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2d Honeycomb Hafnene : Stability & Magnetism by Structural Transition

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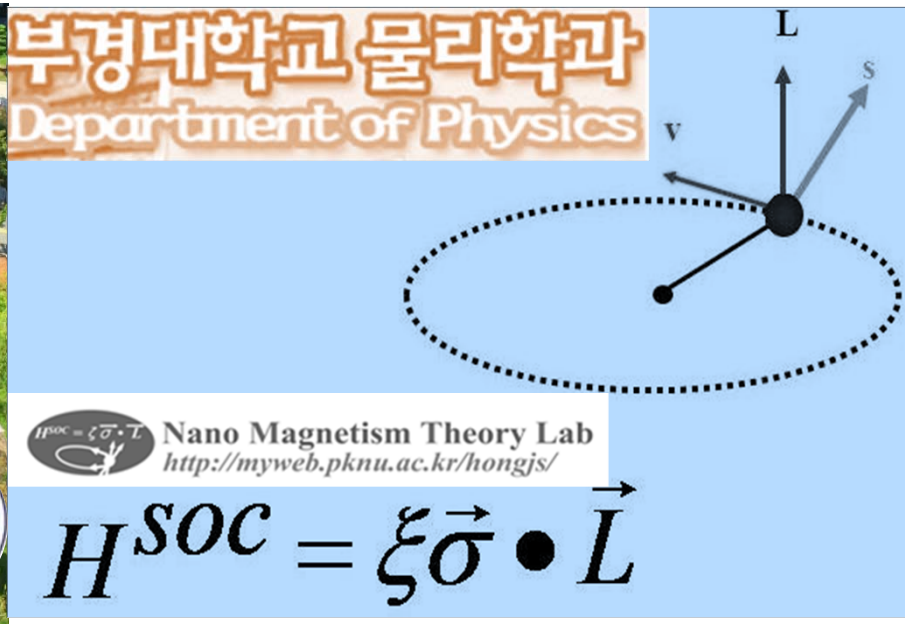

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Introduction

Two-Dimensional Transition Metal Honeycomb Realized: Hf on Ir(111)

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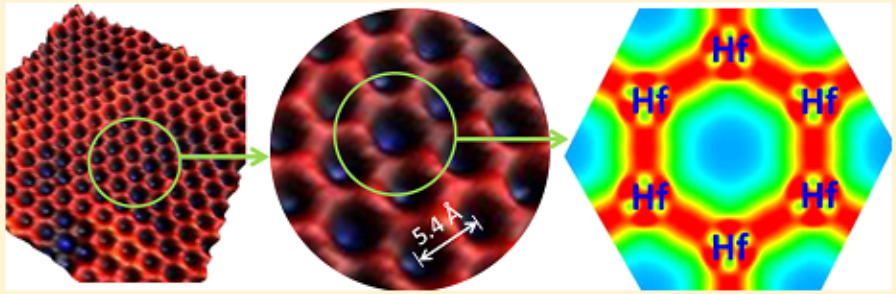
Supporting Information

ABSTRACT: Two-dimensional (2D) honeycomb systems made of elements with d electrons are rare. Here, we report the fabrication of a transition metal (TM) 2D layer, namely, hafnium crystalline layers on Ir(111). Experimental characterization reveals that the Hf layer has its own honeycomb lattice, morphologically identical to graphene. First-principles calculations provide evidence for directional bonding between adjacent Hf atoms, analogous to carbon atoms in graphene. Calculations further suggest that the freestanding Hf honeycomb could be ferromagnetic with magnetic moment μ/Hf = 1.46 μ_B. The realization and investigation of TM honeycomb layers extend the scope of 2D structures and could bring about novel properties for technological applications.

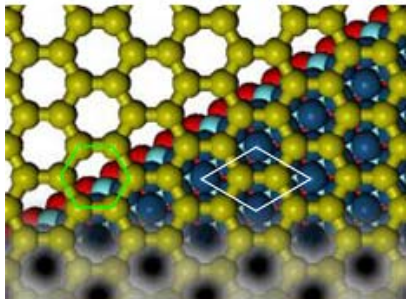


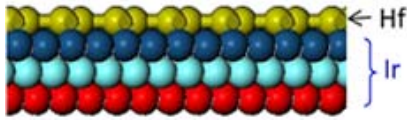
KEYWORDS: *Honeycomb lattice, hafnium, epitaxial growth, STM*

Background - I

Experimental study on Hafnene

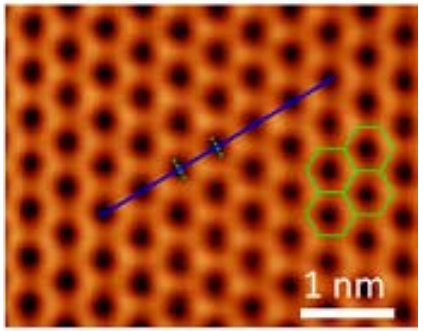
Linfei Li et al, (Nano Letter, 2013) did a combined experimental and theoretical study on Hafnium monolayer , namely Hafnene.





