Moiré-driven multiferroic order in twisted $CrCl_3$, $CrBr_3$ and CrI_3 bilayers

arXiv:2207.01416

Adolfo O. Fumega[1] and Jose L. Lado[1]

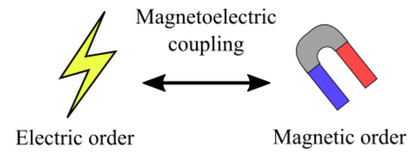
[1]Department of Applied Physics, Aalto University, 02150 Espoo, Finland

ACADEMY OF FINLAND

Introduction

Multiferroics

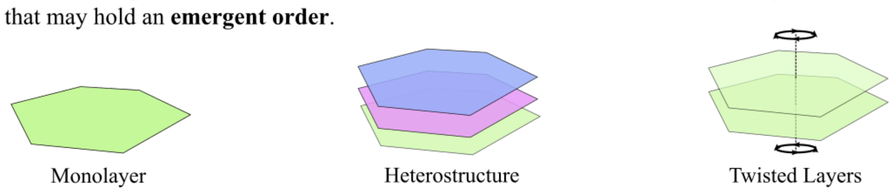
Multiferroic materials display more than one ferroic order at the same time, and in particular, they can **simultaneously host magnetic and ferroelectric orders**.



The existence of multiple symmetry-breaking orders allows having a **coupling between electric and magnetic** degrees of freedom called **magnetoelectric coupling**. Finding a material with a strong magnetoelectric coupling would allow to develop a new kind of technology based on the electric control of magnetic orders. This would have a disruptive impact, leading to the **efficient energy management** of computational processes.

Layered van der Waals compounds

The **weak bonding between layers** in van der Waals materials allows to easily reach the two-dimensional (2D) limit. **Monolayers** can display **different symmetry-breaking orders**, constituting a family of minimal **building blocks** that can be used to artificially engineer other emergent orders combining monolayers in **heterostructures**. In particular, van der Waals layers can be combined with a **twist angle** leading to a **moiré pattern** that may hold an **emergent order**.



Our Goal

Here we demonstrate the **emergence of a multiferroic state** in the family of twisted chromium trihalide CrX_3 (X=Cl, Br and I) bilayers (FIG. 1a). Using effective **spin Hamiltonians**, we first show the emergence of a non-collinear spin texture due to the modulation of the interlayer exchange coupling in the moiré unit cell (FIG. 1b). Associated with the spin texture, an electric polarization emerges in the moiré domains (FIG. 1c). We analyze the emergent magnetoelectric coupling in the system. Using **ab initio calculations** we extract the value of the electric polarization and demonstrate its dependence on the halide of CrX_3.

