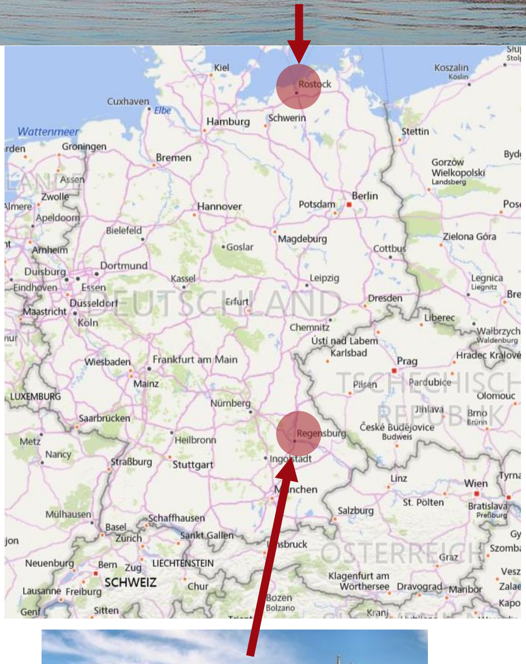
Interlayer excitons in twist-controlled van der Waals heterostructures

Tobias Korn

Geography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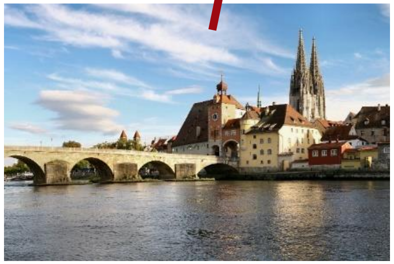



Rostock
Daejeon

Overview

Introduction

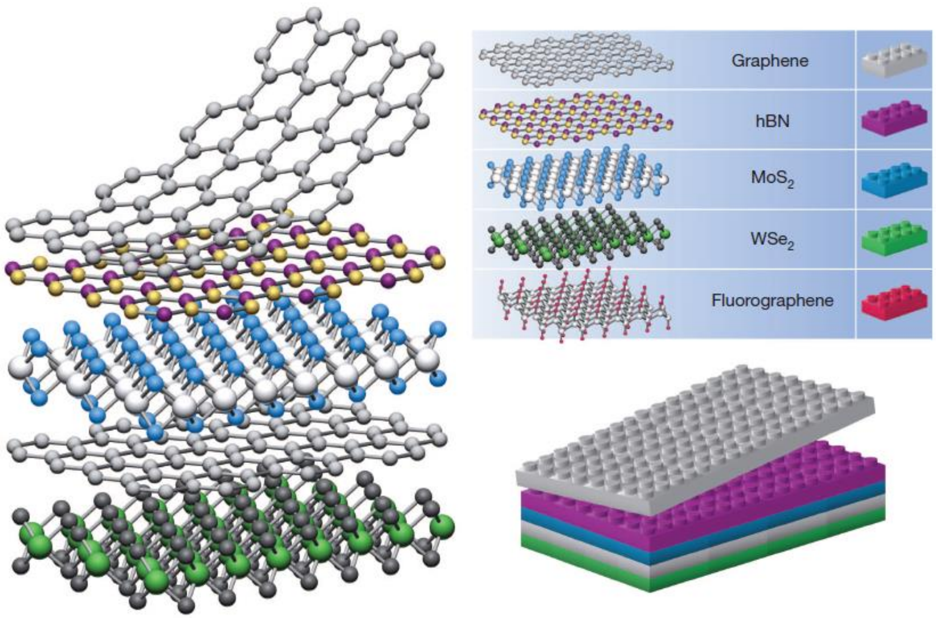
- van der Waals heterostructures
- Stacking TMDC monolayers
- Interlayer excitons

Results: our two sets of Lego

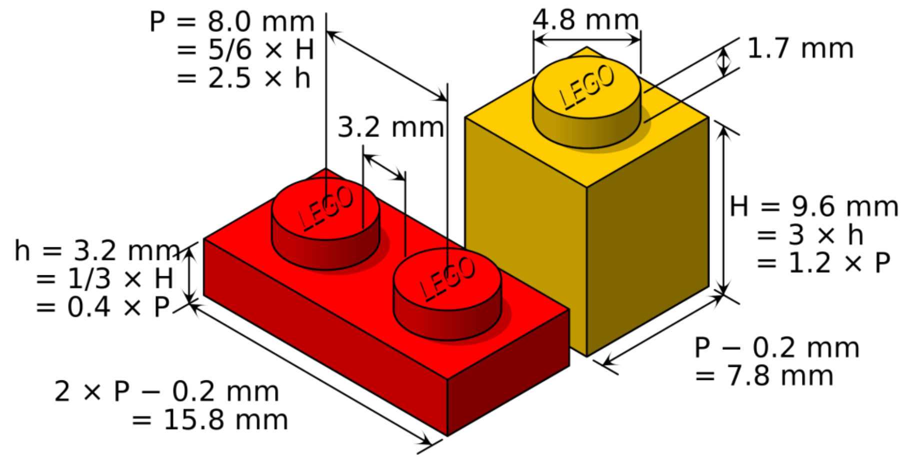
- MoS_2-WSe_2
  - Interlayer exciton character revealed by interlayer twist
- $MoSe_2$-WSe_2
  - Exciton-exciton interaction
  - Interlayer excitons in large magnetic fields

Summary

Artificial 2D crystals & heterostructures

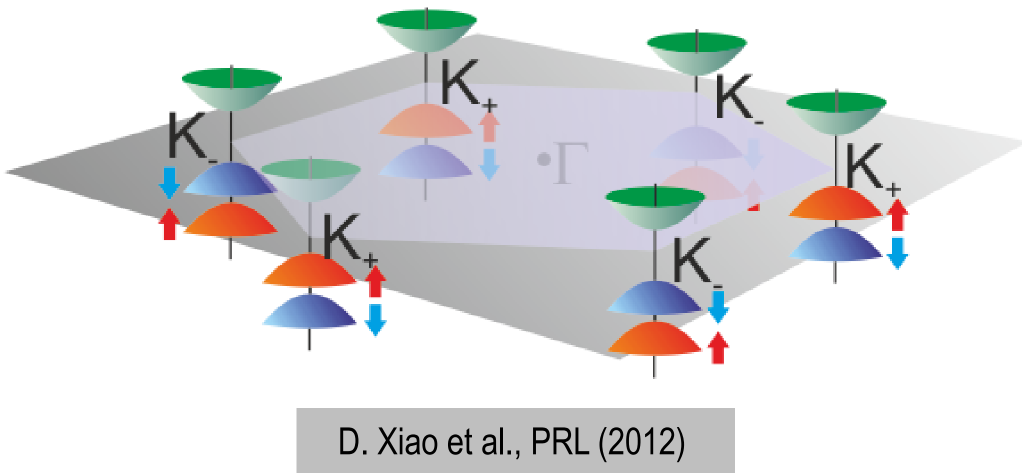


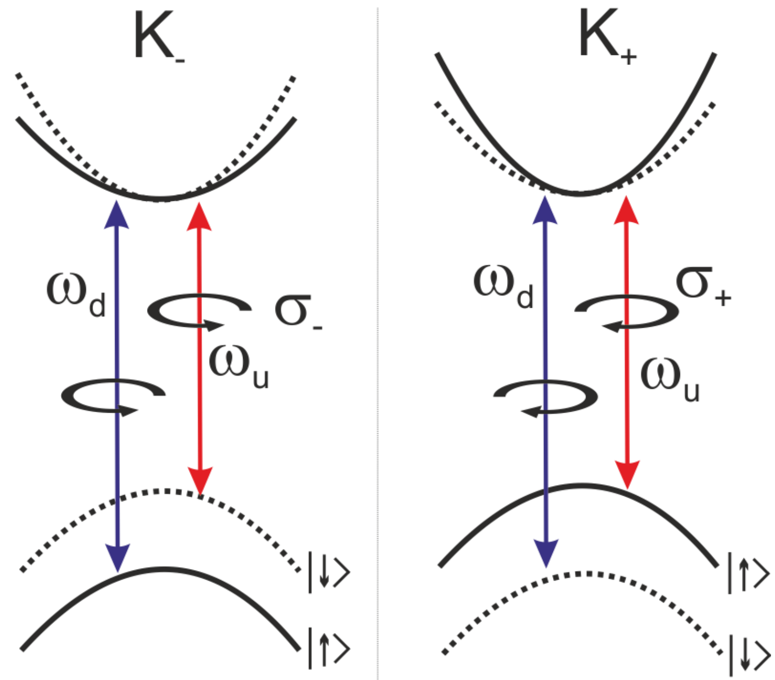
Geim & Grigorieva, Nature 2013



- 2D LEGO: combining different materials with monolayer precision
- Limits of LEGO analogy:
  - Relative orientation of layers not limited to 90° angles
  - Lattice parameters and symmetry are different for different materials