Main features of their study.

- They synthesized Hafnene on a Ir(111) substrate.
- Through STM images they proved that the Hafnene have flat layer (FL) honeycomb structure.
- Then on the bases of DFT study on free standing monolayer they clamed that the Hafnene have a ferromagnetic stat with magnetic moment of μ/Hf = 1.46 μB.



Two main issues regarding there claims

- They had not provided any experimental observation regarding magnetism.
- In their DFT calculation they have ignored the important substrate effect.

Background - II

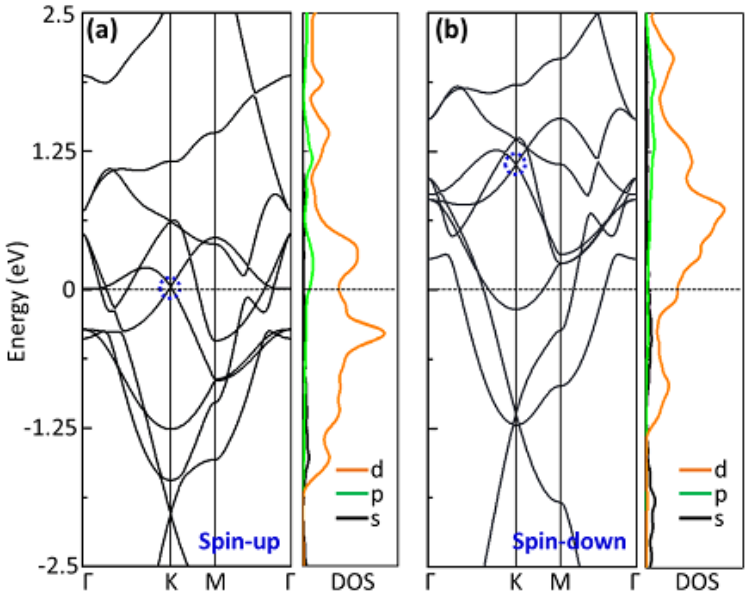
Hafnene can be very interesting regarding magnetism.

- Hafnene observed to have graphene like honeycomb lattice structure .

- The band structure of free standing Hafnene is observed to have some daric cone like band dispersions.

- Since the 5d electron system has a strong SOC, therefore Hafnene can have strong magnetic crystalline anisotropy (MCA).

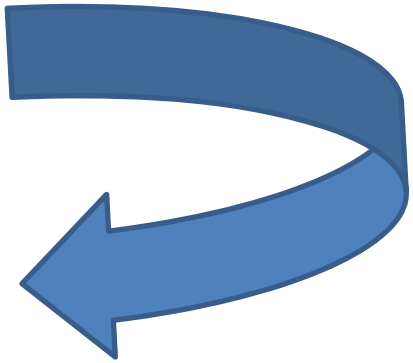
- The strong MCA can leads to a room temperature 2D ferromagnetic material. Which can open up another route in magnetic device application through Van der Waals hetero structuring.



Purpose

■ Hf belongs to the transition metals of group IV in the periodic table. In this column, the materials usually have a hexagonal close-packed (HCP) non-magnetic (NM) bulk structure and it may not be stable enough to preserve a Flat layer geometry.

In this study, we explored the following subjects



■ Possibility of free-standing 2D honeycomb Hafnene lattice structure

■ Structural modification of Hafnene on the Ir(111) surface

■ Magnetism dependent on the crystal structure & hybridization effect on the 2D Hafnene magnetism

■ Possibility of giant magnetocrystalline anisotropy (MAE) in this 2D layer.

