A phase diagram for band inversion of topological materials as a function of interactions between two involved bands

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Abstract – Basing on first-principles calculations, we predicate that Bi on a graphene derivative, g-C$_{14}$N$_3$, which involves a $3 \times 3$ unit cell of graphene with four C atoms substituted by three N atoms, is a topological insulator with a gap of 50 meV. With the help of maximally localized Wannier functions, we find that its band inversion gap can be determined by examining a pair of interaction parameters between the two involved bands. Accordingly, a phase diagram for band inversion of topological materials as a function of the interactions is obtained. The conclusion also holds for Sb, Ir and Rh on g-C$_{14}$N$_3$. These materials are topological nontrivial either insulator or semimetal, indicating that g-C$_{14}$N$_3$ is a good platform for conceiving topological materials.

A topological insulator (TI) exhibits a novel state that possesses simultaneously insulating bulk and conducting surface (edge) in one material. This is impossible to achieve in conventional materials [1,2]. The exotic physical properties of TI has potential applications in quantum devices and spintronics. [3–7] There are three keys to realizing a TI: time-reversal symmetry (TRS), spin-orbit coupling (SOC) and band inversion (BI) [1,2]. TRS and SOC are dependent on atomic configuration and the atom properties themselves. Therefore, the primary challenge in the field falls centrally in BI, which can be manipulated by applying stress [8–11] and controlling the alloy component [12,13]. Recent research has suggested that a distortion in metal dichalcogenides could cause an intrinsic BI between chalcogenide-$p$ and metal-$d$ bands to ultimately form TI [14]. Applying stress, controlling the alloy component and distorting the lattice can affect the relevant interactions. However, little research to date has examined how BI depends on these interactions, and this is of direct importance in the application of TI.

In the present work, we study the BI dependence on the interactions of the involved bands for Bi on g-C$_{14}$N$_3$ and present a phase diagram for the BI gap as a function of interactions between two involved bands. The phase diagram works also for Sb, Ir and Rh on g-C$_{14}$N$_3$. The results were obtained by performing first-principles calculations in the framework of the density function theory with the projector augmented plane-wave (PAW) pseudopotential method [15], as implemented in the VASP package [16]. The exchange-correlation potentials were described by the local density approximation (LDA) [17], which well described interactions in the graphene-based structures [18]. The energy cutoff for the plane-wave basis was 600 eV throughout all calculations. The $k$-points in the 2D Brillouin zone (BZ) of the $3 \times 3$ size unit cell of graphene were sampled on a Γ-centered $7 \times 7$ mesh. All atoms could be relaxed until the Hellmann-Feynman forces on the atoms were less than 0.001 eV/Å. The SOC interaction was included. Spin-polarization was performed in the calculations. However, no spin-polarization effects were identified for the systems concerned. Maximally localized Wannier functions (MLWF) methods were implemented in the Wannier90 package for tight-binding parameters [19].

Firstly, we focused on Bi/g-C$_{14}$N$_3$. The stability of g-C$_{14}$N$_3$ and Au on it has been examined in our previous work [20]. The most stable adsorption site of Bi on g-C$_{14}$N$_3$ can be expected to be the same as that of Au/g-C$_{14}$N$_3$. We further performed a phonon calculation for Bi/g-C$_{14}$N$_3$ with the same calculation setup [21] for Au/g-C$_{14}$N$_3$ [20]. No imaginary frequencies can be found.

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for Bi/g-C\textsubscript{14}N\textsubscript{3}. The most stable structure of Bi/g-C\textsubscript{14}N\textsubscript{3} is quite similar to that of Au/g-C\textsubscript{14}N\textsubscript{3} [20] and the topview of its atomic configuration is shown in fig. 1. Bi is lifted by 1.66 Å away from the graphene layer and the shift of three N atoms upwards to the graphene layer is smaller than 0.01 Å. Each N is bonded to two neighbor C atoms with the length of C-N being 1.37 Å. At 123°, the C-N-C angle is slightly larger than that of the C atoms in graphene (120°). Taking the energy of Bi/g-C\textsubscript{14}N\textsubscript{3} with Bi fixed at the center of vacuum as a reference, Bi on g-C\textsubscript{14}N\textsubscript{3} obtains an energy of 3.0 eV, meaning that Bi on g-C\textsubscript{14}N\textsubscript{3} is quite stable.

