Nature of interfacial Dzyaloshinskii-Moriya interactions in graphene/Co/Pt(111) multilayer heterostructures

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Density-functional theory calculations utilizing the generalized Bloch theorem show that interfacial Dzyaloshinskii-Moriya interactions (DMI) at both interfaces of graphene/Co/Pt(111) multilayer heterostructures are decoupled for $n \geq 3$. Unlike the property of magnetocrystalline anisotropy, DMI in this system is not strongly affected by stacking defects in the Co layer. The effect of graphene (Gr) is to invert the chirality of the vacuum/Co interfacial DMI, overall reducing the DMI of the heterostructure, which is nevertheless dominated by the strong spin-orbit coupling (SOC) of Pt. A spectral analysis in reciprocal space shows that DMI at both the Gr/Co and Co/Pt interfaces have similar contributions from the strongly hybridized SOC-split $d$ bands. Our analysis proves that the DMI in this family of Gr-capped $3d/5d$ metal heterostructures displays richer physics than what is expected from the prediction of single-band models, such as the Rashba DMI model.

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I. INTRODUCTION

When the magnetic exchange interactions are subject to sufficiently intense spin-orbit coupling (SOC) in an environment with broken inversion symmetry, an antisymmetric term appears that leads to a canted and chiral orientation of spins, known as Dzyaloshinskii-Moriya interaction (DMI). First observed for oxides [1] and modeled as orbital-magnetic-spins, known as Dzyaloshinskii-Moriya interaction (DMI), as hybridization with the spin-orbit split [5]. DMI is usually active at surfaces and interfaces, where it trig-

ates the needed spin-flip electron excitations. Hence Co/Pt has become a paradigmatic system [19–21]. Alternatively, DMI strength and handedness can also be manipulated by adsorption of light element atoms, e.g., hydrogen [22,23] and oxygen [24,25], or capping with graphene (Gr) [23,26] and hexagonal boron nitride [27]. This DMI variation upon adsorption stems from the charge density redistribution at the surface and it is correlated with the electric dipole at the surfaces [24], where the correlation is endorsed by an analytical expression [28]. The prospect of connecting DMI to other, more accessible, properties of the system, such as electrostatic ones, has motivated the search for DMI descriptors that allow its predictability in systems of potential interest. For example, at a $3d/5d$ interface, it correlates with the spin moment $m_S$ of the $3d$ atoms but not with the $m_S$ induced at the interfacial $5d$ atoms [19–21,28,29], neither with the spin dipole nor with the orbital magnetic moments [28]. Direct modification of DMI merely based in electric field manipulation by a STM tip is questionable, as it may be mistaken for a variation of the magnetic exchange coupling strength [30].

In an attempt to classify DMI into types, it has been argued that Co/Pt and Gr/Co interfacial DMI are of different nature, namely Fert-Levy-like and Rashba-like, respectively [31]. In the former interface, the DMI energy contribution localizes at Pt, which has strong atomic SOC strength $\xi$. In the latter, Gr/Co, the aforementioned induced electrostatic potential change $VV'$ is modeled by a one-band Rashba Hamiltonian in the presence of a Heisenberg exchange term [32–34], leading to a linear term in the electron wave vector $k$. These models...
can be considered as limits of the strongly hybridized SOC-split $d$-bands behavior.

Motivated by recent experimental work on multilayer Gr/Co$_n$/Pt(111) heterostructures [26,35] and by the existing density-functional theory (DFT) work on the individual interfaces of them, in this paper we show that DMI cannot be satisfactorily described in either limit model. Our DFT calculations reveal that the Pt SOC dominates overall and that there are sizable contributions from Co SOC locally, although cancellations occur for Co from both interfaces. The DMI chirality induced by the graphene capping is opposite although cancellations occur for Co from both interfaces. We draw the important conclusion that this result cannot be simply attributed to specific states in the reciprocal space, i.e., a single-band Rashba model cannot account for it. This finding can be extrapolated to other 2$p$/$3d$/$5d$ heterostructures, where SOC will split bands that undergo a similar strong hybridization of the 3$d$ bands upon interface formation, as it happens in, for example, the cases of Gr/Co/Ir(111) [35] and O/Fe/Ir(100) [24].