Computational Method

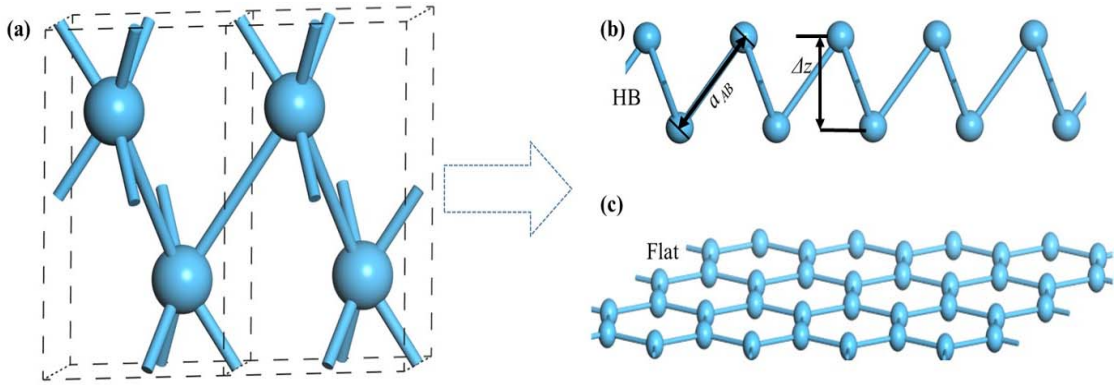
We investigated free-standing Hafnene, Hf/Ir(111) & Hf/BN/Ir(111).

- Vienna ab initio simulation package (VASP)
- ***Exchange correlation interaction:*** Perdew–Burke–Ernzerhof (PBE)
- ***Plane-wave Cut-off*** **:** very high ➔ 700eV
- ***11x11x1 k-points*** are used for all systems
- To understand the role of Ir(111) substrate & BN as a spacer layer, 4 layers of (2 × 2) Ir(111) & 1ML of (4 × 4) BN were considered.
- To simulate the buckled and flat hafnene geometries on Ir(111), we considered both a (2 × 2) & (1 × 1) unit cell respectively.
- SOC was implemented in VASP in a non-collinear. Self-consistent calculations with the magnetic axis oriented perpendicular and parallel to the surface were performed and the magnetocrystalline anisotropy (MCA).
- The total energy convergence criterion was 10^{-8} eV per atom, & the converged MCA energy results were obtained with fine grids of 41 × 41 × 1 k-mesh.

Results & Discussion

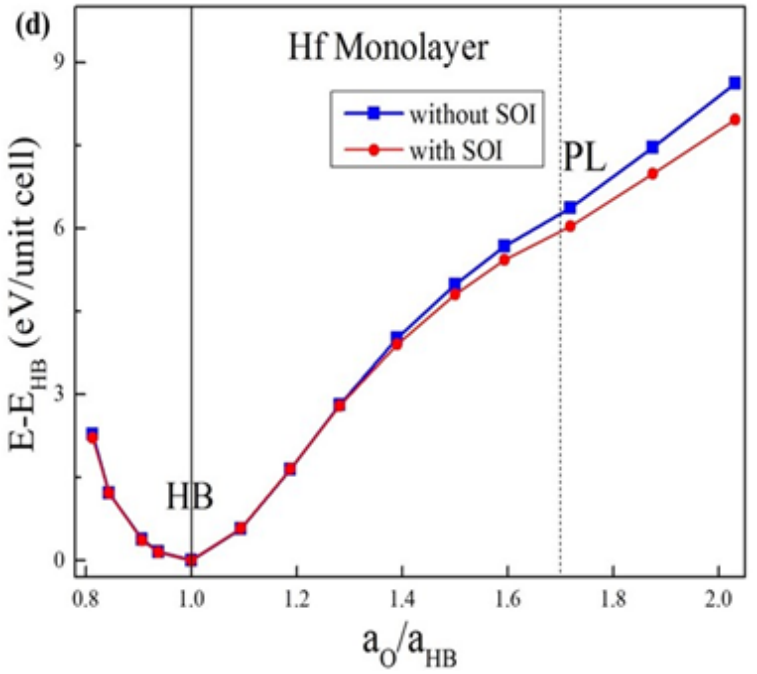
Bulk to Monolayer Hf Structure

- Bulk hafnium ➔ HCP structure space group of P63 (No. 194).
- Hf atoms are connected through covalent bonding with each other.
- Hf–Hf bond length in the HCP structure is 3.127 Å with a buckling height of 2.52 Å.



2D layer

- Total energy minimization was carefully checked in a wide range of lattice constants with changing buckling height.
- Contrary to the previous report, the honeycomb high buckled (HB) hafnene (Fig. b) was more stable and lower in energy than the FL honeycomb structure displayed in Fig. (c).
- Freestanding hafnene had a typical honeycomb lattice with a symmetry of $P\bar{3}m$.



