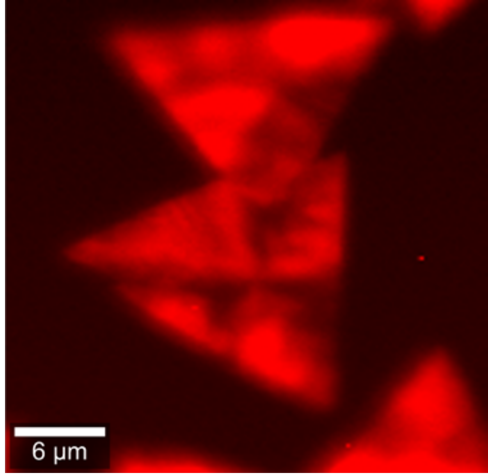
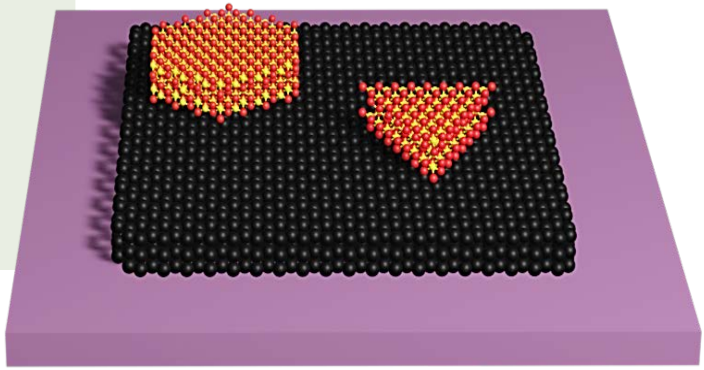
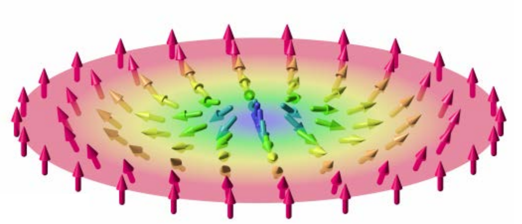
Engineered 2D Quantum Materials, ICTS Bengaluru, 15-26 July 2024

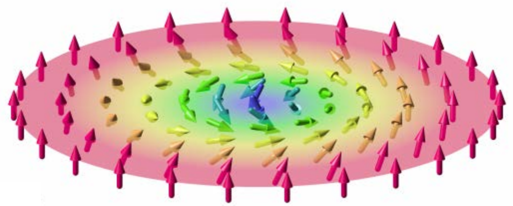


VAN DER WAALS EPITAXIAL GROWTH OF 2D/QUASI-2D MATERIALS & THEIR PROSPECTS FOR OPTOELECTRONIC AND SPINTRONIC DEVICES



Vidya Kochat
IIT Kharagpur
vidya@matsc.iitkgp.ac.in



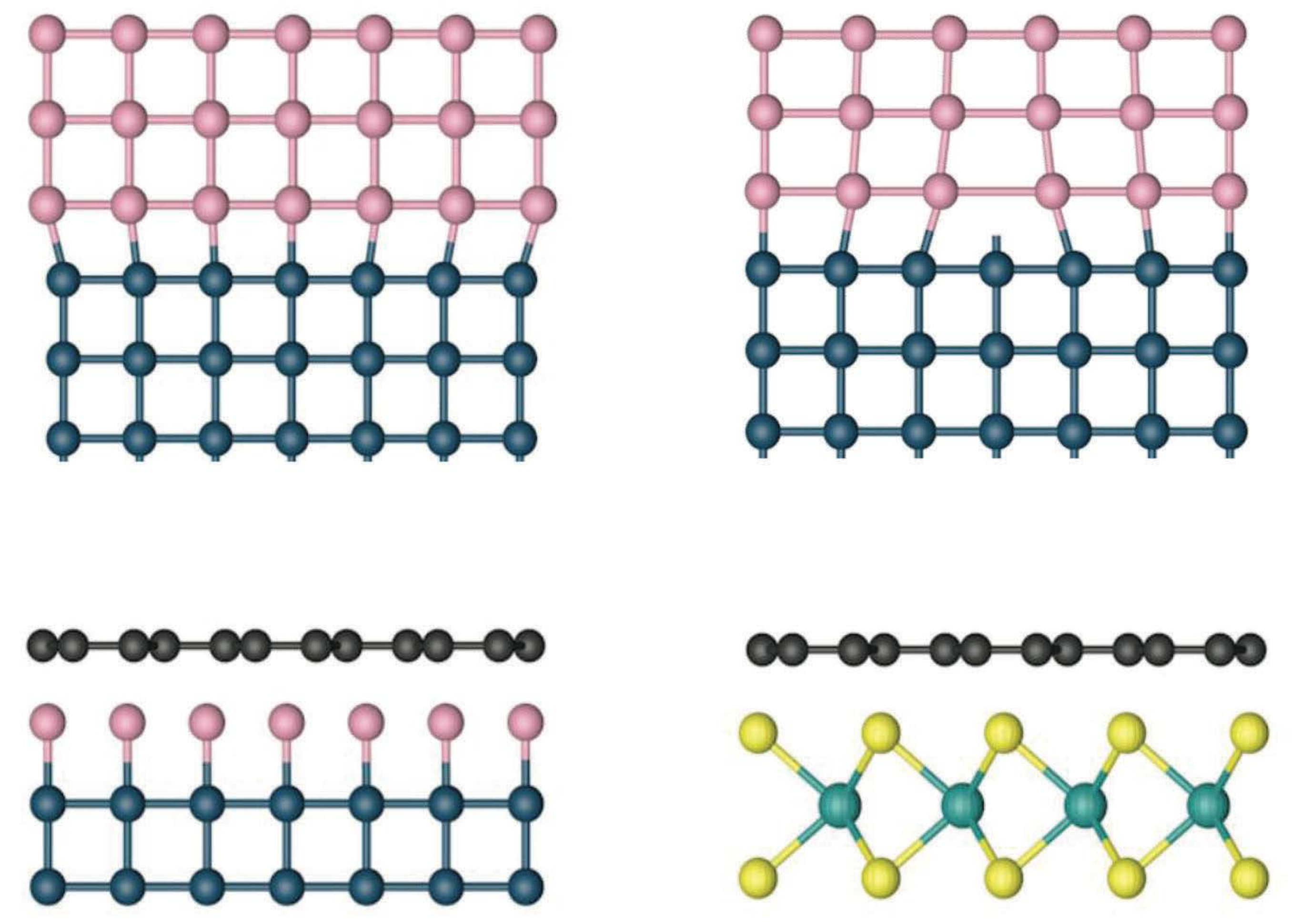


van der Waals epitaxy

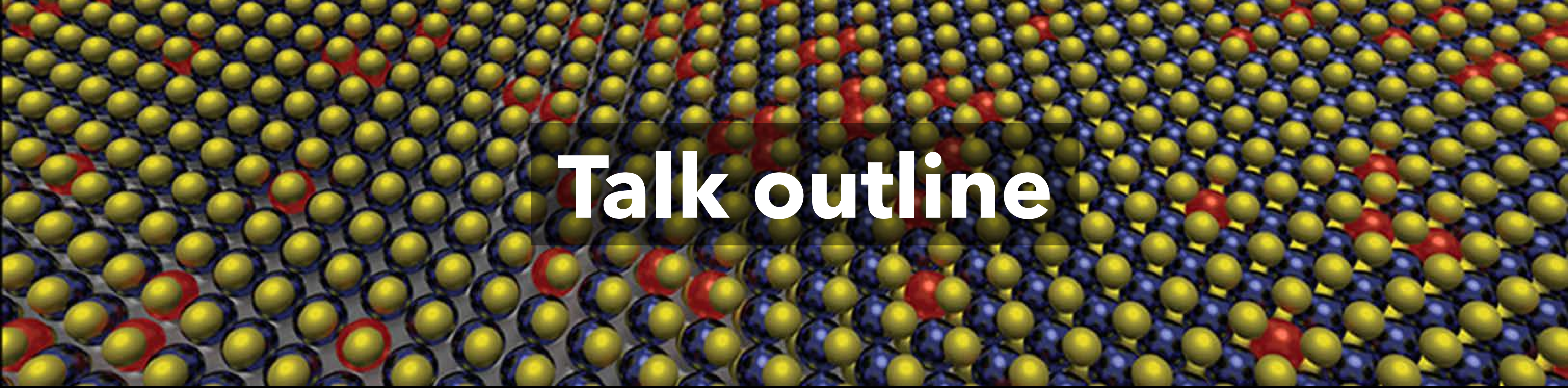
vdW epitaxy is the growth mechanism of epitaxial layers on crystalline substrates governed by weak van der Waals forces between the epilayer and substrate.

Heterointerfaces with negligible strain, despite large lattice mismatch and thermal expansion coefficients.

