Intrinsically patterned 2D transition-metal halides

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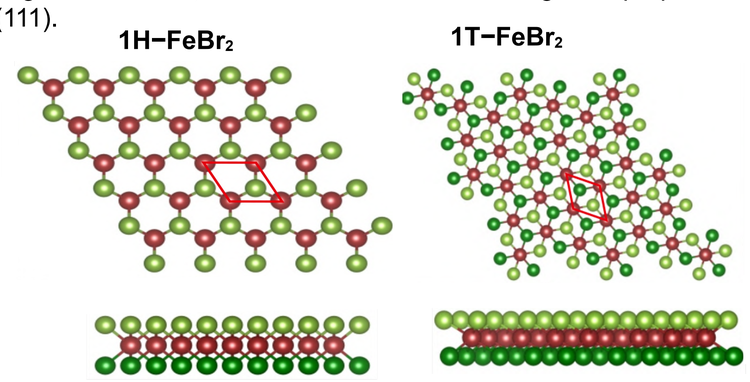
Introduction

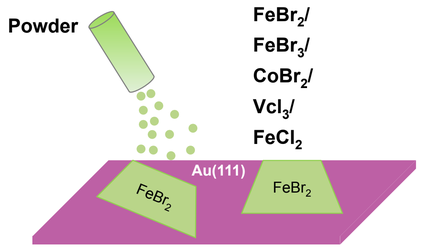
The discovery of graphene paved the way for a surge of interest in novel 2D materials, alluring researchers with their exceptional properties achieved through the quantum confinement effect [1]. This study presents the first vacancy lattice in 2D materials with atomic precision over several hundred nanometers created by controlled patterning in 2D via strain engineering, using single-layer **transition metal halides (TMHs)** as an example. TMHs have gained considerable interest since the recent discovery of intrinsic ferromagnetism in 2D vdW-materials in CrI_3 in 2017 [2]. However, little is known so far about the growth, structure, and intrinsic defects of TMHs at the atomic scale by means of well-defined experimental and theoretical studies. In this work, we leverage Density Functional Theory (DFT), as implemented in the **Vienna Ab-initio Simulation Package** (VASP), to support novel experimental findings. We systematically investigate structural, electronic and collinear magnetic properties of intrinsically patterned $FeBr_2$ monolayers on Au (111).

TMH (MX_2 or MX_3)

• M	• Ti	• V	• Cr	• Mn	• Fe	• Co	• Ni
• X	• I	• Br	• Cl				

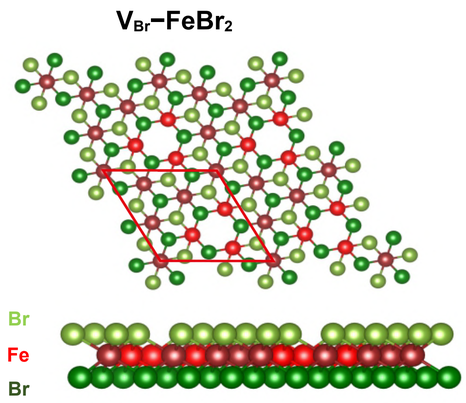
1H−$FeBr_2$ **1T−$FeBr_2$**





- *In-situ* growth of **2D materials** on metal surfaces

V_{Br}−$FeBr_2$



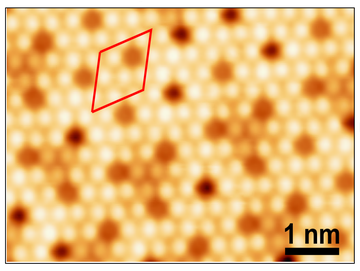
Experimental Methods

Low-temperature & variable temperature scanning probe microscopy & spectroscopy:

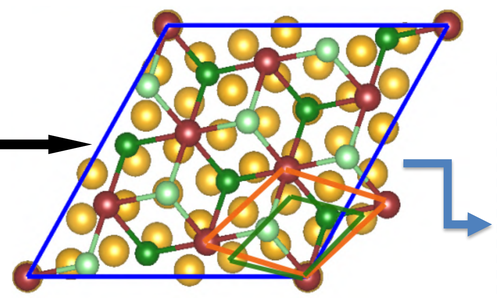
- Scanning tunneling microscopy & spectroscopy (**STM / STS**)
- Atomic force microscopy (**nc-AFM**)
- Kelvin probe force microscopy (**KPFM**)

Computational Model

Low Temperature STM



I = 560 pA, U = 5 mV; 450K



$FeBr_2$ lattice: $\vec{V}_{FeBr2}=(3,1)$
Au lattice: $\vec{V}_{Au}=(4,1)$

We rationalized the $V_{Br\text{-}FeBr2}$ superstructure based on the superposition of two rotated commensurate hexagonal lattices.

Experiments(SEM/LEED)

$FeBr_2$ unit cell, a_{FeBr2}= 3.92 ±0.30Å
$FeBr_2$ superstructure, L= 10.37±0.3Å
Gold unit cell, a_{Au}=2.88Å

Simulation Model

a_{FeBr2}= 3.71 Å, a_{Au}= 2.89 Å
L= (√7×√7)19.10°= 10.42 Å

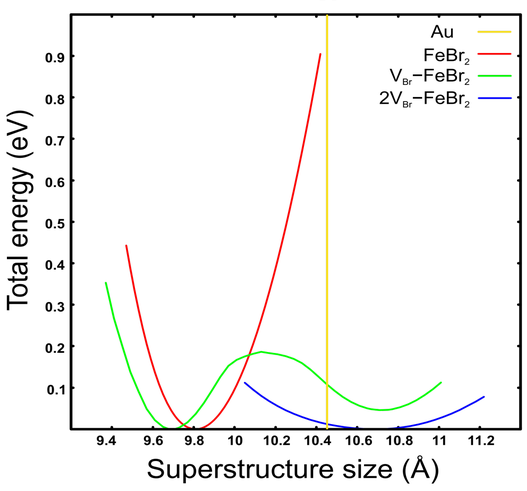
$\phi_{vac\text{-}lattice,FeBr2}$= 19.10°,
$\Phi_{vac\text{-}lattice,Au}$= 13.90°, $\Theta_{feBr2,Au}$= -5.21°

Method

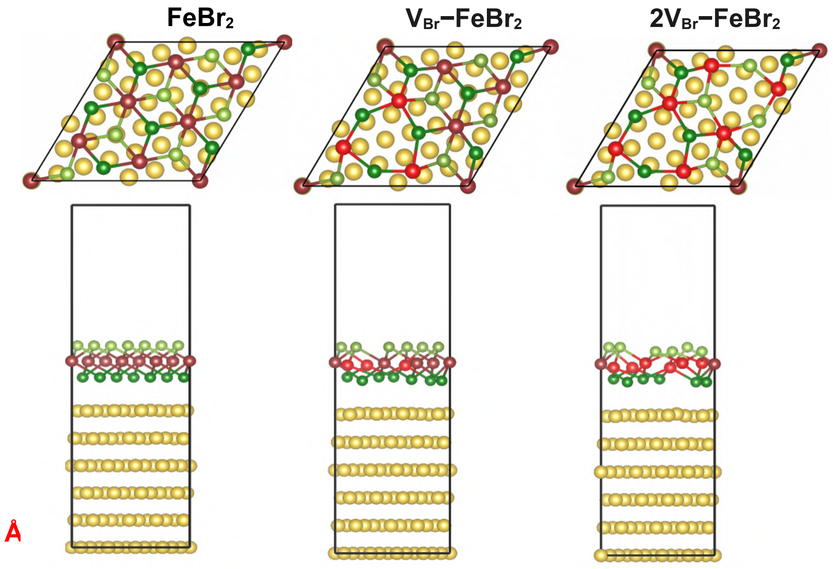
Simulation Package	VASP v-6.3.0
Methodology	Density Functional Theory (SP-DFT)
Exchange-Correlation Functional	GGA-PBE, Fe d7s1, Br s2p5
Dispersion Correction	DFT-D3 (Becke–Johnson damping)
Brillouin Zone Sampling	6x6x1 (geometry optimization), 18x18x1 (electronic structure)
Electron-core interactions	Projector Augmented Wave (PAW)
Energy Convergence	0.00001 eV
Forces on each atom	0.001 eV/Ang
Mesh Cutoff for the Plane Wave	400 eV
Smearing	Methfessel–Paxton smearing (σ = 0.2 eV)
Vacuum spacing	16 Å for slabs, 30 Å for monolayers (z-direction)
STM/nc-AFM simulations	Tersoff–Hamann model and Hapala model.