Before discussing the electronic properties of Bi/g-C\textsubscript{14}N\textsubscript{3} in more detail, it is worth briefly reviewing the features of the g-C\textsubscript{14}N\textsubscript{3} band structure that were described in depth in our previous work [20], as shown in fig. 2(a). The g-C\textsubscript{14}N\textsubscript{3} keeps the main electronic feature of graphene, the Dirac point with a small gap of 0.2 eV below the top of the \(\pi\) band. However, since four C atoms are replaced by three N atoms, the Fermi level lies 0.2 eV below the top of the \(\pi\) band, resulting in a +1\(\epsilon\) hole. The intercation bands between three N lone pairs are fully occupied and the Fermi level lies at the band top. The \(\pi^*\) band consisting of about 25% N\((p_z)\) and 75% C\((p_z)\) degenerates with the \(\pi\) band at the \(\Gamma\)-point. Its antibonding band, \(\pi^{\ast\ast}\), is about 2.5 eV above the Fermi level. Near the \(M\)-point, there exists a crossing of the \(\pi^*\) and \(\pi^{\ast\ast}\), which plays an important role in forming a TI when Bi is deposited on g-C\textsubscript{14}N\textsubscript{3}. In Au/g-C\textsubscript{14}N\textsubscript{3}, one valence electron of Au fills the +1\(\epsilon\) hole, resulting in the Fermi level returning to the Dirac point [20]. Accordingly, when an ion with two valence electrons more than that of Au is deposited on g-C\textsubscript{14}N\textsubscript{3}, the Fermi level could be shifted to the crossing of \(\pi^*\) and \(\pi^{\ast\ast}\), since the \(\pi^*\) band is the lowest conducting band of g-C\textsubscript{14}N\textsubscript{3}. Bi in an \(s^2p^3\) configuration is this type of ion due to its two s-electrons in a deep level of about −7~−8 eV.

The band structures of Bi/g-C\textsubscript{14}N\textsubscript{3}, along the \(M\), \(\Gamma\), \(K\) and \(M\) points with (solid lines) and without SOC (dotted lines), were calculated and are shown in fig. 2(b). The band structure without SOC (dotted lines) reveals that two bands cross over the Fermi level near the \(M\)-point as well as near the \(K\)-points, indicating that the system without SOC is metallic. Furthermore, the two bands cross between \(M\)-\(\Gamma\). The crossing is referred to as \(\Lambda\) in the following. These two bands can be traced to the empty \(\pi^*\) and \(\pi^{\ast\ast}\) bands of g-C\textsubscript{14}N\textsubscript{3}, occupied by p-electrons of Bi. The \(\Lambda\)-point in Bi/g-C\textsubscript{14}N\textsubscript{3} can also be traced to the crossing of the empty \(\pi^*\) and \(\pi^{\ast\ast}\) bands in g-C\textsubscript{14}N\textsubscript{3}. However, in Bi/g-C\textsubscript{14}N\textsubscript{3}, the \(\Lambda\)-point is 1.0 eV above the Dirac point, while in g-C\textsubscript{14}N\textsubscript{3} the crossing is 2.5 eV above the Dirac point. Taking SOC into account, the band structures (solid lines) exhibit a strong SOC splitting, and a gap of 145 meV is opened surrounding the \(\Lambda\)-point. Furthermore, the mixed \(\pi^{\ast\ast}\) band, which is occupied around the \(K\)-point without SOC, shifts up to 160 meV and becomes unoccupied, while the mixed \(\pi^*\) band shifts down to 66 meV. By shifting in opposite direction, the two bands open a gap of 50 meV on the axis \(\Gamma-K-M\), which is overlapped by the gap surrounding the \(\Lambda\)-point and is thus an optical gap. The Fermi level lies in the gap.

The topological nature of Bi/g-C\textsubscript{14}N\textsubscript{3} could be verified by the evolution of the Wannier function Center (EoWFC) [22] and the gapless edge states [23]. We calculated EoWFC in terms of the equivalent method based on
the $U(2N)$ non-Abelian Berry connection [22]. In these calculations, the required parameters were obtained using the MLWF method. The EoWFC with a reference line (dashed line) is shown in fig. 2(c). Figure 2(c) shows that the evolution lines cross the reference line sporadically, indicating that the gap surrounding the Λ-point is topologically nontrivial.

In order to obtain the edge states of Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3}, the periodicity of 2D Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3} in one direction was broken. To achieve this, its 2D structure was viewed as a ribbon (two Bi, six N and 28 C atoms within a 1D unit cell) periodically stacking along the direction perpendicular to its armchair edge, as indicated by the shadow region in fig. 1. Following that, 50 1D ribbons were stacked to a stack ribbon that was employed to calculate the edge states. It was confirmed that this stack ribbon was sufficiently wide to avoid the interaction of two edges over the stack ribbon [20]. The relaxation of edge atoms and the edge correction were not taken into account since these states have been confirmed to be robust against perturbations [1,2]. The interaction parameters obtained by the MLWF optimizing process. This matrix terms of their initial positions.