During pseudomorphic growth by intercalation in Gr/Pt, Co attains a fcc stacking with interplanar spacing contraction (fcc$^*$). Therefore, the central regions of the slab are locally centrosymmetric and DMI is solely an interfacial effect. In the present work we show that this regime is reached at Co$_3$ thickness and that the DMI contributions of the stacking defects cancel out. Interestingly, this DMI behavior contrasts with that of the magnetocrystalline anisotropy of fcc$^*$ Gr/Co$_n$/Pt(111), where a complex evolution as a function of the Co$_n$ thickness is found that depends on the competition between the contributions from the fcc$^*$ bulk (in plane) and twin boundary defects (out of plane) [35].

The paper is organized as follows. In Sec. II we describe the model structures of Gr/Co$_n$/Pt used in this work and the details of the DFT calculations based on the generalized Bloch theorem with SOC. The Results and Discussion section is split into a collection of thickness-dependent and layer-resolved DMI energies (Sec. III A), as well as an analysis in the reciprocal space (Sec. III B), where the DMI contributions are energy and wave vector resolved. Finally, conclusions are drawn.

II. THEORETICAL METHODS

The pseudovectors $\mathbf{D}_{ij}$ characterize the DMI between two localized spin moments $\mathbf{S}_i$, $\mathbf{S}_j$, which is expressed as the Hamiltonian term $\sum_{i,j} \mathbf{D}_{ij} \cdot \mathbf{S}_i \times \mathbf{S}_j$. Figure 1 shows the $D$ vectors between the Co atom at the origin unit cell and its six closest Co atoms in the case of a monolayer. The threefold axes and mirror planes in the structure constrain these $D$ vectors to be determined by two free parameters $D_r$ and $D_z$ [36], as indicated in the sketch. Note that the relative positions of the nearest Pt atom with respect to each pair of Co neighbors alternate from right to left in the threefold symmetry and, thus, the $D$ vector out-of-plane component $D_z$ alternates in sign. As this work is restricted to relatively small angles between spins, we will use an effective model of the energy that maps all Co-Co interactions in the model slabs onto a two-dimensional Hamiltonian that depends on effective $D_r$ and $D_z$ parameters (see Fig. 1 and Supplemental Material [37] Fig. S1). Being effective constants, $D_r$ and $D_z$ can be interpreted also as micromagnetic-scale properties and can be used as input for simulations. The DFT values can be used directly in the spin dynamics equations of atomistic simulations (e.g., Refs. [17,38]). Alternatively, different procedures can be applied to transform them into energy densities [19] to be used in continuum modeling (e.g., Refs. [11,39]).

DFT calculations in the full-potential linearized augmented plane waves (FLAPW) formalism [40,41] have been carried out with the FLEUR code [42,43]. The Perdew-Burke-Ernzerhof (PBE) formulation is chosen as the exchange and correlation functional [44] for this work. We have used Co layers of one to five atom thicknesses, pseudomorphic on a fcc Pt(111) substrate (lateral periodicity 2.772 Å) of five atomic planes, with the relaxed interplanar spacings found in Ref. [35]. The effect of the substrate thickness on the DMI is shown in the Supplemental Material Fig. S2. For the basis set, a $48 \times 48 \times 1$ Monkhorst-Pack-point mesh [45] is used and plane wave expansion cutoffs of 4, 11, and 9.5 a.u.$^{-1}$ for the wave functions, density, and potential, respectively. The local basis was constructed without local orbitals, with $l_{\text{max}} = 6, 8$, and 10 for C, Co, and Pt, respectively. The smearing energy for the Fermi level determination was 0.03 eV.

Suitable noncollinear spin structures are needed for the model to show DMI. They are modeled as long-wavelength spin spirals in the generalized Bloch theorem (GBT) approach [46], which imposes a longer periodicity of the magnetization density described by a wave vector $\mathbf{q}$. Although, in principle, the charge density can be self-consistently converged for a given $\mathbf{q}$, since the calculations shown here involve long-wavelength spirals, we use the GBT non-self-consistently to calculate new energies and electron wave functions as a perturbation of a $\mathbf{q} = 0$ ground state (see Supplemental Material [37] Supplementary Material 2).
Fig. S3). Our calculations on the minimal model system, a Gr/Co$_1$/Pt$_5$ trilayer, show that this is a fair approximation in the low-$q$ regime (see Supplemental Material Fig. S4). Finally, spin-orbit interactions are added as a first-order perturbation. The implementation of this procedure in the FLAPW code is described in Ref. [47].