Growth Mechanism of Grown 2D Films

Potential Energy Surface



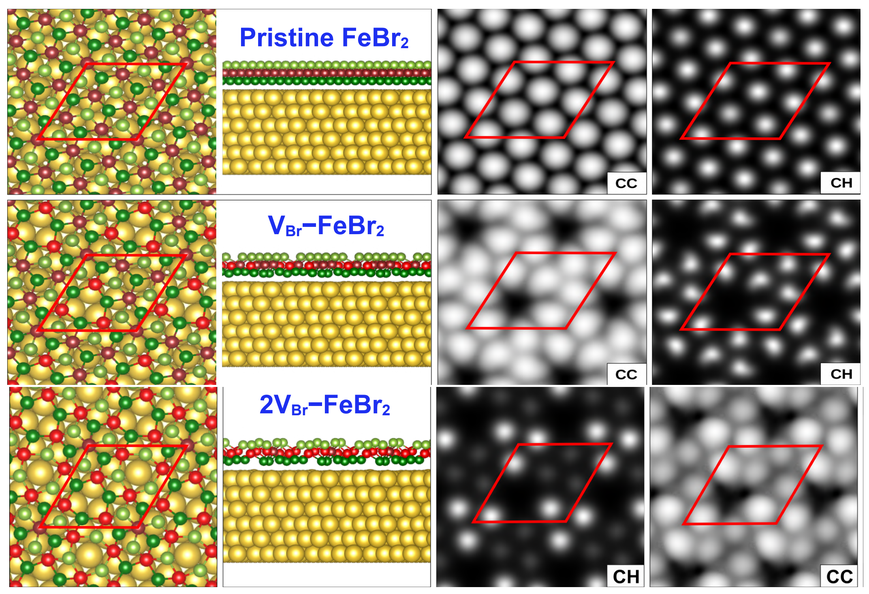
$FeBr_2$ **V_{Br}−$FeBr_2$** **$2V_{Br}$−$FeBr_2$**



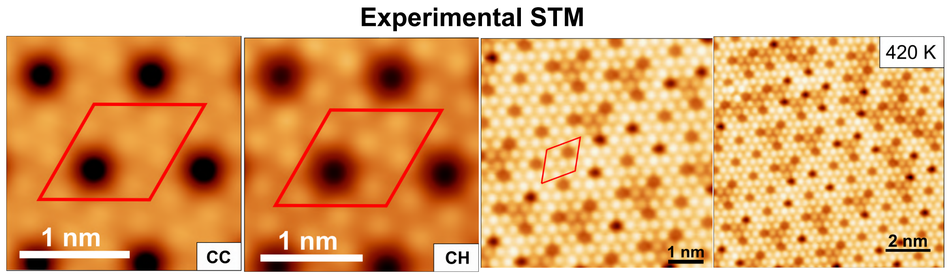
→ Local minimum for **pristine $FeBr_2$** at **9.81 Å**
→ Local minimum for **V_{Br}−$FeBr_2$** at **10.71 Å**
→ Local minimum for **$2V_{Br}$−$FeBr_2$** at **10.70 Å**