The calculated band structures of the stack ribbon are shown in fig. 2(d). The band structures (shadowed region) shown in fig. 2(d) could be seen as the 2D band structures of Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3} projected onto 1D BZ, since the stack ribbon consisted of 50 1D ribbons. Two parts of the projected bands above the Fermi level (0.0–0.2 eV) can be clearly distinguished: one projected by the bands near the K-point, and the other projected by the bands near the Λ-point. Thus, the energy of the optical gap (50 meV) and the topological gap (145 meV) could be identified roughly from the projected bands, whose band edges are mainly determined by the gaps near the K-point and the Λ-point, respectively. Two edge state bands could be seen extended from the projected bands near the Λ-point, and hidden in the background of the projected bands near the K-point. In the blank region of the figure, the solid lines are the edge states of the stack ribbon, indicating that the edge states in the gap are metallic. Clearly, the two edge state bands degenerate at the Π-point and the Fermi level is fixed at this point, indicating the gapless nature of a topological insulator.

Along the axis Γ-K-M, the mixed $\pi^*$ band of Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3} is higher than the mixed $\pi^+$ band, regardless of whether SOC is included (solid lines) or not (dotted lines) in the calculations. This indicates that the $\pi^*$ and $\pi^*$ band are not inverted along the axis Γ-K-M. Considering the importance of Bi, which occurs at the M-point of BZ and 0.1 eV above the Fermi level for Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3} without SOC, as indicated by dotted lines in fig. 2(a), we then turned our attention to identifying which factors determine the BI.

The SOC effects of Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3}, which can be traced to the contribution of $p$-electrons of Bi, were obtained to compare the band structures presented by the dotted (without SOC) and solid (with SOC) lines. As the calculated electronic structures indicate, the SOC effect mainly exists in the bands above ~1.0 eV, as shown in fig. 2(a). In contrast, the difference in the solid and dotted lines below ~1 eV indicates less SOC splitting on these bands. This is because three of five Bi valence electrons fill the bands below ~1 eV: one electron in the +1 eV hole of the g-C\textsubscript{14}N\textsubscript{3} centered at about ~−1 eV, and the other two in the s-level within ~7−8 eV. The bands above ~1.0 eV are fully separated by a gap of 0.3 eV from the bands below, as shown in fig. 2(a). The remaining two electrons of Bi in a doublet $p_x+p_y$ configuration exhibit atomic-like behaviors within a rhombohedral crystal field and fill in the band above ~1 eV. Thus, the bands above ~1 eV could be seen as those involved in ion Bi\textsuperscript{3+} with strong SOC. Accordingly, we focused only on the bands above ~1 eV and will analyze these in more detail below.

During the optimizing process that was designed to transform the involved bands of Bi/\textit{g}-C\textsubscript{14}N\textsubscript{3} above ~1 eV from our first-principles calculations to the MLWF, we chose an inner energy window of ~1.00–0.55 eV including the involved bands across the Fermi level. Thus, the MLWF was performed for 12 bands above ~1 eV as an outer energy window. During the process, four Wannier functions were chosen, two (W\textsubscript{1} and W\textsubscript{2}) for the Bi’s $p_x/p_y$ orbital due to its threefold coordination, and the other two (W\textsubscript{3} and W\textsubscript{4}) for the $\pi^*$ and the $\pi^*$ orbital, respectively.

The optimized centers of four WFs [19] are shown in fig. 1 and indicated by the labels W\textsubscript{1}, W\textsubscript{2}, W\textsubscript{3} and W\textsubscript{4}, independent of their initial positions.

We then used the parameters obtained from the optimizing process to construct the Hamiltonian along the Γ-M axis. In this construction, we ignored interactions with distances larger than third nearest-neighbors, corresponding to the interactions up to the involved WF centers [19] over the unit cell. Despite the truncation of the interactions, the main features of these bands remained. After a unity transformation of

\[
\begin{pmatrix}
\cos \theta & -\sin \theta & 0 & 0 \\
\sin \theta & \cos \theta & 0 & 0 \\
0 & 0 & 1 & 0 \\
0 & 0 & 0 & 1
\end{pmatrix}
\]

with $\theta = \pi/6$, the Hamiltonian matrix

see equation on top of the next page

could be obtained. Here a, b, c, α, β, γ were the parameters for the on-site interaction, and $t_1/t_2$ were the parameters for the interaction between the electrons occupying orbitals W\textsubscript{1} (W\textsubscript{2}) and W\textsubscript{3}/W\textsubscript{4}, which were all obtained from the MLWF optimizing process. This matrix had a form of two 2 x 2 diagonal submatrices. Thus, with $A = a + 2\alpha$, $B = b - \beta$, $C = c - \gamma$, one could easily obtain
self-interaction parameters, the BI were determined by the topological nature of semimetal Sb(Ir)/
are separated into the lower and upper band, as shown in fig. 4. The two concerned bands, referred to as Λ, is broken and the two bands respectively. The stability of Sb(Rh, Ir)/
were obtained by the same processes and are shown in fig. 3, and indicated by the Sb, Rh and Ir labels, respectively.