We use flat spin spirals with a spin rotation axis $\hat{z}_a$, which yield a chirality dependent energy in the presence of SOC. The energy difference between axes pointing in opposite directions $\hat{z}_a^+/\hat{z}_a^-$ is the DMI energy for a given spiral with $q$ periodicity. Our convention is that the spirals are counterclockwise (CCW) with respect to $\hat{z}_a$, so that $\hat{z}_a^+ (\hat{z}_a^-)$ mean CCW (CW) or left-handed (right-handed) spirals. Therefore, if the energy difference $\Delta E_{\text{DMI}}^s(q) = E_{\text{DMI}}(q; \hat{z}_a^+) - E_{\text{DMI}}(q; \hat{z}_a^-)$ is positive (negative), a CW (CCW) spiral is favored. The FLAPW calculations of this work are run for spirals with $q$ vectors along the $\Gamma K$ direction of the two-dimensional first Brillouin zone, i.e., the $q = (\frac{2\pi}{a}, \frac{2\pi}{N}, 0)$ direction in the Brillouin zone. As an example, Fig. 1 shows the spins of a Co atomic plane in the cases of $N = 32, 12, 8$ and $\hat{z}_a = Z$. We used $N$ values between 8 and 48 (the latter is at the resolution limit set by our electron momentum $k$ calculation grid, $48 \times 48 \times 1$).

III. RESULTS AND DISCUSSION

A. Additivity of interfacial DMI

At low $q$ values, the DMI energies for spins rotating around $\hat{z}_a$ pointing in the (positive) $Y$ and $Z$ axes follow a nearly linear in $q$ and a $q^2$ dependence, respectively, as we describe next. These trends are observed in Fig. 2 (red symbols and lines), which show $\Delta E_{\text{DMI}}^s(q)$ for Gr/Co$_n$/Pt$_5$, $n = 1–5$, slabs in the low-$q$ regime. Nevertheless, for the in-plane spins case the energies are too low to extract accurate quantitative results from a fit (note that the energies are one order of magnitude smaller for these spirals). The evolution of $\Delta E_{\text{DMI}}^s(q)$ with the Co layer thickness (red line) shows a significant magnitude variation, but no chirality change (i.e., no sign change). The $D_s$ effective magnetic is extracted from the fit to a 2D model with nearest neighbor interactions in a hexagonal lattice with $C_N$ symmetry, given by the expression (see Fig. S1)

$$\Delta E_{\text{DMI}}^s(q) = 4S^2 \sin \theta \hat{z}_a \cdot \left[0, D_s(1 + 2 \cos \theta), 2D_s(\cos \theta - 1)\right]$$

for flat spin spirals $q = (\frac{2\pi}{a}, \frac{2\pi}{N}, 0)$, where $\theta = \frac{2\pi}{N}$ are the corresponding angles between spins $S$ (assumed to have equal values). This expression has a linear behavior in the low-$q$ limit for spins rotating in the $XZ$ plane,

$$\Delta E_{\text{DMI}}^s(q) \approx 12S^2D_s \frac{2\pi}{N}$$

We use this equation to fit the DFT energies, so that the resulting $D_s$ values are to be interpreted as effective, since other contributions, not considered in Eq. (1), also yield linear terms in $q$ for $\hat{z}_a = Y$, such as interplanar nearest neighbor bonds [36], second nearest, and beyond neighbors.

To obtain $D_y$, we exclude the two largest $q$ values of each curve shown in Fig. 2 and use as spin moment value the average over the Co atomic layers. In the central Co atomic planes we find $m_3(\text{Co}) \approx 1.86 \mu_B$. This value is slightly enhanced at the vacuum/Co and Co/Pt interfaces (1.94$\mu_B$ for $n_{Co} = 5$), while graphene has a demagnetizing effect (1.57$\mu_B$) (see also the Supplemental Material Fig. S5 middle panels). Additionally, at the interfacial Pt atoms a spin polarization of $0.27\mu_B$ is induced. In the model of Eq. (1), this would add to $\Delta E_{\text{DMI}}^Z(q)$ a Co-Pt nearest neighbor contribution one order of magnitude smaller than that of the Co-Co DMI interactions. The resulting $D_y$ values, summarized in Fig. 3, have a very good agreement with linear behavior (the linear fit errors are $\lesssim 4\%$). The $D_y$ values oscillate for $n_{Co} = 1–3$ and converge to $D_y \approx 0.3 \text{ meV } \mu_B^{-2}$ afterwards. The fitted $D_y$ value for Co$_1$Pt$_5$ is in agreement with the literature calculated with GBT and flat spin spirals [20,48], too, which are close to 0.5 meV $\mu_B^{-2}$. This methodology tends to yield larger energies than other electronic structure methods [48].