Freestanding Hafnene: HCP & Flat structure relation

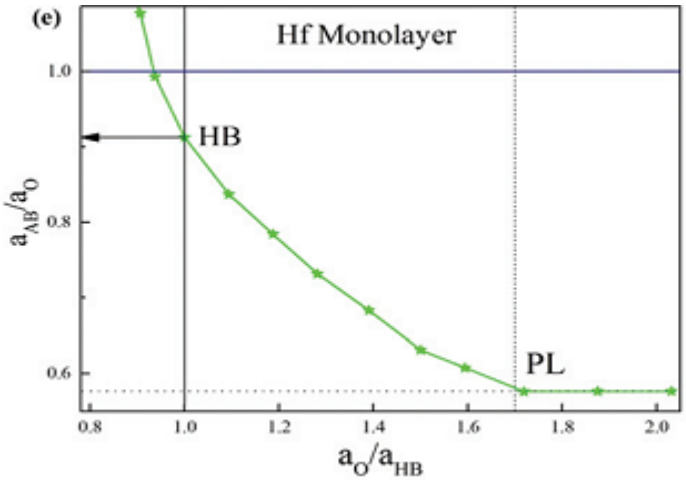
- In an ideal HCP structure, the bond length between two sub-lattice atoms has a relation of $a_{AB} = \sqrt{a_0^2/3 + \Delta z^2}$ ➔ $\Delta z = \frac{\sqrt{2}\, a_0}{\sqrt{3}}$ so that the relation $a_{AB} = a_0$ should hold.

- Lattice constant a_{HB} = 3.2 Å and buckling height Δz = 2.27 Å. Thus, we obtained $a_{AB} = 0.914 a_{HB}$.

- This result indicates that the 2D hafnene is not a perfect HCP, but very close to an ideal HCP structure.

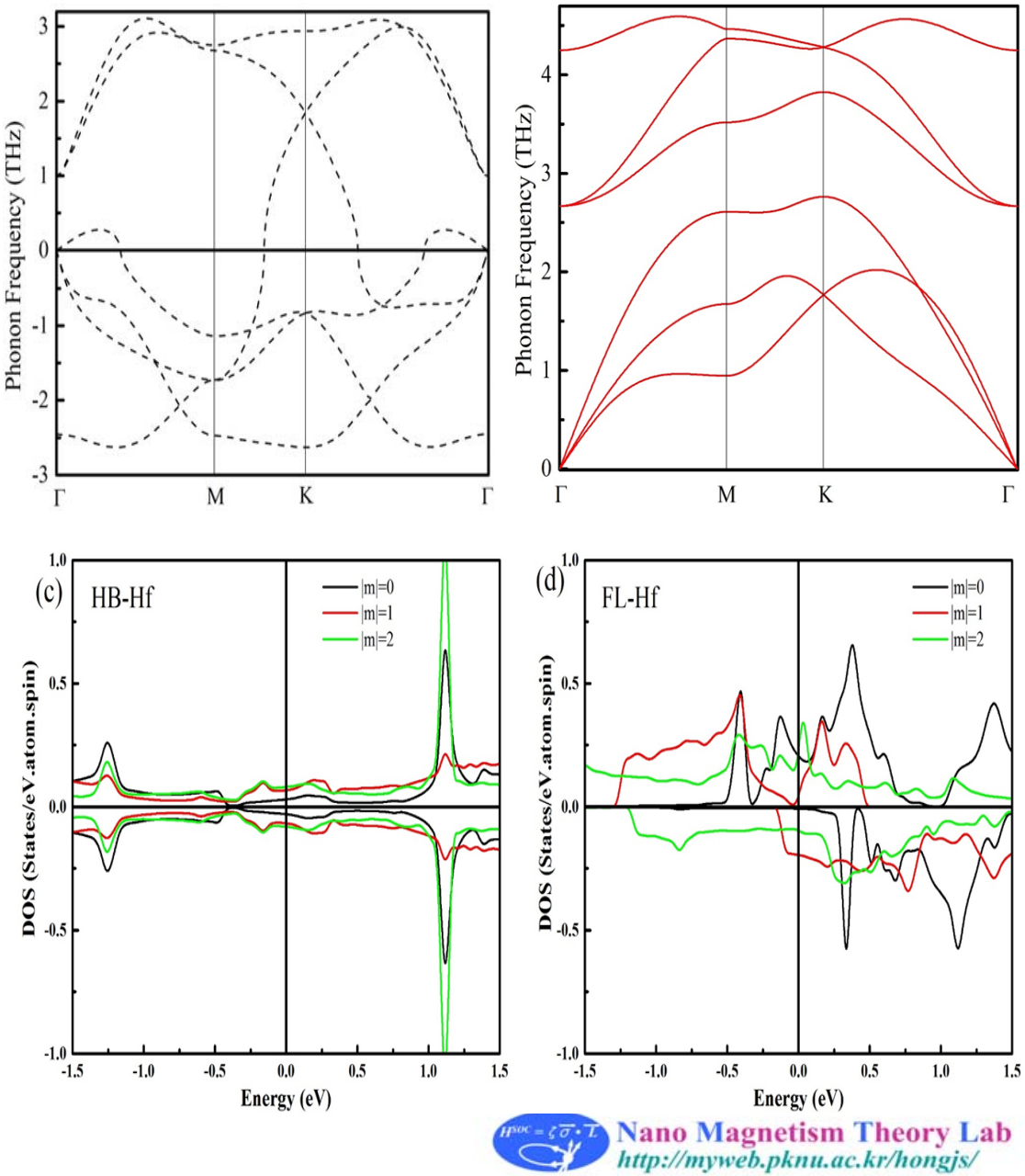
- If the buckling height Δz =0, then the bond length should satisfy the relation $a_{AB} = \sqrt{a_0^2/3}$ in an ideal planar hexagonal lattice. In other words, the planar hexagonal structure will appear at a_{AB}/a_0= 0.577.

