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Magnetism and stability of all primitive stacking patterns in bilayer chromium trihalides

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Chromium trihalides, CrX_3 (with $X = \text{Cl, Br, I}$), are a family of layered magnetic materials that can be easily exfoliated to provide ferromagnetic monolayers. When two layers are stacked together to form a bilayer the interlayer exchange coupling can be either ferromagnetic or antiferromagnetic depending on the stacking sequence. Here we combine crystallographic arguments based on the close-packing condition with first-principles simulations to enumerate all possible stacking patterns in CrX_3 bilayers that preserve the spatial periodicity of each layer. We recover all configurations observed in bulk crystals and disclose stacking sequences with no bulk counterpart where the two layers have opposite *chirality*. Stacking sequences are ranked according to their relative stability and a preferential interlayer magnetic ordering is assigned to each of them. Simulations provide a consistent picture to frame all current experimental observations on bulk and exfoliated CrX_3 crystals, with interesting implications for future measurements, including synthetic bilayers with non-standard stacking patterns.

INTRODUCTION

Van der Waals magnetic materials have always been a source of fascinating phenomena [1] that are now attracting revived interest owing to the possibility of exfoliating these compounds down to the monolayer limit [2–5]. Among these, the family of chromium trihalides (CrX_3 , $X = \text{Cl, Br, I}$) has emerged as a promising playground for experimental [6–17] and theoretical [18–26] explorations. In particular, the magnetic properties of atomically thin CrI_3 [6–10] can be easily manipulated by external controls such as electric fields [27], doping [28, 29], and pressure [30, 31], allowing the realization of spin-sensitive devices [32, 33], although practical applications are limited by the low critical temperature.

Bulk CrX_3 crystals are magnetic insulators where spins are ferromagnetically aligned within each layer, while the interlayer exchange coupling depends on the halogen. In CrBr_3 and CrI_3 , all layers share the same spin orientation, giving rise to an overall ferromagnetic (FM) behaviour [34, 35], while CrCl_3 is a layered antiferromagnet with neighbouring layers having spins pointing in opposite directions (so called “A-type” ordering) [36, 37]. Another difference arises from the lighter atomic number of Cl atoms, which leads to reduced spin-orbit coupling effects, so that spins are oriented parallel to the layers in CrCl_3 and perpendicular in CrBr_3 and CrI_3 .

In addition to the magnetic phase transition at low temperature, CrX_3 crystals undergo a structural phase transition at higher temperatures from a high-temperature monoclinic phase to a low-temperature rhombohedral phase [35, 38–40]. Across the transition, the structure of each layer remains essentially unaffected, with the main difference between the two phases being the stacking sequence of the layers [35]. At room tem-

perature, only CrBr_3 is already in the low temperature structure, while CrI_3 and CrCl_3 are still in the monoclinic phase. At temperatures below the magnetic transition, instead, all members of the chromium trihalide family share the same rhombohedral structure (see table I).

When thinned down to few atomic layers, CrI_3 has been reported to display A-type antiferromagnetic (AF) order [6], giving rise to a strong spin-filtering effect and a large magnetoresistance in tunnelling devices [7–10]. The different magnetic ordering of atomically thin and bulk CrI_3 has been long puzzling, especially in view of the apparently similar behaviour of CrBr_3 and CrCl_3 multilayers with respect to their 3D counterparts [11–15, 17]. First-principles simulations have provided a possible solution to this conundrum by demonstrating a strong connection between the stacking pattern and the magnetic ground state [9, 18–22], predicting that for CrI_3 the monoclinic phase should be AF while the rhombohedral phase is FM.

Raman spectroscopy [41] and non-linear optical measurements [42] have validated this picture by showing that bulk CrI_3 is rhombohedral at low temperature, consistently with the bulk FM ordering, while in atomically-thin samples the stacking sequence is monoclinic, thus explaining the AF interlayer coupling (also present in superficial layers [43, 44]). A monoclinic structure has been reported also in thin CrCl_3 , while keeping the same A-type AF order as in its bulk rhombohedral form, although with an enhanced interlayer coupling [13]. For CrBr_3 , no experimental result is currently available on the stacking pattern in thin crystals, although clear indications exist that they preserve the bulk FM interlayer coupling [11, 15, 17].

To close the circle and provide a consistent picture for all current experimental results on atomically thin CrX_3

TABLE I. Low-temperature magnetic order (ferromagnetic, FM, or antiferromagnetic, AF) and stacking symmetry (rhombohedral or monoclinic) in bulk and multilayer chromium trihalides CrX_3 as experimentally reported in the literature.

	CrCl_3	CrBr_3	CrI_3
bulk	AF ^{36,37} rhom. ³⁸	FM ³⁴ rhom. ⁴⁰	FM ³⁵ rhom. ^{35,39}
multilayers	AF ¹²⁻¹⁵ monocl. ¹³	FM ^{11,15,17} –	AF ⁶⁻¹⁰ monocl. ^{41,42}

samples, here we combine general crystallographic arguments with first-principles simulations to explore the magnetic ground state and the relative stability of all possible stacking patterns in bilayer chromium trihalides that preserve the spatial periodicity of each layer (i.e. primitive). We extend previous results on CrI_3 to CrBr_3 and CrCl_3 and disclose stacking sequences that have no bulk counterpart but could be relevant in synthetic crystals [45]. The theoretical scenario that arises suggests that atomically thin CrBr_3 should display a rhombohedral structure, differently from the other chromium trihalides CrI_3 and CrCl_3 , as a result of the higher critical temperature for the structural phase transition, which makes CrBr_3 rhombohedral –and not monoclinic– at the temperatures at which exfoliation takes place.