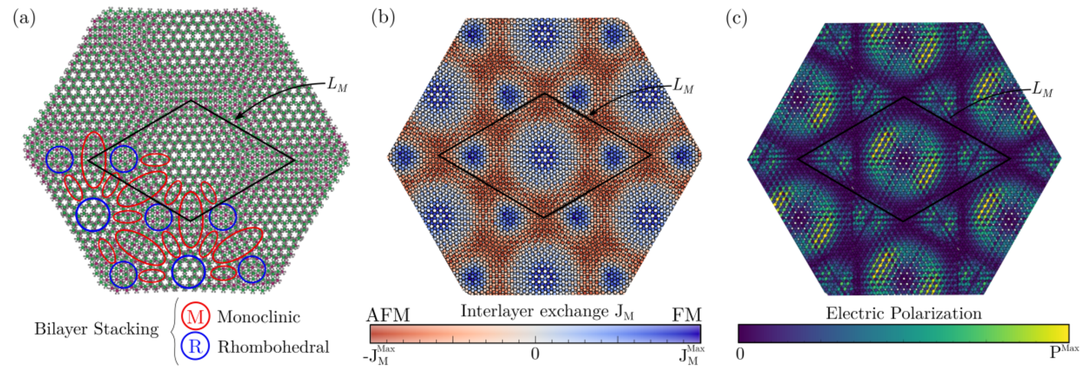


FIG. 1. (a) Top view of the twisted CrX_3 bilayer at small angles. Ligand atoms X are represented in gray, and Cr atoms of the bottom (top) layer in pink (green). The moiré unit cell is described by a lattice parameter of the moiré length scale L_M.The emergent moiré pattern leads to regions with monoclinic (M) and rhombohedral (R) stackings, highlighted in red and blue respectively. (b) Moiré profile for the interlayer magnetic exchange J_M originated from the different stackings. The interlayer magnetic exchange interaction is antiferromagnetic (ferromagnetic) in the monoclinic (rhombohedral) stacking. (c) Module of the local electric polarization associated with the moiré ground state spin texture.

Spin Hamiltonian

Emergent multiferroic order

The magnetic behavior of CrX_3 monolayers can be described by a spin Hamiltonian in a honeycomb lattice

$$\mathcal{H} = -\frac{J}{2}\sum_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j - \frac{A_v}{2}\sum_{\langle i,j\rangle}S_i^zS_j^z - A_u\sum_i(S_i^z)^2 + \mathcal{V}$$

where J is the first neighbor intralayer ferromagnetic exchange. A_v is the anisotropic magnetic exchange. A_u is the single-ion anisotropy, which is dominated by A_v. The term $\mathcal{V}$ contains additional contributions that do not qualitatively affect our analysis. In the case of twisted bilayers a site-dependent interlayer magnetic exchange $J_M(\mathbf{r}_i, \mathbf{r}_j)$ arises due to the different stacking (FIG. 1ab)

$$\mathcal{H}_{Inter} = -\frac{1}{2}\sum_{i,j}J_M(\mathbf{r}_i,\mathbf{r}_j)\mathbf{S}_i\cdot\mathbf{S}_j$$

The spin Hamiltonian for the twisted system can be solved classically. The ground state magnetic order is depicted in FIG. 2a. A non-collinear magnetic texture emerges between ferromagnetic and antiferromagnetic regions. In the presence of spin-orbit coupling (SOC), non-collinear magnetism leads to the emergence of an electric polarization $\mathbf{P}_{ij}$ between neighboring spins separated by a distance $\mathbf{r}_{ij}$

$$\mathbf{P}_{ij} = \lambda_{SOC}\,(\mathbf{r}_{ij}\times(\mathbf{S}_i\times\mathbf{S}_j))$$

where λ_{SOC} is a coefficient that controls the strength of the SOC. For the emerging ground state spin texture of the twisted system (FIG. 2a), the associated electric polarization when SOC is introduced is shown in FIG. 2b, with P_z the dominant component. The electric polarization emerges in both layers in the areas where the non-collinear spin texture occurs. The polarization emerges locally, and for the ground state spin texture the net electric polarization is zero. The moduli of the electric polarization in the moiré system associated with the ground state spin texture can be seen in FIG. 1c. FIG. 2c shows the average polarization as a function of the maximum interlayer exchange. At low values, the twisted system behaves like two independent layers, remaining ferromagnetic, no spin texture emerges and consequently, there is no electric polarization. By increasing the interlayer coupling, non-collinearity appears and with it an associated electric polarization. FIG. 2d shows the average polarization as a function of the anisotropic exchange A_v. At high values, the twisted system tends to align the magnetic moments out of the plane. Therefore, no spin texture occurs and thus there is no electric polarization. This situation happens for $A_v/J>0.1$, so CrI3 would be on the verge of displaying a multiferroic behavior due to its strong uniaxial anisotropy.