- In Fig (e), we observe a FL structure was near $a_0 \sim 1.7 a_{HB}$ and confirms that our calculations are consistent.



Phonon Dispersion & Magnetic state

- In perfect FL geometry, an imaginary phonon dispersion in a large portion of the Brillouin zone with mixed optical and acoustical branches.
- In contrast, both optical and acoustical branches were well separated, and all branches had positive frequencies in HB geometry.
- HB structure has a crystal symmetry of D_{3d}, and this high symmetry results in a non-magnetic state.
- However, in flat geometry, it adopts the D_{6h} symmetry of a honeycomb structure, like graphene, and the major contributions to the magnetic moment originate from out-of-plane orbitals $|m| = 0$ (d_{z^2}) & $|m| = \pm 1$ (d_{xz}, d_{yz}).
- This finding implies that the structural characteristic is a key factor for both stability and magnetism of free-standing 2D hafnene.



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Hafnene in the presence of Ir substrate

- Our results suggest that the Ir substrate strongly affects Hf structure.

Table 1 Formation enthalpy of a layer of Hf honeycomb on Ir(111)

System	fcc + hcp	atop + hcp	atop + fcc
HB	4.39	7.15	7.22
Flat structure	−1.07	−0.26	−0.08

- The strong hybridization between the Ir & Hf film made the FL planar structure much more stable than the HB geometry.

- 2D hafnene lattice is a compact graphene-like structure on Ir substrate, good agreement with the experimental report.

- The free-standing FL hafnene had a FM ground state with a large magnetic moment, while we found no magnetic state in the Hf/Ir(111) structure.