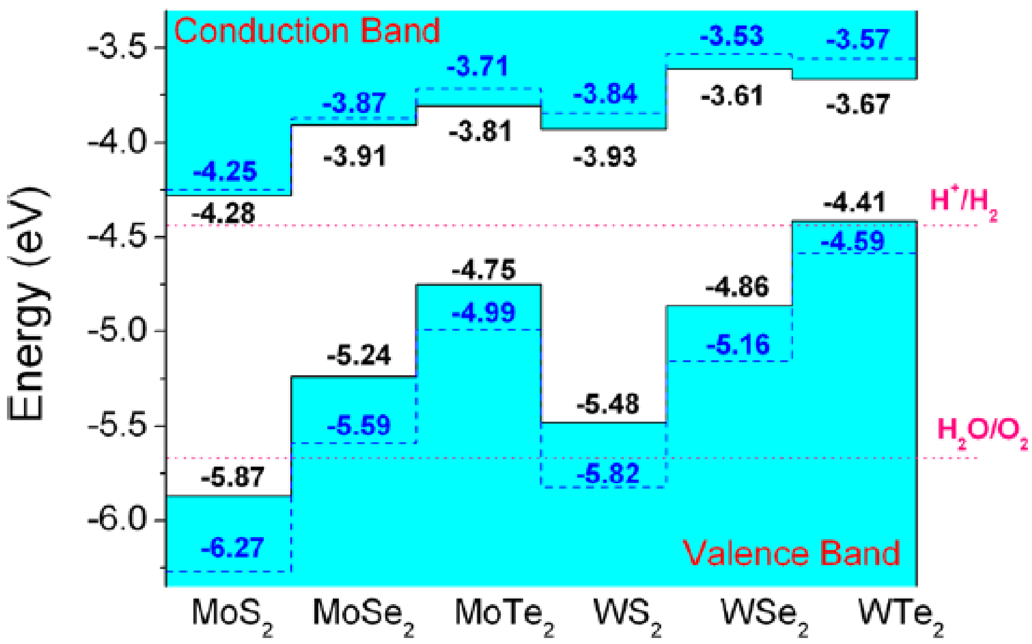
Our favorite LEGO: TMDC monolayers

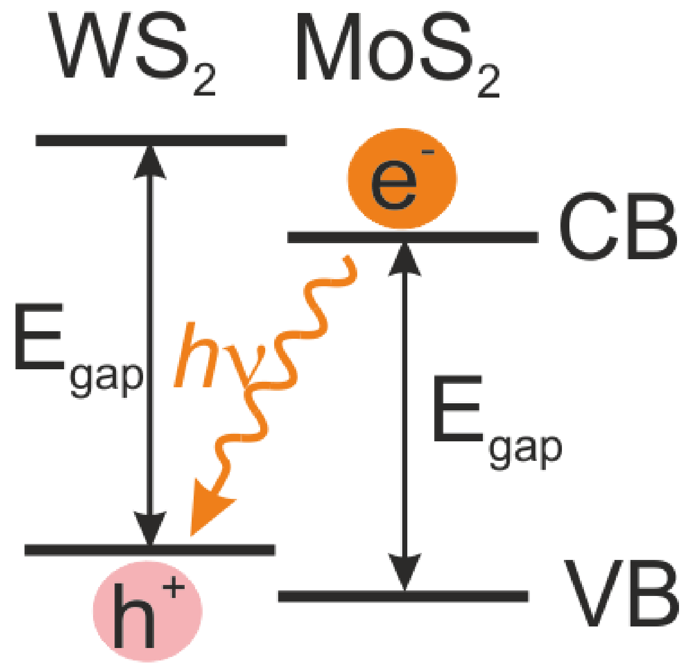




- Direct band gap in the monolayer limit
- Gap located at K points (corners of Brillouin zone)
- Large (150-500 meV) and opposite valence-band spin splitting at $K_{+/-}$
- Spin and valley degrees of freedom are coupled
- Direct access to individual valleys via circularly polarized light

Stacking TMDC monolayers

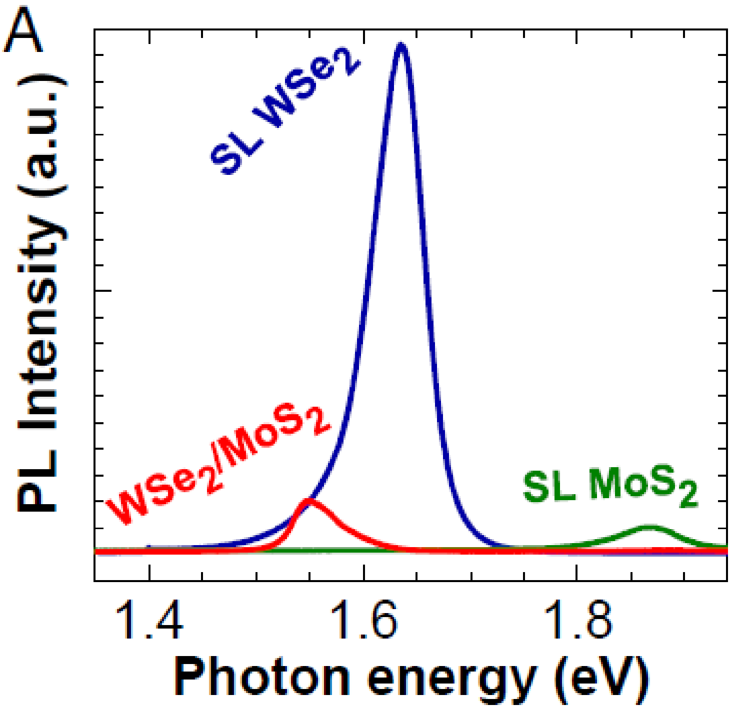




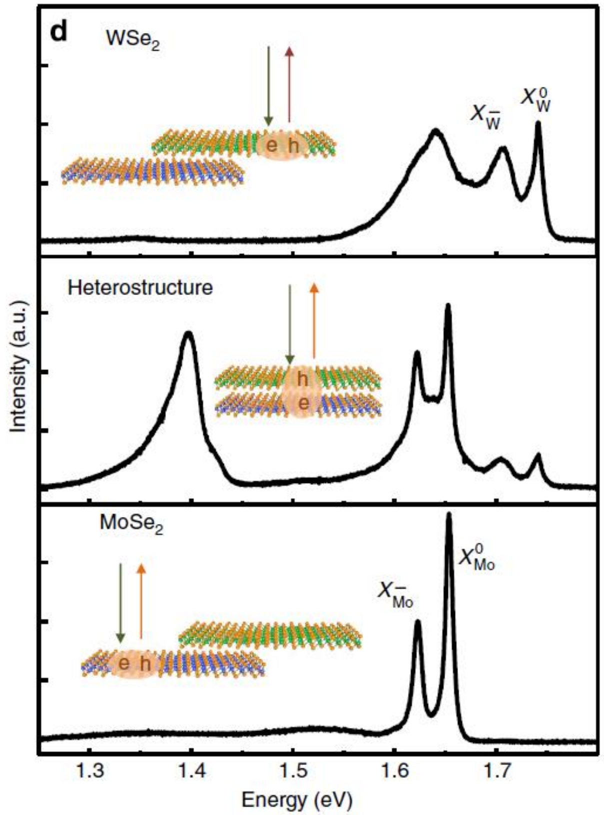
Kang et al., APL 2013
See also: Kosmider et al., PRB 2013

- Many TMDC combinations lead to staggered band alignment
- ➢ Separation of electron-hole pairs into different layers
- ➢ Relevant for device applications, e.g., photovoltaics
- ➢ Formation of interlayer excitons

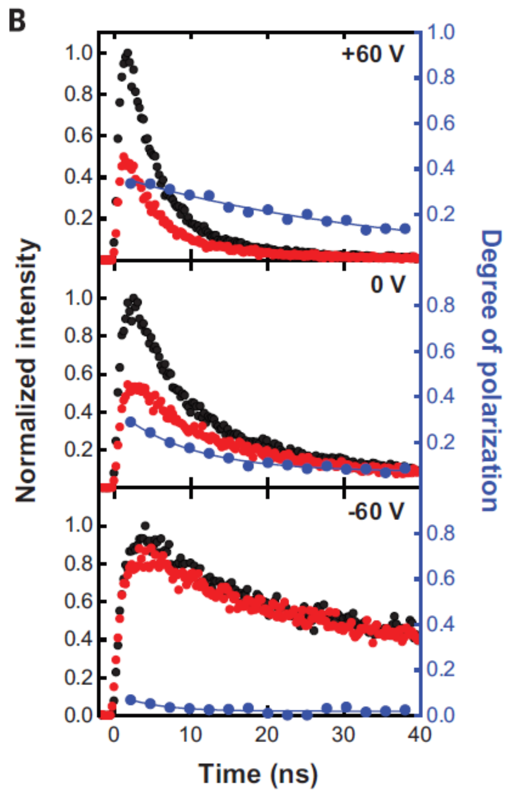
Interlayer excitons in TMDC heterostructures



Fang et al., PNAS (2014)



Riviera et al., Nature Comms. 2015

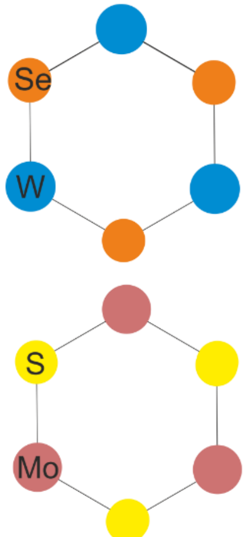


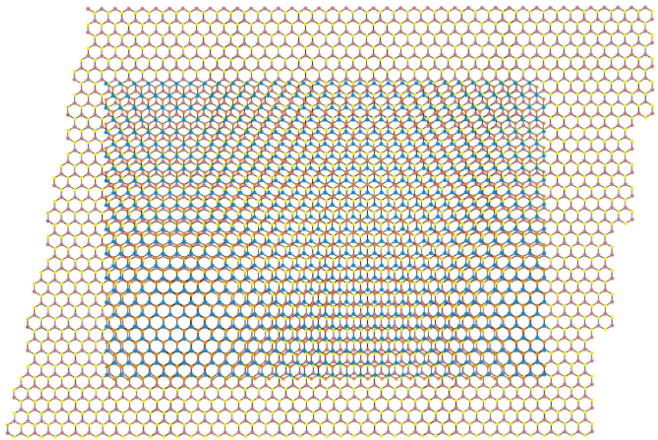
Riviera et al., Science 2016

- Attractive properties:
- ➢ Long exciton and valley lifetime
- ➢ Permanent electric dipole moment (manipulation by electric fields)
- ➢ High binding energies (stability at high temperature & density)