METHODS

First-principles simulations are performed within density-functional theory (DFT) using the Quantum ESPRESSO distribution [46, 47]. To account for van der Waals interactions between the layers, the spin-polarised extension [48] of the revised vdw-DF2 exchange-correlation functional [49, 50] is adopted, truncating spurious interactions between artificial periodic replicas along the vertical direction [51–53]. The Brillouin zone is sampled with a $8 \times 8 \times 1$ Γ -centered Monkhorst-Pack grid. Pseudopotentials are taken from the Standard Solid-State Pseudopotential (SSSP) accuracy library [54–56] (v1.0) with increased cutoffs of 60 Ry and 480 Ry for wave functions and density, respectively. Total energy calculations as a function of the relative displacement between the layers are performed without atomic relaxations, by taking the structure of DFT-relaxed monolayers with the experimental lattice parameter and interlayer separation. For line scans, atomic positions are relaxed by reducing the force acting on atoms below a threshold of 26 meV/Å, while keeping fixed the in-plane coordinates of Cr atoms. The threshold is reduced to 3 meV/Å without constraints to evaluate the relative stability of the different stacking configurations, while also optimising the lattice parameter and

cell angle (for non-hexagonal systems) using an equation-of-state approach. Calculations are managed and automated using the AiiDA materials informatics infrastructure [57, 58].

RESULTS AND DISCUSSION

The crystal structure of monolayer CrX_3 is reported in Fig. 1a), and consists of three atomic planes: a layer of chromium atoms (grey) sandwiched between halogen layers, reported with different colours (orange and blue) to distinguish the top and bottom plane. The structure can be rationalised by noting that each halogen layer forms a planar triangular sublattice (although slightly distorted) and that the two planes are close-packed (see the top right corner of Fig. 1a). Chromium atoms occupy octahedral interstitials, which themselves form a third triangular lattice, although only 2/3 of the sites are occupied. The three close-packed triangular sublattices are shown in Fig. 1b) with different colours (blue, grey, and orange) and named a, b, and c. Because 1/3 of the octahedral interstitials are empty, the unit cell of CrX_3 (black solid line) is larger than the unit cell of a single triangular sublattice (red shade), and represents a $\sqrt{3} \times \sqrt{3}$ supercell rotated by 30°.

Once the halogen triangular sublattices are specified, the Cr sublattice is enforced by the close-packing condition and the only degree of freedom is the choice of the empty site among three possibilities (marked A, B, and C, in Fig. 1). Thus the structure of a monolayer can be identified by specifying the two halogen triangular sublattices and the empty site in the chromium layer. For instance, in Fig. 1a) the bottom halogen plane corresponds to the “a” sublattice, while the top halogen plane to the “c” sublattice. Cr atoms belong to the “b” sublattice with the “A” site empty. We denote this structure as “aA_bc”, where the left (right) small letter denotes the bottom (top) halogen sublattice while the capital letter identifies the empty site in the Cr layer, with a subindex specifying the corresponding sublattice.

We can thus see that CrX_3 monolayers can exist in two inequivalent forms. Fixing an arbitrary choice of the origin at the empty site uniquely determines the Cr layer to be A_b. The close-packing condition allows only two possible choices for the halogen planes: aA_bc (as in Fig. 1a) and cA_ba (with top and bottom halogen planes exchanged). The difference between the two can be best visualised by considering the halogen atoms forming the octahedral cage around the empty site. In the aA_bc case of Fig. 1a), the top (bottom) halogens make a right (left) pointing triangle, while the opposite is true in the cA_ba case. We thus have two possible *chiralities* for a monolayer, identified by the direction of the triangles in the top plane. The left chirality arises when the labels of the sublattices in the three atomic planes are an even permu-

TABLE II. Possible primitive stacking patterns in bilayer CrX_3 that satisfy the close-packing condition. Assuming the first layer to be in the aA_bc configuration (see text for details), the second layer can either display the same or opposite chirality. In each case, the configuration of the second layer is reported, together with the in-plane component of the relative translation between the layers. Inequivalent stacking patterns are given short names for simplicity and associated with the corresponding point group, reported in both the International and Schönflies (in parenthesis) notation.