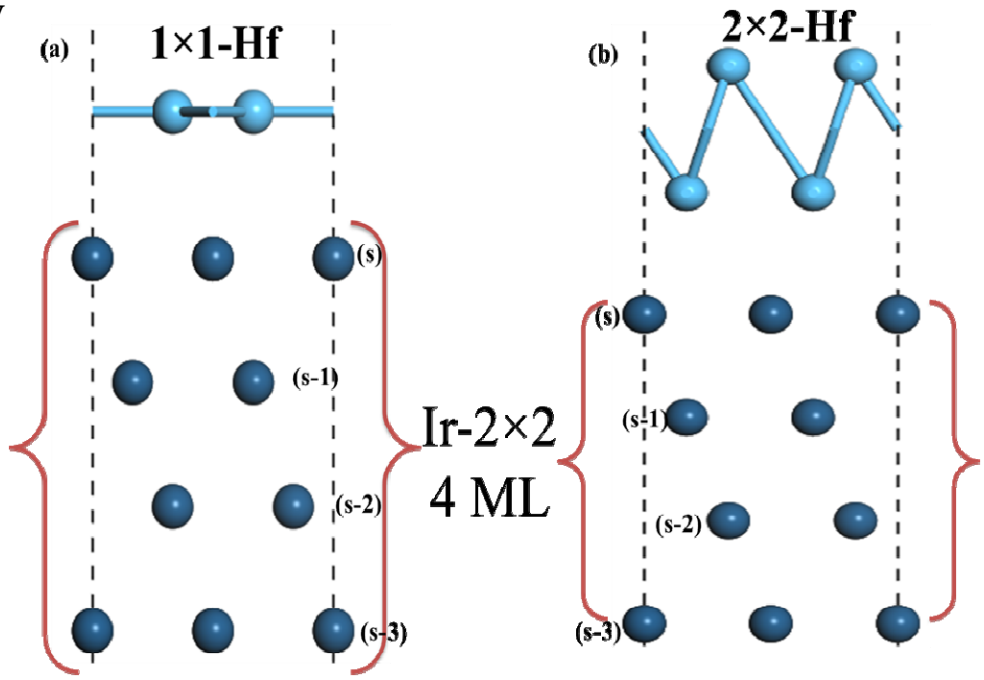
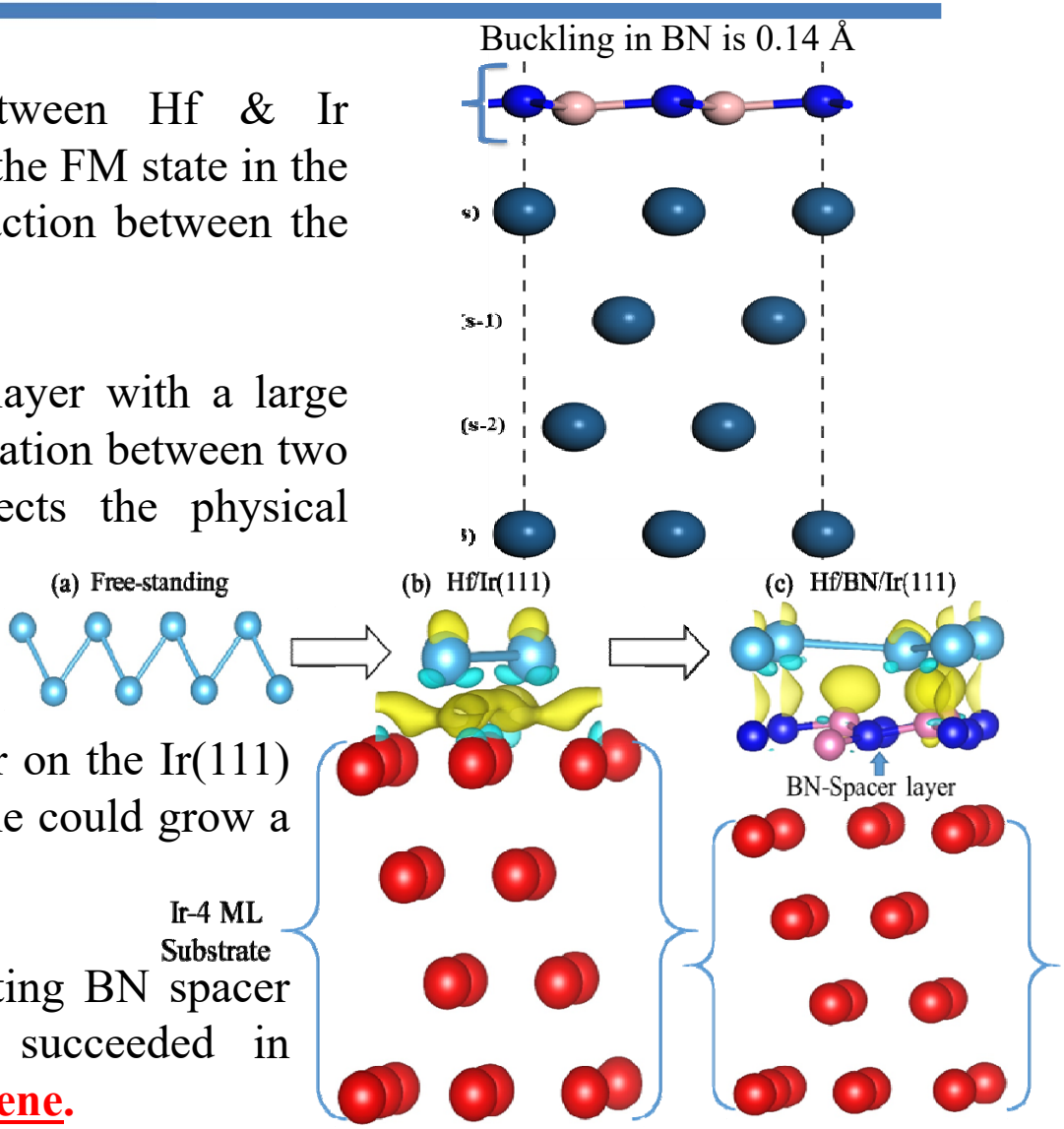


Table 2 Total energy difference (in meV) and spin magnetic moment in μ_B (per unit cell) of free-standing FL and supported hafnene on Ir(111)

System	NM	FM	AFM	μ_B
Free-standing FL Hf	104	0	Not observed	3.073
Hf on Ir(111)	NM only	—	—	—

NM to FM Hafnene : Hf/BN/Ir(111)

- Considering strong hybridization between Hf & Ir substrate, it seems that we can reinstate the FM state in the 2D layer if we can minimize the interaction between the substrate and hafnene.
- We propose that an insulating spacer layer with a large band gap may reduce the direct hybridization between two conducting materials and greatly affects the physical properties.



