Tunability of Magnetic Anisotropy of Co on Two-Dimensional Materials by Tetrahedral Bonding

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Pairing of \(\pi\) electronic state structures with functional or metallic atoms makes them possible to engineer physical and chemical properties. Herein, we predict the reorientation of magnetization of Co on hexagonal BN (h-BN) and graphene multilayers. The driving mechanism is the formation of the tetrahedral bonding between \(sp^3\) and \(d\) orbitals at the interface. More specifically, the intrinsic \(\pi\)-bonding of h-BN and graphene is transformed to \(sp^3\) as a result of strong hybridization with metallic \(d_{z^2}\) orbital. The different features of these two tetrahedral bondings, \(sp^2\) and \(sp^3\), are well manifested in charge density and density of states in the vicinity of the interface, along with associated band structure near the \(K\) valley. Our findings provide a novel approach to tailoring magnetism by means of degree of the interlayer hybrid bonds in 2D layered materials.

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I. INTRODUCTION

Two-dimensional (2D) materials, down to one or a few atomic thick, have been still active in modern material physics, including spintronics [1,2], spin-orbitronics [3], and spin Hall effects [4,5], owing to the intriguing properties associated with their unique atomic and electronic structures. In particular, intense research efforts continue to seek possibilities for engineering the physical and chemical properties of transition metal (TM) atoms. On the other hand, the presence of graphene can also substantially alter the electronic and magnetic properties of transition metal (TM) atoms, which depends on the degree of hybridization between the metal \(d\) and graphene \(\pi\) orbitals [11]. In these contexts, the exploration in other archetypal 2D structures such as hexagonal boron nitride (h-BN), which is a structural analogue of graphene with broken sublattice symmetry, emerges one of central interests from both fundamental and technological stand points.

In spintronics, perpendicular magnetic anisotropy (PMA) is of crucial significance, where its tunability is essential to enhance the performance. Furthermore, combination with 2D materials is yet to explore the possibilities for manipulating the magnetism and magnetic anisotropy of TM atoms on graphene [12,13]. For example, unexpectedly large PMA up to an order of 100 meV was predicted in cobalt dimer-benzene pairs [12]. Nevertheless, subsequent experiments have shown that the individual Co atoms adsorbed onto graphene on a Pt\((111)\) exhibit in-plane magnetic anisotropy [13]. Interestingly, it is further identified that the preferable magnetization direction of Co adatoms on graphene depends on the underlying metallic substrate: magnetization is perpendicular in graphene/Ru\((0001)\) and in-plane in graphene/Ir\((111)\) [14], where different graphene/metal interactions are responsible, i.e. chemisorption in graphene/Ru, physisorption in graphene/Ir [14], and graphene/Pt [13]. In recent studies, through \(C\) \(p_z\)-Co \(d_{z^2}\) hybridization, the presence of fullerene molecules necessitates magnetization reorientation of the underlying Co films in-plane to perpendicular [15].

In addition to these remarkable findings, the promising alternative for tailoring the magnetic anisotropy of TM atoms seemingly resides in the use of even stronger bonding features between the tetrahedral \(sp^3\) and metallic \(d\) orbitals. In this article, the reorientation of magnetization of Co is predicted on h-BN via \(sp^2 - sp^3\) transition. The bond transition includes hybridization with metallic \(d\) orbitals, where the \(sp^3-d_{z^2}\) hybridization is crucial for the magnetization reversal. Moreover, the bond transition also accompanies the sign change in Berry curvature, which may invites experiments to verify using the spin Hall [4,5,8,38] and the inverse spin Hall effect [36,37]. Further investigations demonstrate the reorientation of magnetization in similar phase transition involving carbon \(sp^3\)-bonds from graphene layers [16].