First layer	Chirality	Second Layer	Translation	Short name	Point group	
aA _b c ▷	same	aA _b c ▷	(0,0)	AA	$\bar{3}m (D_{3d})$	
		aB _b c ▷	$(0, a/\sqrt{3})$	AB	$\bar{3} (S_6)$	
		aC _b c ▷	$(a, a/\sqrt{3})/2$	AC		
	opposite	bA _c a ▷	$(a/3, 0)$	HT	rHT	$2/m (C_{2h})$
		bB _c a ▷	$(a, a\sqrt{3})/3$			
		bC _c a ▷	$(-a, a\sqrt{3})/6$			
aA _b c ▷	opposite	aA _c b ◁	$(a/3, 0)$	rHT	$m (C_s)$	
		aB _c b ◁	$(a, a\sqrt{3})/3$			
		aC _c b ◁	$(-a, a\sqrt{3})/6$			
	opposite	bA _a c ◁	$(a, a\sqrt{3})/6$	rHT'	$m (C_s)$	
		bB _a c ◁	$(2a/3, 0)$			
		bC _a c ◁	$(-a, a\sqrt{3})/3$			

tation of “abc” (as in Fig. 1a), while the right chirality occurs for odd permutations (e.g. “cba”). The two chiral structures can be obtained one from the other either by exchanging the top and bottom halogen planes, or equivalently by a 60° rotation or a mirror reflection (as it is typical of enantiomers).

We now turn our attention to the possible configurations of bilayer CrX_3 . We restrict to *primitive* stacking arrangements that preserve the translational invariance of each layer, that is with the same (primitive) unit cell as a monolayer. The most stable configurations of the bilayer are expected to follow the same close-packing conditions of the monolayer. Choosing for definiteness the bottom layer in the aA_bc form, the bottom halogen plane of the second layer needs to be in the “a” or “b” sublattice. In each case, we have then two possible choices for the top halogen plane sublattice that are compatible with the close-packing condition, and three possibilities for the empty site of the Cr layer. We thus expect $2 \times 2 \times 3 = 12$ possible stable configurations of the bilayer, listed in table II. In half of them the two layers share the same chirality, while the chirality is different in the other six cases.

In Fig. 2 we report a schematic picture of the different stacking sequences in table II, where the orange and blue dashed (solid) lines highlight the triangles corresponding respectively to the top and bottom halogens around the empty site in the first (second) layer. When the chirality

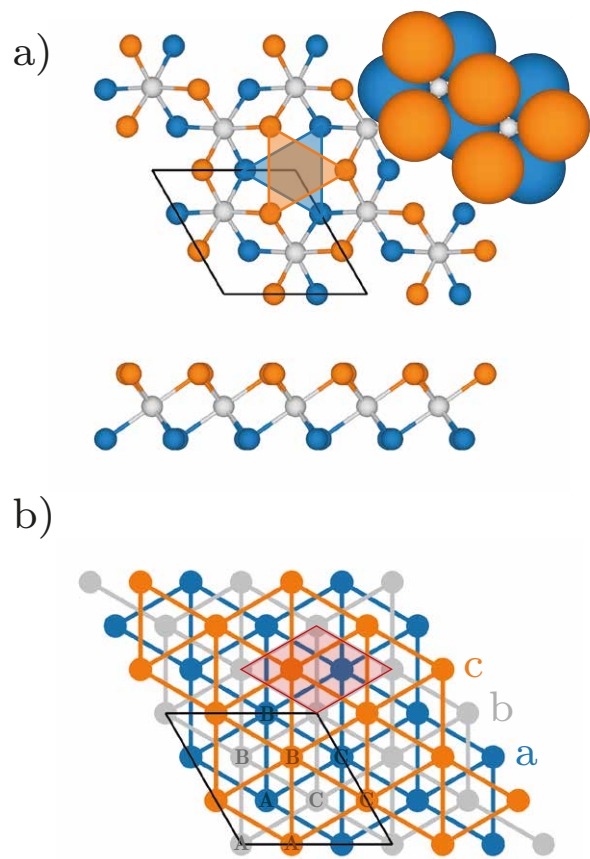


FIG. 1. Panel a): Top and later views of the crystal structure of monolayer CrX_3 , with a black solid line showing the perimeter of the unit cell. Chromium atoms are reported in grey, while halogens are shown with different colours (orange and blue) to distinguish the planes above and below the layer of Cr atoms. In the top right corner the size of halogen atoms is exaggerated to emphasise their close-packed arrangement. Cr atoms occupy $2/3$ of the octahedral interstitials, with a single empty octahedron per unit cell. The vertices of the empty octahedron are highlighted with orange and blue shaded triangles in the top and bottom halogen plane, respectively. Panel b): Three possible triangular sublattices (grey, orange, and blue) that are consistent with a close-packed arrangement. The primitive unit cell of the triangular sublattices is highlighted with a red shade, while the overall unit cell of CrX_3 is shown in black (and corresponds to a $\sqrt{3} \times \sqrt{3}$ supercell rotated by 30°).

is the same, we can interpret the second layer as obtained from the first one by a rigid translation, which has both an in-plane (shown in the figure) and out-of-plane component. When the chirality is different, the second layer can still be obtained from the first one by a rigid translation, but we need to perform first a rotation by 60° (or a vertical mirror reflection).