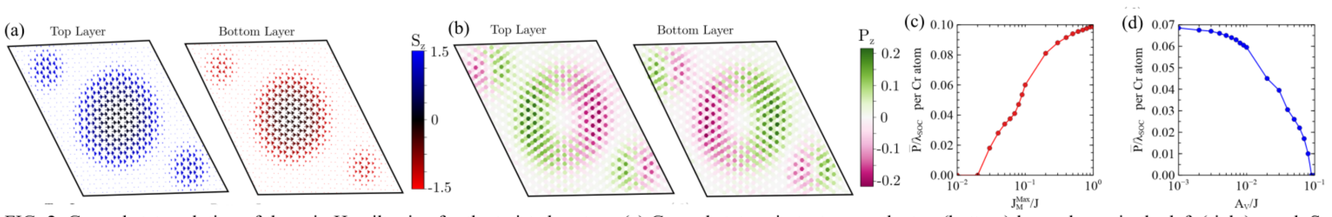


FIG. 2. Ground state solution of the spin Hamiltonian for the twisted system. (a) Ground state spin texture on the top (bottom) layer shown in the left (right) panel. S_x and S_y components are depicted as a vector field. The color of the vectors shows the S_z component. (b) Associated electric polarization (P_z component) to the ground state magnetic texture. (c) Electric polarization average of the ground state as a function of the interlayer exchange maximum J_M ($A_v/J=0.01$ and $A_u/J=0.001$). At low values of J_M no spin texture is formed. (d) Electric polarization average of the ground state as a function of the anisotropic magnetic exchange A_v ($J_M/J=0.1$ and $A_u/J=0.001$). At high values of A_v no spin texture is formed.

Magnetoelectric coupling

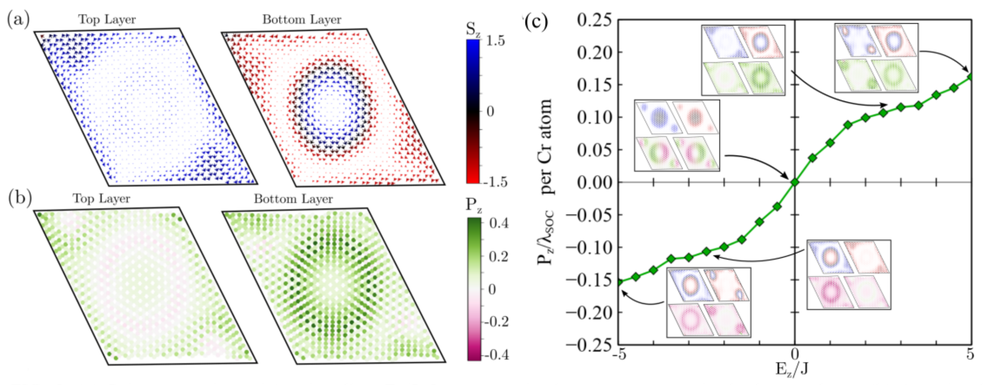


FIG. 3. (a) Spin texture in moiré unit cell at Ez/J=3, a magnetic skyrmion emerges in the bottom layer. (b) Associated electric polarization to the spin texture. (c) Evolution of the net electric polarization in the z-direction P_z as a function of the electric field. Different spin textures appear as a function of the electric field: ground state spin texture at $E_z/J=0$, a magnetic skyrmion appears in the AA stacking area in one of the layers at $E_z/J=\pm3$, and a second pair of magnetic skyrmions emerge in the other layer around the AB/BA stacking regions at $E_z/J=\pm5$.

We analyze the magnetoelectric coupling present in twisted CrX_3 bilayers. To do so, we include in the low energy Hamiltonian a coupling to an external electric $\mathbf{E}=(0, 0, E_z)$ field perpendicular to the twisted system in the z-direction

$$\mathcal{H}_E = \frac{1}{2}\sum_{ij}\mathbf{E}\cdot\mathbf{P}_{ij}$$

This interlayer bias allows controlling the magnetic order due to the emergent multiferroicity. FIGs. 3a and 3b show the spin texture and the associated electric polarization at Ez/J=3. We can observe that the ground state spin texture (FIG. 2a) gets significantly modified due to the strong magnetoelectric coupling, leading to the formation of a magnetic skyrmion around the AA rhombohedral stacking in one of the layers.