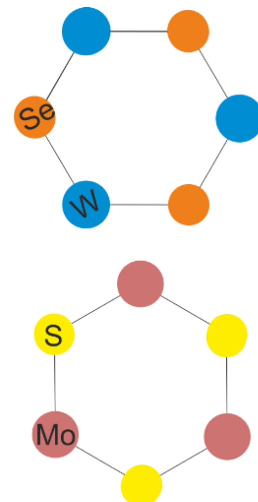
Our first set of LEGO: MoS_2 and WSe_2

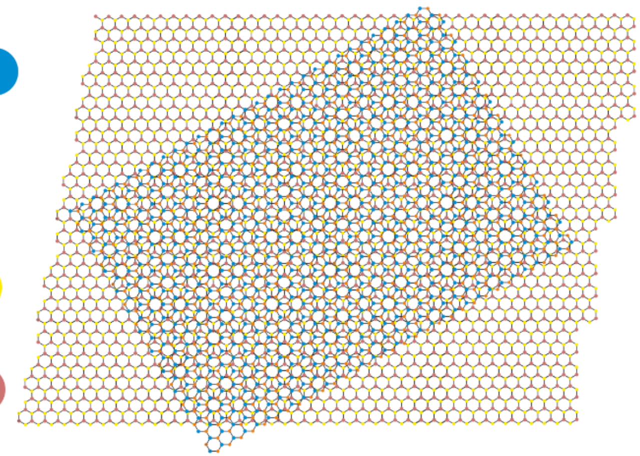
twist angle: 0°





twist angle: 30°



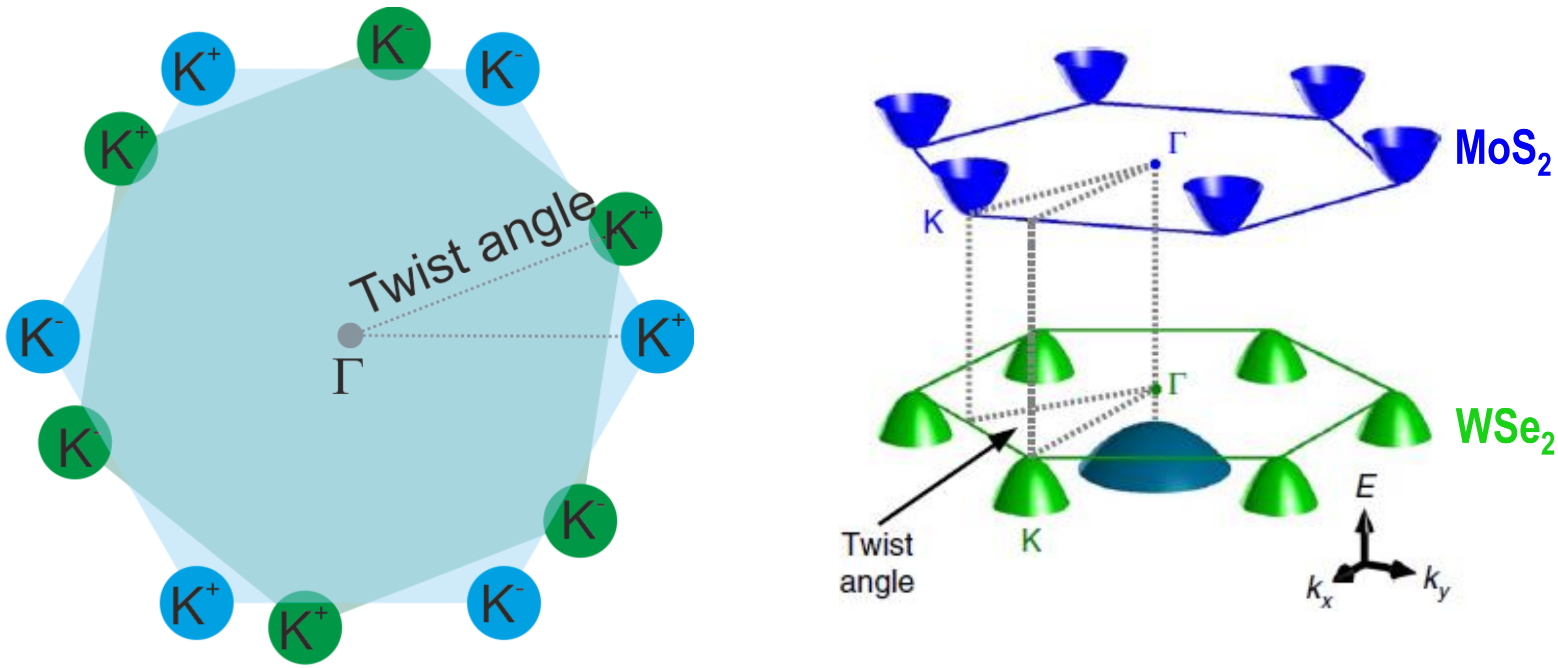


Material	MoS_2	WSe_2
Lattice vector a_0 (nm)	0.316 [1]	0.329 [1]
Rel. CB offset (eV)	0.67 [2]	
Rel. VB offset (eV)	1.0 [2]	

[1]Kormanyos et al., 2D Mat. 2015
[2]Kang et al., APL 2013

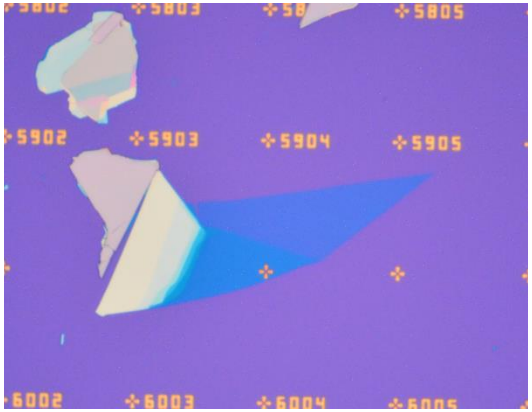
- Staggered band alignment
- 4 % lattice mismatch:moiré pattern even for aligned layers

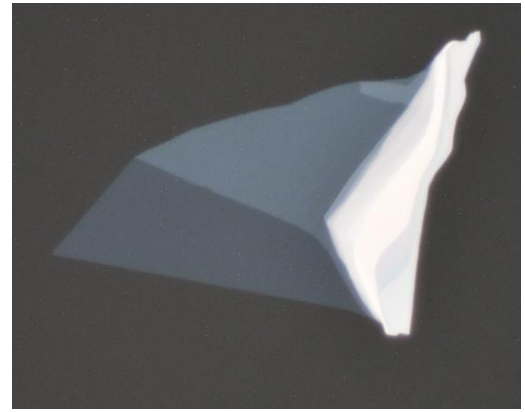
Twist angle and k space alignment

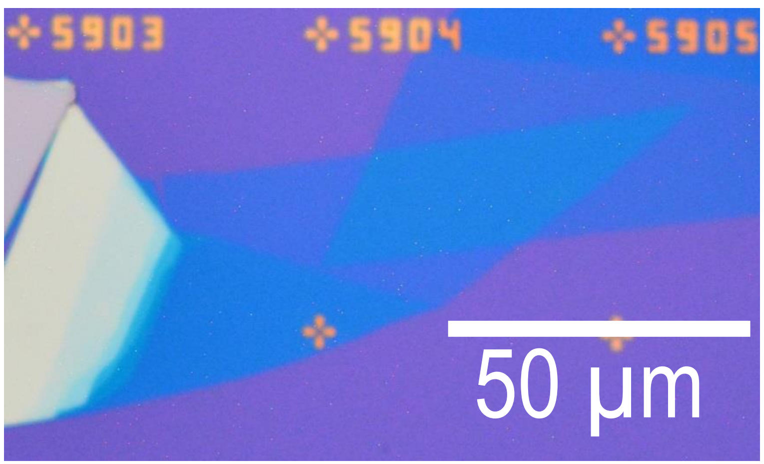


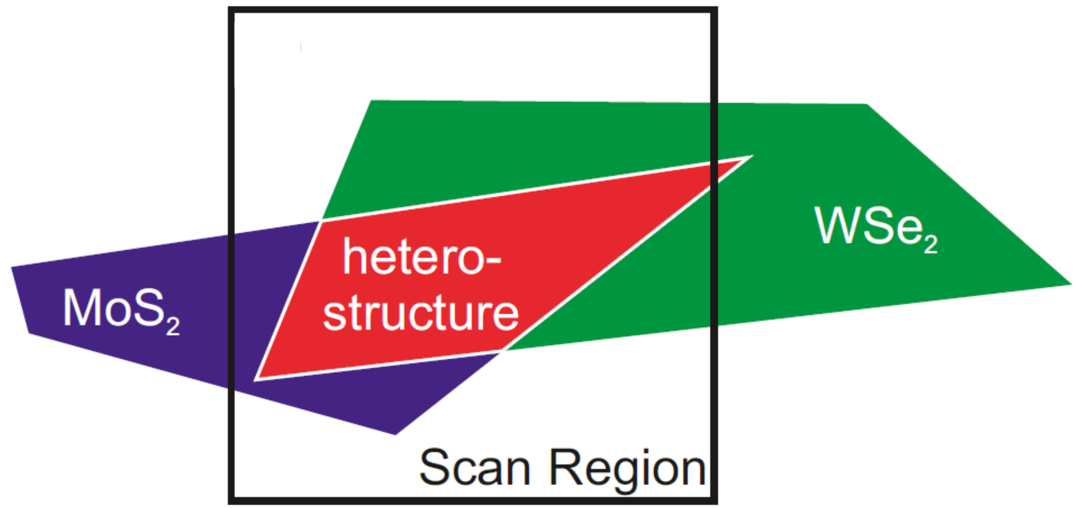
- Twist angle determines interlayer *k* space alignment
- Lattice mismatch corresponds to Brillouin zone size mismatch
- K-K transition only (almost) direct for 0 and 60 degree alignment

A typical MoS_2-WSe_2 heterostructure



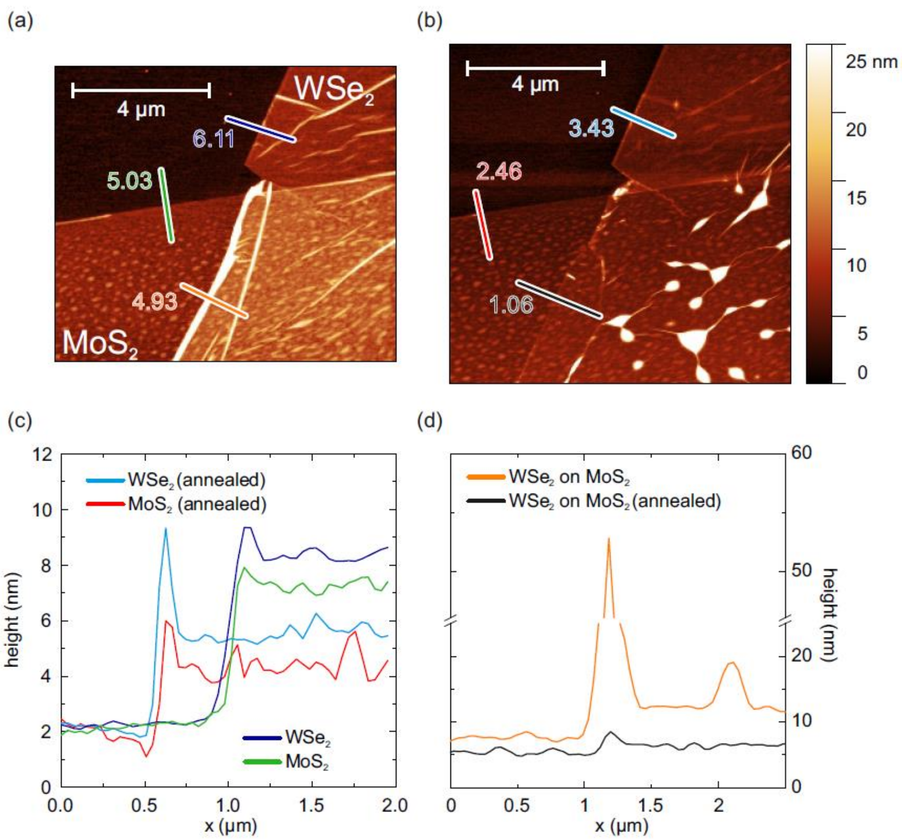






- MoS_2 flake (bottom layer) covered with WSe_2 flake (top layer)

Improving interlayer contact

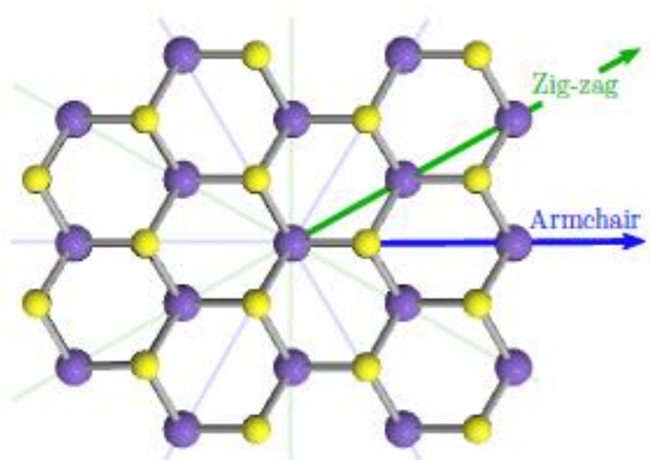


- Annealing (150°C in vacuum) increases mobility of adsorbates trapped between layers
- Formation of bubbles, good contact in between bubbles