Conventional epitaxy



van der Waals epitaxy



Talk outline

01

Epitaxy of 2D/ quasi-2D materials growth

02

Quasi-2D magnet - $Cr_{1+x}Te_2$

Growth, non-collinear magnetism and prospects for spintronics

03

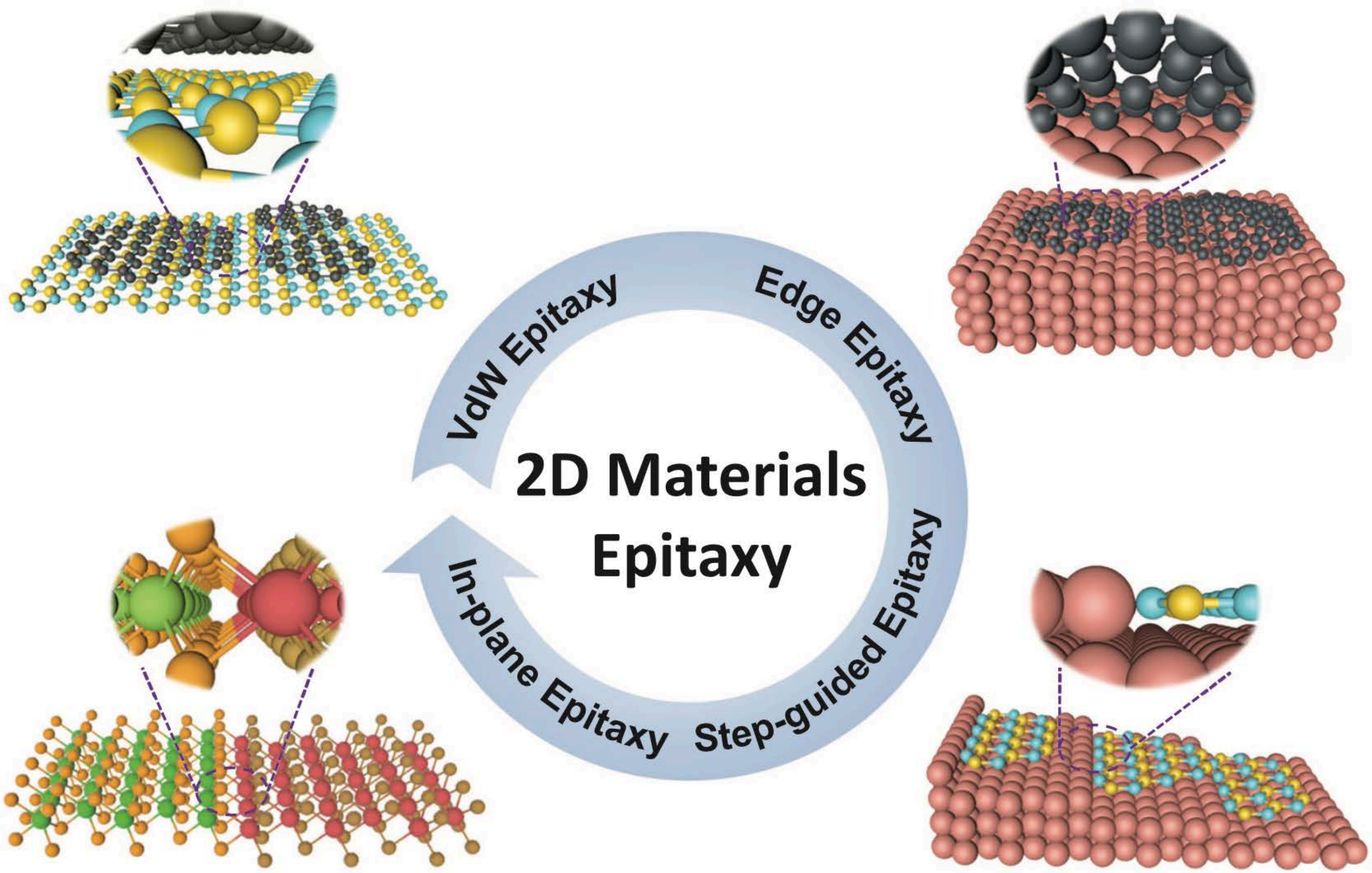
2D semiconductors – WSe_2

Optical emission signatures and prospects for optoelectronics

04

Conclusions
The future

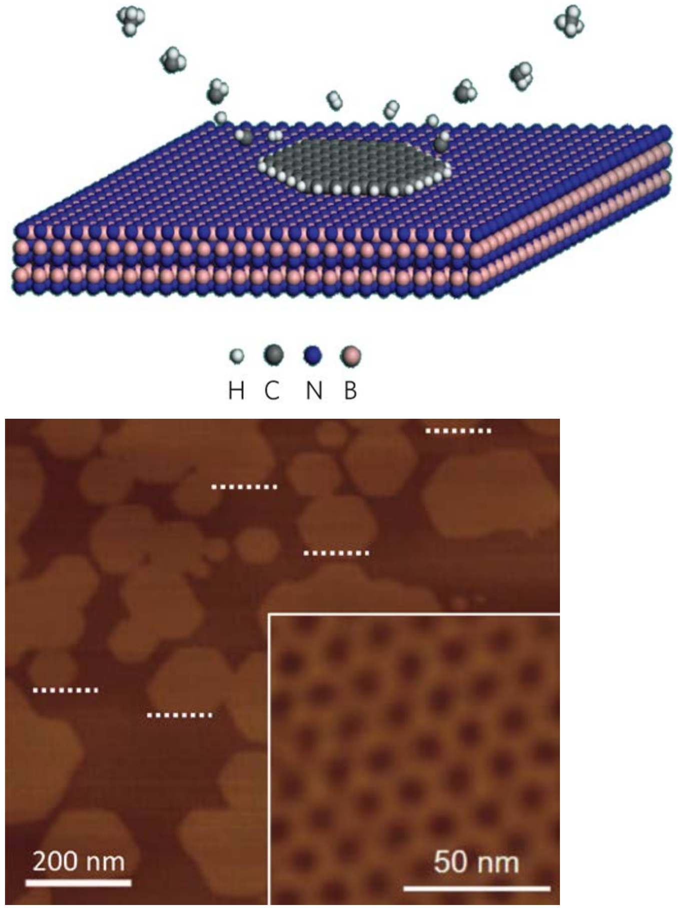
Epitaxy of 2D materials growth



Adv. Sci. **2022**, *9*, 2105201

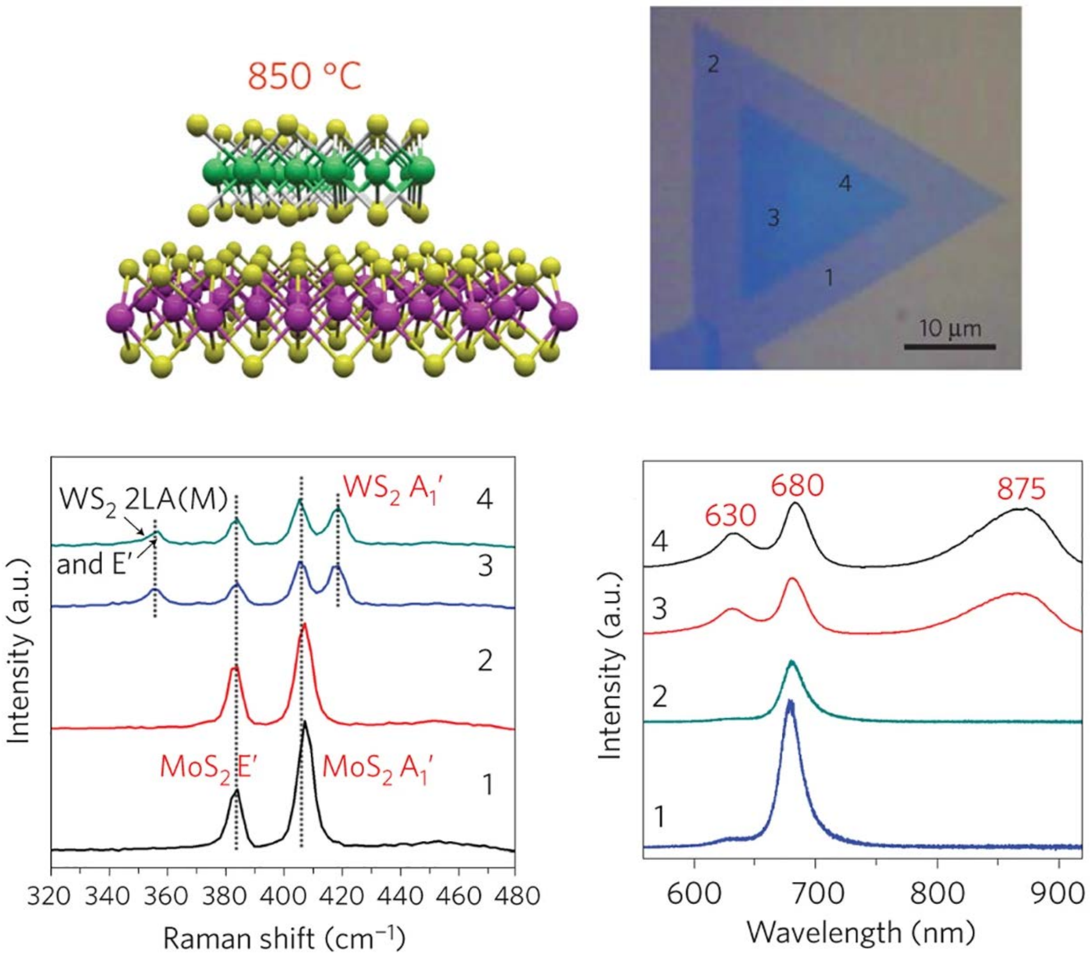
van der Waals epitaxy

Epitaxial growth of graphene on hexagonal boron nitride



Nat. Mater. **2013**, *12*, 792

Vertical heterostructures from WS_2/MoS_2monolayers

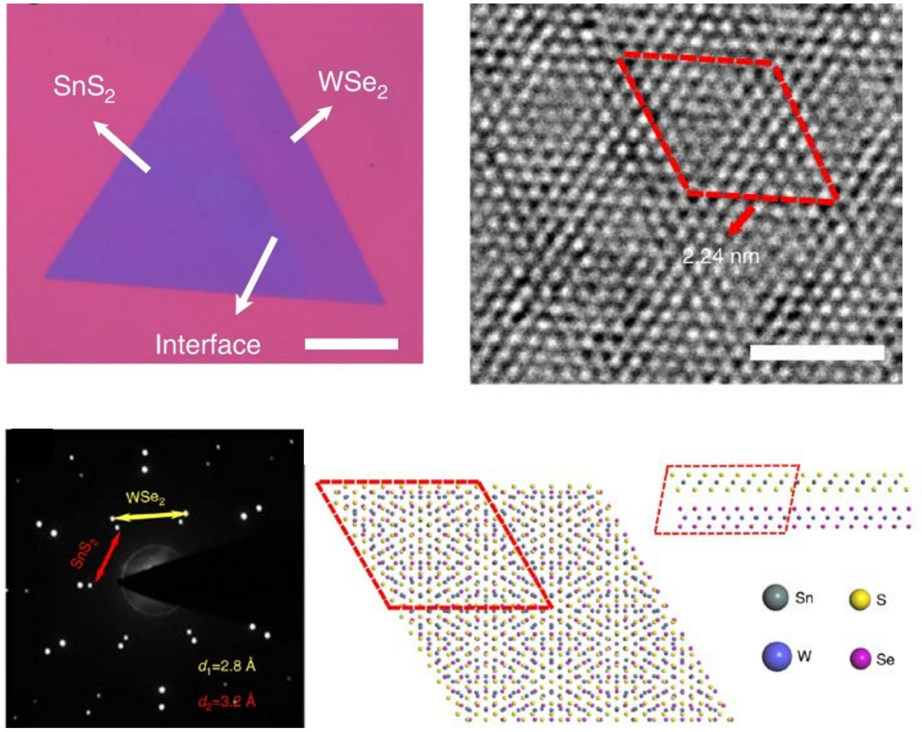


Nat. Mater. **2014**, *13*, 1135

van der Waals epitaxy

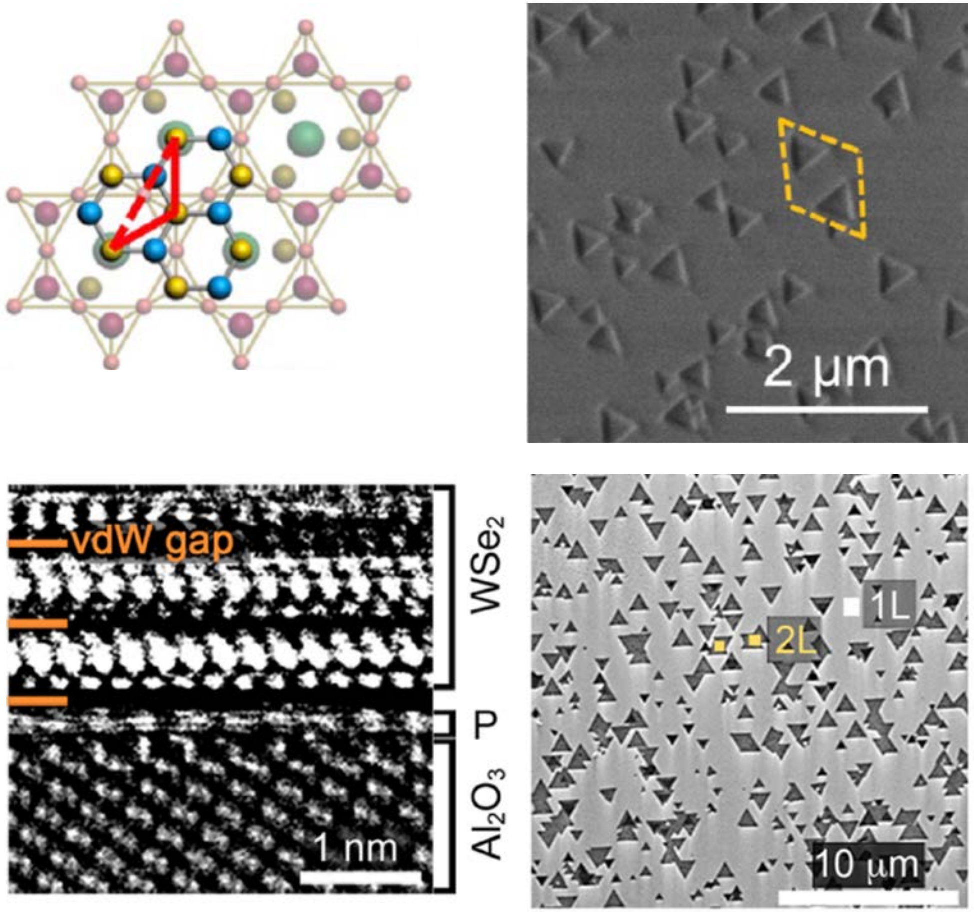
Possible with large lattice mismatch (as high as 50%) and between different crystal structures

WSe_2/SnS_2 vertical heterostructures



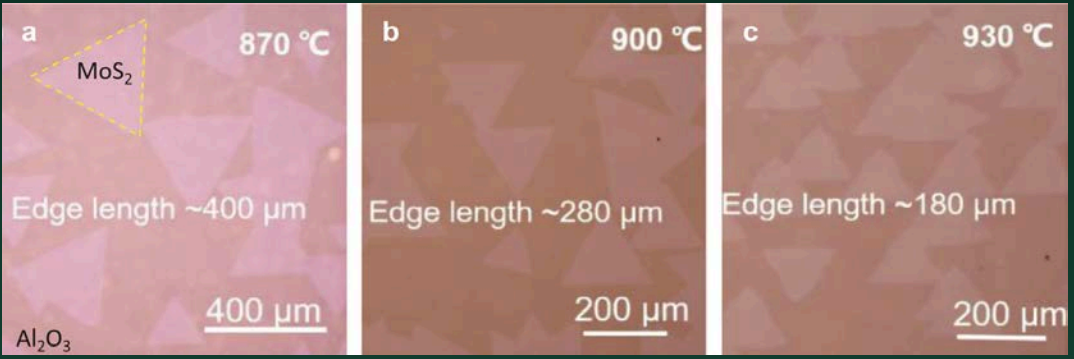
Nat. Commun. **2017**, *8*, 1906

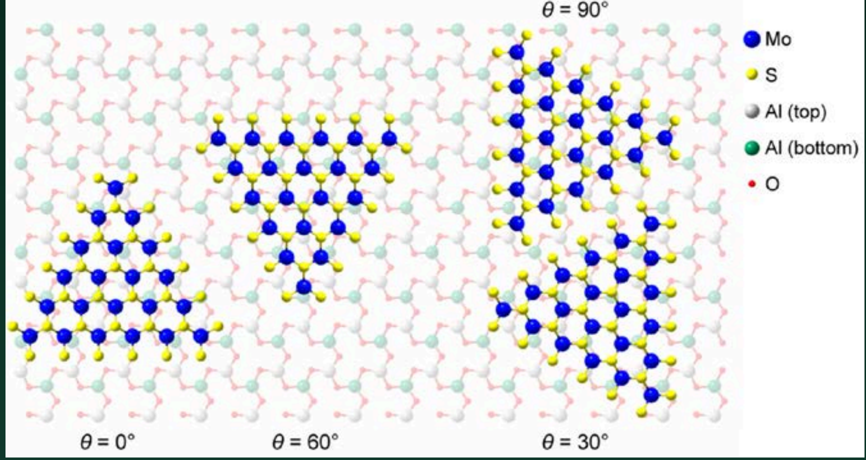
Epitaxial TMD monolayers on mica and sapphire



Nano Lett. **2013**, *13*, 3870
ACS Nano **2018**, *12*, 965

Modulating vdW epitaxy





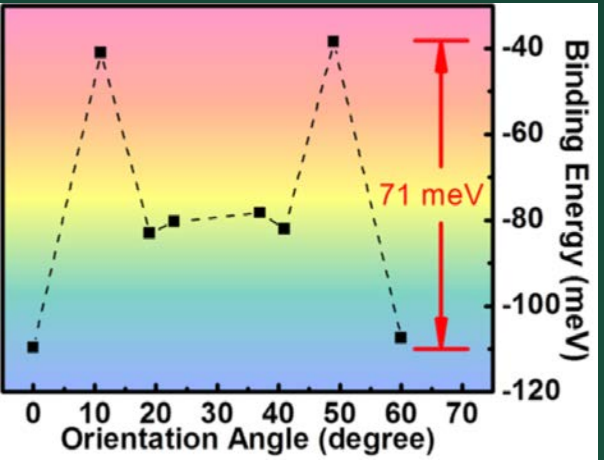
ACS Nano 2015, 9, 4611

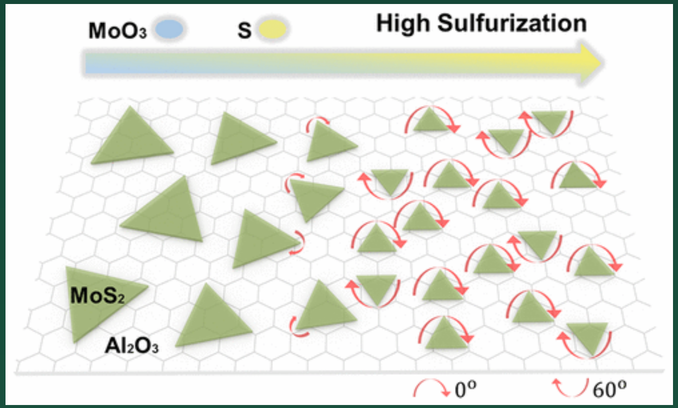
Nano Lett. **2020**, *20*, 7193
Nano Lett. **2015**, *15*, 198

Temperature

Precursor concentration

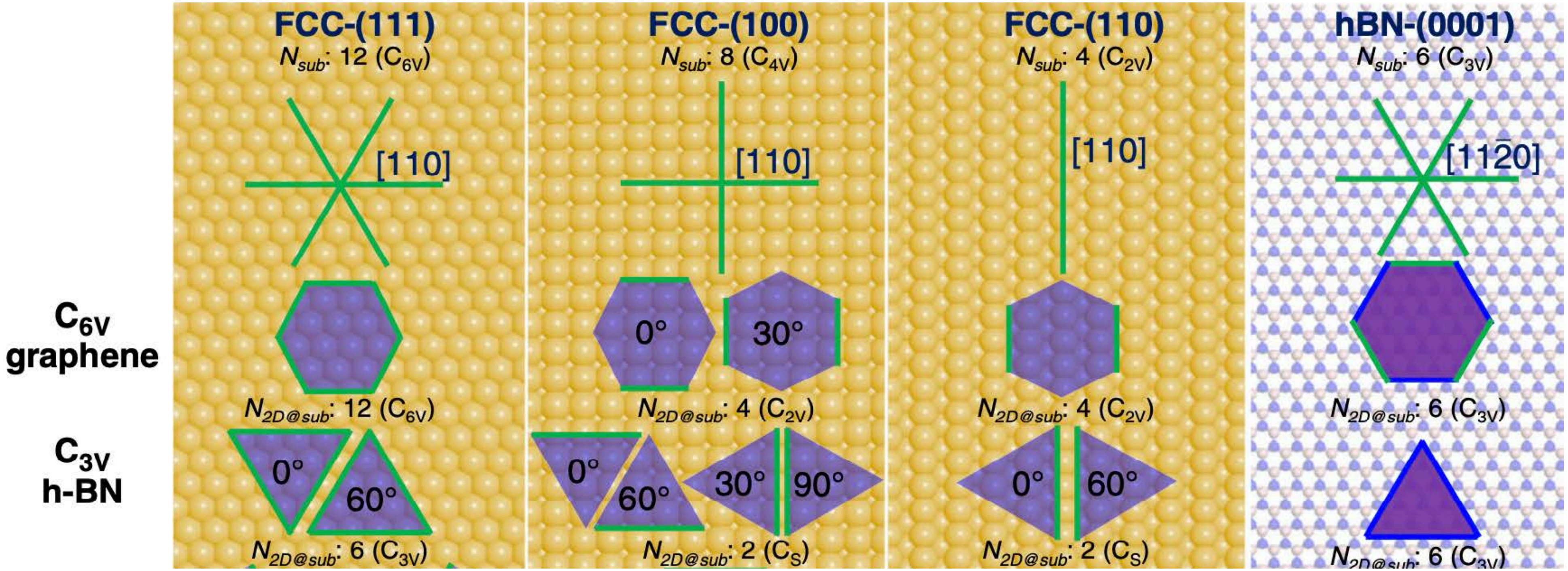
Substrate symmetry





ACS Nano **2017**, *11*, 9215

Interplay of the symmetries of the 2D material and the substrate



The propagating edge of a 2D material tends to align along a high symmetry direction of the substrate.

1, 2, 1 and 1 equivalent but different alignments for a 6-fold symmetric 2D material on 6-, 4-, 2- and 3-fold symmetric substrates

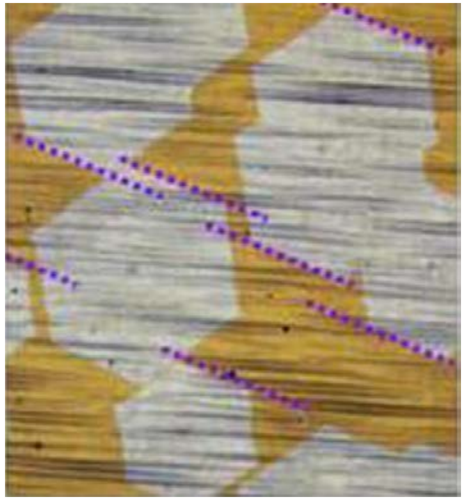
2, 4, 2, and 1 equivalent but different alignments for a 3-fold symmetric 2D material on 6-, 4-, 2- and 3-fold symmetric substrates

Nat. Commun. **2020**, *11*, 5862

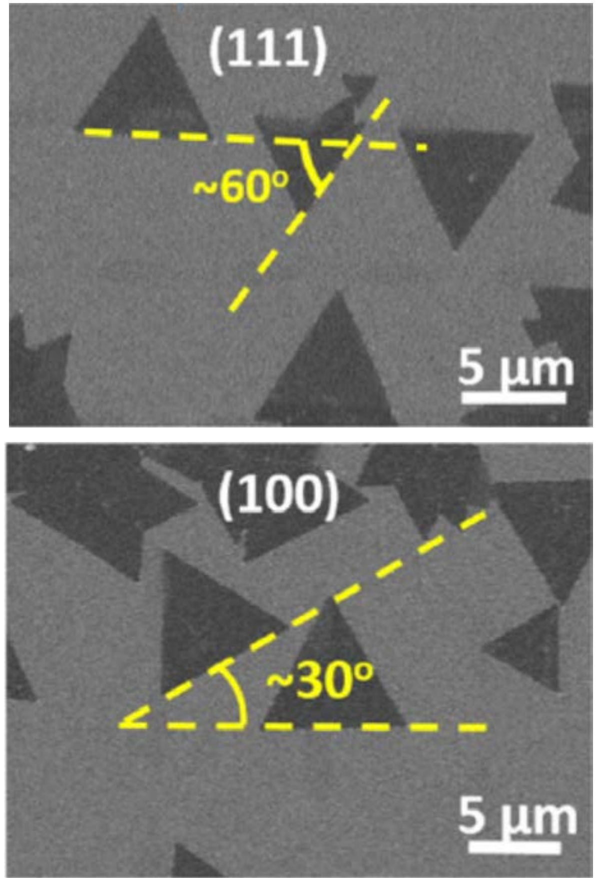
Interplay of the symmetries of the 2D material and the substrate