For spins rotating in the interface ($XY$) plane, the DMI energy is a third order effect in $q$,

$$\Delta E_{\text{DMI}}^Z(q) \approx -4S^2D_y \frac{(2\pi)}{N}^3.$$

This means that at this geometry the interfaces sustain an effective $D$ vector with an out-of-plane component $D_y$ (note that a spin spiral with $q$ vector along $\Gamma M$ would not allow one to resolve $D_y$, although the magnitude of this effect is small. The second column of Fig. 2 shows that, indeed, the energies are an order of magnitude smaller than for spins rotating in
the $XZ$ plane. These data sets do not allow for a good quality fit to a $q^3$ law, since the large $\xi(Pt)$ value magnifies finite size effects. Slabs with a single Pt layer as substrate, which are shown in the Supplemental Material Fig. S6, have a smoother behavior. In them $\Delta E_{y}^{\text{DMI}}(q)$ changes its sign, i.e., alternating chirality of $D_3$, as the Co layer grows beyond the monolayer thickness and tends toward small values when interfaces are decoupled at $n_{Co} = 3$. A sizable nonzero $D_3$ component can result in hybrid Bloch-Néel domain walls \cite{49} and it has been postulated that it is responsible for an asymmetric skyrmion layer have been used.

In the remainder of the paper we focus the analysis on the $D_3$ component only. To ascertain whether the crossover at $n_{Co} = 3$ is correlated with the additivity of interfacial DMI, we have decomposed the heterostructure model slab into Co$_{1-5}$/Pt$_5$ and Gr/Co$_{1-5}$ partial slabs with the same atomic positions (green and blue lines and symbols, respectively, in Fig. 2 and Fig. 3). In the following, we call this form of analysis “partial slab decomposition” (PSD). The sum of the corresponding $\Delta E_{y}^{\text{DMI}}(q)$ and effective $D_3$ (black lines and open symbols) follows closely the Gr/Co$_{2-5}$/Pt$_5$ values, while there is a large difference for $n_{Co} = 1$. Although this would suggest that the Co/Pt and Gr/Co interfaces are already decoupled at $n_{Co} = 2$, their individual values still depend on the Co thickness. Hence effective decoupling does not occur until at least $n_{Co} = 3$. In particular, for Gr/Co$_2$/Pt$_5$ the maximum value $D_3 = 0.5$ meV $\mu_B^{-2}$ is obtained.

The contribution of the Co/Pt interface accounts for most of the $\Delta E_{y}^{\text{DMI}}(q)$ energy in the heterostructure. Importantly, at the Gr/Co interface the chirality is opposite (except in the GrCo bilayer) and of comparable magnitude to that of Co/Pt. This type of analysis, however, cannot determine if the effect of the Gr capping layer is to invert the chirality of the vacuum/Co interface. For this, we have calculated $\Delta E_{y}^{\text{DMI}}(q)$ with atomic SOC contributions selected in the respective atomic spheres \cite{47}, a method we denote in the following with the acronym ASOD (atomic spin-orbit decomposition). These results are shown in Fig. 4. This alternative method allows one to assess the individual atom contributions to interfacial DMI energy in a given system, since it is additive in the atomic SOC strength ($\xi$) by construction. With ASOD we find that the contribution of the interfacial Pt atomic plane, Pt$_{Co}$, dominates the whole DMI effect, showing similar energies in both Gr/Co$_5$/Pt$_5$ and Co$_5$/Pt$_5$ slabs, whereas the Co plane in that same interface, Co$_{Pt}$, has a negligible contribution compared to Co$_{Gr}$, as also reported in the literature for similar 3d/5d interfaces \cite{19,20}. This is explained in part by the strength of SOC at Pt, which is one order of magnitude larger than at Co ($\xi_{Co} = 76$ meV and $\xi_{Pt} = 618$ meV, given by the present FLAPW calculations). In the case of a bare Co$_5$ slab, the two outermost atomic planes contribute with opposite chiralities and sizable values, namely $|D_3| = 0.175$ meV $\mu_B^{-2}$. Importantly, we find that the Co contribution changes from positive to negative $D_3$ and it is nearly doubled in magnitude when it is in contact with graphene in the Gr/Co$_5$ slab (the contribution of graphene itself is negligible due to the small $\xi_C$ value). Therefore, graphene has the effect of reducing the net DMI of Gr/Co$_5$/Pt heterostructures by inducing in the topmost Co plane an opposite chirality to that of the Co/Pt interface. This has been observed by MOKE microscopy in domain wall propagation experiments, although the graphene effect on the DMI was reported there to be about one-half of that of the Co/Pt interface (the reported spatial micromagnetic averages are 1.4 and $-0.8$ mJ/m$^2$ for the Co/Pt \cite{12} and Gr/Co \cite{26} interfaces).