Interestingly, such a magnetic state features a non-zero total electric polarization in the z-direction. The evolution of the total electric polarization in the moiré supercell in the z-direction as a function of the external electric field is shown in FIG. 3c. The different bumps in P_z as a function of the electric field indicate transitions to different non-trivial spin textures (insets in FIG. 3c). As a reference, J≈3meV and $\lambda_{SOC}\approx10^{-4}$e in twisted $CrBr_3$ bilayers, implying that such magnetic transitions can be experimentally driven via gating at voltages of 1 −10V. This brings twisted CrX_3 bilayers as apromising platform for the electric control of non-trivial magnetic textures, and ultimately as a platform for magnetoelectric skyrmionics.

Ab initio calculations

We now demonstrate and quantitatively quantify using first-principles density functional theory calculations the emergence of an electric polarization due to the non-collinear order at the domain wall. Performing first principles calculations in a full twisted CrX_3 bilayer with spin-orbit coupling and non-collinear magnetism is well beyond the current computational capabilities. However, since the electric polarization arises locally, the ab initio analysis can be performed in a system like the one shown in FIG. 4a by imposing a magnetic texture in the CrX3 layer like the one shown in FIG. 4b. We set the same out-of-plane spin texture to the three compounds to systematically extract the effect of the halide atom. The associated polarization of a non-collinear texture given can be rewritten in terms of an spin spiral propagation vector **q** and the spin rotation axis **e** =(0, −1, 0), leading to an electric polarization of the spin texture

$$\mathbf{P} = \lambda_{SOC}(\mathbf{q}\times\mathbf{e})$$

To demonstrate the emergence of an electric polarization in the magnetic texture shown in FIG. 4b, we now perform calculations in two equivalent configurations (FIG. 4b) with the same spin rotation vector **e**, but with opposite spin propagation vector **q**. Therefore, an opposite electric polarization will emerge in each of the configurations.

The emergence of the electric polarization in the spin texture is directly obtained by taking the difference between the two equivalent configurations. This procedure provides a direct methodology to extract electric polarization stemming from non-collinear magnetic order.

The emergence of an electric polarization is accompanied by a reconstruction of the electronic density ρ and a ferroelectric force in the atoms with the spin texture in the direction of the emergent electric polarization. We can analyze the difference in the electronic density δρ between both configurations (FIG. 4c) and the force difference between both configurations (FIG. 4b) to provide a direct quantification of the electric polarization in CrX_3. The forces emerge on the z-direction only in the Cr atoms in which the non-collinear magnetism is present. We can quantify the dependence on the halide by taking the average of the force module among Cr-atoms for each of the compounds (FIG. 4d). Taking a heavier halide produces an increase in the ferroelectric force and in the electronic reconstruction (FIG. 4c), as expected from the increase of the SOC. This confirms that spin textures produced in twisted CrX_3 bilayers lead to the emergence of an electric polarization with a strong magnetoelectric coupling.