Experimental observations

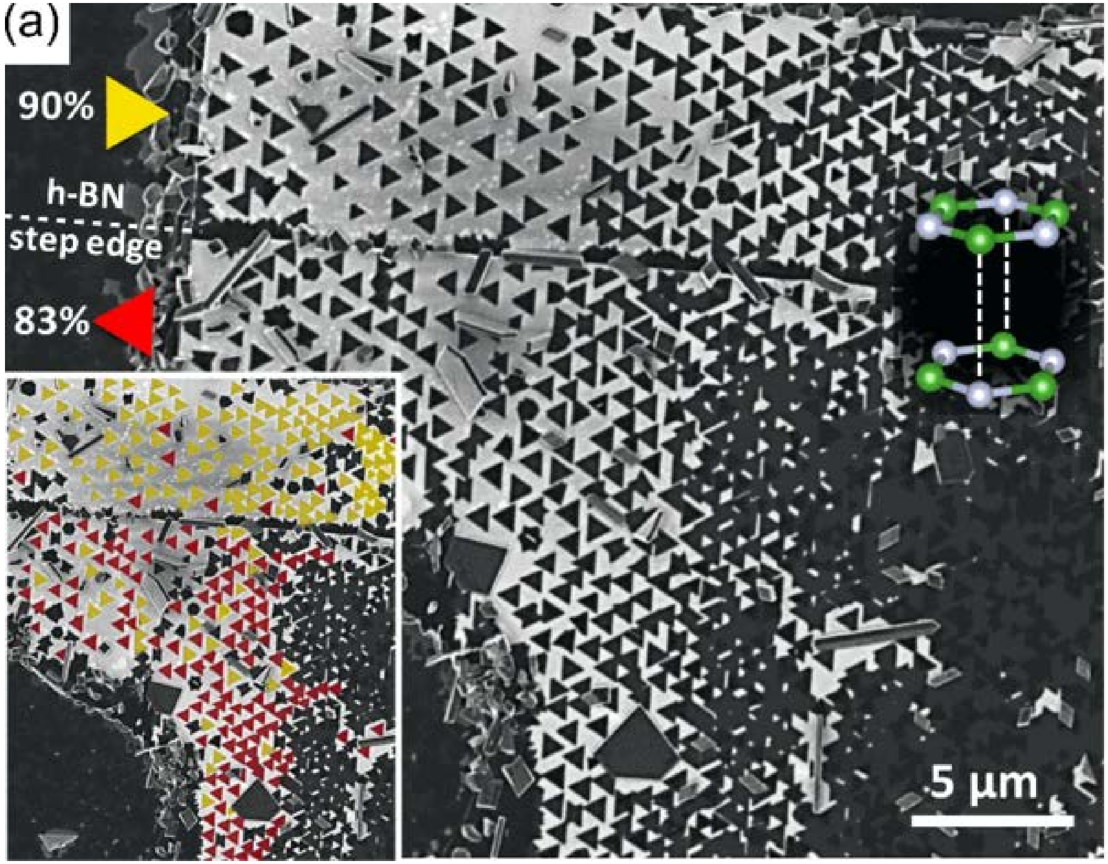
Graphene on Cu(111)



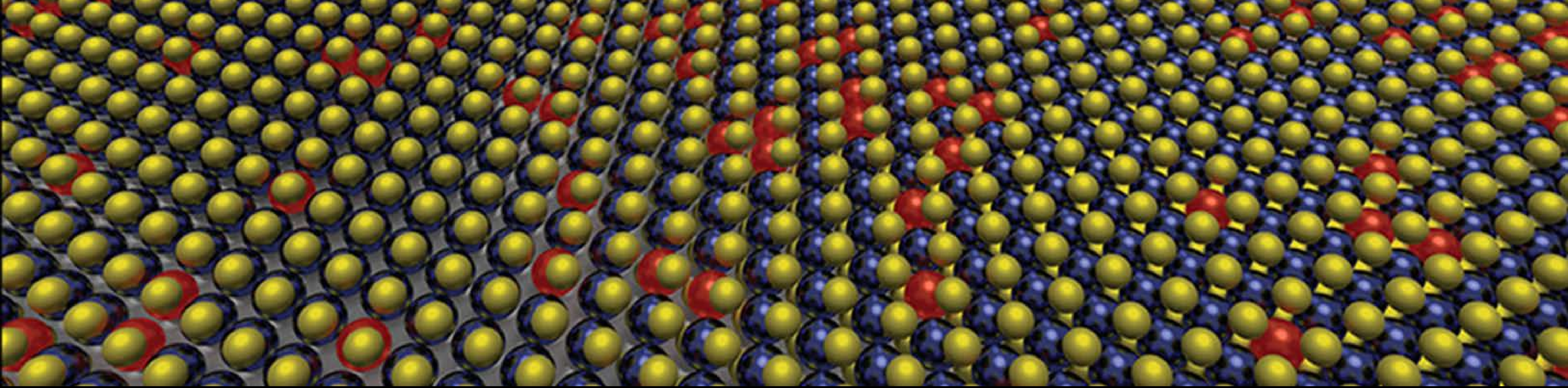
h-BN on Cu (111) & Cu (100)



MoS_2 on h-BN



Sci. Bull. **2017**, *62*, 1074
Nano Res. **2015**, *8*, 3164
Phys. Rev. B **2019**, *99*, 155430

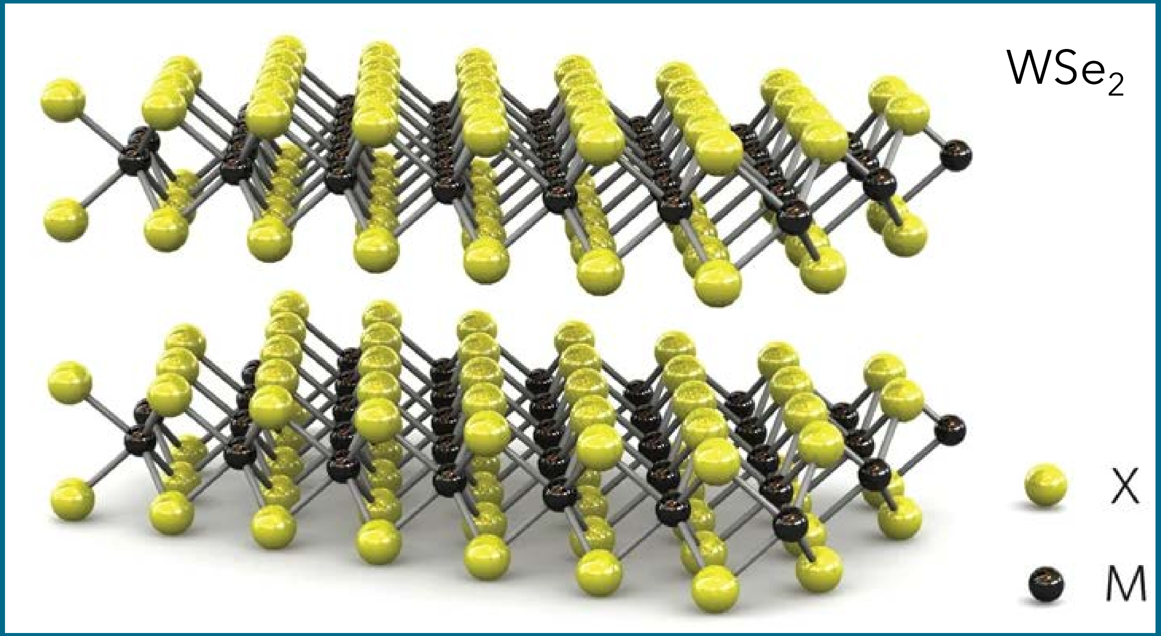


Quasi-2D magnet - $Cr_{1+x}Te_2$

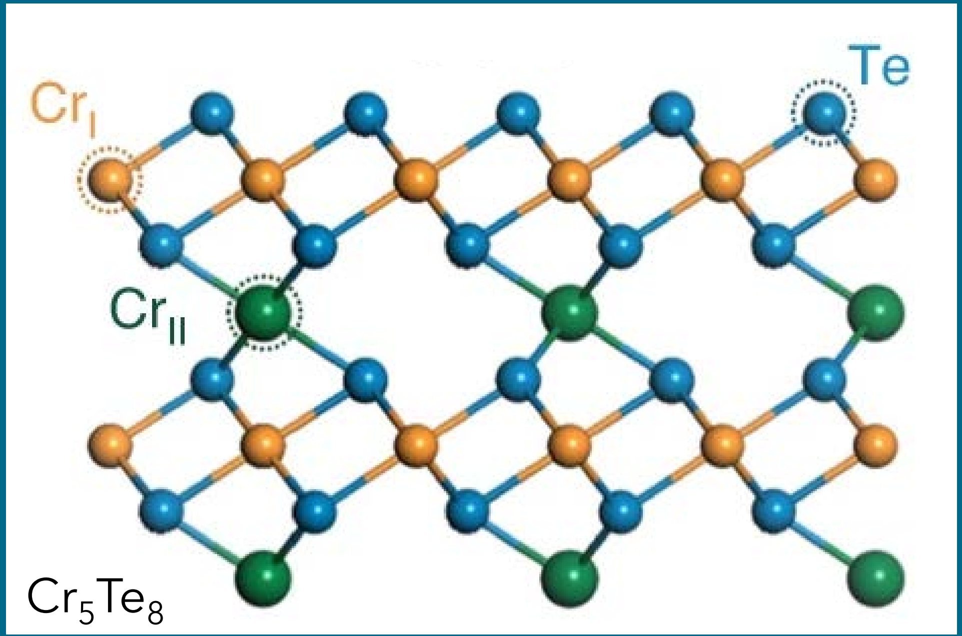
Growth, non-collinear magnetism and prospects for spintronics

Quasi-2D materials

Two dimensional materials manifest two distinct forms: layered and non-layered, based on the strength of the interlayer coupling effect.

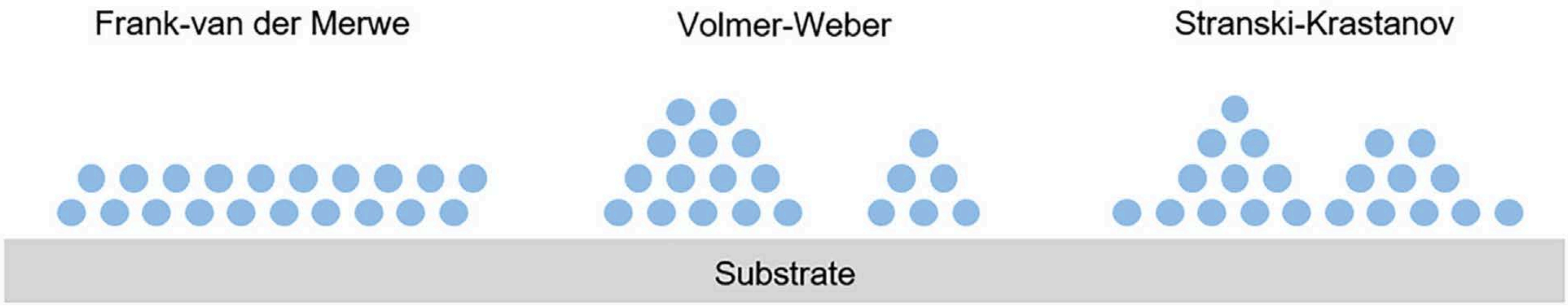


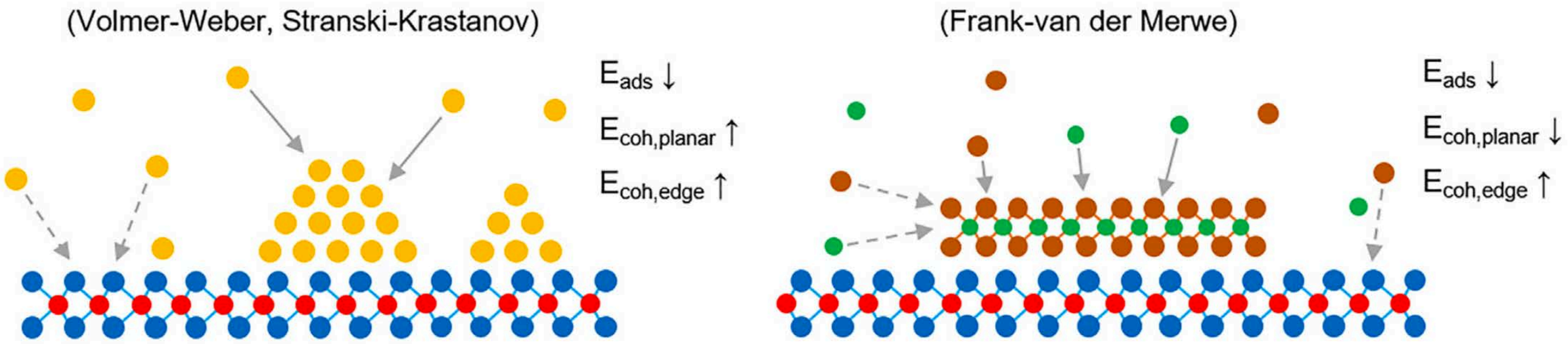
2D materials : atomically thin layers interconnected by vdW forces



Quasi-2D materials : 2D non-vdW materials with covalently bonded intercalants between layers of unit cell thickness

Epitaxial growth of quasi-2D materials

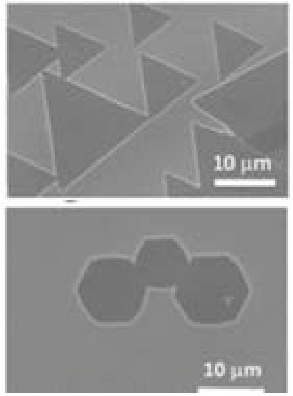




Kinetics of growth

ATTACHMENT-LIMITED GROWTH

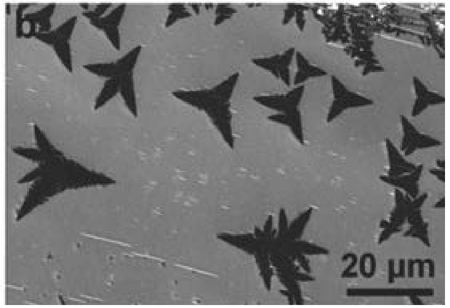
The precursor concentration on the whole substrate is nearly a constant and therefore the growth is dominated by the attachment of precursor atoms at the growing edges of a 2D material.



Single crystalline polygonal domains

DIFFUSION-LIMITED GROWTH

In barrierless attachment of precursor to the edges of a 2D material, there will be a depletion zone around a growing 2D material and the growth must be determined by the diffusion of atoms/molecules on the substrate.



fractal-like shapes

$$R_G = \left(c \cdot v \cdot e^{-E_{ba}/kT} - n_0 \cdot v \cdot e^{-E_{bd}/kT}\right) \cdot s_0$$

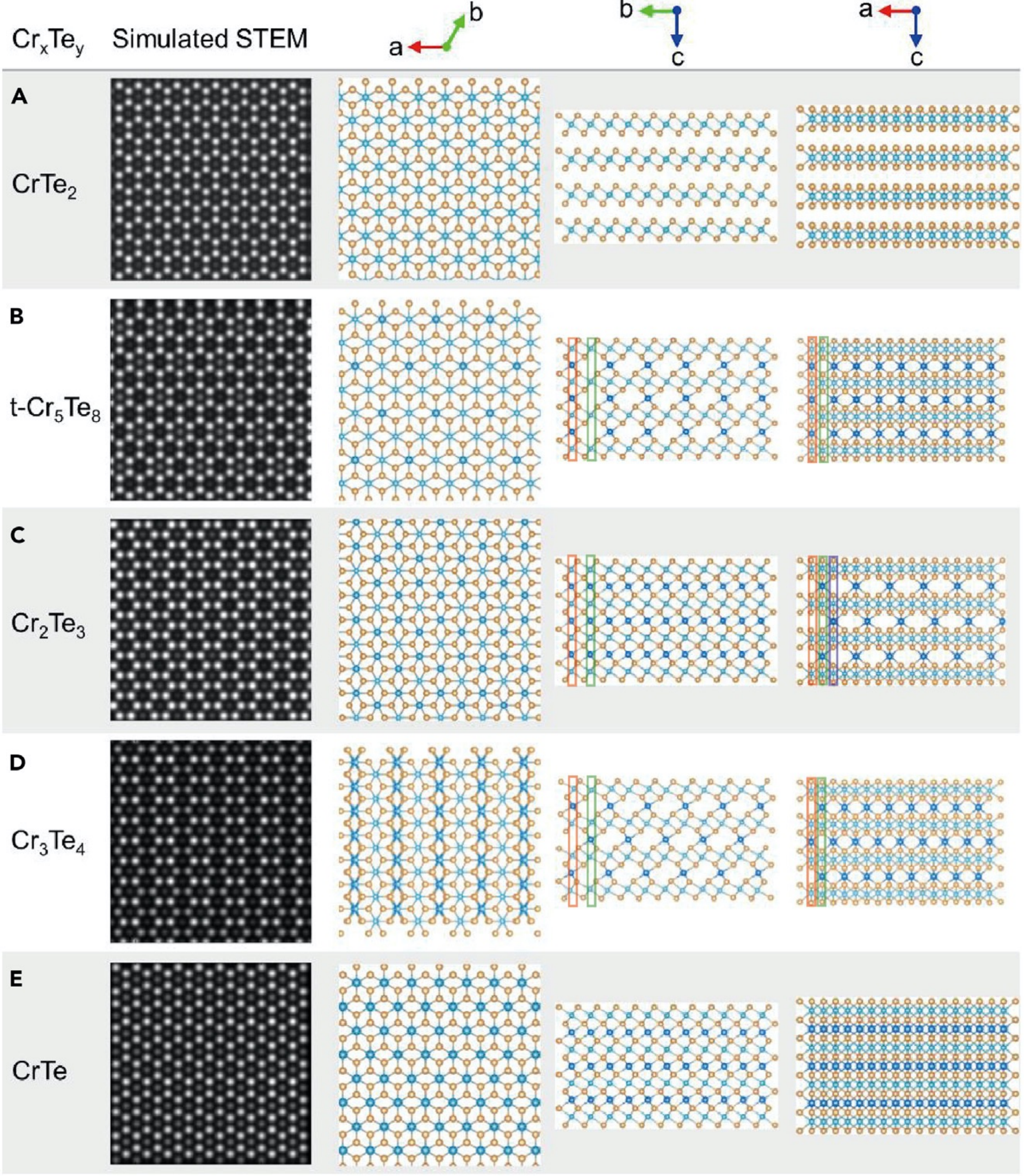
For growth of material :

$$E_{bd} - E_{ba} < kT \times \ln\left(\frac{c}{c_0}\right)$$

Conditions for attachment-limited growth of 2D single crystals

1) *Atomic attachment/detachment is very slow (E_{bd} & E_{ba} large)*
2) *Diffusion of atoms on the substrate is extremely fast*
3) *Atomic flux is sufficient large*