We have used two methods for the resolution of the DMI energy into its individual interfacial terms. The PSD method accounts for the joint effect of (i) the SOC strength and (ii) the electronic structure modification at the interface when the constituents are brought together. In the ASOD method only the relativistic effect is being probed. The latter method is less realistic, but more informative. The importance of effect

![Graph showing in-plane components of the effective D vector obtained from fits of the data in the left-hand column of Fig. 2 to a linear law up to $q = 0.25 |\Gamma K|$, where the averaged $m_s(Co)$ values over the Co layer have been used.](image1)

![Graph showing contributions to the DMI energy $\Delta E_{y}^{\text{DMI}}(q)$ (spins rotating in the plane perpendicular to $Y$ axis and spiral wave vector along the $\Gamma K$ reciprocal direction) from the individual interfacial atomic planes in the Gr/Co$_5$/Pt$_5$ slab and its constituents. The labels indicate the contributing atom and the subindices indicate the interface the atom belongs to, e.g., Co$_5$ is the Co at the vacuum interface.](image2)
TABLE I. Electric dipole (atomic units) in the direction perpendicular to the interfaces inside the FLAPW muffin-tin spheres \( (p_z) \) for the interfacial atoms in the Gr/Co\(_n\)/Pt\(_{3}\), Co\(_{3}\)/Pt\(_{3}\), and Gr/Co\(_n\) slabs with \( n = 1, 5 \). The subindex in the first column indicates the neighboring atomic layer in the interface. At graphene, the \( p_z \) of the two sublattice C atoms is averaged.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Gr/Co(<em>n)/Pt(</em>{3})</th>
<th>Co(<em>{3})/Pt(</em>{3})</th>
<th>Gr/Co(_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.014</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>-0.111</td>
<td>0.153</td>
<td>-0.267</td>
</tr>
<tr>
<td>Pt(_{co})</td>
<td>-0.092</td>
<td>-0.088</td>
<td></td>
</tr>
<tr>
<td>Atom</td>
<td>Gr/Co(<em>n)/Pt(</em>{3})</td>
<td>Co(<em>{3})/Pt(</em>{3})</td>
<td>Gr/Co(_n)</td>
</tr>
<tr>
<td>C</td>
<td>0.013</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co(_{Gr}) (Co(_n))</td>
<td>-0.043</td>
<td>0.197</td>
<td>-0.043</td>
</tr>
<tr>
<td>Co(_{Pt}) (Co(_n))</td>
<td>-0.059</td>
<td>-0.060</td>
<td>-0.195</td>
</tr>
<tr>
<td>Pt(_{co})</td>
<td>-0.077</td>
<td>-0.077</td>
<td></td>
</tr>
</tbody>
</table>

(ii) is manifested in the DMI tuning by adsorption of light atoms. For example, H adsorption on Ni/Co/Pd/W induces chirality change [22], with the advantage that H uptake and desorption is a reversible process [22,23]. DMI changes have also been characterized during oxidation of 3d/5d layered systems [24,25]. This DMI behavior is associated to a charge density redistribution upon adsorption and, based on this mechanism, electrostatic properties such as surface dipoles, work functions, and electronegativity have been proposed as DMI descriptors [24,28].

Table I shows the perpendicular electric dipole \( p_z \) of the interfacial C, Co, and Pt atoms of the three partial slabs in the limit cases \( n_{Co} = 1 \) and 5. It is evaluated as \( p_z = -|e|\langle \hat{z}\rangle_{MT} \), where the average position is evaluated as an integral over the charge density distribution inside the muffin tin. For the interfaces at the top of the slab, \( p_z > 0 \) \( (p_z < 0) \) means that the dipole points outward (inward) and vice versa for the interfaces at the slab bottom. For \( n_{Co} = 1 \), \( p_z(Co) \) depends strongly on the interface type: the dipole points inward when coated with graphene and outward when not. At the top of the \( n_{Co} = 5 \) slab a sign inversion of \( p_z \) due to graphene is observed, too, alongside a reduction of the \( p_z \) magnitude from 0.197 to 0.043 a.u. (a factor 4.6). At the buried Co/Pt interface, Pt has also the effect of reducing the dipole of the interfacial Co plane atom by a factor 3.25 with respect to Co\(_{Gr}\), but no sign inversion occurs. As reported in Ref. [28], the \( p_z \) are correlated with DMI energies. In the present case of the slabs with \( n_{Co} = 5 \), there is agreement between the signs of the \( p_z \) of interfacial Co atoms (Table I) and the signs of the contributions of these atoms to \( \Delta E_{DMI}^{p} \) (Fig. 4). However, there is no proportionality between the two magnitudes. Note that dipoles and electronegativity are related to the \( D \) vector by a nonlinear analytical expression, which results in an approximately linear correlation between these properties for different adsorbed species [28].