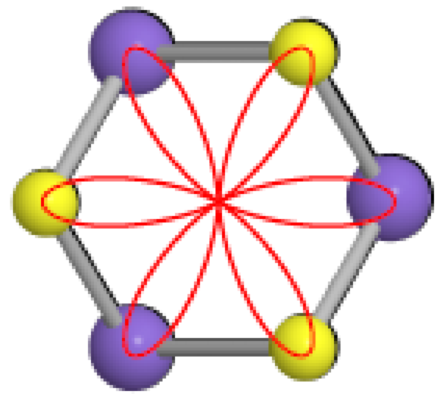
Recipy: Tongay et al., Nano Letters 2014

Second harmonic generation microscopy of TMDs

Top view of MoS_2 monolayer



Polar plot of SHG intensity

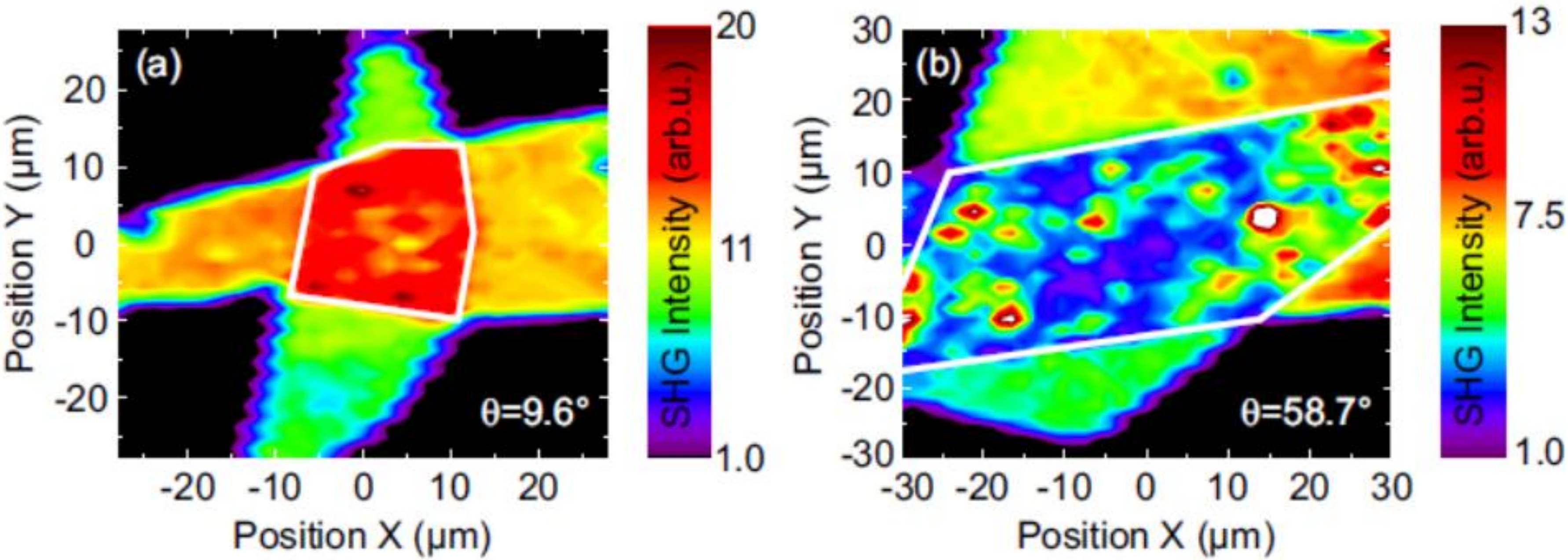


c.f. Li et al., Nanoletters (2013)

- No inversion center in monolayer and odd-layered TMDs
- ➢ Second harmonic generation allowed

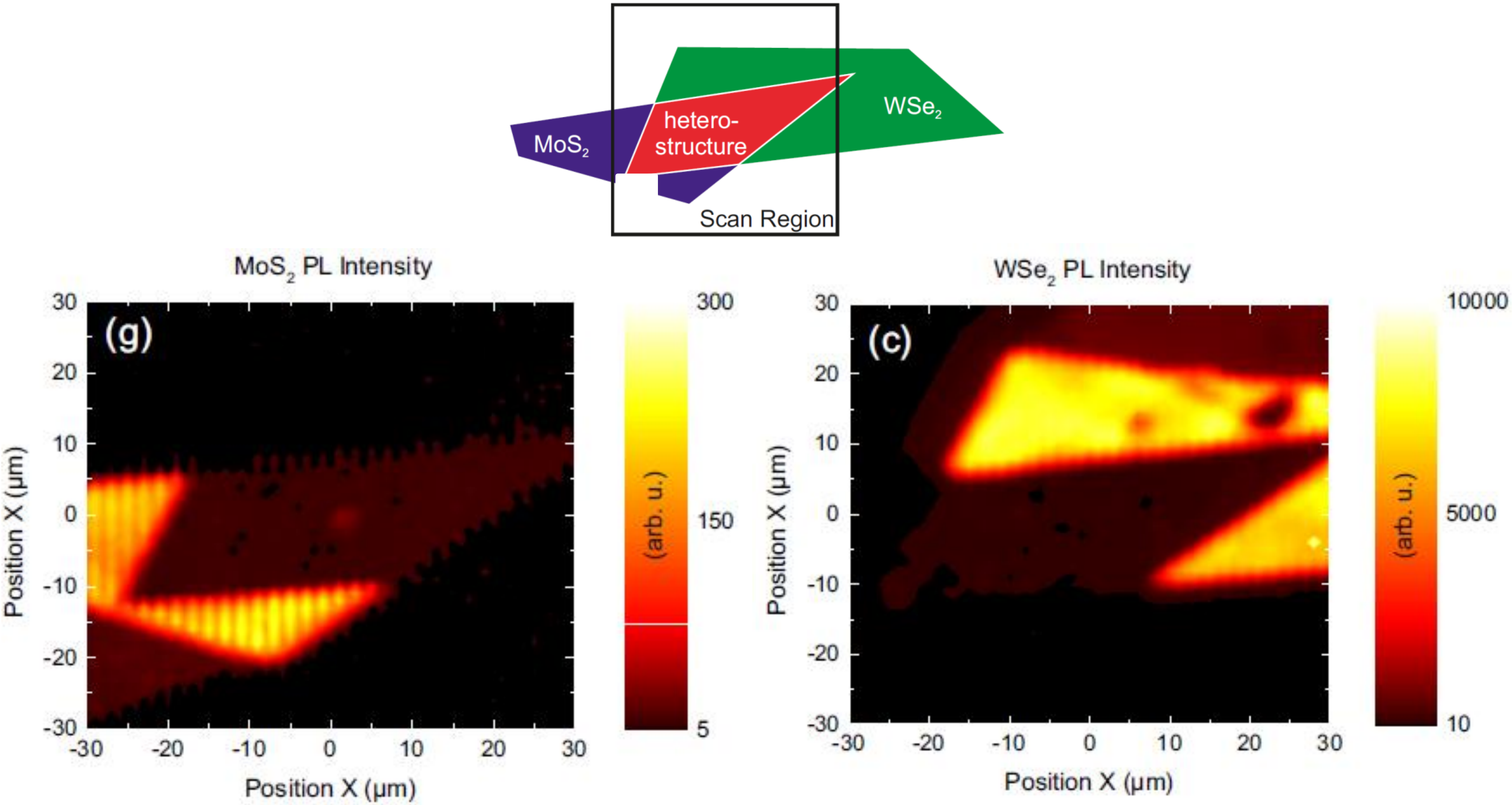
- Angular dependence of SHG intensity:
  - SHG with parallel polarization maximum for armchair directions
  - ➢ Crystal orientation can be determined

Checking for (anti-)alignment



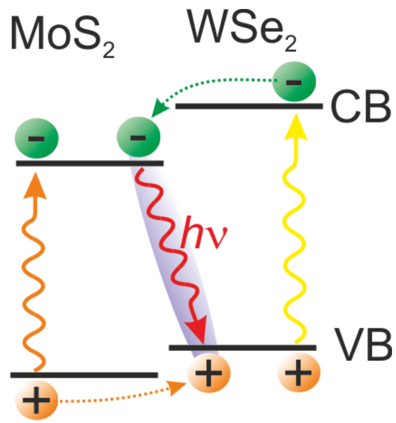
- SHG with circularly polarized excitation: interference between adjacent layers
- Aligned layers: constructive interference
- Anti-Aligned (60°) layers: destructive interference

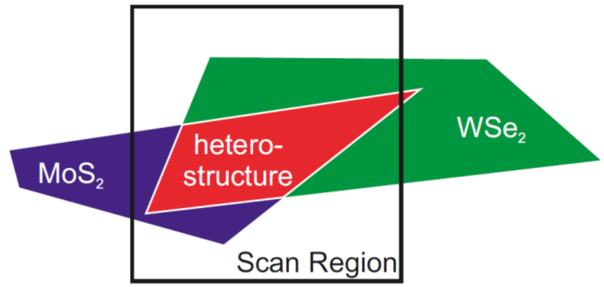
Heterostructure characterization

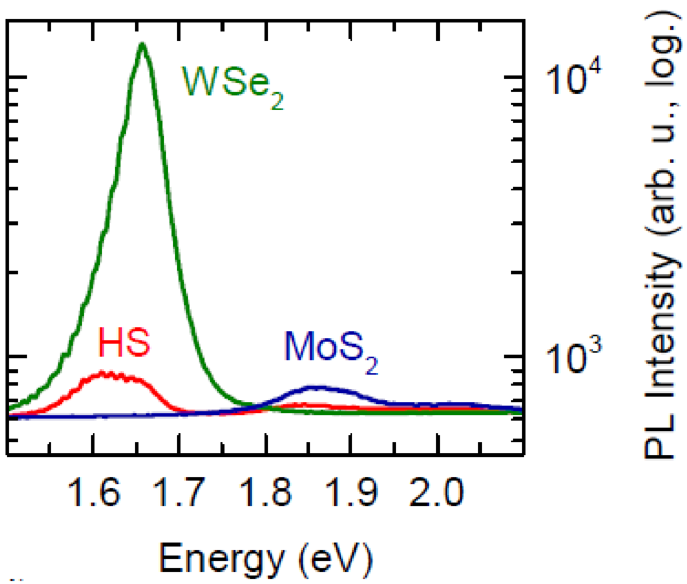


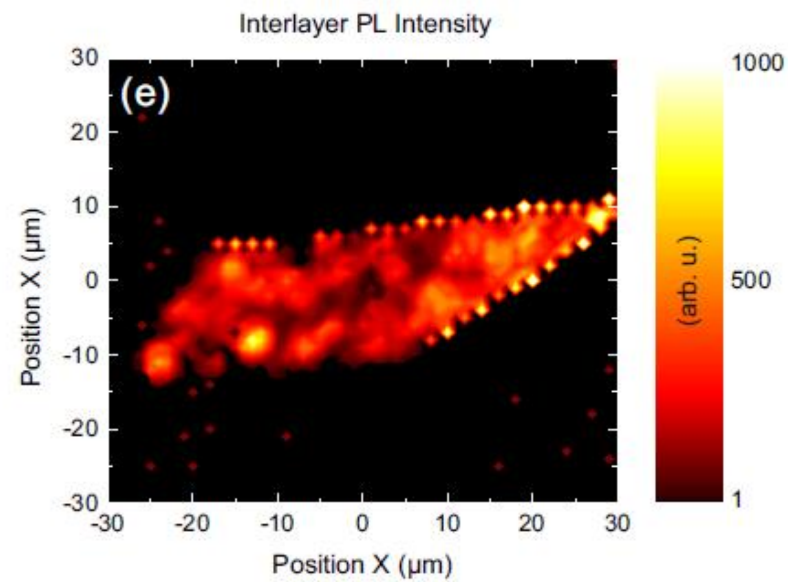
- Drastic drop of intralayer exciton PL intensity for both materials in HS region