In the bulk form, all layers have the same chirality, so we should expect to find the bulk stacking sequences among these cases. Indeed, two consecutive layers in the

rhombohedral phase share the same sublattices in the halogen planes, while the position of the empty site is different. In table II, this situation corresponds to the second layer being either $aB_b c$ or $aC_b c$ (with the first one being $aA_b c$). Since the information on the halogens is redundant in the two layers, these configurations are typically denoted simply as AB or AC from the position of the empty site, and they are equivalent up to a re-definition of the lattice vectors (and thus have the same point group). In principle, also another possibility arises when the two layers share the same halogen sublattices, that is when also the empty position is the same, thus corresponding to an AA stacking sequence. The high-temperature (HT) monoclinic stacking arrangement can also be recovered. It corresponds to the second layer being $bA_c a$, $bB_c a$, or $bC_c a$, corresponding to a rigid translation along one of three equivalent high-symmetry directions. Translations along the same lines but in opposite directions would give rise to a HT' configuration (with the second layer being either $cA_a b$, $cB_a b$, or $cC_a b$). This HT' configuration is indistinguishable from the standard HT bulk arrangement when only Cr atoms are considered. Nonetheless, it does not satisfy the close-packing condition as the halogen planes facing the van der Waals gap share the same "c" sublattice and thus sit on top of each other, so that this configuration is expected to be unstable.

Stacking sequences where the two layers have different chirality do not have a bulk counterpart, although they can be realised in synthetic bilayers grown by molecular beam epitaxy [45]. Among the six possibilities, listed in table II, that satisfy the close-packing condition, only two are inequivalent up to a redefinition of the lattice vectors. They correspond to the same relative translation between the layers as the HT and HT' discussed above, but with the second layer now rotated by 60° , and are thus denoted rHT and rHT'. Differently from the case of pure translations when the HT configuration is stable while the HT' is not, the rHT and rHT' stacking sequences both satisfy the close-packing condition. Even more compelling, the two arrangements are energetically indistinguishable as they differ only by the definition of the positive vertical direction. The only symmetry element is a vertical mirror plane that contains the translation vector between the layers, so that such configurations are monoclinic.

To verify that the configurations listed in table II, predicted from crystallographic arguments based on the close-packing condition, are the only (meta)stable primitive stacking sequences for bilayer CrX_3 , we perform first-principles DFT simulations as a function of the relative in-plane displacement $\mathbf{d} = (d_x, d_y)$ between the two layers, with either the same or opposite chirality. The vertical separation d_z between the layers is either kept fixed or optimised as specified below. Calculations are carried out assuming both a FM and a AF alignment between the layers, with a corresponding to

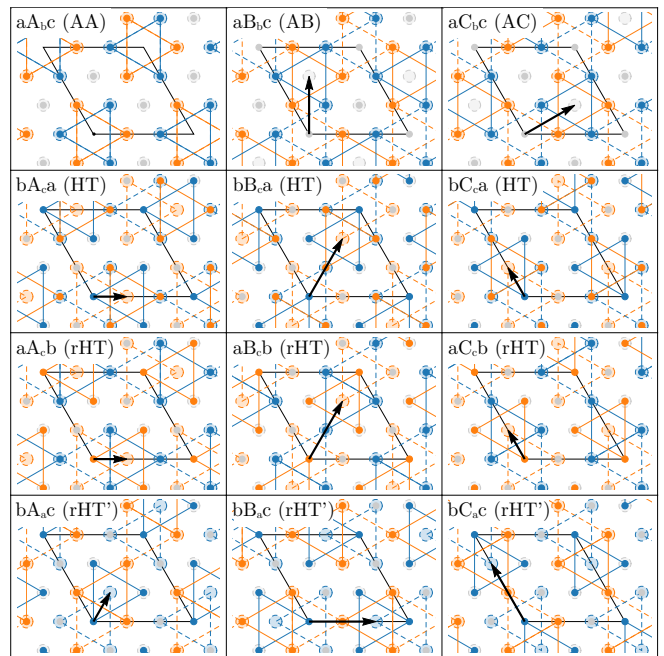


FIG. 2. Graphical representation of the primitive stacking patterns listed in table II. Chromium atoms are shown in grey, while halogens above and below the Cr sheet are reported in orange and blue, respectively. The first (bottom) layer is assumed to be in the $aA_b c$ configuration (see text for details) and is shown with bigger, shaded symbols with dashed contours. The second (top) layer takes the configuration specified in the upper left corner, with the corresponding short name in parenthesis, and is shown with full symbols. Dashed (solid) orange and blue triangles highlight the configuration of the top and bottom halogen atoms around the empty site in the Cr sublattice of the first (second) layer. The black solid line marks the primitive unit cell contour, while thick arrows denote the in-plane component of the relative translation between the layers (folded inside the unit cell).

tal energy $E_{\text{FM}}(\mathbf{d})$ and $E_{\text{AF}}(\mathbf{d})$. For each displacement \mathbf{d} , it is then possible to evaluate the ground-state energy $E_{\text{min}} = \min\{E_{\text{FM}}, E_{\text{AF}}\}$ and the energy difference $E_{\text{FM}} - E_{\text{AF}}$ expressing the preference towards a FM/AF alignment. In particular, we can relate the energy difference to an effective interlayer exchange coupling J_{eff} , i.e. $2J_{\text{eff}} = E_{\text{FM}} - E_{\text{AF}}$, with $J_{\text{eff}} > 0$ leading to an AF state while a FM alignment is expected when $J_{\text{eff}} < 0$.