Quasi-2D magnet - $Cr_{1+x}Te_2$



$P\bar{3}m1$

1T $CrTe_2$ – layered material

$P\bar{3}m1$
25%

$Cr_{1+x}Te_2$ compounds:
Cr self-intercalation of the $CrTe_2$ backbones

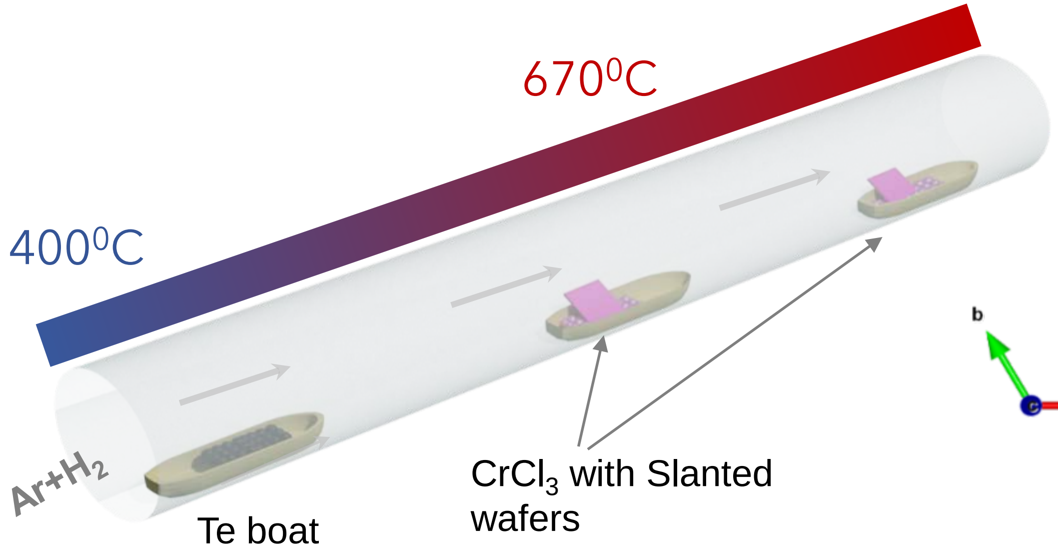
$P\bar{3}1c$
33.3%

By self-intercalation of the native Cr atoms, the in-plane anisotropy of $CrTe_2$ can be switched to perpendicular magnetic anisotropy.