We investigate next the influence of the Co stacking on the DMI, known to be a key factor to explain the magnetocrystalline anisotropy of Gr/Co/Pt heterostructures. When Co is pseudomorphically grown by intercalation in Gr/Pt(111), it results in a fcc* stacking rather than hcp [26,51], with stacking defects scattered throughout, nucleating predominantly near the Pt(111) substrate steps [35]. In a perfect fcc* heterostructure, DFT calculations show that the magnetocrystalline anisotropy energy (MAE) follows a bulklike behavior with in-plane anisotropy starting at \( n_{Co} = 8 \) (0.09 meV per Co atom, imposed by the lateral fcc* lattice strain) and the critical thickness for perpendicular to in-plane switching at \( n_{Co} = 4 \). However, the experimental switch occurs later, at \( n_{Co} \approx 20 \) (about 4 nm), due to defects. The theory shows that each twin boundary contributes with nearly 1 meV to out-of-plane anisotropy, as it introduces locally a hcp stacked structure [35].

Figure 5 shows atom-resolved \( \Delta E_{DMI}^{p} (q) \) for Gr/Co\(_5\)/Pt\(_5\) with Co in three different stackings [panels (a)–(c)]: Perfect hcp, fcc* stacking with a twin boundary defect at the middle Co plane, labeled \( \tilde{b}3 \) in the following, and perfect fcc*. As in the original fcc* heterostructure, with the hcp and \( \tilde{b}3 \) stackings the large \( \xi_{P} \) dominates the net DMI, contributing similar energies (black symbols). In the case of a perfect fcc* growth, the central region of the Co layer is locally almost centrosymmetric and therefore will not contribute to DMI. Nevertheless, in this finite-thickness model, we observe that the Co atomic plane contributions oscillate around zero. Oscillating values occur for the \( \tilde{b}3 \) and the hcp slabs, with larger energies in the latter. Note that for bare Co\(_5\) slabs with the same geometries, i.e., in the absence of interfaces with Gr and Pt, cancellations at the Co planes are almost total irrespective of the stacking type [red symbols in Fig. 5(d)]. There is an overall negative contribution of the Co planes to the DMI [black symbols in Fig. 5(d)] that has its main origin at the Gr/Co interface. Sizable DMI occurs at the Gr/Co and Co/Pt interfaces, while buried interfaces in Co that break inversion symmetry locally contribute almost negligibly. This behavior contrasts with that of the magnetic anisotropy, despite both properties sharing a common origin in the SOC, with MAE being of \( \xi_{P}^2 \) order at this symmetry and DMI being linear in \( \xi \). Therefore, in the Gr/Co/Pt heterostructure DMI and magnetocrystalline anisotropy are at play on an equal footing only close to the critical thicknesses, when the fcc* bulk limit and the defect contributions compensate each other to give a low MAE. The effect of the strained Co lattice constant on the Gr/Co interfacial DMI contribution is negligible, as long as the Gr-Co interplanar distances are similar, which ensures a similar hybridization [52–55]. This has been checked in a calculation for the Gr/Co\(_5\) slab with the experimental hcp Co lattice constant (see Supplemental Material Fig. S7).

B. Reciprocal space analysis

So far, in the literature, interfacial DMI has been discussed in terms of two different mechanisms: A Rashba-like behavior in Gr/Co triggered by the surface potential change \( \nabla V \) induced by graphene adsorption [31] or, alternatively, a Fert-Levy-like behavior in Co/Pt, where Pt SOC mediates the spin flip of the Co itinerant electrons. The aim of this section is to identify the nature of DMI at those interfaces based on information gathered at the reciprocal space. The explicit dependence of DMI on each Bloch eigenstate \( \epsilon_{ab} (q) \) is too intricate to be analyzed by a bare eye, due to the high density of dispersive bands in the Gr/Co\(_n\)/Pt\(_3\) models (see Supplemental Material Fig. S8). Note that each band is subject...
to lateral shifts due to the spin spirals and to degeneracy liftings, mainly at crossings between bands, due to SOC (see Supplemental Material Fig. S8), as shown by Sandratskii for the CoPt bilayer [21]. Instead, in our analysis we use quantities integrated in energies and in electron wave vectors \( k \).