- To this aim, we considered a BN layer on the Ir(111) substrate. Indeed, it was reported that one could grow a BN layer on an Ir(111) surface
- Remarkably, by inserting a NM insulating BN spacer layer between Ir and hafnene, we succeeded in reinstating the **FM ground state in hafnene**.

Magnetic Anisotropy : Giant Perpendicular anisotropy (PMA)

- Since Hf has 5d orbital characteristics, we expect a very large magnetic anisotropy energy (MAE) due to large SOC.

- Collinear in-plane and out-of-plane as well as non-collinear (NC) configurations of spin alignments, shown in Fig. (a–f).

- Free-standing PL Hf and Hf/BN/Ir, collinear FM out-of-plane magnetic alignment is the most stable spin configuration.

- Freestanding PL Hf had PMA of 1.42 meV, it's even enhanced on the BN/Ir(111) surface with PMA energy of 3.41 meV.

- The spin and orbital magnetic moments were anti-parallel and this agrees with the Hund's rule, and the spin magnetic moment

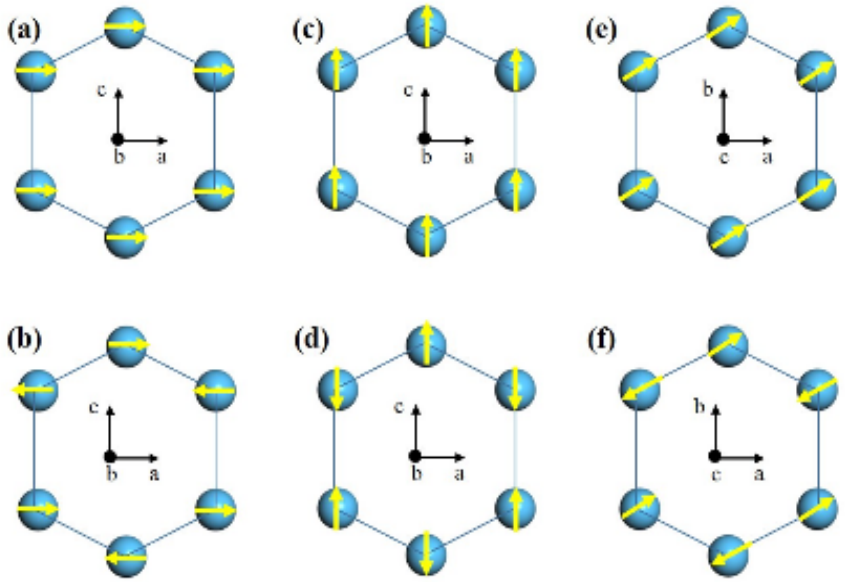


Table 3 Spin μ_s, orbital μ_L, and total μ_{tot} magnetic moments (all in μ_B) of a free-standing flat hafnene layer and on a BN/Ir(111) substrate per unit cell. The MAE is given in meV

	Without SOC	Including SOC			
	μ_s	μ_s	μ_L	μ_{tot}	MAE
Unsupported FL hafnene	3.073	2.849	−0.170	2.679	1.42
Supported hafnene on BN/Ir(111)	2.162	2.308	−0.172	2.136	3.41