II. COMPUTATIONAL METHOD

Density functional theory (DFT) calculations are performed using Vienna \(ab\) initio simulation package (VASP) [17–19]. The exchange-correlation interactions are treated by the generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof (PBE) [20]. The long-range dispersion corrections for the interlayer interaction were taken into account within the semi-empirical DFT-D2 approach suggested by Grimme [21]. We used \(2\times2\) graphene and \(h\)-BN cells in the lateral 2D-lattice for all the calculations. More details of our model geometries are provided in the following section. We use an energy cutoff of 400 eV, a \(21\times21\times1\) \(k\)-mesh, and relaxation with force criteria of \(10^{-2}\) eV/\(\AA\). The spin-orbit coupling (SOC) is included in a second-variational way employing scalar-relativistic calculations of the valence states [22]. Magnetic anisotropy energy (MAE) is calculated from the total energy differences between when the magnetization is along the \(xy\) plane (\(E^{\parallel}\)) and along the \(z\) axis (\(E^{\perp}\)). MAE = \(E^{\parallel} - E^{\perp}\). A dense \(k\) points of 41\(\times\)41\(\times\)1 is used in non-collinear calculations, which is sufficient to get reliable results
Prior to explore the Co/h-BN heterostructures, we first examine the stacking and binding affinity of h-BN layers. Top and side views of three distinctive stacking configurations of h-BN bilayers are shown in Fig. 1 (a) AA'-stacking, (b) AA-stacking, and (c) AB-stacking (often referred to Bernal-type). In the AA'-stacking configuration, each atomic column along the c-axis consists of alternating B and N atoms. In the AA-stacking configuration, two h-BN layers are laterally superimposed. In the AB-stacking configuration, while B (N) atoms of the top layer sit right above B (N) of the bottom layer, the other atoms are above the hollow-site. With the same pattern of the AB-stacking, one may consider two more configurations, i.e., A'B and AB' [23], where B (N) atoms of the top layer sit right above B (N) of the bottom layer. These two stacking structures have been excluded in the present study owing to higher energies than AB-stacked h-BN in previous ab initio calculations [23]. Optimized in-plane lattice \( a \), the interlayer distance \( d \), and the binding energy \( E_b \) are listed in Table I for the AA', AA, and AB stacked h-BN bilayers. Here, \( E_b = E_{(BN \ bilayer)} - 2E_{(BN \ monolayer)} \), where \( E_{(BN \ bilayer)} \) and \( E_{(BN \ monolayer)} \) are the total energies of bilayer and monolayer h-BN, respectively. Overall, our structural results agree well with experimental [24, 25] and other theoretical studies [23, 26]. The AB stacking is more stable by \( \sim 3 \) meV than the bulk-like AA' stacking, in agreement with the previous calculations (4 meV) [23]. Experiments have also reported that both the AA' and AB stackings can exist [23], as their energy difference is quite small in our calculations.

The structural stability of Co/h-BN, upon functionalization of the bottom surface, is then explored, where we adopt only the AB-stacked h-BN bilayer, whose structures are shown in Figs. 1(a) and (b). In Fig. 1(a), Co(0001) monolayer is weakly physisorbed onto h-BN bilayer with AB-stacking, where vacuum region separating the periodic slabs is taken no less than 15 Å thick. The most preferred adsorption site of the Co adatoms on h-BN is N-top site, where the Co-BN interlayer distance, denoted as \( d_1 \), is 3.32 Å (Table II). In usual experiments, functional atoms in gas phase can cover up to half the surface of graphene in a uniform pattern [27, 28]. As such, fluorine atoms preferably bind with B at the bottom surface of h-BN bilayer [29] as shown in Fig. 2(b). Consequently, the latter structure, Co/h-BN/F, is energetically favored than the former, fluorine-free Co/h-BN, by \( \sim 1.8 \) eV/Co, from formation energy, \( H_f \) [10], as shown in Fig. 2(c), where \( H_f = [E_{(Co/BN/F)} - E_{(Co)} - E_{(BN)} - E_{(F)}] / N \); \( E_{(Co/BN/F)} \), \( E_{(Co)} \), \( E_{(BN)} \), and \( E_{(F)} \) are the total energies of Co/BN/F, h-BN bilayer, and F atom in \( F_2 \)-gas phase, respectively; \( N \) is the number of \( 1 \times 1 \) unit cell of h-BN in 2D lattice.