To analyze the spectral behavior of the DMI chirality, we plot the corresponding energies integrated in \( k \) as a function of the number of electrons \( n_e \) for each spin spiral vector \( q \). This is similar to the MAEs in the force theorem approach [56,57]:

\[
\Delta E_{DMI}^Y(n_e; q) = \sum_{nk} \left( \epsilon_{nk}^Y(q) - \epsilon_Y^F(n_e; q) \right) - \epsilon_{nk}^Y(q) f \left( \epsilon_{nk}^Y(q) - \epsilon_Y^F(n_e; q) \right),
\]

where \( q \) is a spin spiral wave vector along \( \Gamma K \), the sum runs over the eigenvalues \( \epsilon_{nk} \) calculated for opposite spin rotation axes (\( Y^+ \) and \( Y^- \)), and the Fermi levels correspond to the filling up with \( n_e \) electrons of the bands of each individual calculation with \( q \) and \( Y^+ \) or \( Y^- \). The \( \Delta E_{DMI}^Y(n_e; q) \) curves for Gr/Co5/Pt5, Co5/Pt5, and Gr/Co5 slabs are qualitatively stable (see Fig. 6): The nodes in the curves are almost invariant and peaks only increase in amplitude with \( q \), resulting in the linear dependence observed in the previous section. This behavior occurs also in the less complex CoPt bilayer, where it has been explained [21] by the hybridization of the spiral electron states with wave vectors \( k \) and \( \pm q \), which have similar character regardless of \( q \), giving rise to the dependence of Eq. (1) [58]. As observed in Fig. 6, this scenario is not affected by the presence of the large number of additional bands of a thicker Pt substrate, which is the reciprocal space confirmation that the DMI is localized within a very short spatial range (bond length distance) of the interface. At neutrality (\( n_e = 0 \)) the known positive \( \Delta E_{DMI}^Y(0; q) \) values for Gr/Co5/Pt5 and Co5/Pt5 and negative for Gr/Co5 are retrieved. The sign of the DMI energy is kept under small variations of \( n_e \) around the neutrality condition. When represented as a function of binding energies, \( \Delta E_{DMI}^Y(n_e; q) \) has the last node before neutrality at the filling corresponding to \( E_F = -0.5 \text{ eV} \) in the three slabs, as shown in the Fig. 6(d) panel for \( q = \frac{\pi}{a} \left( \frac{1}{12}, \frac{1}{12}, 0 \right) \).

FIG. 6. (a)–(c) DMI energy \( [\Delta E_{DMI}^Y(q)] \) as a function of the band filling for the Gr/Co5/Pt5, Co5/Pt5, and Gr/Co5 slabs. The color scale bar indicates the \( q \) magnitude on a scale from 0 (\( \Gamma \)) to 1 (\( K \)).

(d) The same curves plotted as a function of energy (referred to the Fermi levels of each slab calculated without SOC) for the particular point \( q = 0.25(\Gamma K) \).

FIG. 5. (a)–(c) Top panels: cross section of the Gr/Co5/Pt5 slabs with different Co stacking geometries: Perfect hcp, fcc* with a twin boundary introduced in the middle Co plane (tb3) and perfect fcc. A red line indicates the stacking sequences. Bottom panels: For each geometry, total DMI energies \( [\Delta E_{DMI}^Y(q)] \) for spins rotating in the plane perpendicular to \( Y \) (black filled circles) and those obtained when SOC is applied only to the indicated atomic planes (colored filled circles for Pt layer and empty for individual atomic planes). (d) Co layer contributions from Gr/Co5/Pt5 slabs (black symbols) compared to bare Co5 slabs with the three stacking types (red symbols).
energies in this energy window of 0.5 eV would effectively reproduce the net DMI, albeit nonzero DMI contributions occur throughout the whole available energy spectrum. This is evident with a Pt substrate, since the $4d - 3d$ hybrid bandwidth spans several eV. However, Figs. 6(c) and 6(d) show the same qualitative behavior for Gr/Co interface, pointing out that there is a similar DMI mechanism here due only to the Co SOC contributions. Note that the 0.5 eV window coincidence for the three slabs is fortuitous, as it depends on the particular details of each band structure.