Heterostructure characterization



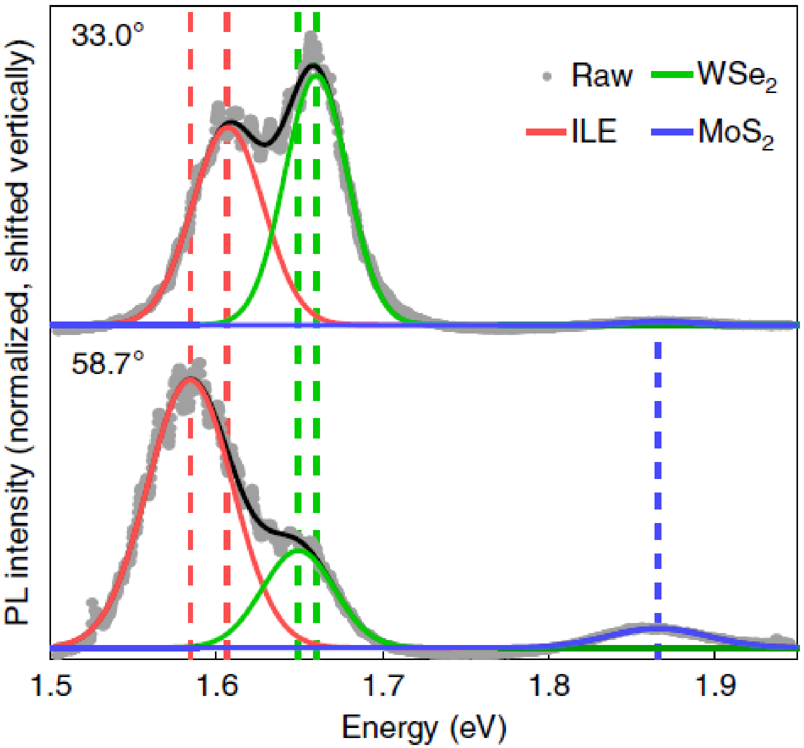


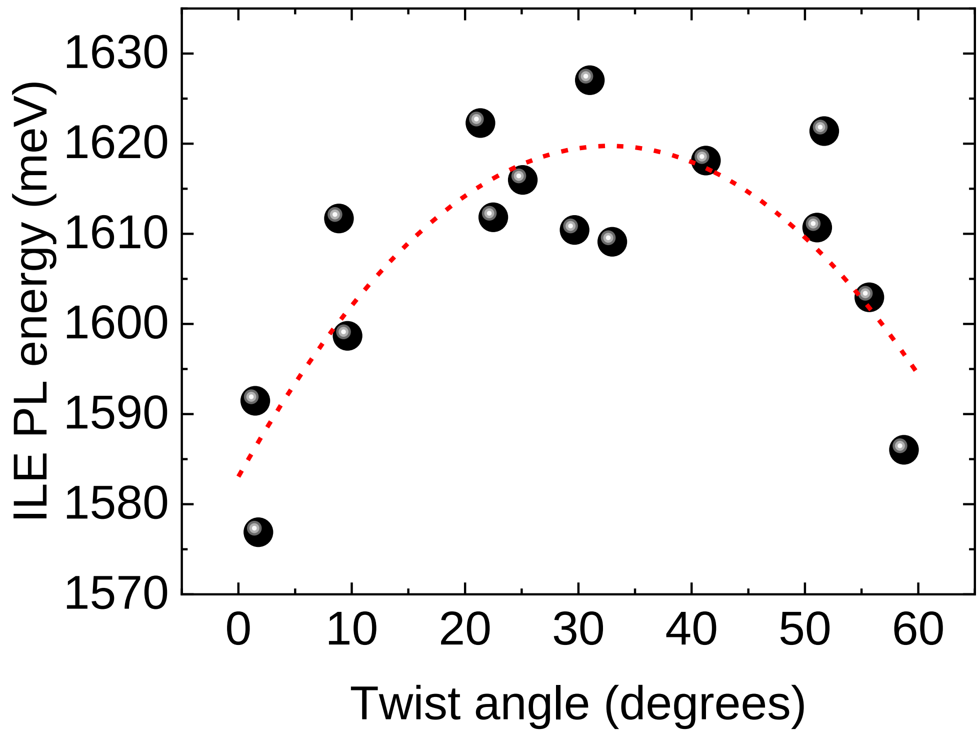




- New (interlayer exciton) PL peak observed in HS region

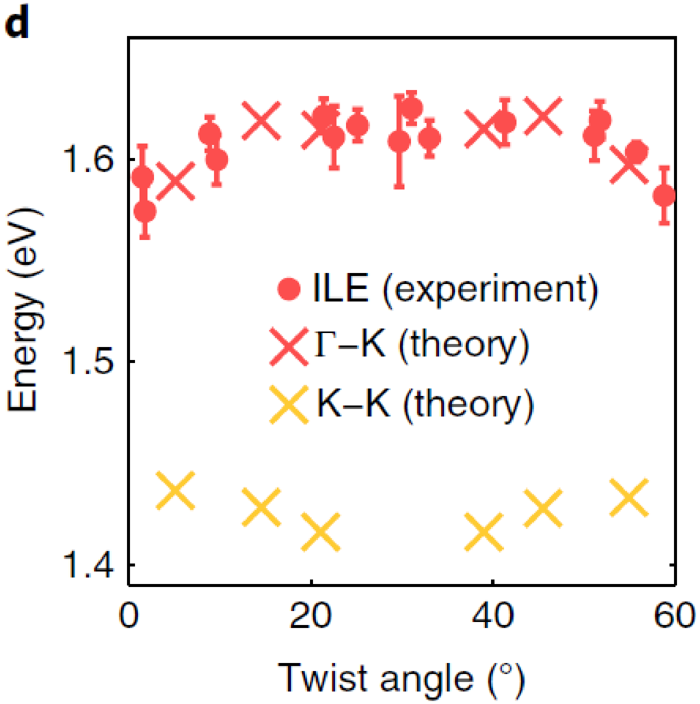
Interlayer excitons in MoS_2-WSe_2 HS

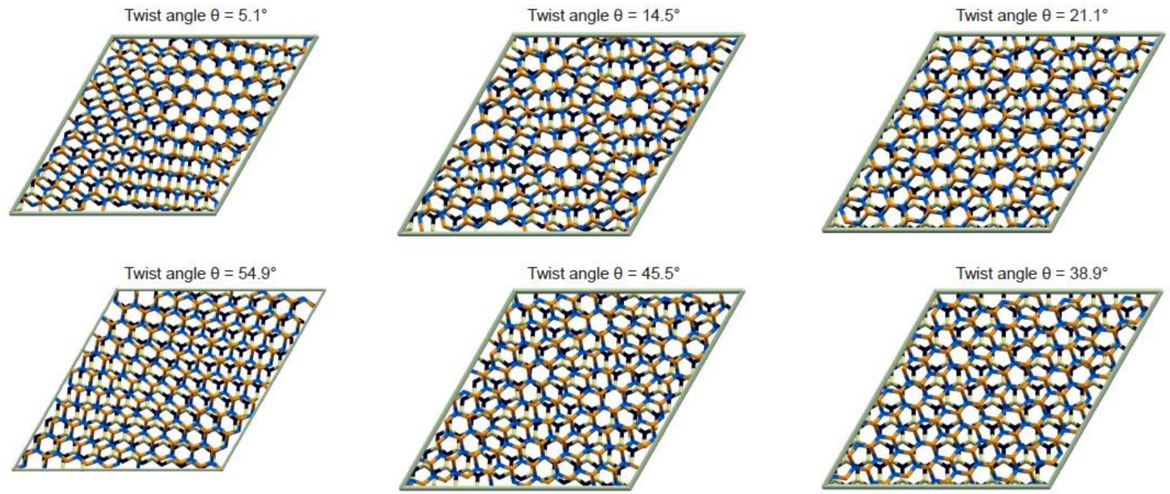




- Strong ILE PL emission for all twist angles – how?
- Systematic 50 meV shift of IEX PL position with twist angle –why?