Upon functionalization, h-BN layers either retain the van der Waals distance [Fig. 2(a)] or form covalent interlayer bonds [Fig. 2(b)]. The optimized interlayer distance between the BN layers, denoted as \( d_{2} \), of the former and the latter structures are 3.24 and 1.56 Å, respectively (Table I). The reduced value of the latter characterizes \( sp^3 \) bond in cubic BN structure (c-BN). Remarkably, the Co/\( sp^3 \)-BN structure is

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**TABLE I.** Optimized in-plane lattice \( a \) (Å) and interlayer distance \( d \) (Å), and binding energy \( E_b \) (eV per 1 \times 1 \) unit cell) of h-BN bilayer for the different stacking configurations shown in Fig. 1.

| Stacking | \( a \) | \( d \) | \( E_b \) |
|----------|-------|-------|---------|
| AA'      | 2.513 | 3.145 | -0.138  |
| AA       | 2.500 | 3.250 | -0.082  |
| AB       | 2.513 | 3.152 | -0.141  |

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**FIG. 1.** Top- and sideview of three kinds of h-BN stacking: (a) AA', (b) AA, and (c) AB-stacking, where orange and blue sphere denote B and N atoms, respectively.

**FIG. 2.** Side views of the optimized atomic structures of a Co monolayer on the (a) \( sp^3 \) and (b) \( sp^3 \) BN bilayers. Red, blue, orange, and gray spheres represent the Co, N, B, and F atom, respectively. The arrows through the Co atoms denote the direction of Co magnetic moments. (c) The formation energy \( H_f \) of the physisorbed and chemisorbed Co|BN. The case of metal-free chemisorbed BN bilayer is shown in open circle. Total energy of Co adatoms on functional-free h-BN is taken as reference energy.
To better appreciate the significance of the $sp^3-d_{xz}$ hybridization, partial density of states (PDOS) of the bonded Co and N atoms are shown in Figs. 3a–d for the physisorbed and chemisorbed Co/BN, respectively. PDOS of the free-standing Co and $h$-BN monolayers remain almost unchanged in the physisorption. The two doublets, $d_{xy}+d_{yz}$ ($m = \pm 2$) and $d_{xz}$ ($m = \pm 1$) states, retain during the $sp^2 - sp^3$ transition, where $m$ is the magnetic quantum number. In contrast, the chemisorption alters Co-$d_{xz}$ and N-$p_z$ states, where common peak in PDOS, owing to hybridization, is apparent. Notably, the N-$p_z$ states into the majority- and minority-spin subbands are split by such strong hybridization, which in turn leads to a large majority-spin peak at the Fermi level ($E_F$).

The split N-$p_z$ state in $E_F$ exhibits the feature of the metal-induced gap states (MIGS), which penetrates two- or three-layer-thick (~0.5nm) into the c-BN layers. Fig. 4a analyzes the electron density profile, $\Delta \rho = \rho(\text{Co/BN}) - \rho(\text{Co}) - \rho(\text{BN})$, where the MIGS is clearly manifested; the larger electronegativity (3.04) of the N than the Co (1.91) drives the spin-polarized charge transfer from the metal atom. On the other hand, the strong hybridization between the Co-$d$ and N-$p$ states causes charge redistribution in the metal layer. From the integration of the occupied Co-PDOS, the $d_{xz}$ orbital in the majority-spin loses 0.09$e$ under the formation of Co|sp$^3$-BN while the $d_{xy}$ in the minority-spin and $d_{xz}$ in the minority-spin gain 0.02 and 0.03$e$, respectively.