With focus on the DMI chirality inversion of the vacuum/Co interface upon capping with graphene, we first verify that the $\Delta E_{\text{DMI}}(0; n_e)$ values reproduce the sign change when evaluated with only the corresponding interfacial individual atomic SOC strength $\xi_{\text{Co}}$ [see Fig. 7(a)]. We now turn to a $\mathbf{k}$-resolved analysis of these quantities. Figures 7(b) and 7(c) show that DMI is not localized in the $\mathbf{k}$ space, but broad regions of the Brillouin zone (BZ) contribute with opposite chiralities to the final net $\Delta E_{\text{DMI}}(0; q)$ in both vacuum/Co and Gr/Co interfaces. Owing to the found effective energy window, in Figs. 7(d) and 7(e) we restrict the $\mathbf{k}$-resolved analysis to an integral over states within a window of 0.5 eV below the Fermi level. We observe that the Co-C hybrid bands, with nearly conical dispersion at the $K$, $K'$ special points, yield a positive contribution to $\Delta E_{\text{DMI}}(0; q)$ (red spots at the BZ vertices), whereas the rest of the BZ contributes with negative values. In other words, the distinctive feature of the graphene adsorption on the band structure, namely the conical band of C-$p_z$ and Co-$d_{z^2}$ character, as well as a small weight in $d_{x^2-y^2}$ orbitals, actually contributes to a chirality opposite to the observed one. The conclusion is that the DMI of the Gr/Co interface cannot be attributed to individual Co-C hybrid bands near the Fermi level. For this reason, a model where the $D$ vector is estimated from a Rashba Hamiltonian $\alpha_{\text{Rashba}}(\mathbf{\sigma} \times \mathbf{K})$, of a single band in a ferromagnetically coupled environment [27,31,33,34] is not suitable for the Gr/Co interface. In particular, the expression $D = 4\alpha_{\text{Rashba}}m^*A/\hbar^2$, where $A$ is the exchange stiffness [33], is no longer valid beyond the Rashba approximation [59]. Instead, the contributing Co-C interactions extend to the whole spectrum. On this basis we can state that the interfacial DMI at Gr/Co and Co/Pt has similar contribution from the strongly hybridized SOC-split $d$ bands. We recall that Rashba band splitting requires not only a $\mathbf{VV}$, which can be indeed enhanced upon adsorption if this increases the asymmetry of the charge distribution at the surface [60], but also a substantial SOC strength $\xi$ [61,62].

**IV. CONCLUSIONS**

Our interface-resolved DFT study of DMI in Gr/Co$_n$/Pt(111) heterostructures with varying Co layer thickness shows that the regime of additivity of interfacial DMI is reached already at $n = 3$ atomic planes and also that the $D$ vectors have an almost negligible out-of-plane component. As the perpendicular magnetocrystalline anisotropy prevails up to much larger $n$ values [35], a sizable DMI interaction to have spin canting and chiral exchange effects are expected to be robust with the film thickness. However, unlike the magnetocrystalline anisotropy itself, interfacial DMI is insensitive to the internal structure of the Co layer. The observed DMI in domain wall propagation suggests a comparable interface DMI strength but opposite sign at Gr/Co and Co/Pt interfaces [35]. This is confirmed by our calculations. Indeed, we find that the graphene layer has the effect of inverting the chirality of the vacuum/Co interface.

The Gr/Co and Co/Pt interfacial DMI has been classified as being of different nature, namely, Rashba and Fert-Levy mechanisms at Gr/Co and Co/Pt, respectively. Our study leads to the conclusion that this classification is subjective. Those models correspond to two limiting cases of the same physics, as illustrated by the Gr/Co$_n$/Pt system. The electrostatic dipole (a magnitude identified as a DMI descriptor) at the vacuum/Co surface is reversed and increases in magnitude upon capping with graphene. Nevertheless, this does not mean that the effects can be explained by an overall Rashba
term acting on all bands with the same strength and sign. Instead, the superposition of many hybridized bands with weight on the Co atoms can contribute to the interfacial DMI at both Gr/Co and Co/Pt. A band-dependent and generalized (nonlinear in \( k \)) Rashba model is probably more appropriate for the accurate description of DMI at the Co/Gr interface. In other heterostructures with 2p/3d/5d composition, where nontrivial hybridization of the 3d bands with the ones of the 5d substrate and the 2p orbitals is foreseen, the DMI should be analyzed in the same way. This means that all bands must be treated on an equal footing and with no approximations on the functional form of the SOC terms.

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