System	Lattice Misfit w.r.t Au(111) Δa %	Vacancy Formation energy (gas phase) eV/Br	Formation energy (on surface) eV
1. V_{Br}−$FeBr_2$	-2.5%	0.045	0.09
2. $2V_{Br}$−$FeBr_2$	-2.4%	0.056	-1.175

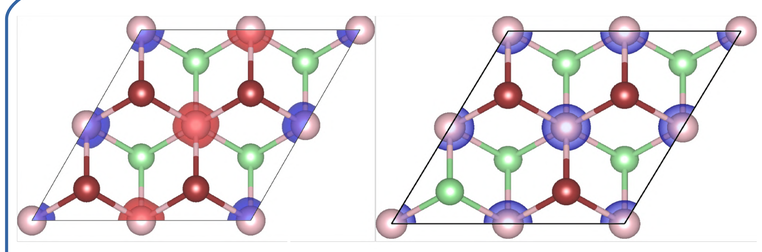
STM Simulations



Experimental STM

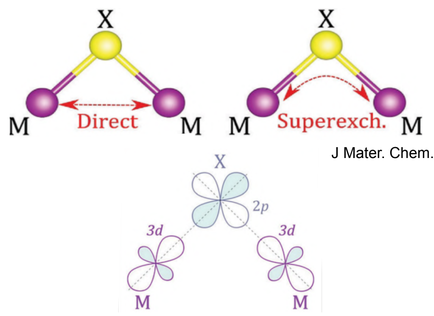


Magnetic Structure



Ferromagnetic **Antiferromagnetic**

Exchange energy E_{ex} = E_{AFM} - E_{FM}
E_{ex}=48 meV



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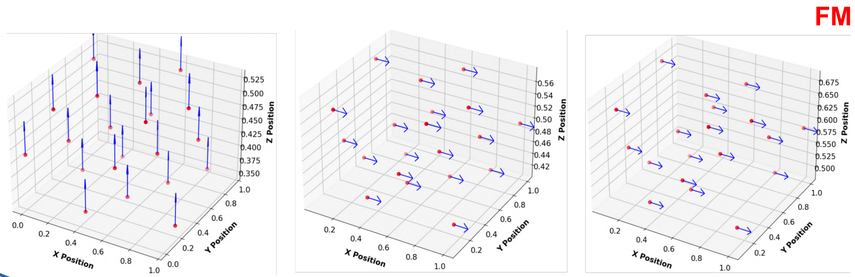
Goodenough–Kanamori–Anderson (GKA) formalism
FM superexchange is dominating



Magnetic Anisotropy Energy(meV)

Pristine $FeBr_2$	:	**0.99 (Out-of-Plane)**
V_{Br}−$FeBr_2$	:	**-0.45 (In-Plane)**
$2V_{Br}$−$FeBr_2$	:	**-0.77 (In-Plane)**

Conclusions

- Periodic **Br-vacancy lattices** identified in $FeBr_2$ monolayers on Au(111) via STM, nc-AFM, LEED, and DFT.
- Vacancy superstructure formation driven by low Br-vacancy formation energy, **reduced lattice-mismatch strain**, and enhanced structural flexibility of TMH monolayers.
- The vacancy lattice enables creation of **noncollinear spin textures**.
- Demonstrated a computational strategy for predicting long-range ordered defect-patterned structures in 2D materials.

References

1. Novoselov, Kostya S and Geim, Andre K and Morozov, Sergei V and Jiang, De-eng and Zhang, Yanshui and Dubonos, Sergey V and Grigorieva, Irina V and Firsov, Alexandr A,Science,306,666–669 (2004).

2. Huang B, Clark G, Navarro-Moratalla E, Klein DR, Cheng R, Seyler KL, Zhong D, Schmidgall E, McGuire MA, Cobden DH, Yao W, Xiao D, Jarillo-Herrero P, Xu X,Nature,546(7657),270-273 (2017).

DFG Deutsche Forschungsgemeinschaft