Remarkably, the $sp^2 - sp^3$ transition accompanies reorientation of magnetization. Calculated MAE and orbital moment

| TABLE II. Optimized in-plane lattice $a$ (Å), interlayer distance $d_1$ between the Co and the top BN layer and $d_2$ between the BN layers (Å), and spin magnetic moment $\mu_\alpha$ ($\mu_B$) of the bonded Co and N atoms for the physisorbed and chemisorbed Co/BN. Orbital anisotropy $\Delta \mu_\alpha (\times 10^{-2} \mu_B)$ and MAE (meV) are also listed. |

|          | $a$  | $d_1$ | $d_2$ | $\mu_\alpha^{Co}$ | $\mu_\alpha^{N}$ | $\Delta \mu_\alpha^{Co}$ | MAE   |
|----------|------|-------|-------|-------------------|-----------------|-------------------------|-------|
| Physisorption | 2.49 | 3.32  | 3.24  | 1.98              | 0.00            | -0.79                   | -0.62 |
| Chemisorption | 2.56 | 1.94  | 1.56  | 1.95              | 0.05            | 0.82                    | 0.76  |

FIG. 3. The $d$-orbital PDOS of the Co atom (a) physisorbed and (b) chemisorbed on BN bilayer. (c) and (d) The corresponding $p$-orbital PDOS of the N atom underlying the Co atom. The blue and red areas denote the spin-up and spin-down states, respectively. The Fermi level is set to zero energy.

FIG. 4. (a) Isosurface plot of the charge density difference $\Delta \rho$, where red (blue) corresponds to charge accumulation (depletion) in unit of $5 \times 10^{-2} e$/bohr$^3$. (b) The planar average of the $\Delta \rho (e)$ along the $z$ axis in the case of Co/BN with $sp^3$-bonding (chemisorbed). The notation of the atomic symbol is the same as used in Fig. 1. In (b), the planar average of the $\Delta \rho$ for the physisorption is also shown in red line.
anisotropy, $\Delta \mu_0 = \mu_{\uparrow} - \mu_{\downarrow}$, are listed in Table I for the physisorbed and chemisorbed Co/BN, respectively. The sign change for both MAE and $\Delta \mu_0$ emerges from the physisorption ($-0.62$ meV and $-0.79 \times 10^{-2} \mu_0$) to the chemisorption (0.76 meV and 0.82 $\times 10^{-2} \mu_0$), which indicates that the Co magnetization reorients from in-plane to perpendicular direction during the $sp^2 - sp^3$ transition. Moreover, these MAE values are fairly reproduced by the force method [31] from the $k$-resolved MAE according to $\text{MAE}(k) \approx \sum_{n \in \text{occ}} \left( \epsilon(n,k) \| - \epsilon(n,k) \perp \right)$ in 2D Brillouin zone (BZ), where $\epsilon(n,k) \|$ and $\epsilon(n,k) \perp$ are eigenvalues of occupied states for in-plane and perpendicular magnetization, respectively. Summing over $k$ points, we find the MAE values of $-0.59$ and 0.76 meV for the Co/Sp^2-BN and Co/Sp^3-BN, respectively, and both of them mainly arise from the MAE($k$) at/around the $\Gamma$ point.