Interlayer excitons in MoS_2-WSe_2 HS

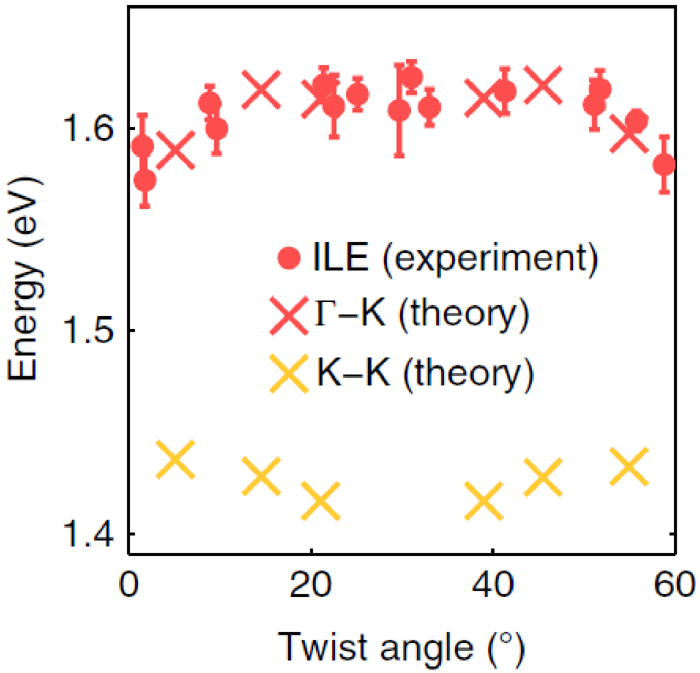


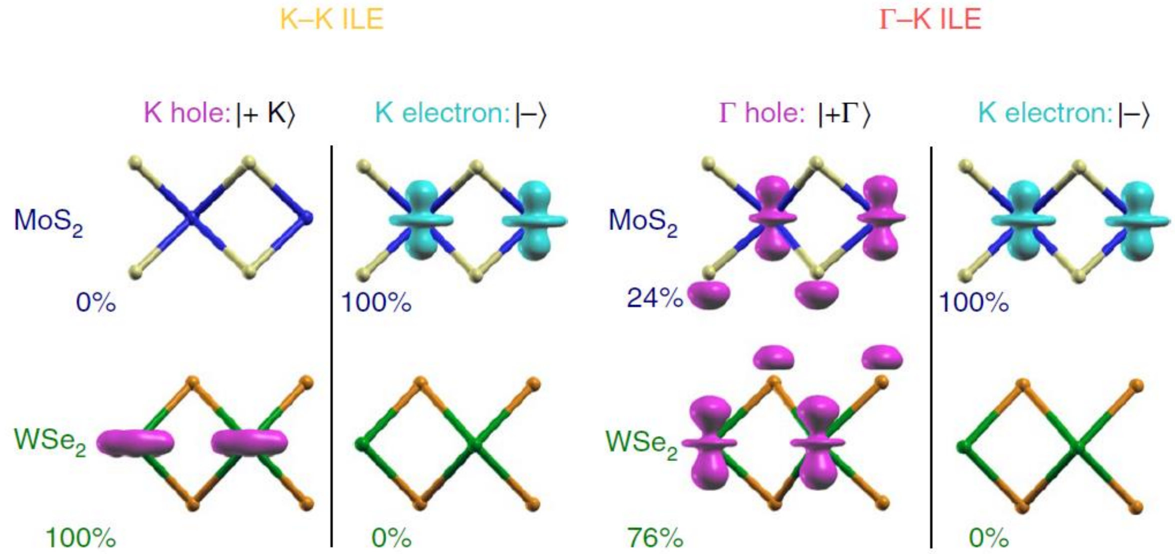


J. Kunstmann, F. Mooshammer, P. Nagler, TK et al., Nature Physics 2018

- Calculation of twist-dependent joint band structure for large supercells
- Calculation of twist-dependent interband transition energy change for K-K, K-Q, Γ-K etc.
- Only Γ-K transition matches experimentally observed shift of ILE energy

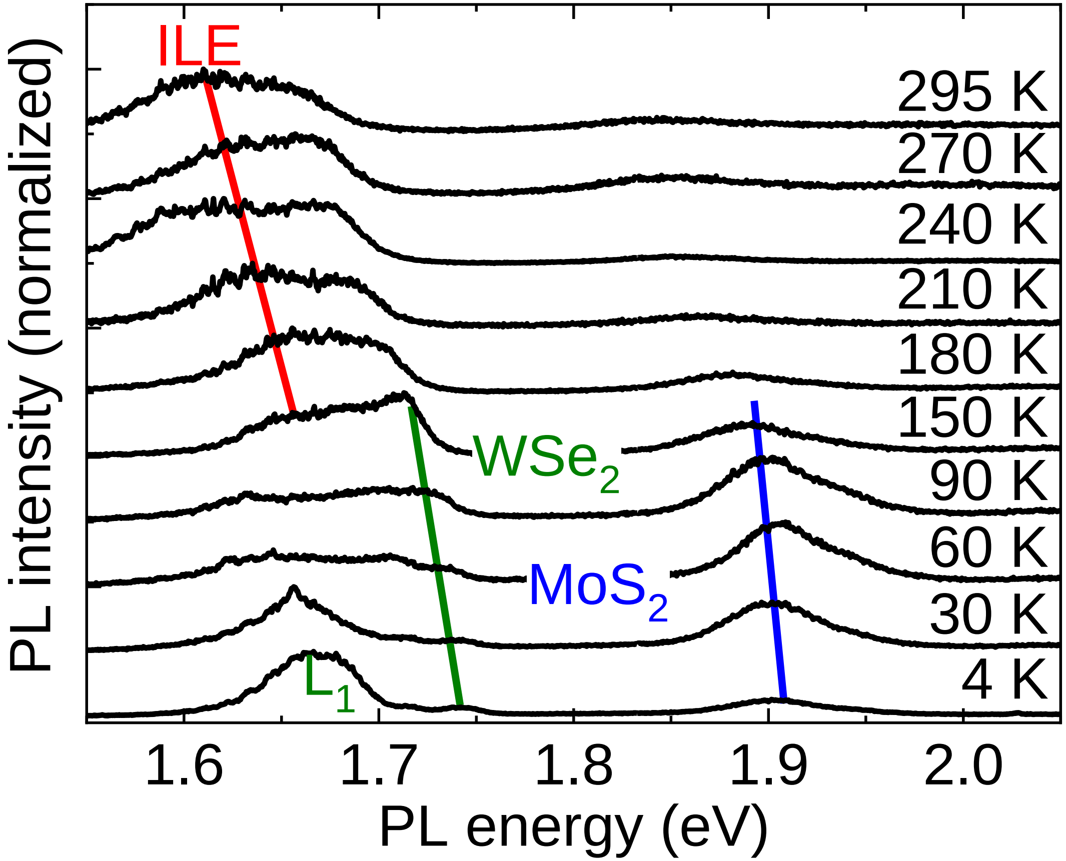
„Interlayer“ excitons in MoS_2-WSe_2 HS





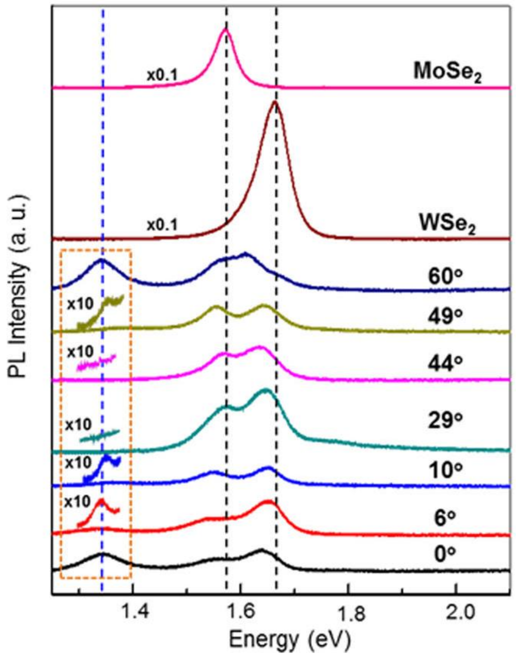
- DFT reveals state hybridization within band structure
- hole strongly delocalized at Γ
- Γ-K ILE has larger wave function overlap and binding energy than K-K ILE
- ➢ Momentum-indirect ILE dominates PL emission
- ➢ Transition has only partial interlayer character

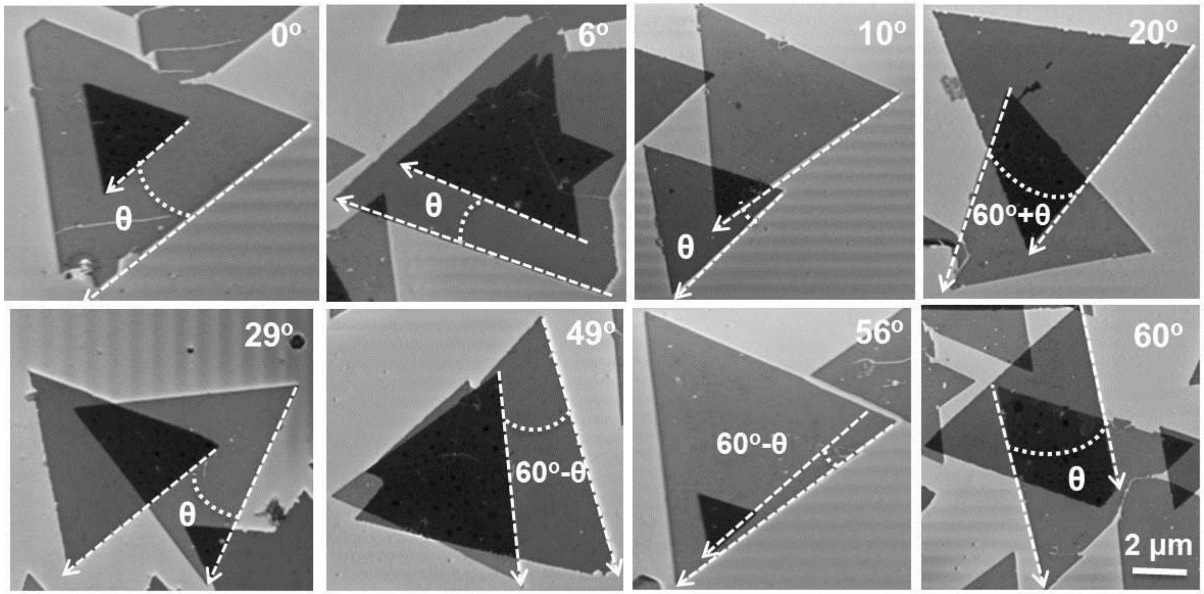
Limits of ILE in MoS_2-WSe_2 HS



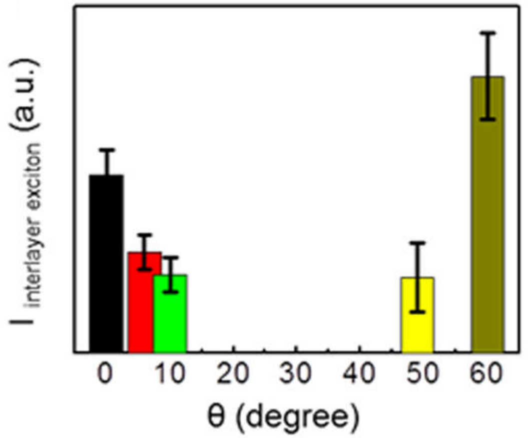
- ILE linewidth and intensity do not improve wth decreasing temperature
- Defect emission in WSe_2 overlaps ILE
- ➢ Study of subtle effects like exciton-exciton interaction and valley physics difficult

Alignment matters in $MoSe_2$-WSe_2 HS



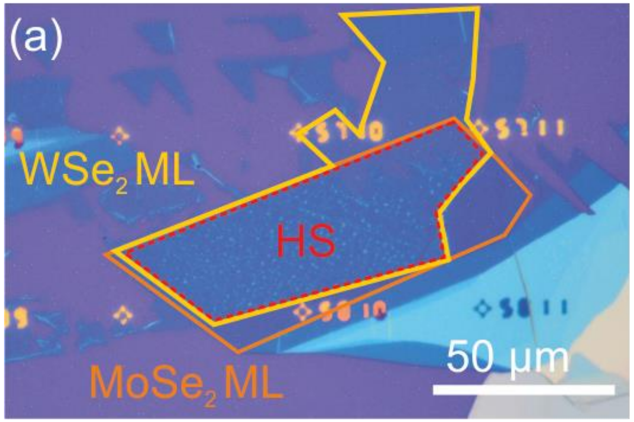


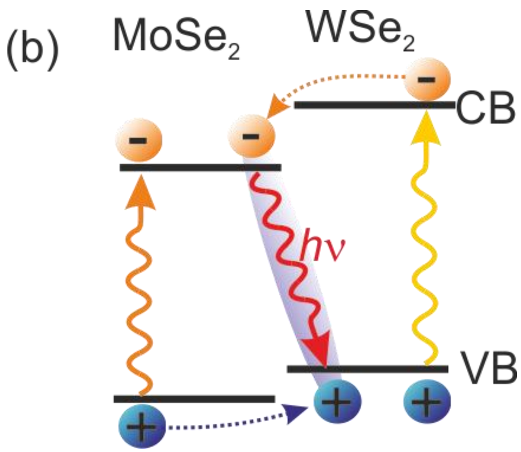
Nayak et al., ACS nano (2017)