\[
\begin{pmatrix}
  a + \alpha (1 - \cos k) & 0 & 2t_1 (1 - e^{-ik}) & 0 \\
  0 & a + \alpha (1 - \cos k) & 0 & -2t_2 (1 - e^{ik}) \\
  2t_1 (1 - e^{ik}) & 0 & b + \beta (2 \cos k + \cos 2k) & 0 \\
  0 & -2t_2 (1 - e^{-ik}) & 0 & c + \gamma (1 + 2 \cos k)
\end{pmatrix},
\]

the BI gap [14] as

\[
\delta_{BI} = C - B - \sqrt{(A - C)^2 + 64t_1^2} + \sqrt{(A - B)^2 + 64t_2^2}.
\]

Since \(a, b, c, \alpha, \beta, \Gamma\) in the Hamiltonian are on-site and self-interaction parameters, the BI were determined by the \(t_1\) and \(t_2\) parameters, which describe the interactions for \(W_1-W_4\) and \(W_2-W_4\), respectively. The \(t_1/t_2\) optimized by the MLWF method for Bi/g-C\(_{14}\)N\(_3\) reads 0.180/0.150, corresponding to a BI gap of 0.29 eV, as shown in fig. 3(a). \(t_1/t_2\) can be used to tune the BI gap: if \(t_1/t_2\) is taken as 0.142/0.188 and 0.104/0.226, the BI gap is zero and -0.29 eV, respectively, as shown in fig. 3(b) and (c).

The electronic structures of Sb, Rh and Ir on g-C\(_{14}\)N\(_3\) were obtained by the same processes and are shown in fig. 4, and indicated by the Sb, Rh and Ir labels, respectively. The stability of Sb(Rh, Ir)/g-C\(_{14}\)N\(_3\) was also examined by the phonon calculation [21]. In the figure, the top and bottom panels correspond to the band structure and EoWFC, respectively. The EoWFC, for all three cases exhibit an odd winding number, indicating a topological nontrivial gap along the \(M-\Gamma\) axis. However, due to the fact that they exhibit a different band structure along the \(\Gamma-K\) axis, Sb and Ir on g-C\(_{14}\)N\(_3\) are topological semimetal,

\[\text{1If SOC is introduced in the calculation, the cross-point of the two concerned bands, referred to as} \Lambda, \text{is broken and the two bands are separated into the lower and upper band, as shown in fig. 4. The topological nature of semimetal Sb(Ir)/g-C\(_{14}\)N\(_3\) is determined by the electron behaviors near the} \Lambda \text{-point. Therefore, the lower band will be entirely taken into account for calculating the evolution of the Wannier function center, although its small piece is unoccupied near the} M \text{-point.}\]

whereas the Rh case is a topological insulator with a gap of 30 meV.

Through applying similar processes to the case of Bi on g-C\(_{14}\)N\(_3\), we also obtained the optimized parameters in eq. (1) for cases of Sb, Rh and Ir on g-C\(_{14}\)N\(_3\); that is, the BI gap as a function of the interaction between the involved bands for Sb, Rh and Ir on g-C\(_{14}\)N\(_3\). Equation (1) indicates that positive, zero and negative values for the BI gap could be tuned by pairs of the interaction parameters \(t_1/t_2\).

Accordingly, a phase diagram of the BI as a function of the interaction parameters between two involved bands could be obtained from the equation. This is shown in fig. 5, in which the red region indicates a topological trivial phase, while the blue region indicates a topological nontrivial phase. The optimized interaction parameters \(t_1/t_2\) for Bi, Sb, Rh and Ir on g-C\(_{14}\)N\(_3\) all lie in the blue region (with positive BI gap), labeled by Bi, Sb, Rh and Ir, respectively, revealing that all four cases have a topological nontrivial gap. This indicates that g-C\(_{14}\)N\(_3\) is a good platform for conceiving topological nontrivial materials.

In conclusion, we demonstrated that Bi/g-C\(_{14}\)N\(_3\) is a topological insulator with a topological nontrivial gap of 145 meV and an optical gap of 50 meV. The study also confirmed that depositing Sb (Ir and Rh) on g-C\(_{14}\)N\(_3\) could also form topological nontrivial materials (either
A phase diagram for BI of topological materials

Fig. 5: (Color online) Phase diagram of the band inversion gap as a function of interaction parameters \( t_1/t_2 \). The blue and red regions correspond to the topological nontrivial and trivial phase, respectively. The Bi, Sb, Rh, and Ir labels indicate the optimized parameter pairs of \( t_1/t_2 \) for the case of Bi, Sb, Rh and Ir on \( g\)-C\(_{14}\)N\(_3\), respectively. The yellow region corresponds to either positive or negative BI gap, case by case.

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