We first consider the case of two layers with the same chirality. The first column of Fig. 3 shows the minimum energy E_{min} as a function of d_x and d_y while keeping fixed d_z at the bulk (rhombohedral) value for all CrX_3 bilayers with $X = \text{Cl}, \text{Br}, \text{and I}$. In all cases, two equivalent global minima are found at a relative displacement corresponding to the AB and AC configurations, and thus to the rhombohedral stacking sequence. This is consistent with the rhombohedral structure being the most stable phase at low temperature. Additional local minima are present and correspond to the HT and AA configurations. In par-

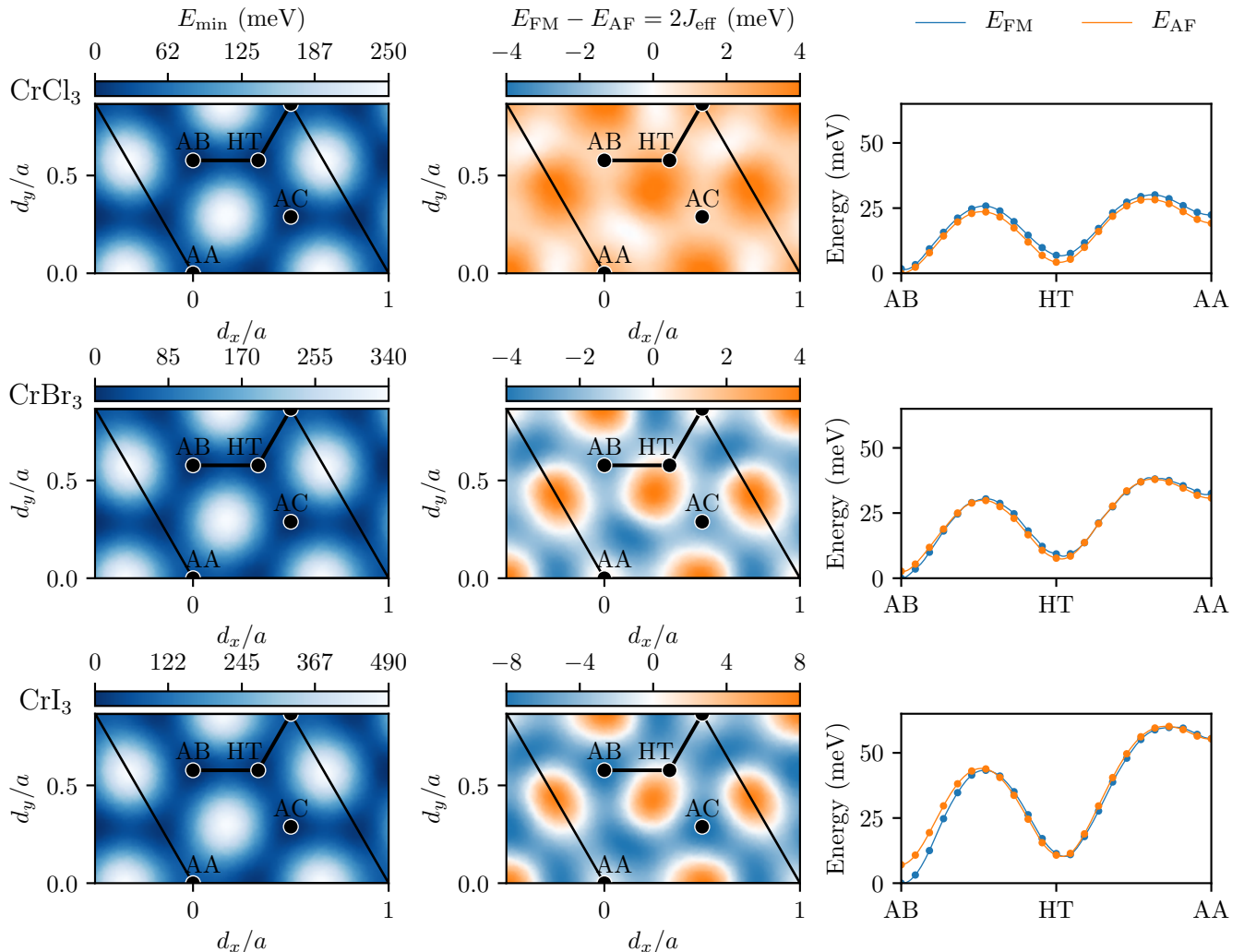


FIG. 3. Relative stability and interlayer magnetic order in CrX_3 bilayers when both layers share the same chirality. Left: Minimum energy between the ferromagnetic (FM) and antiferromagnetic (AF) configurations, $E_{\min} = \min\{E_{\text{FM}}, E_{\text{AF}}\}$, for bilayer CrX_3 ($X = \text{Cl}, \text{Br}, \text{I}$, from top to bottom), as a function of the relative in-plane displacement $\mathbf{d} = (d_x, d_y)$ between the layers at fixed interlayer distance d_z . Black circles with a white contour mark the positions corresponding to the stacking patterns listed in table II that satisfy the close-packing condition. Only one of the three equivalent HT configurations is highlighted. Center: Similar plot as on the left, but for the energy difference between the FM and AF configuration, related to the effective interlayer exchange coupling J_{eff} . Blue regions correspond to a preferential FM order, while orange regions correspond to an AF interlayer coupling. Right: Energy of the FM (blue) and AF (orange) configurations of bilayer CrX_3 along the path highlighted with a thick black line in the left and center panels. For each point along the path the atomic structure, including the interlayer distance, is now optimised while keeping the in-plane positions of Cr atoms fixed.