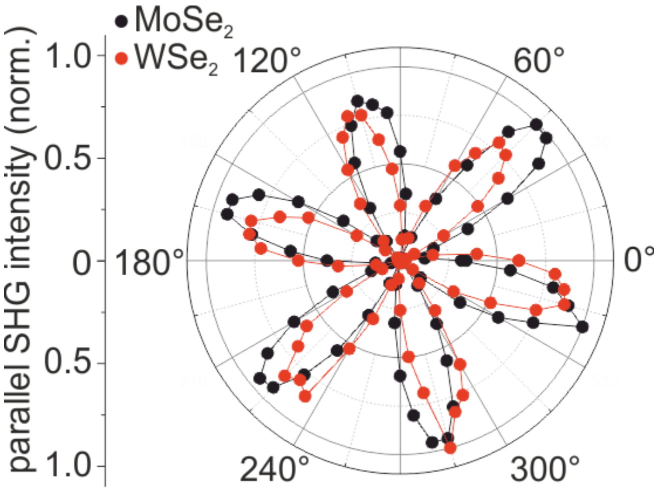


- Strong suppression of ILE PL in twisted $MoSe_2$ - WSe_2 HS
  - ➢ Twist generates momentum mismatch for interlayer transition
  - ➢ Indication that $MoSe_2$ - WSe_2 ILE is momentum-direct

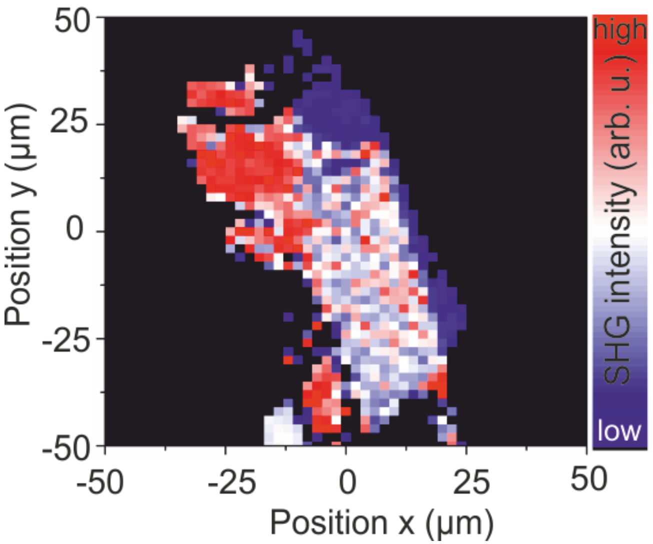
A better set of LEGO blocks? $MoSe_2$-WSe_2





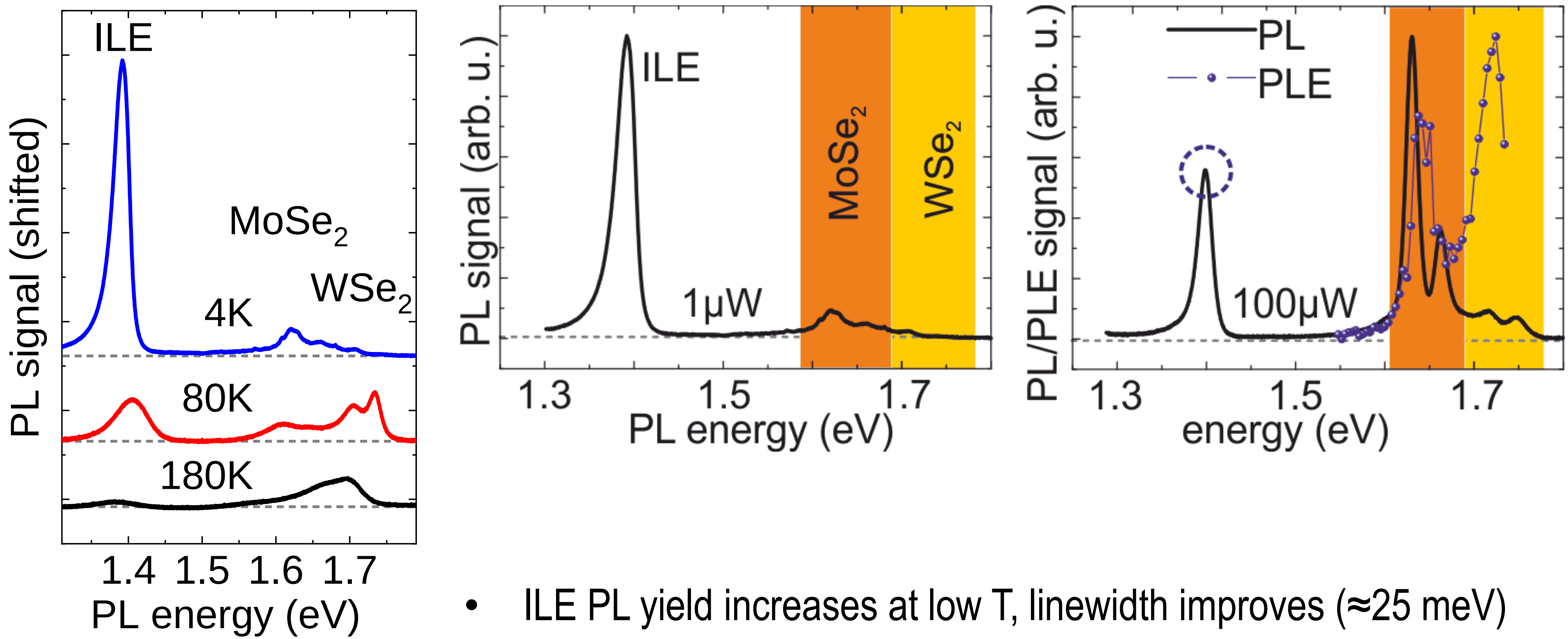


P. Nagler, TK et al., 2D Mat. 2017



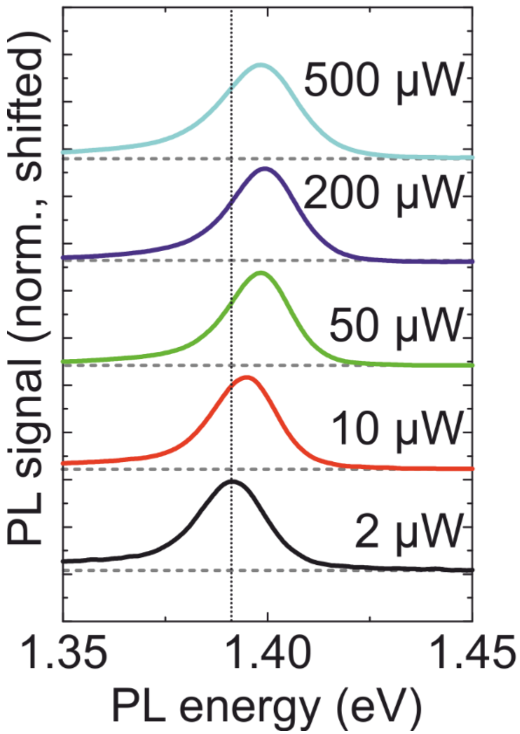
- (almost) no lattice mismatch between $MoSe_2$ and WSe_2
- ➢ Crystallographic alignment allows k-space alignment
- Our structure: 54° alignment between layers (destr. SHG)

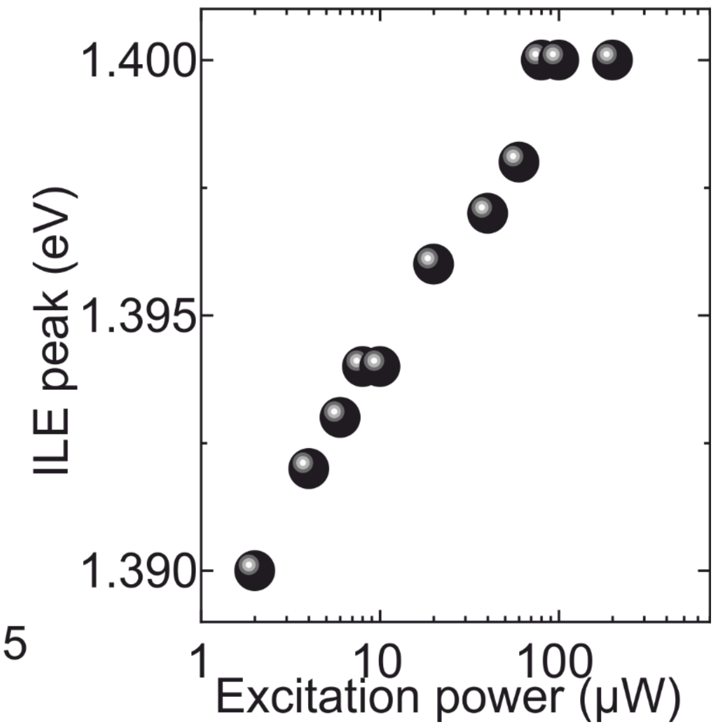
Low-temperature ILE PL

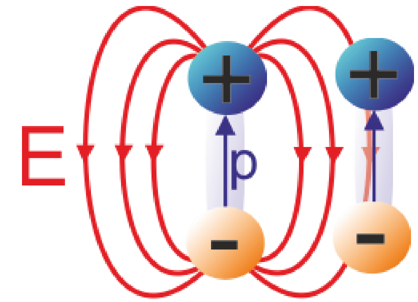


- ILE PL yield increases at low T, linewidth improves (≈25 meV)
- Large spectral separation between ILE and monolayer peaks
- Strong power dependence of ILE-monolayer ratio
- Monolayer absorption resonances identified in PLE

Exciton-exciton interactions (1)







Blueshift due to dipolar interaction:

(1) TMDC interlayer excitons

Rivera et al., Nature Comms. (2015)

Miller et al., Nano Lett. (2017)

(2) GaAs QW indirect excitons

…..