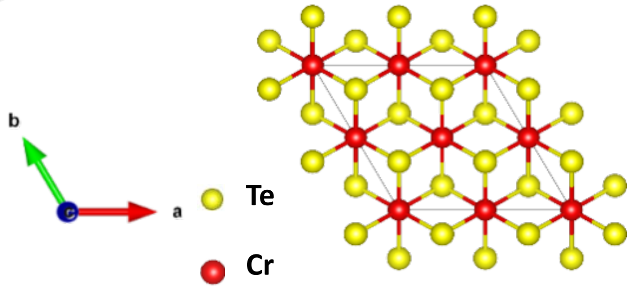
$P2/m$
50%

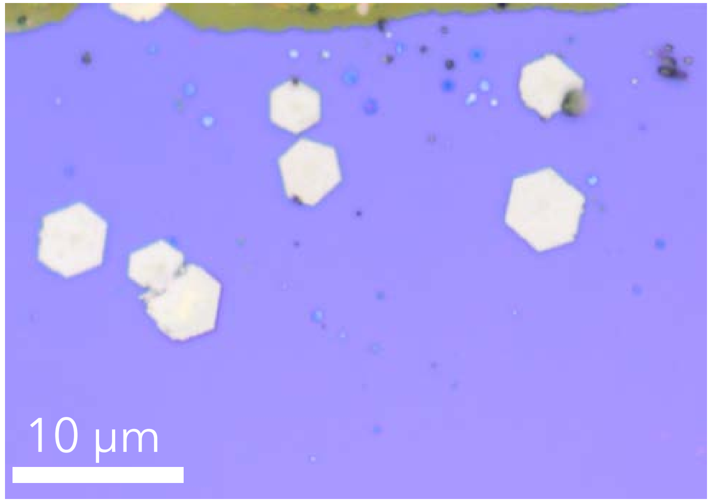
$P6_3/mmc$

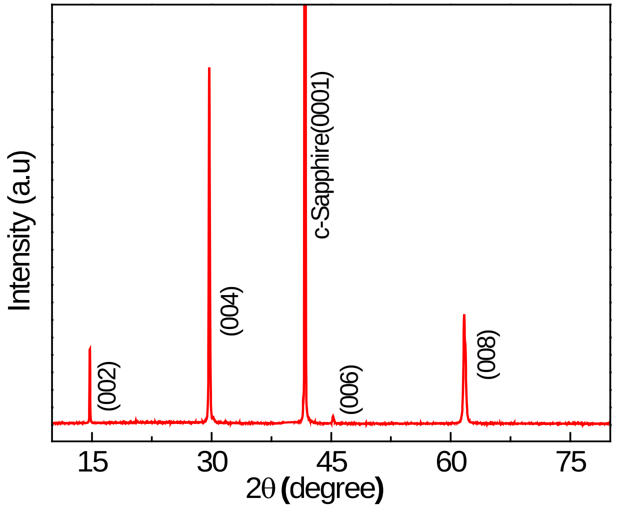
Growth of Quasi-2D Cr_5Te_8

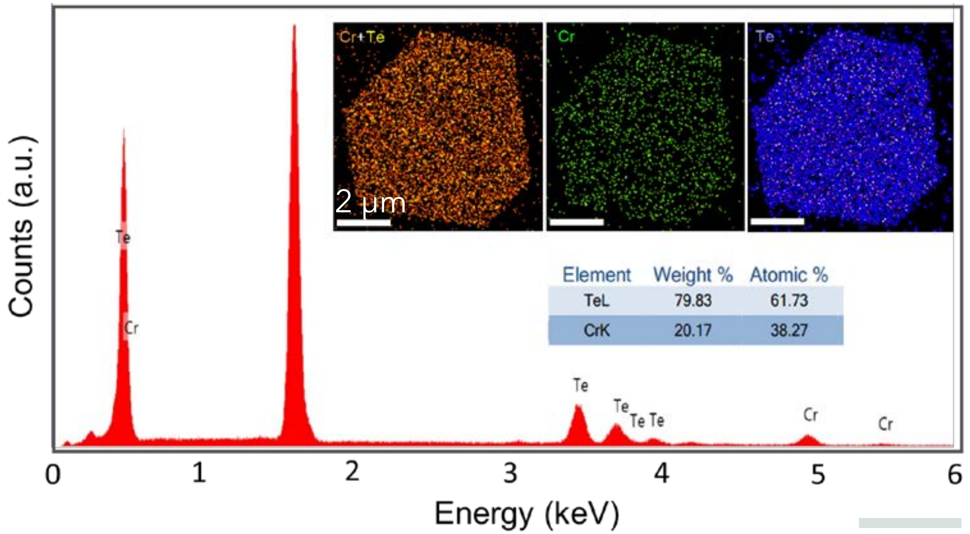


t-Cr_5Te_8









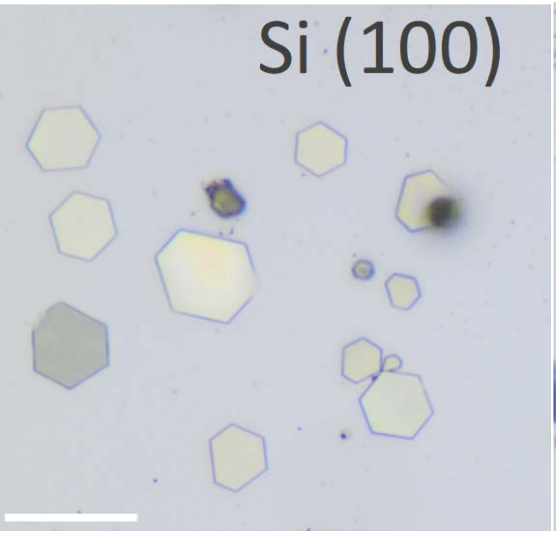
Growth conditions

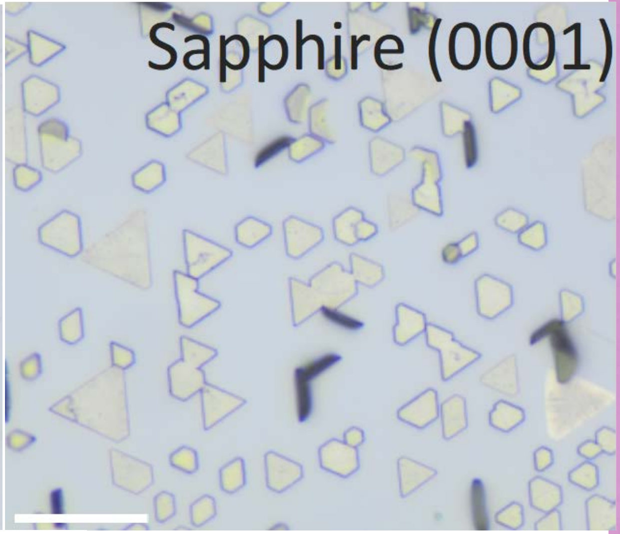
Precursors: 60 mg Te, 5 mg $CrCl_3$

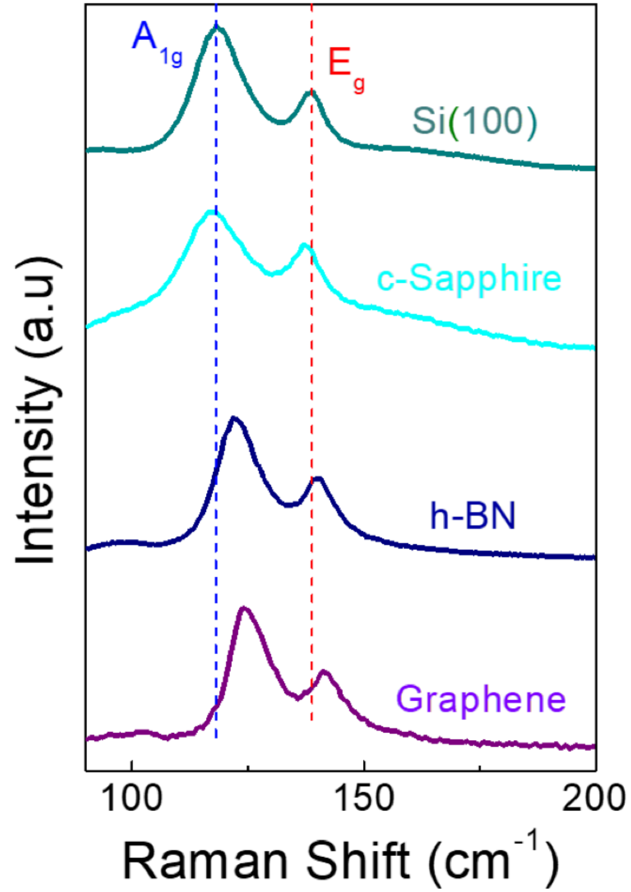
Gas flow: 100 sccm Ar + 10 sccm H_2

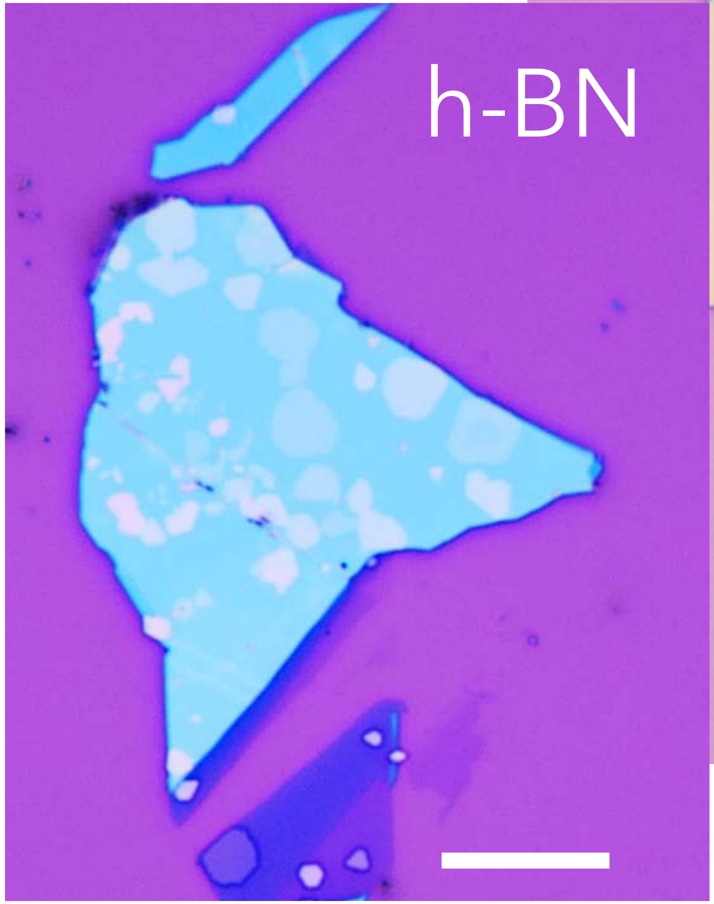
Growth time : 4 min

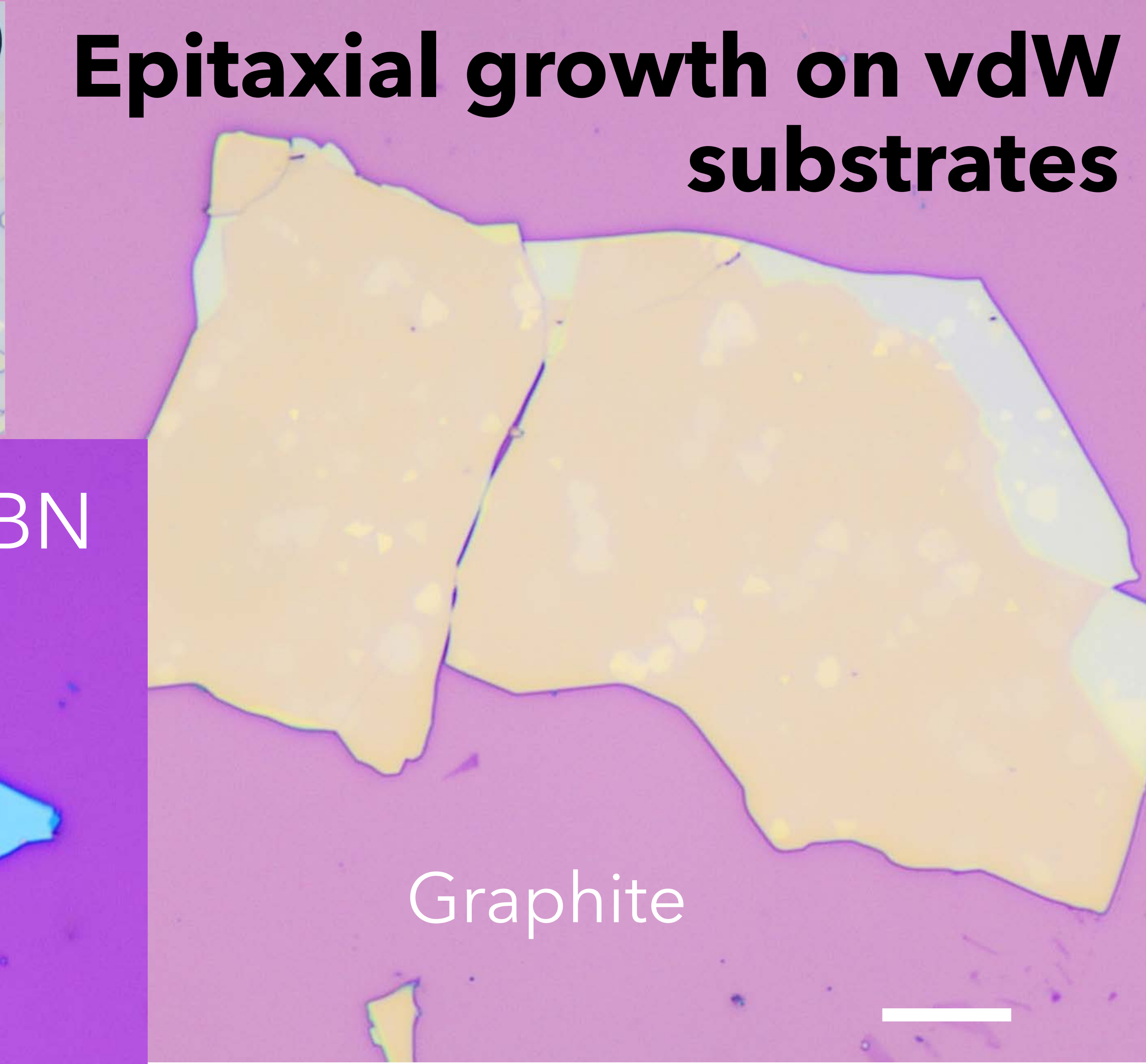
Epitaxial growth on vdW substrates





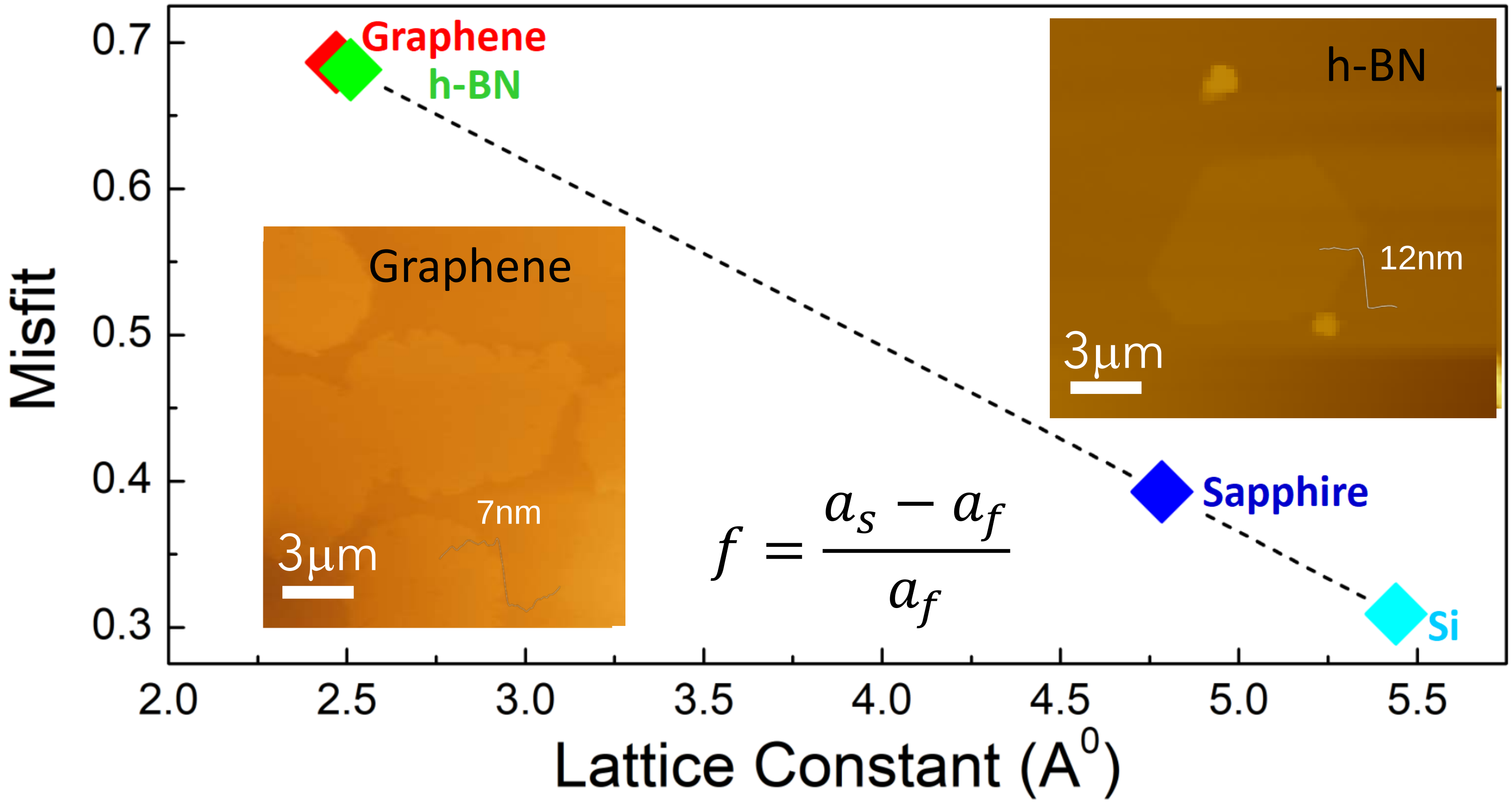






Scale bar = 10 μm

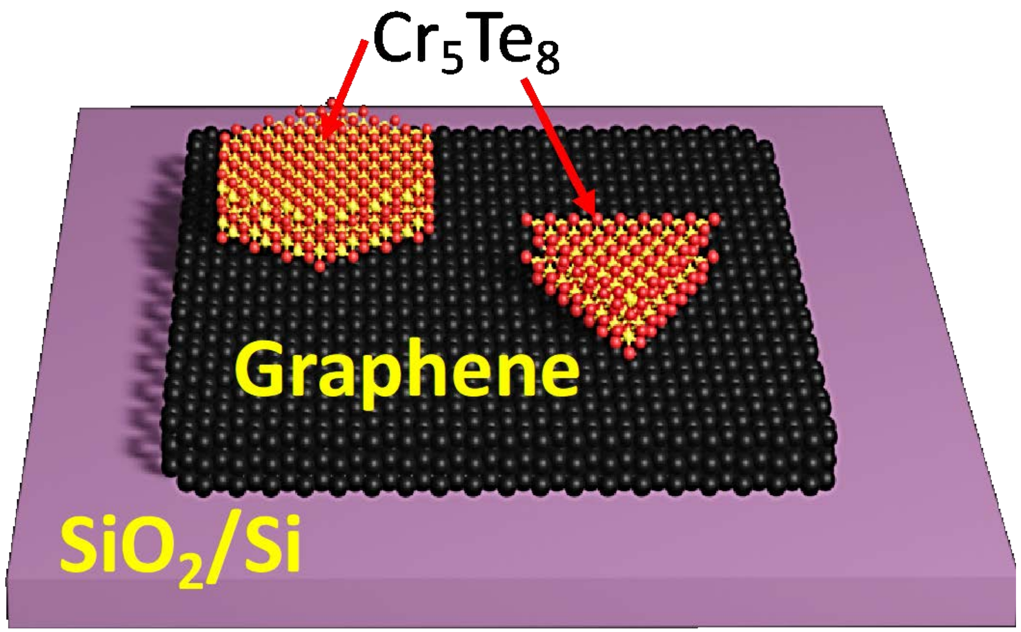
Substrate criticality in vdW epitaxy



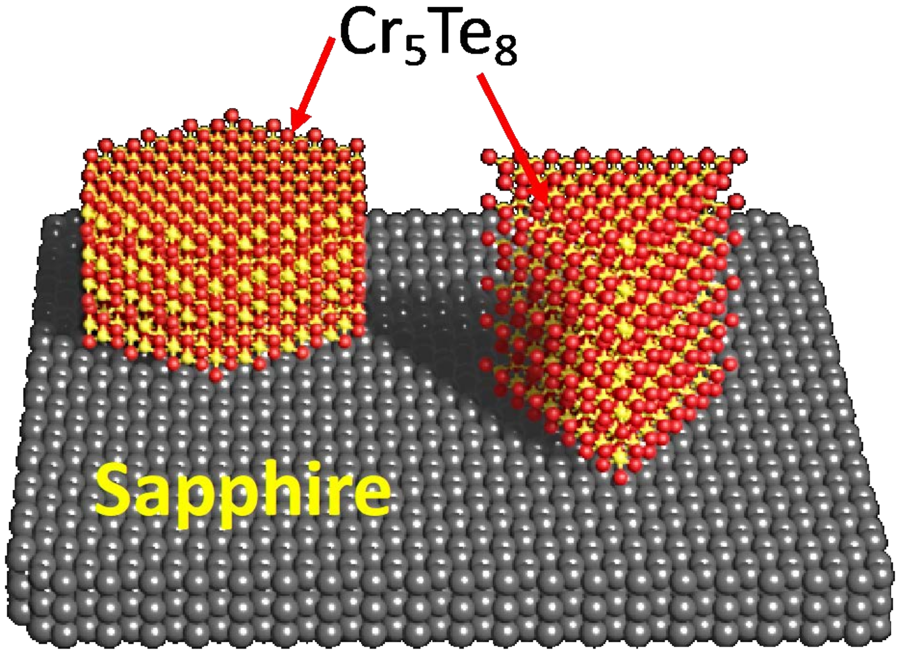
$$f = \frac{a_s - a_f}{a_f}$$

Strain effect in vdW epitaxy

Frank – van der Merwe growth
Layer-by-layer growth

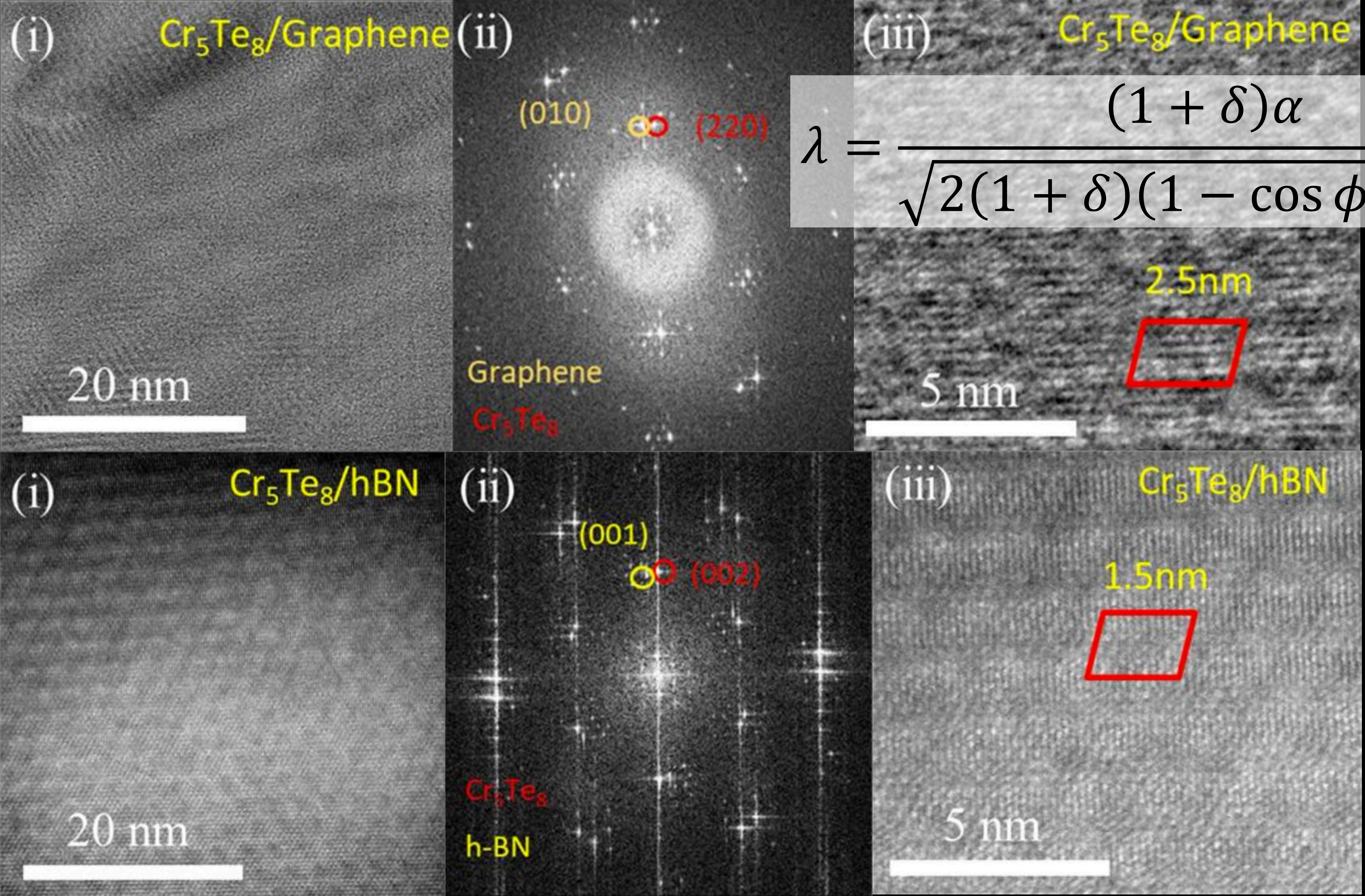


Volmer – Weber growth
Island growth



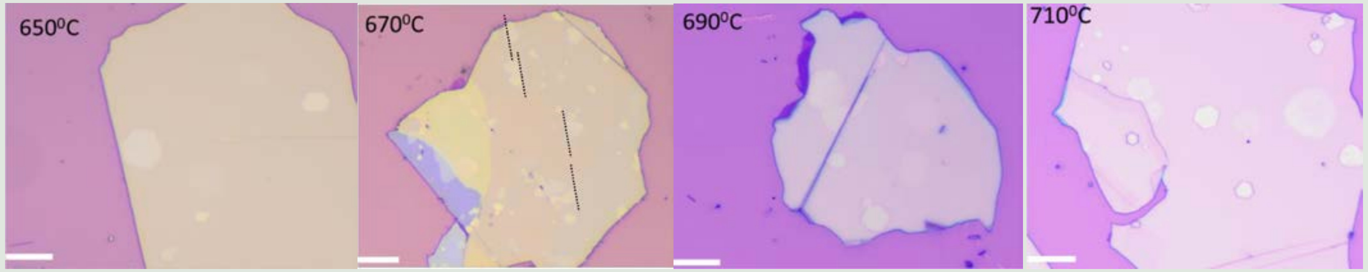
Moiré superlattice

$$\lambda = \frac{(1+\delta)\alpha}{\sqrt{2(1+\delta)(1-\cos\phi)+\delta^2}}$$

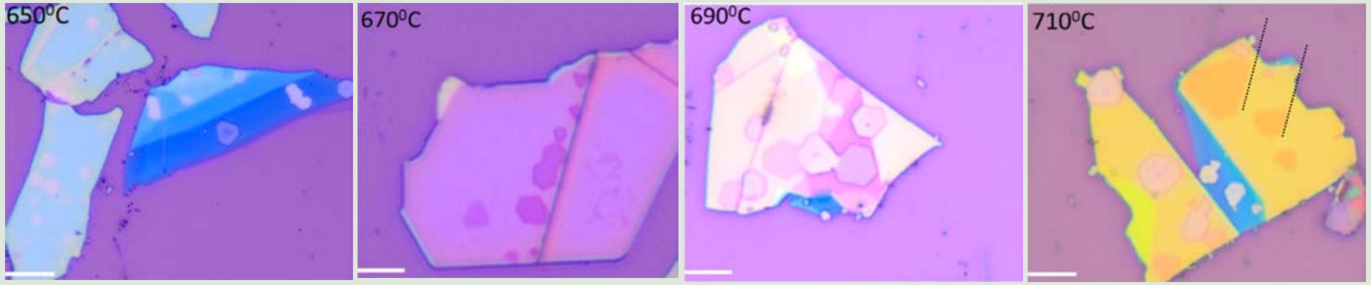


Effect of growth parameters

Temperature



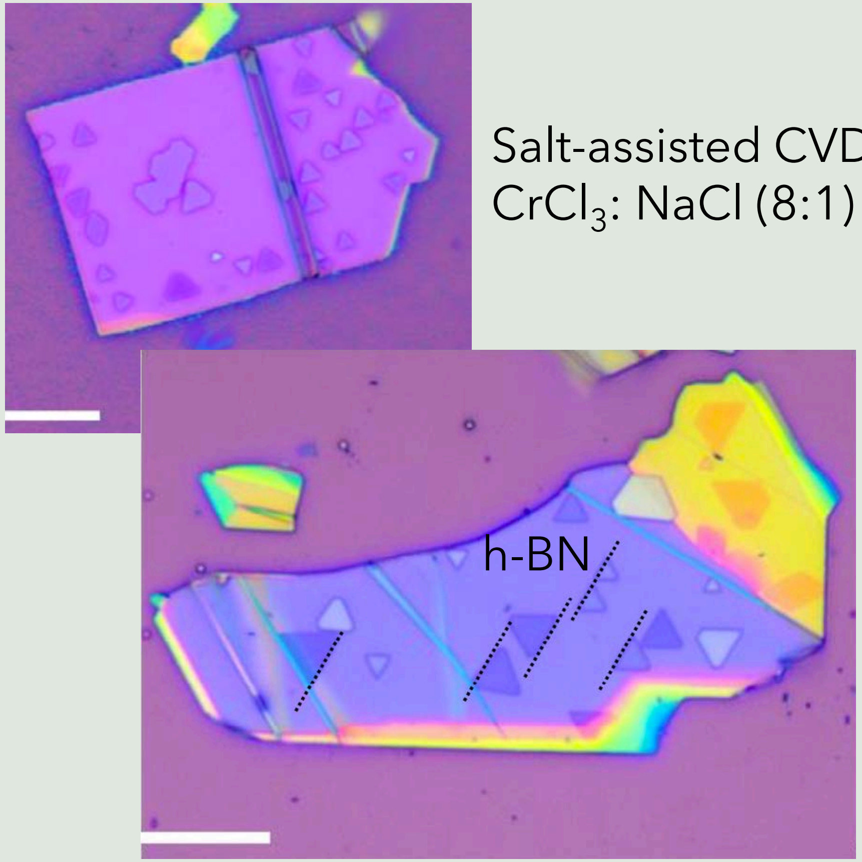
Graphite



h-BN

Scale bar = 10 μm

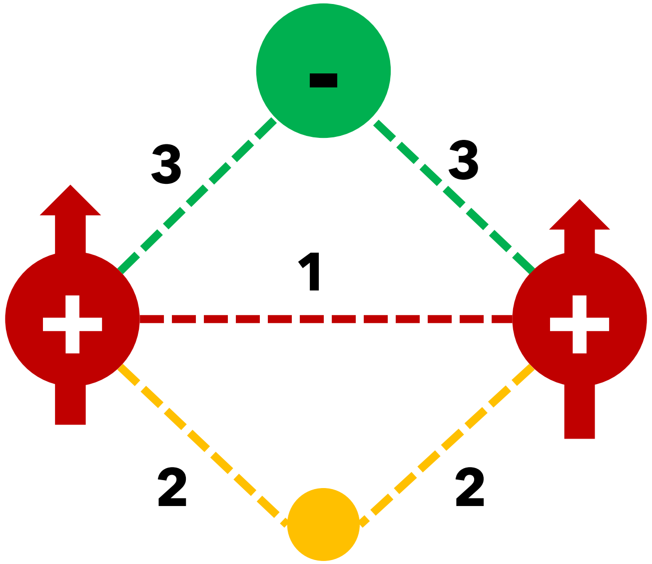
Precursors



Salt-assisted CVD
$CrCl_3$: NaCl (8:1) and Te

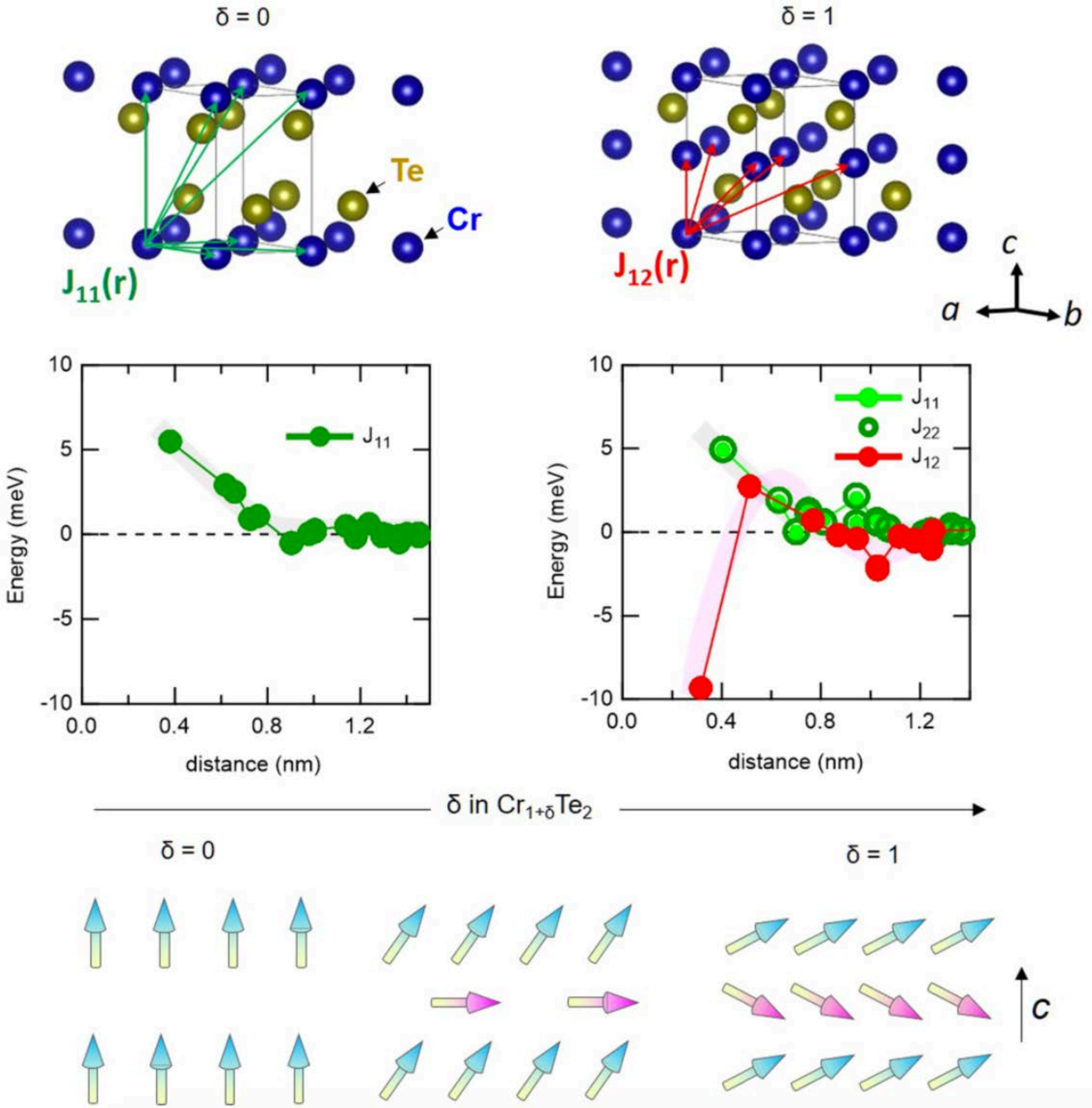
Magnetism in $Cr_{1+\delta}Te_2$

Exchange interaction



1. Antiferromagnetic Cr-Cr direct exchange interaction