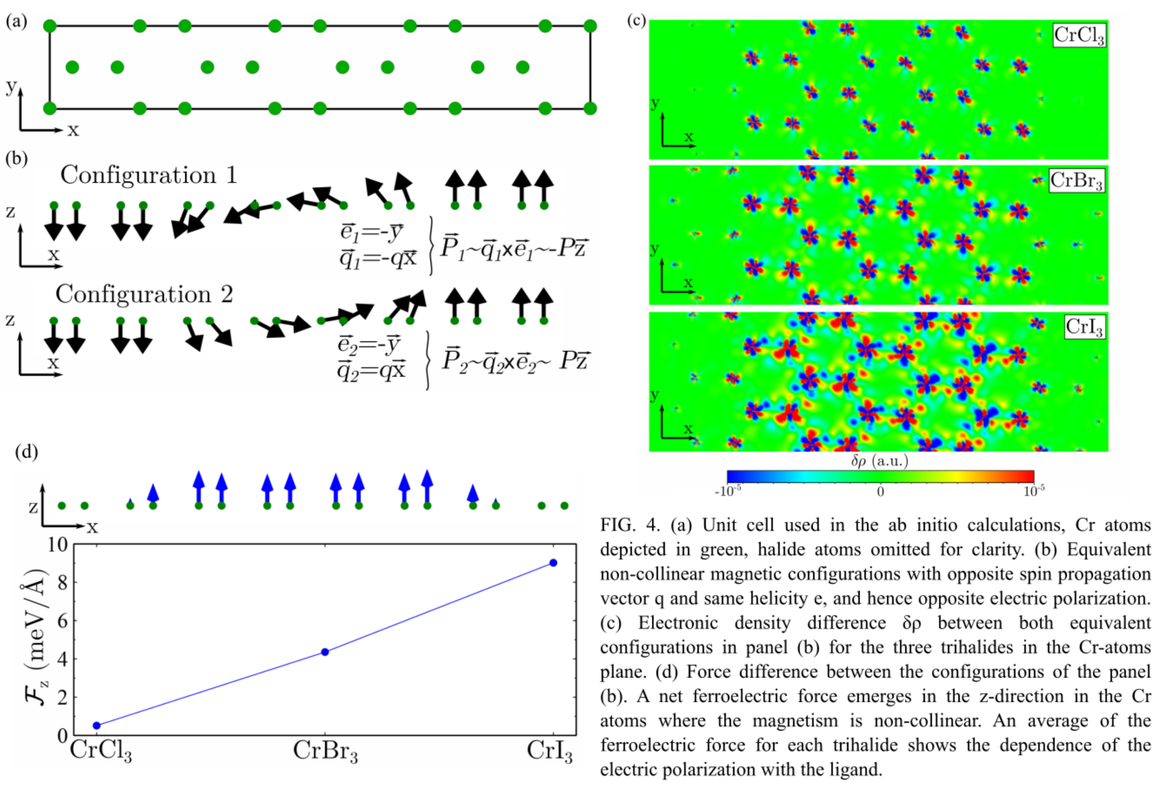


FIG. 4. (a) Unit cell used in the ab initio calculations, Cr atoms depicted in green, halide atoms omitted for clarity. (b) Equivalent non-collinear magnetic configurations with opposite spin propagation vector q and same helicity e, and hence opposite electric polarization. (c) Electronic density difference δρ between both equivalent configurations in panel (b) for the three trihalides in the Cr-atoms plane. (d) Force difference between the configurations of the panel (b). A net ferroelectric force emerges in the z-direction in the Cr atoms where the magnetism is non-collinear. An average of the ferroelectric force for each trihalide shows the dependence of the electric polarization with the ligand.

Conclusions

In short, ab initio density functional theory methods show that as the halide becomes heavier, the ferroelectric polarization becomes stronger, while the spin model shows that the anisotropic exchange has a detrimental impact on the formation of the spin texture and hence on the multiferroic order. In particular, in CrI_3 the strong anisotropic exchange might partially quench the formation of a sizable non-collinear magnetic texture. In $CrCl_3$, the small SOC would yield a weak ferroelectric polarization despite the formation of the non-collinear texture. Therefore, the optimal twisted bilayer yielding the strongest ferroelectric polarization would be $CrBr_3$, or ultimately, a bilayer of an intermediate stoichiometry between $CrBr_3$ and CrI_3. Our results put forward a strategy to design a new family of artificial multiferroics with a strong magnetoelectric coupling based on twisted magnetic van der Waals materials allowing to electrically control non-trivial magnetic textures.