ticular, the monoclinic HT arrangement is very close in energy to the stable AB configuration, consistently with the experimental observation of the monoclinic phase at sufficiently high temperature. As expected, the HT' configuration is unstable and represents a local maximum for E_{\min} .

In the central panels we show the energy difference between the FM and AF configurations in order to assess the preferential interlayer magnetic order of a given stacking arrangement. As already pointed out [9, 18–22], for bilayer CrI_3 there is a strong connection between the

stacking sequence and the interlayer spin alignment. The AB arrangement is FM, while the AA and HT configurations have a mild preference for an AF order. A similar situation is found for CrBr_3 , although with a tendency to increase $E_{\text{FM}} - E_{\text{AF}}$ with respect to CrI_3 , and thus to suppress FM order in favour of the AF state. The suppression is further enhanced for CrCl_3 , where the AF alignment is preferred irrespective of the relative translation between the layers, although $E_{\text{FM}} - E_{\text{AF}}$ largely depends on d_x and d_y . In all cases, the largest AF interlayer exchange coupling is obtained for a configuration

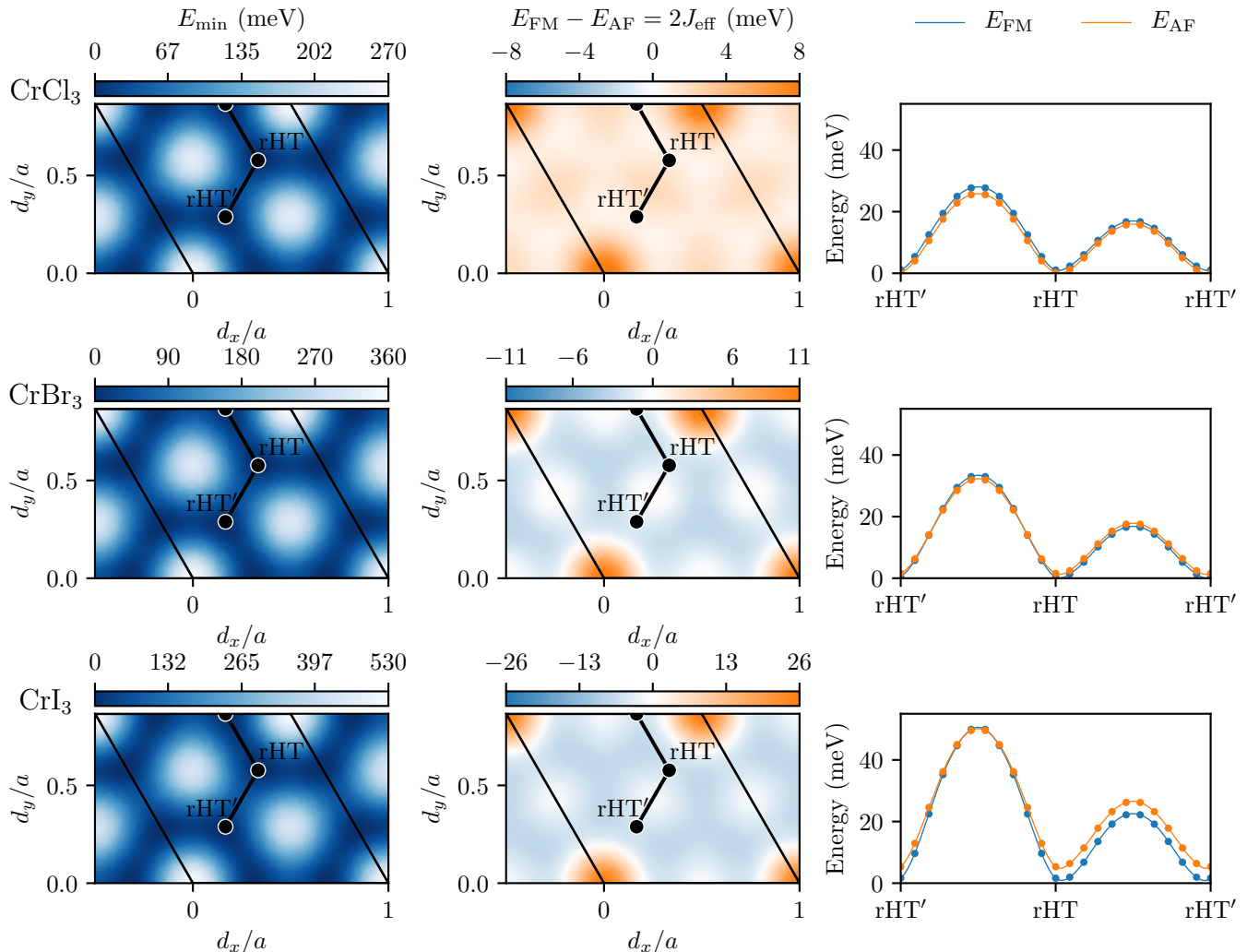


FIG. 4. Relative stability and interlayer magnetic order in CrX_3 bilayers when the layers have opposite chirality. Left: Minimum energy between the ferromagnetic (FM) and antiferromagnetic (AF) configurations, $E_{\min} = \min\{E_{\text{FM}}, E_{\text{AF}}\}$, for bilayer CrX_3 ($X = \text{Cl}, \text{Br}, \text{I}$, from top to bottom), as a function of the relative in-plane displacement $\mathbf{d} = (d_x, d_y)$ between the layers at fixed interlayer distance d_z . Black circles with a white contour mark the positions corresponding to the stacking patterns listed in table II that satisfy the close-packing condition. Only one of the three equivalent rHT and rHT' configurations is highlighted. Center: Similar plot as on the left, but for the energy difference between the FM and AF configuration, related to the effective interlayer exchange coupling J_{eff} . Blue regions correspond to a preferential FM order, while orange regions correspond to an AF interlayer coupling. Right: Energy of the FM (blue) and AF (orange) configurations of bilayer CrX_3 along the path highlighted with a thick black line in the left and center panels. For each point along the path the atomic structure, including the interlayer distance, is now optimised while keeping the in-plane positions of Cr atoms fixed.

corresponding to $\mathbf{d} = (a/2, a/2)$, dubbed “special” in Ref. 45. This is consistent with the AF order measured in Ref. [45] for synthetic CrBr_3 bilayers. Nonetheless, it is surprising that this configuration is experimentally accessible since, according to the present simulations, it should not be dynamically stable as it does not represent a local minimum (nor a local maximum) in the energy landscape.

To compare in more detail the energy of the FM and AF alignments, in the right panels we show their dependence on the stacking sequence along a path (passing

through the metastable configurations) highlighted with thick black lines in the left and central panels. In this case, the atomic structure is fully relaxed, including the interlayer distance d_z , while keeping fixed the in-plane coordinates of the Cr atoms in order to maintain a given configuration during the force minimisation. All ground-state magnetic orderings discussed above are confirmed, although with a better estimation of the interlayer J_{eff} . These plots also give more insight on energy barriers separating the three metastable configurations. In particular, the very small potential barrier protecting the AA-