2. Ferromagnetic t^3-t^3 superexchange interaction in the Cr-Te-Cr unit

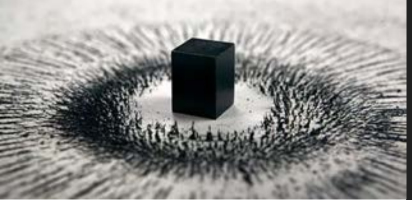


Non-collinear Magnetism in $Cr_{1+\delta}Te_2$

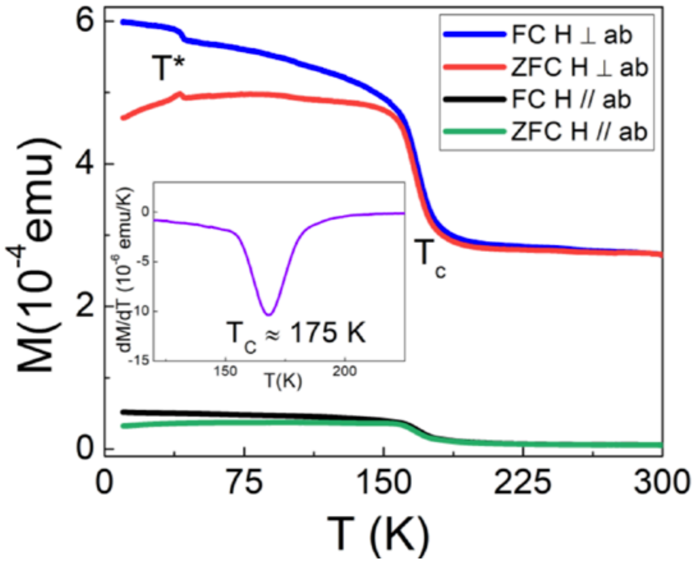
DFT-calculated direct exchange interactions for pairs of atoms intra-sublattice (J_{11}, J_{22}) and inter-sublattice (J_{12}) as a function of atomic separation

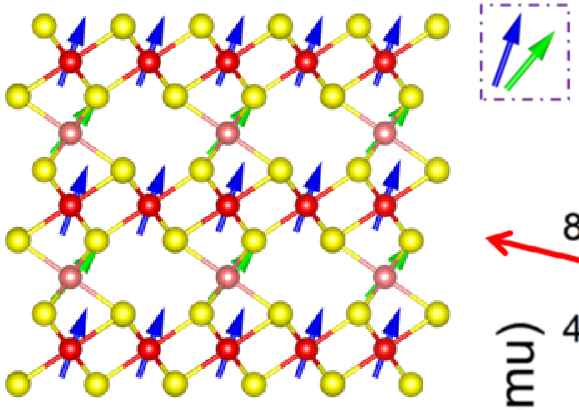
Evolution of ground-state magnetic configuration of $Cr_{1+\delta}Te_2$

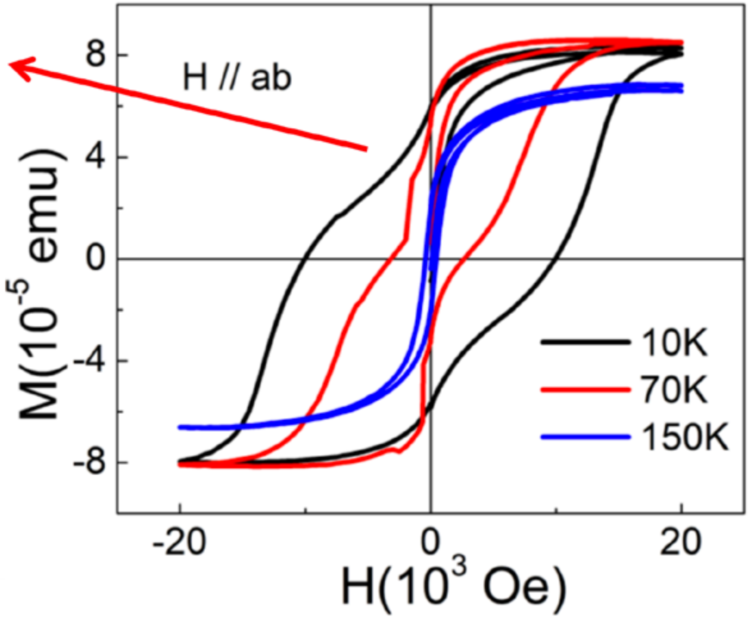
PHYSICAL REVIEW MATERIALS **4**, 114001 (2020)

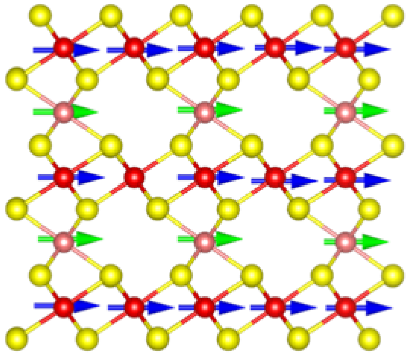


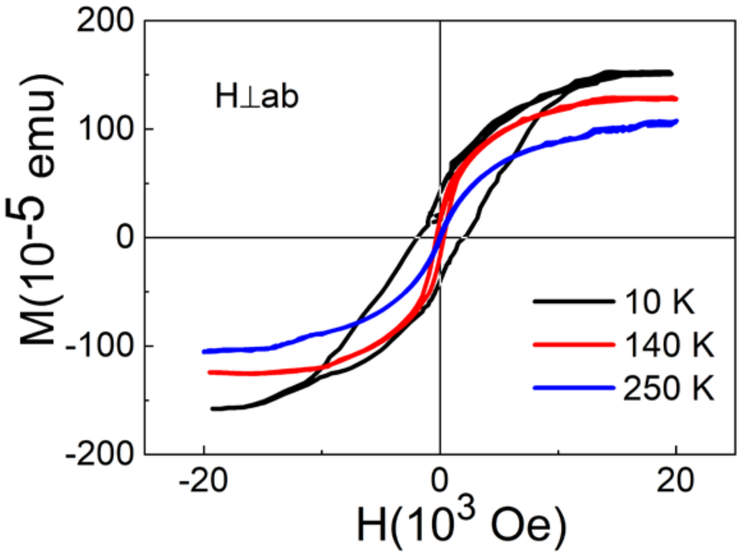
Magnetism in Cr_5Te_8

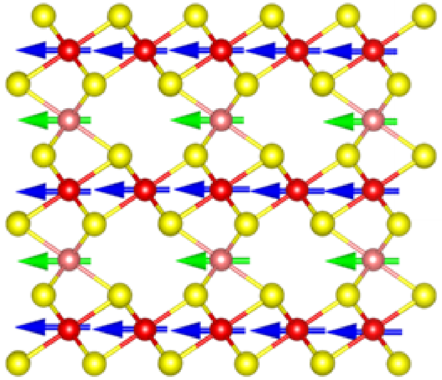


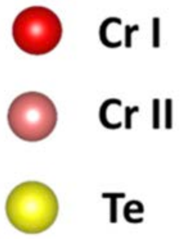




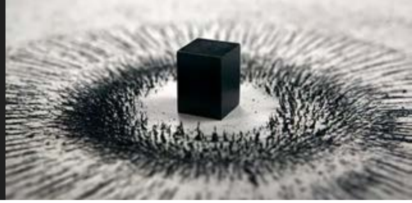








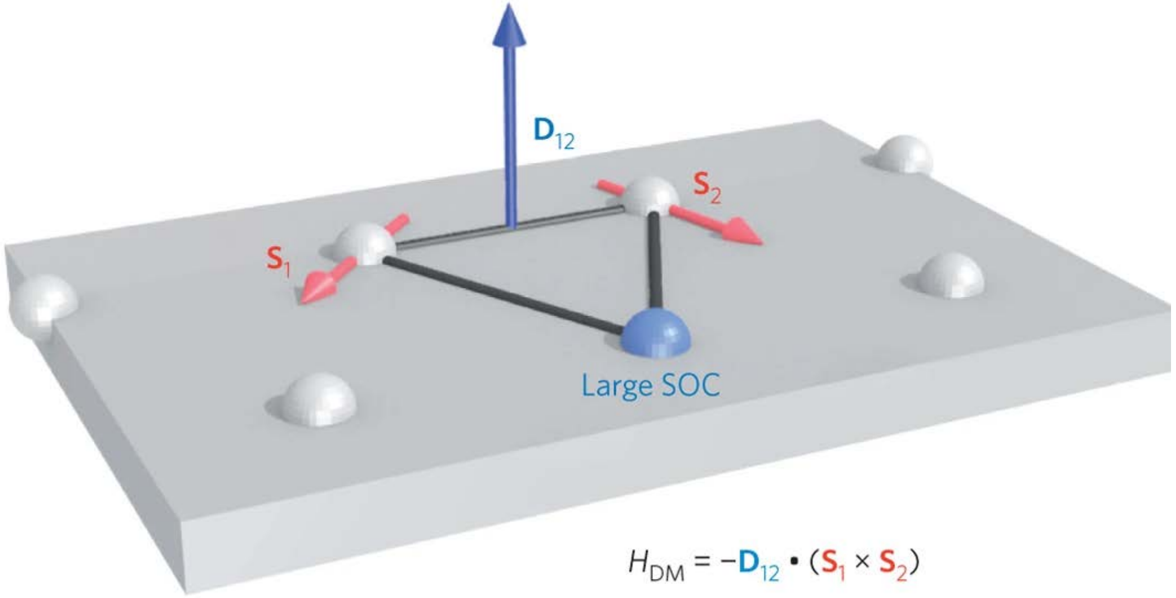
Implications of non-collinear magnetism



Self-intercalated $Cr_{1+\delta}Te_2$: Lacks inversion symmetry

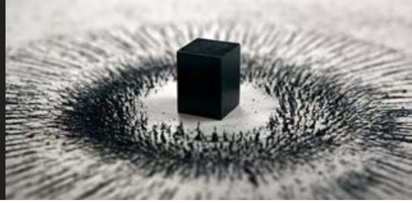
Dzyaloshinskii-Moriya interaction (DMI) / antisymmetric exchange : Additional contribution to total magnetic exchange interaction in systems with broken inversion symmetry, when an atom with large spin-orbit coupling mediates a super-exchange interaction between two magnetic atoms.

$$\mathcal{H}_{DM} = -D_{12} \cdot (S_1 \times S_2)$$

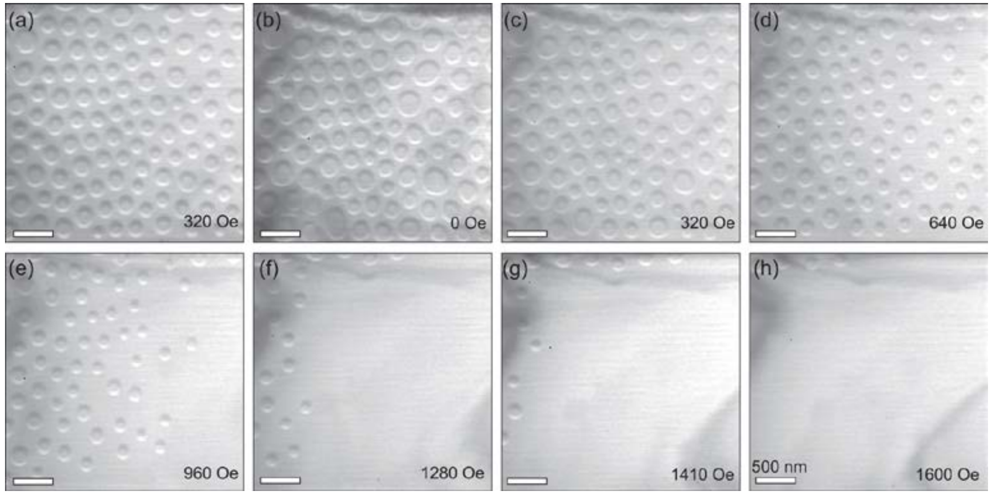


Nature Nanotech **8**, 152–156 (2013)

Skyrmions in chromium tellurides

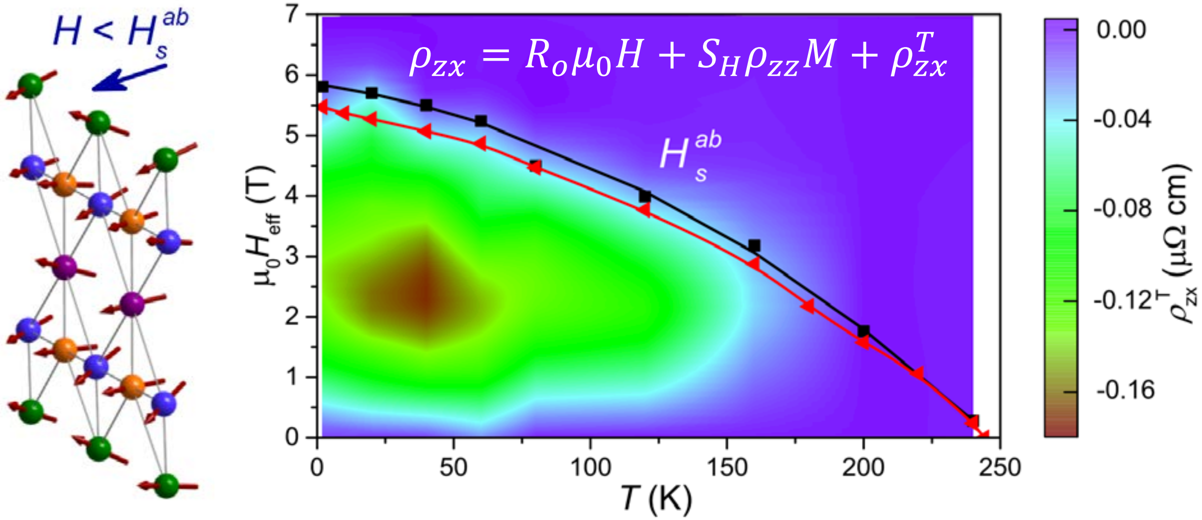


Evolution of Néel-type textures in $Cr_{1+\delta}Te_2$ as a function of magnetic field at 100 K



