(g\)-C\(_4\)N\(_3\) structure with uniaxial strain along the \(x\) direction is performed and shown in Fig. 4(c). The magnetic moments are mainly attributed to the \(p_z\) orbit of the three N atoms and the effect of the \(sp^2\) orbit is very small. The contribution of the \(p_z\) orbital magnetic

![Fig. 3](image1.png)

**FIG. 3.** Calculated magnetic moments (a), formation energy (c), and energy differences (b) between valence band maximum value and Fermi level at the \(\Gamma\) point of the \(g\)-C\(_4\)N\(_3\) structure with different external strain, respectively. The fluctuation in temperature is shown as a function of the molecular dynamic simulation step at 300 K of \(g\)-C\(_4\)N\(_3\) structure with 10\% uniaxial strain along \(x\) direction.

![Fig. 4](image2.png)

**FIG. 4.** Energy difference \(\Delta E_{AFM-FM}\) between the AFM and FM configurations (a) and magnetic coupling strength (b) of the \(g\)-C\(_4\)N\(_3\) structure with different external strain, respectively. Projected magnetic moments on the \(p_z\), \(sp^2\) orbit (c) and \(\Delta E_{AFM-FM}\) as a function of \(p_z\) orbital magnetic moments (d) in \(g\)-C\(_4\)N\(_3\) structure. The inset shows the high symmetry points of the Brillouin zone.
moment to the $\Delta E_{AFM-Fm}$ is considered and shown in Fig. 4(d) and the $p_z$ orbital magnetic change is mainly responsible for the $\Delta E_{AFM-Fm}$ behavior.

In summary, in the $g$-C$_4$N$_3$ structure, magnetism can be controlled by asymmetric deformation. It diminishes gradually to 0.33 ($x = 10\%$) and 0.83 $\mu_B$ ($y = 11\%$) and then increases slowly to 0.56 ($x = 16\%$) and 0.98 $\mu_B$ ($y = 16\%$). Meanwhile, this system transforms from half-metallicity to metallicity. This phenomenon is different from the magnetic behavior of symmetric deformation induced by biaxial strain. It should be noted that the previously proposed strategies to regulate magnetism may be difficult to control experimentally because a strong external electric field or careful selective doping is required. In contrary, since the external strain can be easily applied by means of a specific substrate in fabrication, the strategy to apply external strain in engineering of spintronic materials has large potential.

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11A. K. Geim and K. S. Novoselov, Nat. Mater. 6, 183 (2007).