To elucidate the origin of magnetization reversal, we show the $d$-orbital-projected contributions to the difference in SOC energies for in- and out-of-plane magnetization orientation, $\Delta E_{soc} = E_{soc}^{\|} - E_{soc}^{\perp}$, in Figs. 5(a) and (b) for the physisorbed and chemisorbed Co/BN, respectively. Here, $E_{soc} = \langle k^2 - \frac{1}{2m^*} \frac{d^2}{dr^2} L \cdot S \rangle$, where $V(r)$ is the spherical part of the effective potential within the PAW sphere, and $L$ and $S$ are the orbital and spin angular momentum operators, respectively. The expectation value of $E_{soc}$ is twice the actual value of the total energy correction to the second-order in SOC, i.e., $\text{MAE} \approx 1/2 \Delta E_{soc}$ [32]. Our test calculations indicate that the second-order perturbation theory is a reasonable approximation as the total MAE overall agrees within a few percent accuracy with those obtained from the atom and orbital projected calculations. The other 50% of the SOC energy translates into the crystal-field energy and the formation of the unquenched orbital moment [33]. It is obvious as seen in the top panel in Fig. 5(a) that the negative MAE of the Co/Sp^2-BN is dominated by the $\langle \chi z, yz | L_z | z^2 \rangle$, where $L_z$ is the orbital angular momentum operator of the $z$ component, which serves as negative (positive) contribution to MAE [34]. Two positive contributions, involving the $m = \pm 1$ and $m = \pm 2$ states, are rather small [bottom panel in Fig. 5(a)]. Interestingly, as shown in Fig. 5(b), these negative and positive contributions are reversed in sign under the $sp^2 - sp^3$ transition.

In order to understand more, we show energy- and $k$-resolved distribution of the Co $d$-orbital character of the majority- and minority-spin bands along the high-symmetry $\overline{M}K\overline{M}$ line in Figs. 6(a) and (b) for the physisorbed and chemisorbed Co/BN, respectively. From this, in Fig. 6 we sketch a schematic diagram of Co $d$-orbital energy levels at the $\overline{K}$. For reference, the same for the free-standing Co(001) monolayer is also compared. In the free-standing Co, without BN, Co $d$ states are split into a singlet ($m = 0$) and two doublets ($m = \pm 1, \pm 2$). In the physisorption, while Co $d$ orbitals hybridize weakly with BN via $sp^2$ bonding, energy levels do not change very much. The SOC split energy between the occupied and unoccupied states near $E_F$ is $\epsilon_{xz, yz}(\downarrow) - \epsilon_z(\uparrow) \approx 1.09$ eV, which occurs in the minority-spin channel (\downarrow). We simply ignore the $\uparrow\uparrow$- and $\uparrow\downarrow$-channel couplings as the majority-spin states are completely filled. On the other hand, in the chemisorbed case, as discussed earlier, the strong hybridization at the interface splits the Co $d_z$ and $N p_z$ into some hybrid bonding states, denoted as $p_z \otimes d_z$ [right panel in Fig. 6]. In particular, the hybrid $p_z \otimes d_z$ in the majority-spin channel (\uparrow) contributes to the MIGS at $E_F$, as shown in the bottom panel in Fig. 6(b).
FIG. 7. Schematic diagram of the interlayer bond splitting of the Co d- and N p-orbital levels at the \( \mathbf{K} \) point in the 2D BZ. The metal d-orbital states are not much perturbed upon the physisorption with h-BN (middle panel). The interlayer bonds at the Co \( sp^2 \)-BN interface splits the Co \( d_z \) and N \( p_z \) into the hybrid bonding states across the Fermi level (\( E_F \)), denoted as \( p_z \otimes d_z \) in the right panel. The upward red and downward blue arrows represent the majority- and minority-spin states, respectively.

which in turn modifies SOC significantly. Thus, from the energy level analysis along with the second-order perturbation theory of SOC matrix [34], the sign reversal in SOC matrix under the \( sp^2 - sp^3 \) transition mainly originates from two factors: (i) \( \varepsilon_{xz, z\bar{y}}(\downarrow) - \varepsilon_{z\bar{y}, z\bar{y}}(\downarrow) \sim 1.94 \text{ eV} \), which weakens the negative MAE in the magnitude, (ii) \( \varepsilon_{z\bar{y}}(\uparrow) - \varepsilon_{xz, z\bar{y}}(\downarrow) \sim 0.38 \text{ eV} \), which provides an additional strong contribution to PMA through \( \langle \hat{z}^2, \hat{\sigma}_z \rangle \). In addition to the magnetization reorientation, we also address briefly the sign change of Berry curvature across the \( sp^2 - sp^3 \) transition. The Berry curvature is calculated using the Kubo formula [35-38]