range might be responsible (together with the high energy difference with respect to the AB and HT configurations) for its absence in current experiments under standard conditions, both for bulk and atomically thin samples.

Interestingly we also note that the energy minimum associated with the HT configuration does not necessarily occur for the expected translations in table II (e.g. $\mathbf{d} = (a, a\sqrt{3})/3$), and might even be slightly different for the FM and AF state. This is due to the fact that in the HT configuration the symmetry is reduced to monoclinic and the positions of Cr atoms (and thus the relative translation) are not enforced by symmetry, although deviations from the ideal structure are typically small.

The above situation changes when the two layers have different chirality, i.e. when the second layer is obtained from the first one by performing a 60° rotation (or a vertical mirror reflection) before the relative translation. The corresponding energy landscape is reported in Fig. 4. Although stacking configurations are indistinguishable from the ones in Fig. 3 when only Cr atoms are considered, the energy profile is completely different, signalling the uttermost importance of the halogen arrangement in determining the stability of a stacking sequence. Moreover, also the difference between the FM and AF alignment is largely affected. This means that extending the current results to arbitrary rotation angles and non-primitive unit cells (relevant for twisted bilayers) is far from trivial, as the precise location of the halogens –and not only of the Cr atoms– is crucial in determining the stability and magnetic order of bilayers.

A more detailed analysis shows that the only local minima in E_{\min} correspond to the rHT and rHT' identified in table II using crystallographic arguments. Similarly, the local maxima correspond to the rotated analogues of the AA, AB, and AC arrangements (denoted rAA, rAB, and rAC), which are correctly marked as unstable by the close-packing condition as in this case the halogen layers facing the van-der-Waals gap would sit exactly on top of each other. Allowing for atomic relaxation, including the interlayer distance, provides a more accurate estimation of the energy profile between the local minima at the rHT and rHT' configurations, as shown in the right panels for configurations along the path highlighted with thick black lines in the other panels. The two rotated monoclinic sequences are energetically equivalent, as expected, but are separated by different barriers. The highest barrier occurs when passing through a saddle point in between the rAB and rAC configurations, while the barrier is lower when the saddle point is between the rAA and the rAB (or rAC) arrangements.

Concerning the magnetic order, bilayer CrCl_3 prefers an AF alignment irrespective of the relative translation between the layers also in this case of opposite chirality. CrBr_3 and CrI_3 behave similarly, with a FM ground state favoured for most configurations, including in par-

TABLE III. Energy difference (in meV) between the ferromagnetic (FM) and antiferromagnetic (AF) configuration of the (meta)stable stacking patterns of bilayer CrX_3 . In parenthesis the minimum energy (in meV) between the FM and AF state is also reported with respect to the stable AB configuration.