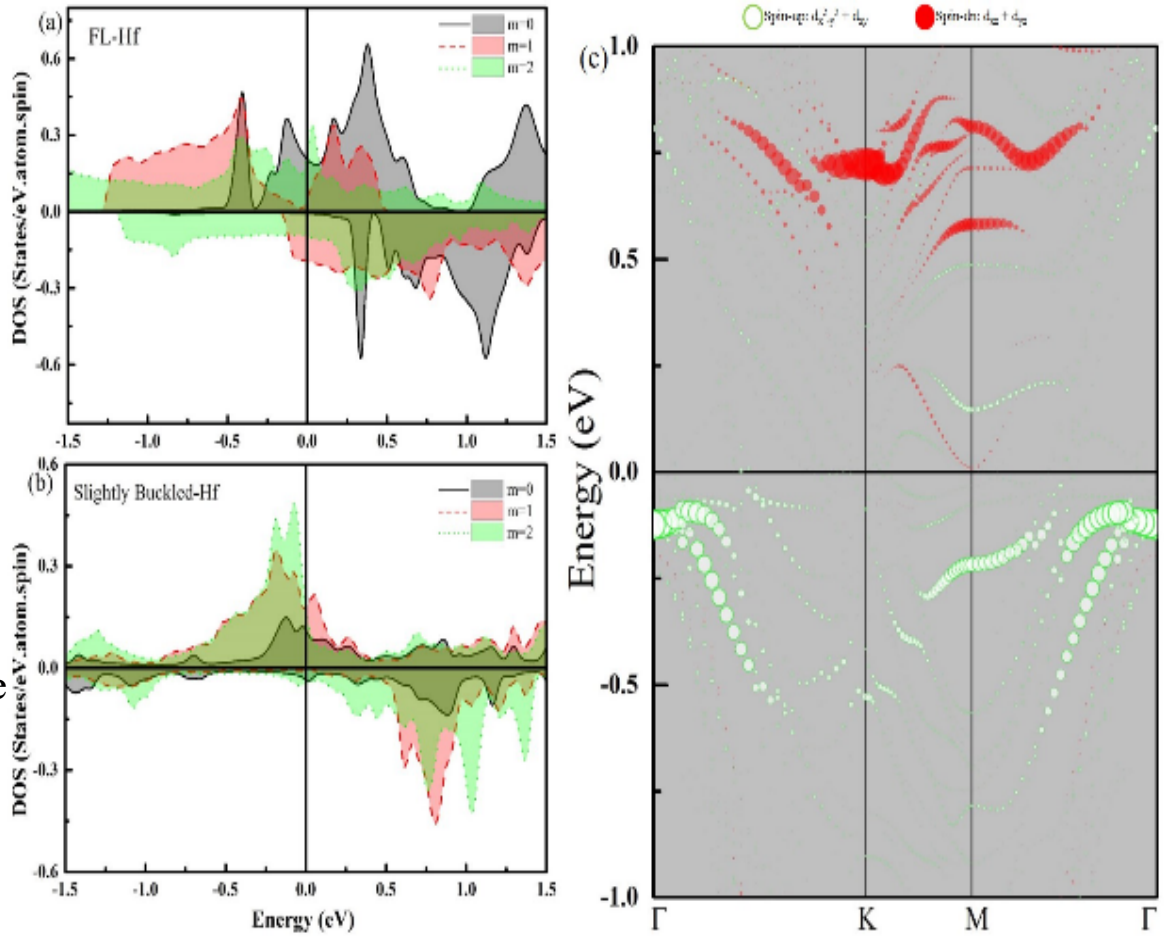
Magnetic Anisotropy : Giant Perpendicular anisotropy (PMA)

- Contribution to the magnetic moment from a pure ➔ out-of-plane orbital |m| = 0 ($d_{z^2-r^2}$) greatly suppressed, resulted in the suppression of the magnetic moment in the substrate supported Hafnene.

- In Hf/BN/Ir(111), in-plane contribution found in the FL Hf disappeared.

- Strongest contribution to the perpendicular magnetization ➔ from the SOC between |m|=2 in the majority spin state & |m|=1 in the minority spin state.

- Major contributions of $d_{x^2-y^2} + d_{xy}$ orbitals near the **Γ point**, while $d_{xz} + d_{yz}$ contributions are strong near **K** & **M points**.



Conclusion

- We investigated the structural and magnetic properties of 2D monolayer Hafnene.

- Unlike the previous report, we found that the 2D hafnene layer had honeycomb buckled geometry in the free-standing structure with NM behavior.

- On the Ir (111) substrate, the structural modification from buckled to flat structure.

- Magnetic state of Hafnene vanished due to hybridization with the Ir(111) surface.

- We reinstated the FM state in the 2D Hafnene ML by inserting a BN spacer layer on the Ir(111) substrate & (BN/Ir(111)).

- We found a giant perpendicular anisotropy energy of 3.41 meV on the BN/Ir(111) surface.

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Two-dimensional honeycomb hafnene monolayer: stability and magnetism by structural transition†

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A few years ago, it was claimed that the two-dimensional ferromagnetic planar Hf monolayer could be synthesized on Ir(111). However, several questions remained unanswered. Herein, we unravel the structural stability of the HF monolayer and its influence on magnetism using first principles calculations. Despite the ferromagnetic state in the planar free-standing Hf layer, extensive systematic calculations with phonon spectra reveal that the planar free-standing Hf layer is unstable and it has a non-magnetic high-buckled structure in the ground state. We also find a structural transition from buckled to flat honeycomb geometry on the Ir(111) substrate. Nonetheless, 2D hafnene has no magnetic state due to strong hybridization with the Ir(111) surface. The evolution from the non-magnetic to the ferromagnetic state combined with structural transition is observed by adding BN as a spacer layer on the Ir(111) substrate (BN/Ir(111)). In addition, we find that 2D Hf on BN/Ir(111) has a giant perpendicular magnetic anisotropy of 3.41 meV.

THANK YOU!