\[
\Omega_{xy} = \sum_{k,n} f(k,n)\Omega_{xy}(k,n)
\]

\[
\Omega_{xy}(k,n) = \sum_{m} \text{Im} \frac{(k,n|j_z|k,m)}{(\varepsilon_{k,n} - \varepsilon_{k,m})^2},
\]

where \( \Omega_{xy}(k,n) \) are Berry curvature at \( k \) and \( n \)-the band, whose summation over occupied bands and \( k \) is \( \sum \). \( j_z = \hbar \frac{\sigma_z}{2} \) is the spin-current operator, where \( \sigma_z \) is Pauli matrix. \( f(k,n) \) is the Fermi-Dirac function; \( \varepsilon_{k,n} \) is eigenvalue of \( k \) at \( n \)-the band. In the physisorption case, the Berry curvature (\( \Omega \)) is 26.83 (\( \Omega \cdot \text{cm}^{-1} \)) while it is –63.35 (\( \Omega \cdot \text{cm}^{-1} \)) in the chemisorption. Hence, the sign change of \( \Omega \) implies the change in spin Hall effect: spin separation occurs in opposite direction during the bond transition. This is quite inspiring that the effect of \( sp^2 - sp^3 \) transition can be verified experimentally using the spin Hall effect or the inverse spin Hall effect [36, 37] by measuring the spin current.

For more feasibility and insights, it would be instructive to explore the other \( sp^2- \) bonded layered structures. Similar calculations are performed for the weakly deposited Co adatoms on bottom surface fluorinated graphene bilayer. The optimized structural and magnetic properties of the Co\( sp^2 \)-graphene and Co\( sp^3 \)-carbon multilayers are tabulated in Table III. In terms of energetics, the formation of hybrid bond between the C-\( sp^3 \) and Co-\( d \) orbitals is favored rather than the \( sp^2- \) interaction, as found in previous experiments [16] and calculations [10, 16]. Notably, both the \( \Delta \mu \) and MAE of the Co\( sp^2 \)-graphene and Co\( sp^3 \)-carbon reveal the similar features to the Co\( BN \) structures. In this sense, switching magnetization of metal adatoms by the formation of \( sp^3- \) hybrid bond seems quite ubiquitous.

### IV. CONCLUSION

In summary, our first-principles calculations predict the re-orientation of magnetization via \( sp^3- \) hybrid bond in the Co adatoms on h-BN and graphene. Moreover, sign change occurs not only in MAE but also in the spin Berry curvature. Chemical functionalization of the bottom surface of h-BN (graphene) layers leads to the transformation into thermodynamically stable \( sp^3 \)-bonded BN (carbon) films, which in turn develops stronger interlayer tetrahedral \( sp^3 \)-metalllic \( d \) bonds. The present study provides a new avenue to tailor magnetization by means of degree of the interlayer hybrid bonds in the layered materials.

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**TABLE III.** The formation energy \( H_f \) (eV/Co), optimized in-plane lattice \( a \) (Å), interlayer distance \( d \) between the Co and the top carbon layer and \( d_z \) between the carbon layers (Å), spin magnetic moment \( (\mu_s) \) and orbital moment difference \( \Delta \mu_s \), and MAE (meV) for the physisorbed and chemisorbed Co bilayer graphene.

|          | \( H_f \) (eV/Co) | \( a \) (Å) | \( d \) (Å) | \( d_z \) (Å) | \( \mu_s^{Co} \) \( (\times 10^{-2} \mu_B) \) | \( \Delta \mu_s \) (meV) | MAE     |
|----------|------------------|------------|------------|-------------|-----------------|-----------------|--------|
| Physisorption | -1.12 2.45 3.29 3.18 1.96 0.00 -0.81 \( \times 10^{-2} \) 0.68 | | | | | | |
| Chemisorption | -2.80 2.50 1.94 1.58 1.14 -0.04 0.3 \( \times 10^{-2} \) 0.41 | | | | | | |

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