	$E_{\text{FM}} - E_{\text{AF}} = 2J_{\text{eff}} (E_{\min})$		
	CrCl_3	CrBr_3	CrI_3
AB	1.3 (0.0)	-2.8 (0.0)	-8.0 (0.0)
HT	2.5 (3.8)	1.3 (7.8)	0.2 (10.7)
AA	3.5 (20.0)	1.3 (32.0)	0.3 (57.1)
rHT	1.0 (5.1)	-1.1 (8.8)	-4.6 (12.8)

ticular the locally stable rHT and rHT', while AF order would be present only close to the unstable rAA stacking sequence. Interestingly, we predict a FM alignment in bilayer CrBr_3 for $\mathbf{d}/a \simeq (0.65, 0.17)$, consistently with the observations in Ref. [45]. Nonetheless, also in this case the experimentally reported stacking sequence, dubbed ‘‘bridge I’’ [45], is predicted to be dynamically unstable.

Having verified that the locally stable primitive stacking configurations are only the ones expected from the close-packing condition in table II, it is of uttermost importance to provide more accurate estimates of the relative stability and effective interlayer exchange coupling for each of them. We thus perform full structural relaxations with tight thresholds for all metastable stacking sequences, allowing also for the lattice parameter and the cell angle (for monoclinic structures) to be optimised. Final results are summarised in table III. In all cases, the rhombohedral AB stacking sequence is the most stable, followed by HT and rHT (or equivalently rHT'). The AA arrangement is typically quite high in energy, consistently with its absence in experiments.

Although numerical values might depend on details of the calculations [21, 26], general trends can be clearly identified concerning the magnetic ground state of different stacking sequences. Irrespective of the configuration, AF order is suppressed –possibly in favour of FM order– as we go from Cl to Br, to I, with J_{eff} decreasing and even going from positive to negative. All metastable configurations are AF for CrCl_3 , while the AB and rHT arrangements are preferably FM for CrBr_3 and CrI_3 , with an effective exchange coupling more negative for the iodide than for the bromide. For all halides, the effective interlayer exchange coupling is largest and positive (i.e. AF) for the AA configuration, followed by the HT sequence, and further decreases for the AB and rHT arrangements (possibly becoming negative for Br- and I-based bilayers).

These trends are consistent with all current experimental observations and have strong implications for future measurements. The AB configuration has a negative J_{eff} for Br- and I- based bilayers, while it is positive for CrCl_3 ,

consistent with the magnetic ordering measured at low temperature in bulk rhombohedral structures. The interlayer alignment becomes AF for CrI_3 when considering the HT configuration, in agreement with the AF state observed in atomically thin samples [7–10] with a monoclinic stacking sequence [41, 42]. Even more compelling, the increase in the AF J_{eff} for CrCl_3 when comparing the AB (rhombohedral) and HT (monoclinic) configurations is perfectly compatible with recent experimental observations of an enhanced interlayer exchange coupling in thin (monoclinic) samples with respect to bulk (rhombohedral) crystals [13]. Finally, although no experimental information is available on the stacking sequence of CrBr_3 bilayers, the current results suggest that the measured FM order [11, 15, 17] would be compatible only with a AB rhombohedral configuration. This prediction is consistent with the fact that CrBr_3 is in the rhombohedral phase at the temperatures at which exfoliation takes place, and the same AB arrangement is inherited by the exfoliated multilayers. On the contrary CrI_3 and CrCl_3 are monoclinic when exfoliated, and apparently thin samples are not able to undergo the bulk structural phase transition [13, 41, 42] and remain monoclinic also at the low temperatures at which magnetism sets in.

CONCLUSIONS

We consider chromium trihalide bilayers and investigate all possible stacking sequences that preserve the translational symmetry of each layer. We first identify a set of configurations based on crystallographic arguments by imposing a close-packing condition. This analysis not only recovers the stacking patterns observed in bulk structures but also predicts configurations with no bulk counterpart where the two layers have different *chirality*, which have been recently observed in synthetic bilayers. By performing first-principles simulations we validate that these configurations are the only (meta)stable primitive stacking sequences and we associate to each of them a preferential interlayer magnetic ordering. These predictions are consistent with (and provide an explanation for) all current experiments on bulk and exfoliated CrX_3 crystals, ranging from the different magnetic order in thin and bulk CrI_3 to the enhanced antiferromagnetic interlayer exchange coupling in CrCl_3 bilayers. For CrBr_3 , our simulations suggest that atomically thin samples should display a rhombohedral stacking sequence to account for the observed FM order, consistently with the fact that bulk crystals are already in the rhombohedral phase when exfoliated. Our results are also compatible with the magnetic ordering observed in non-standard stacking sequences observed in CrBr_3 bilayers grown by molecular beam epitaxy, although we predict that such configurations should not be dynamically stable. Finally, the dramatic differences between bilayers where the two

layer have the same or opposite chirality clearly shows the importance of the precise arrangement of also the halogen atoms in determining the stability and magnetic ground state of a given configuration, so that caution should be used in extending the current results to arbitrary stacking sequences and twist angles.

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