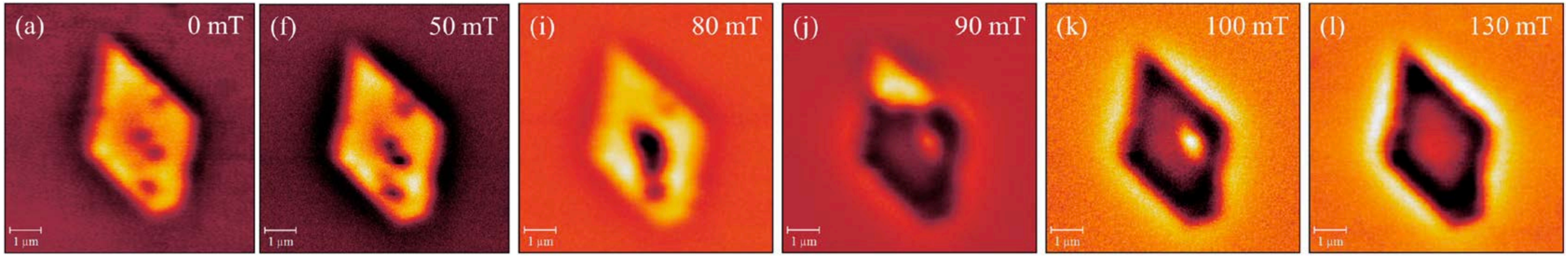
Nat Commun **13**, 3965 (2022)

Topological Hall effect in t-Cr_5Te_8 and Cr_3Te_4



Phys. Rev. B **100**, 024434 (2019)
Materials Today, 57, 66 (2022)

Evolution of magnetic bubbles in 2D Cr_5Te_8



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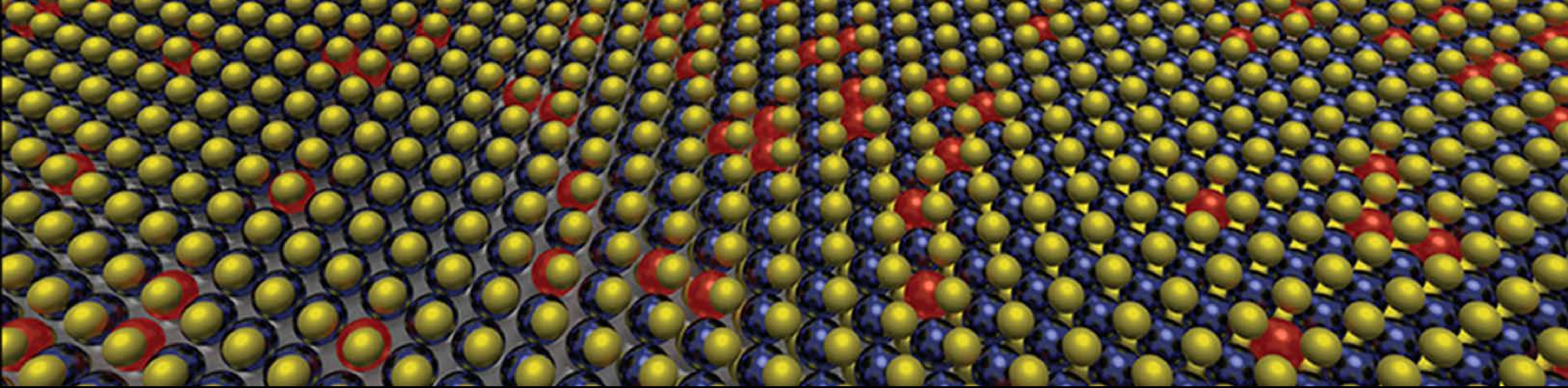
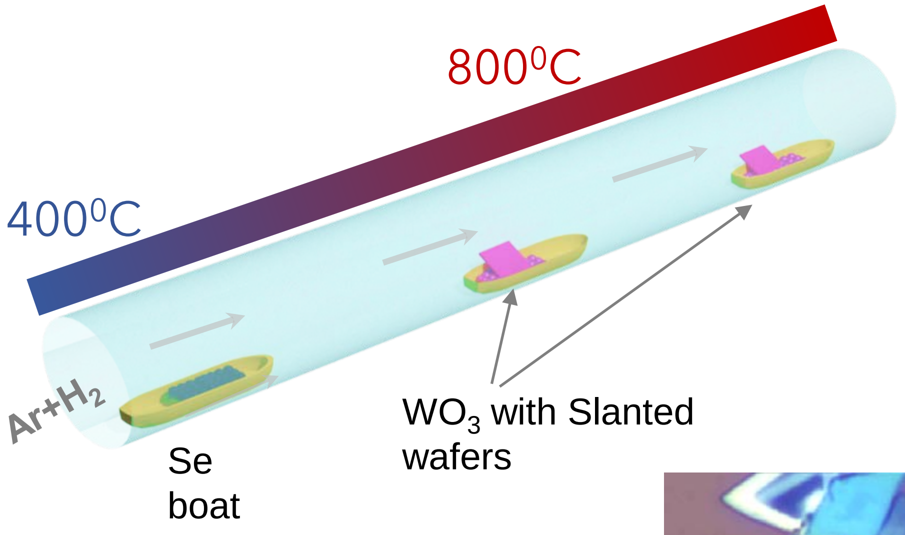
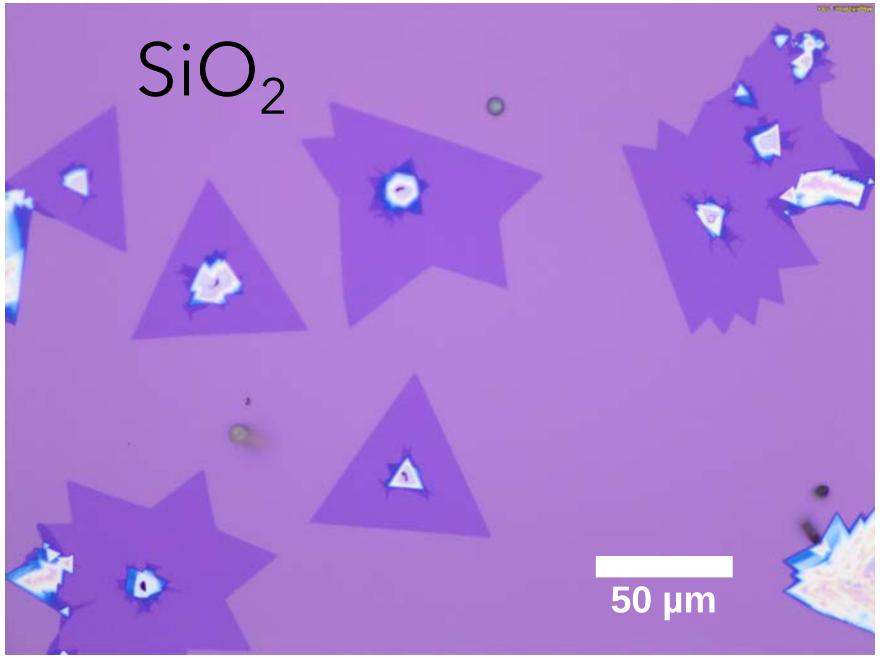


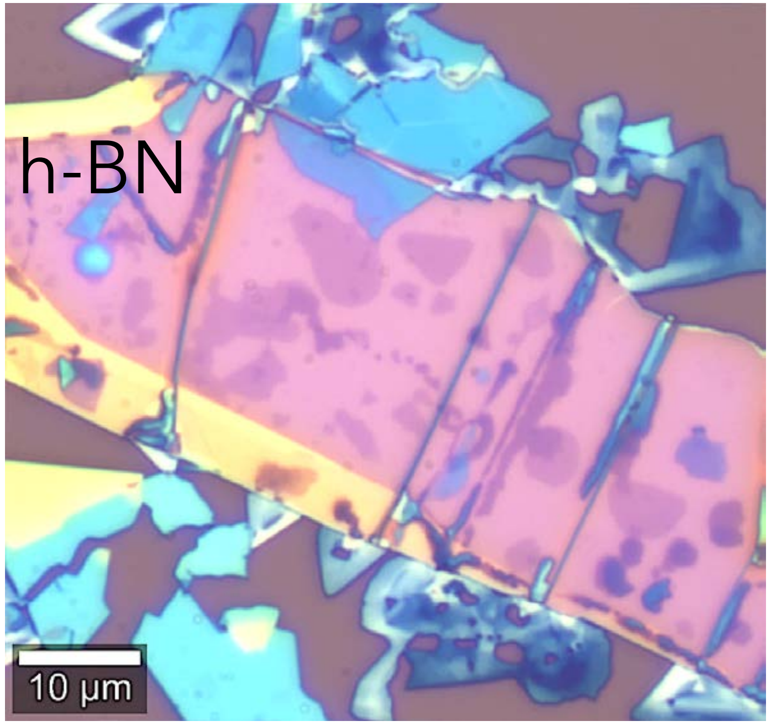
2D semiconductors – WSe_2

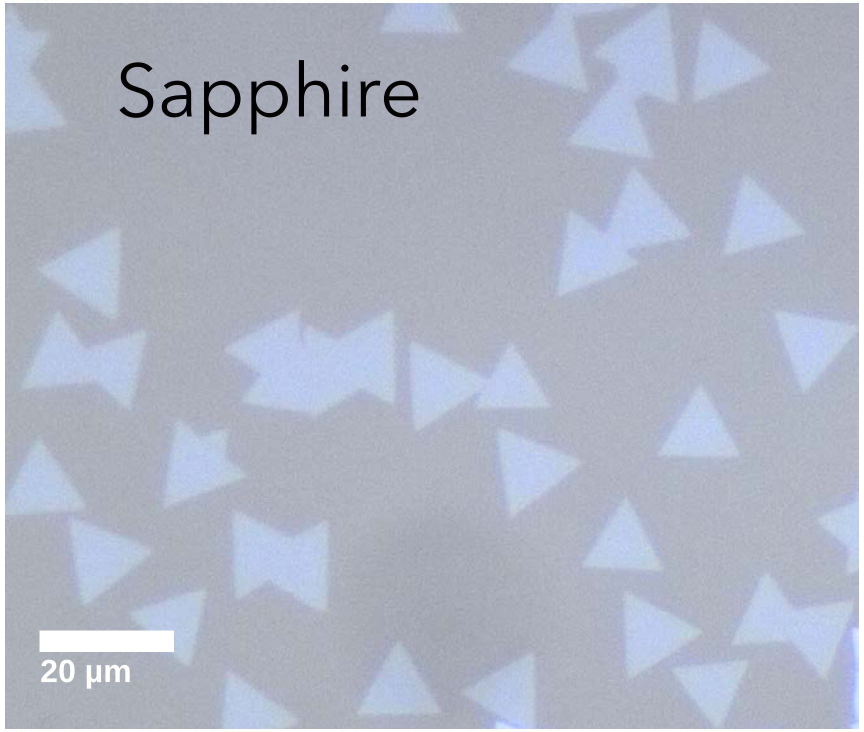
Optical emission signatures and prospects for optoelectronics

CVD growth of WSe_2



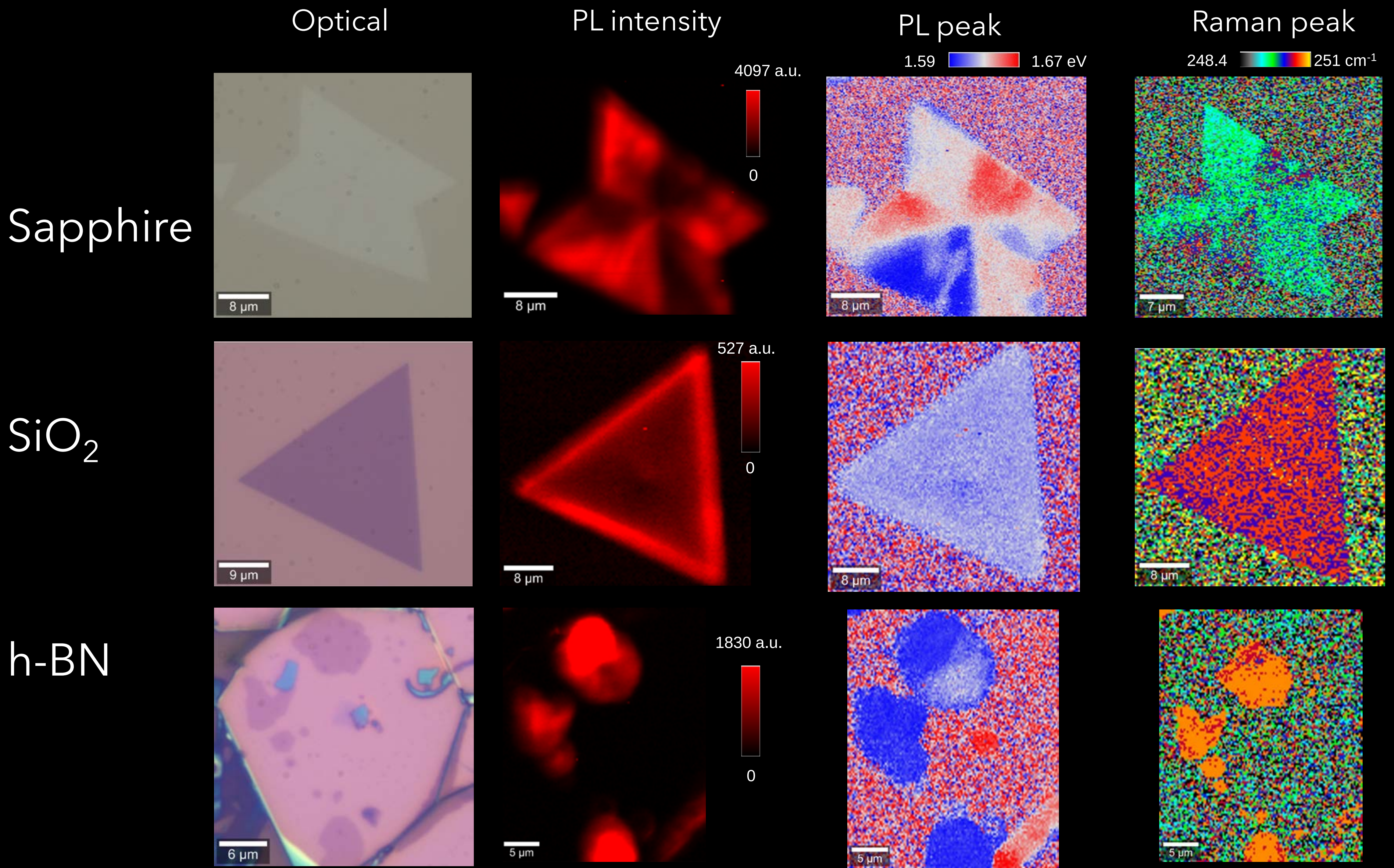






Growth conditions

Temperature: 780- 800°C
Gas Flow: 60 sccm Ar/ 8 sccm H_2
Growth Time: 5 min



Optical
PL intensity
PL peak
Raman peak
1.59
1.67 eV
248.4
251 cm-1
Sapphire
4097 a.u.
0
8 µm
8 µm
8 µm
7 µm
SiO2
527 a.u.
0
9 µm
8 µm
8 µm
8 µm
h-BN
1830 a.u.
0
6 µm
5 µm
5 µm
5 µm

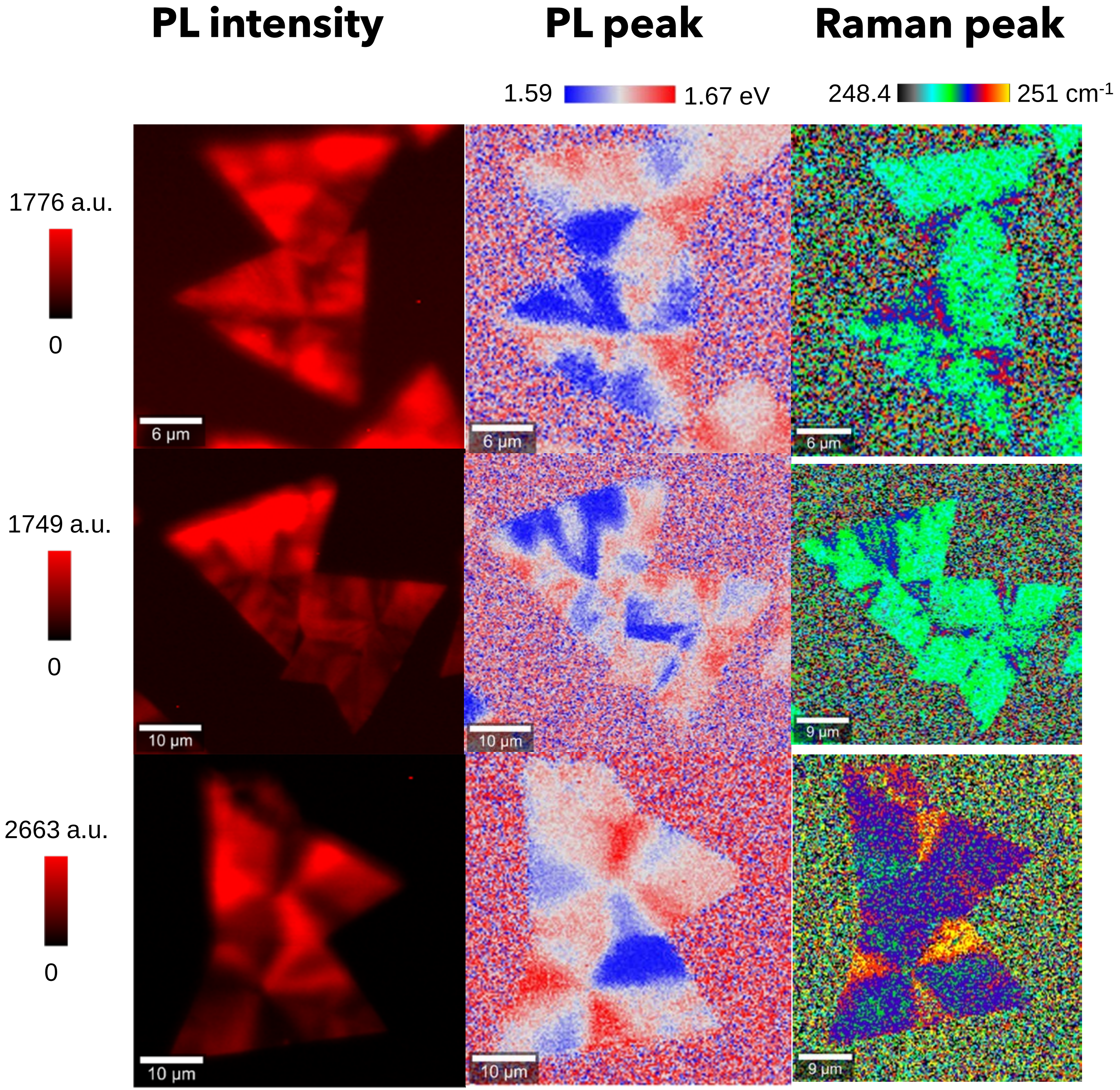
TEC

Sapphire
7.5 – 8.5 µ/K

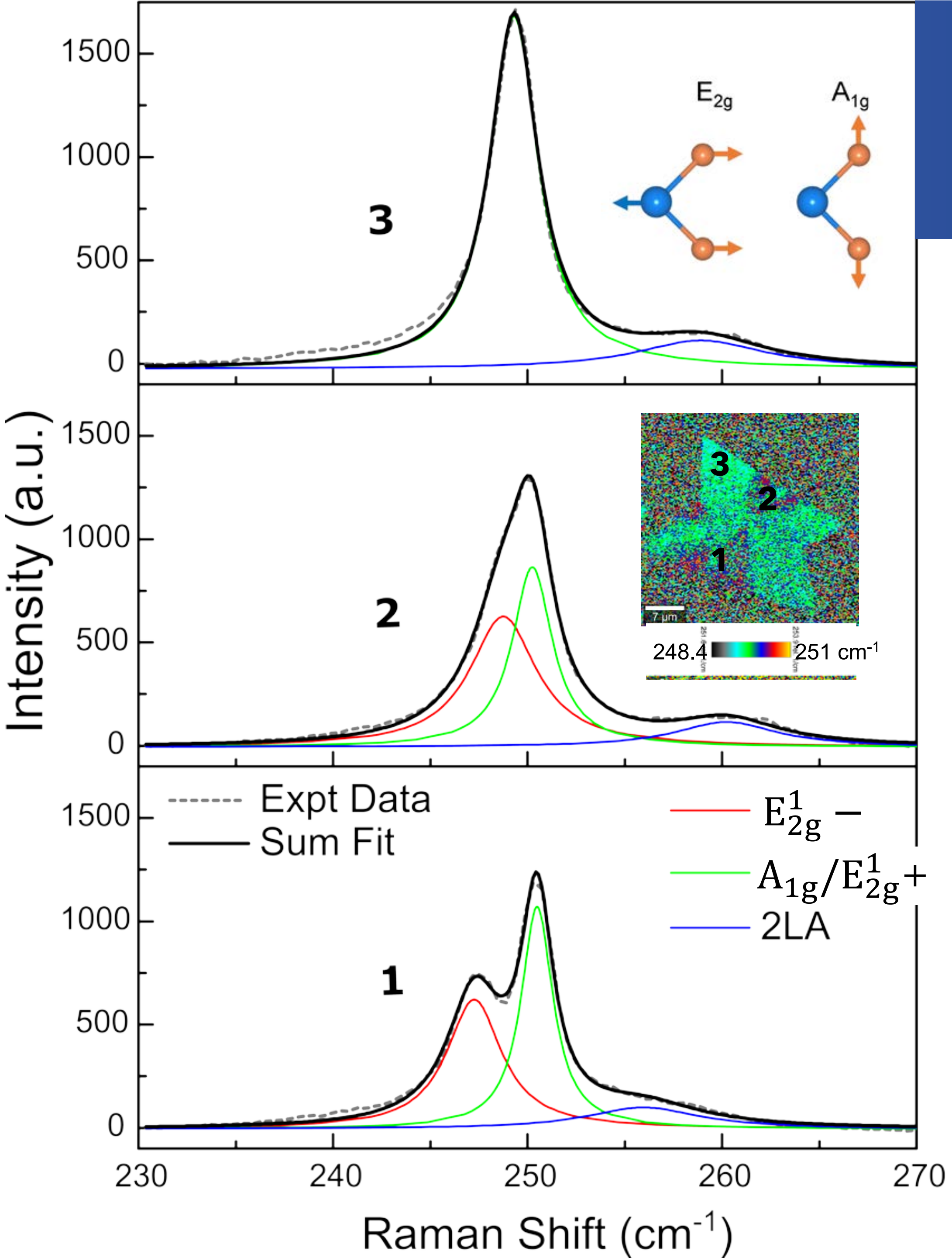
h-BN
-2.72 µ/K

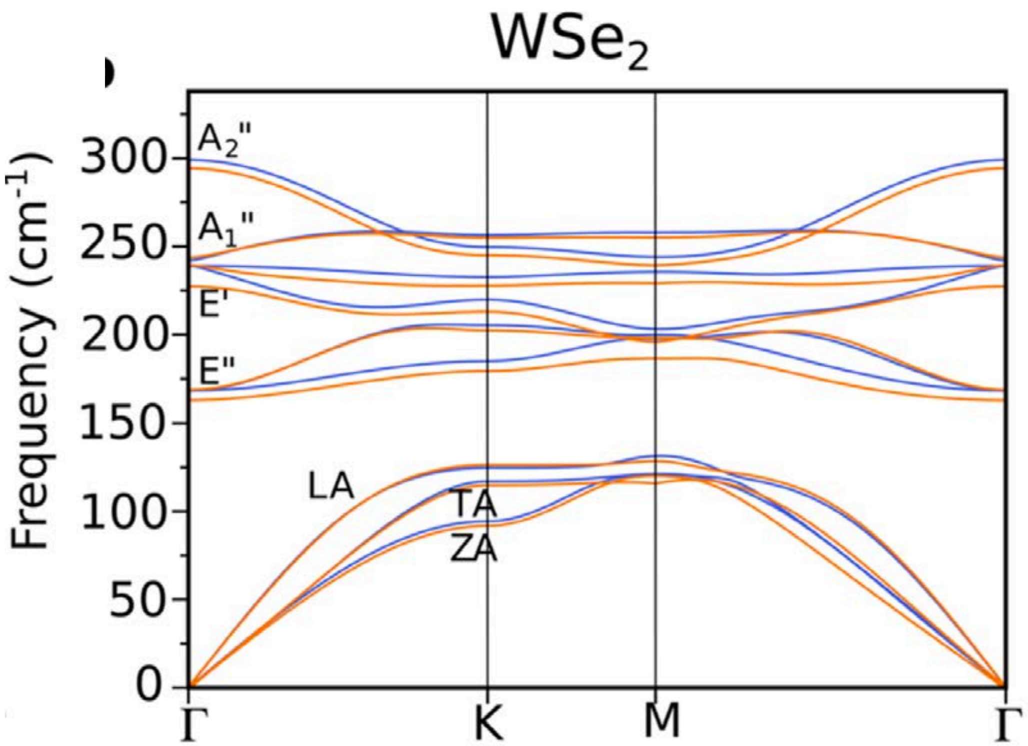
SiO_2
0.5 µ/K

WSe_2
3.5 µ/K



Substrate strain effect on Raman spectra





The displacement eigenvector of the E′+ mode is orthogonal to the direction of strain, while it is parallel for the E′− mode .

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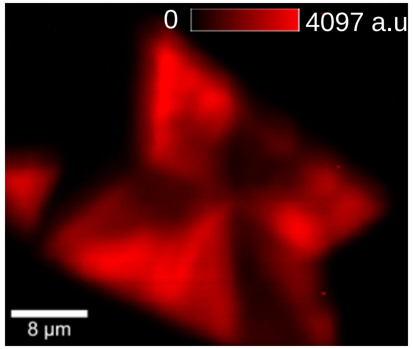
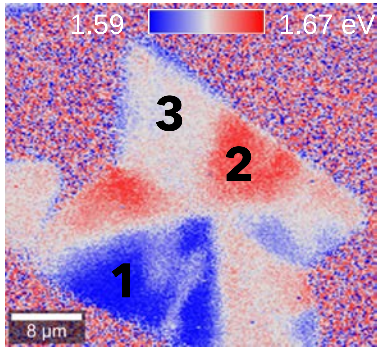
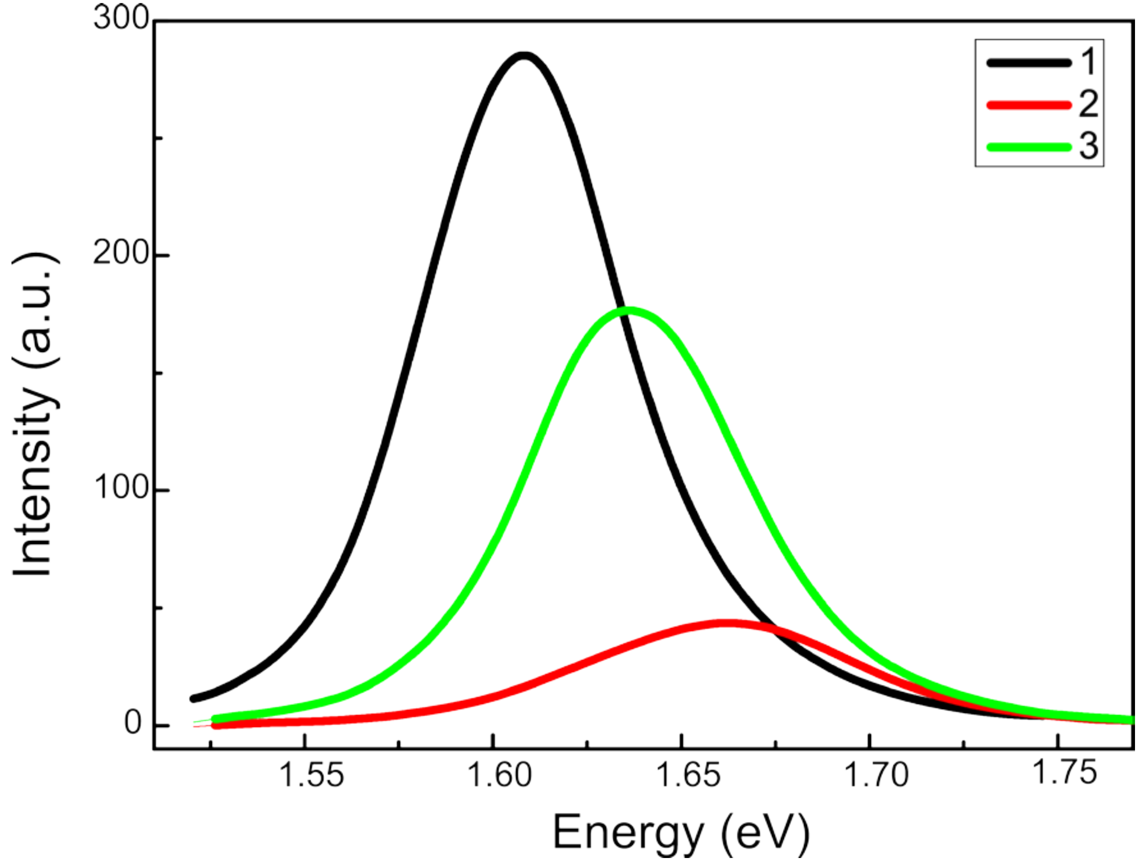
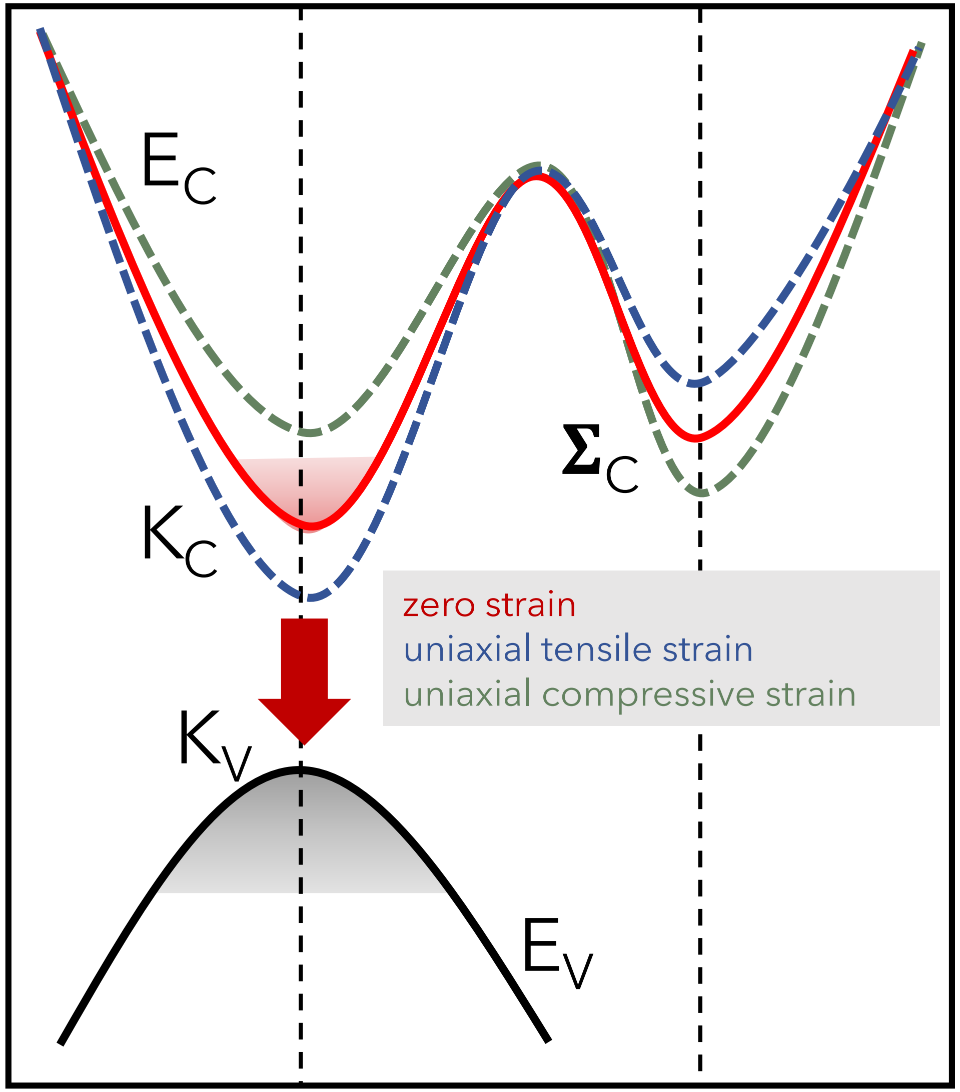
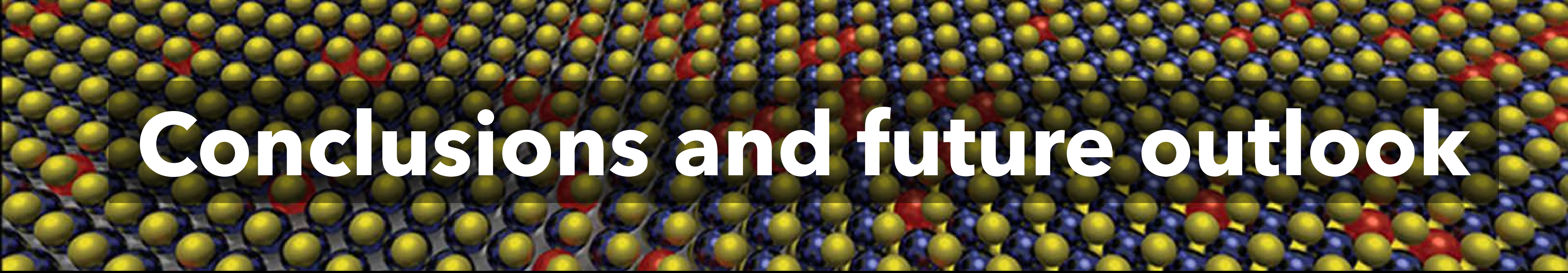
Substrate strain effect on Photoluminescence











Conclusions and future outlook

- Van der Waals epitaxy - Growth mechanism, prospects and challenges for large area growth of 2D/quasi-2D materials
- $Cr_{1+x}Te_2$ system – non-collinear magnetism and prospects for hosting skyrmions
- Substrate interactions in WSe_2 – effect of strain on vibrational modes and band structure

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Thanks for your kind attention…