Butov et al., PRB (1999)

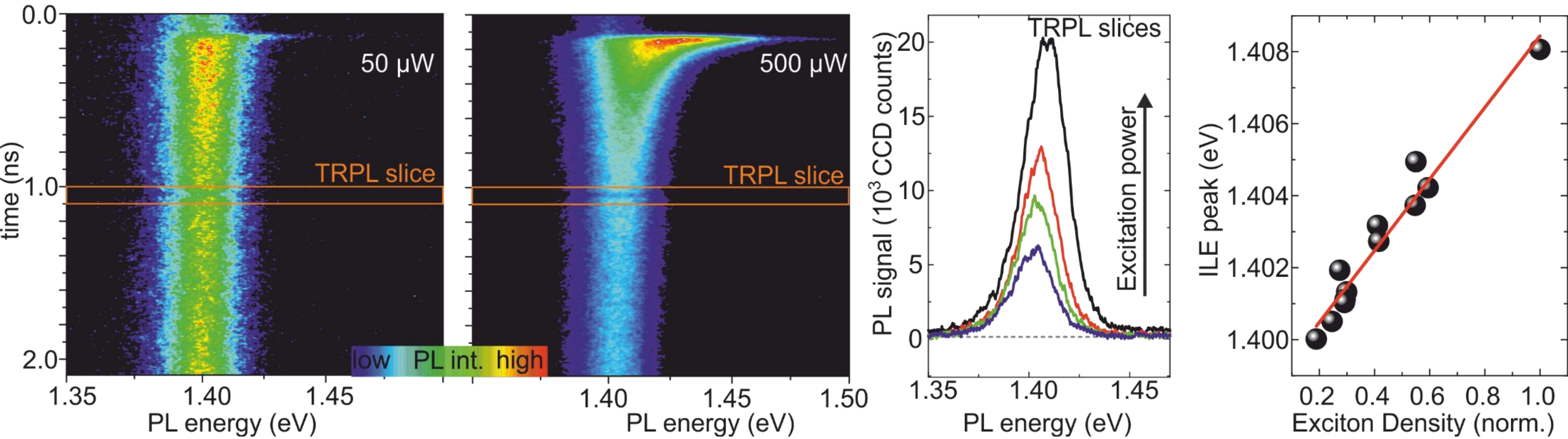
Schindler et al., PRB (2008)

Rapaport et al., PRB (2009)

…..

- Blueshift of ILE PL emission with increasing excitation power
- Dipole-dipole interaction between ILE
- Why near-logarithmic power dependence of blueshift?

Exciton-exciton interactions (2)

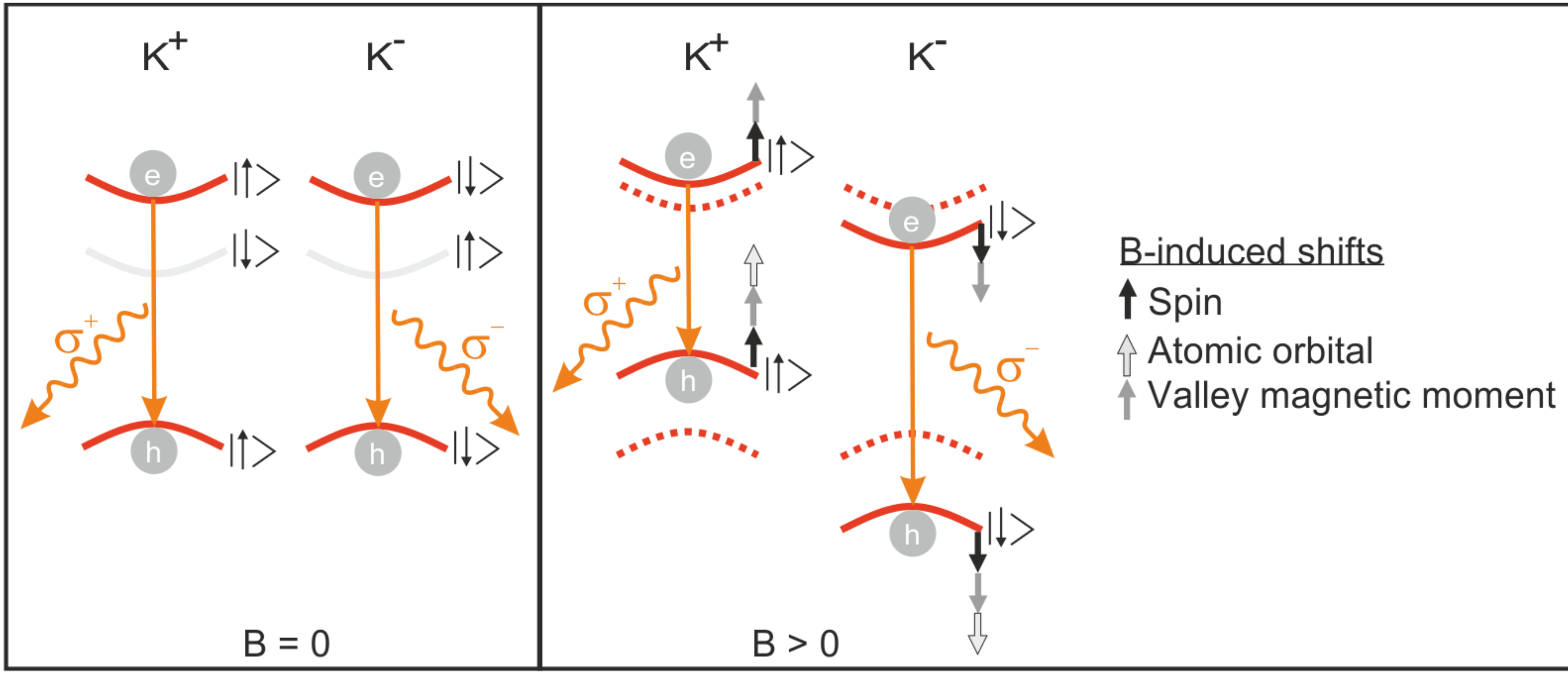


- TRPL shows strong ILE lifetime dependence on excitation power
- TRPL slices extracted after ILE relaxation allow direct intensity comparison
- Assumption: PL intensity within slice proportional to ILE density

➢ **Linear dependence** on ILE peak shift on ILE density

➢ Estimated lower boundary for ILE density: $n_{ILE} \geq 4 \cdot 10^{10} cm^{-2}$

Energetic shifts of monolayer states with B

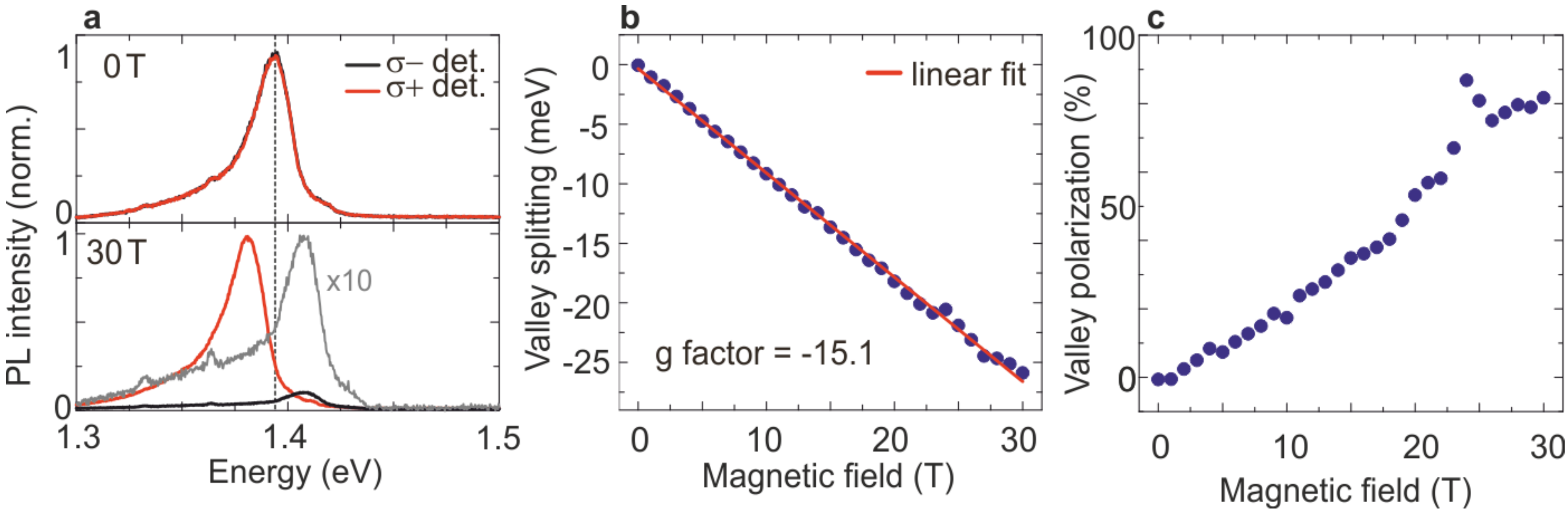


Valley degeneracy is broken by magnetic field, 3 contributions to shifts

- **Spin**: no net effect, CB and VB shift by same amount
- **Orbital magnetic moment**: valley-contrasting shift of valence band, $m_V = \pm 2$
- **Valley magnetic moment**: small net effect, CB and VB shift by similar amounts

g factor of 4 expected, deviation due to CB/VB **valley magnetic moment difference**

Magneto-PL of interlayer excitons

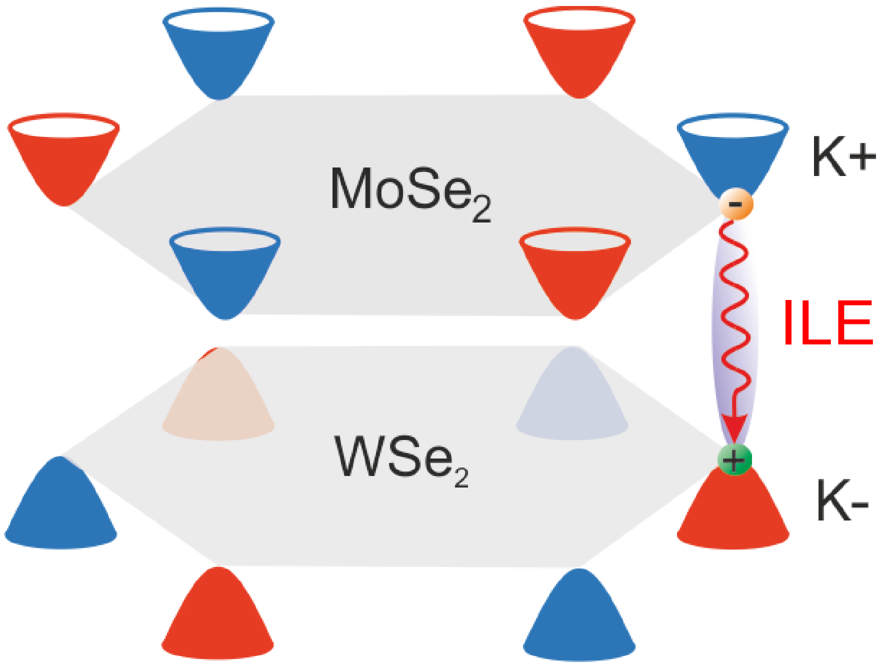


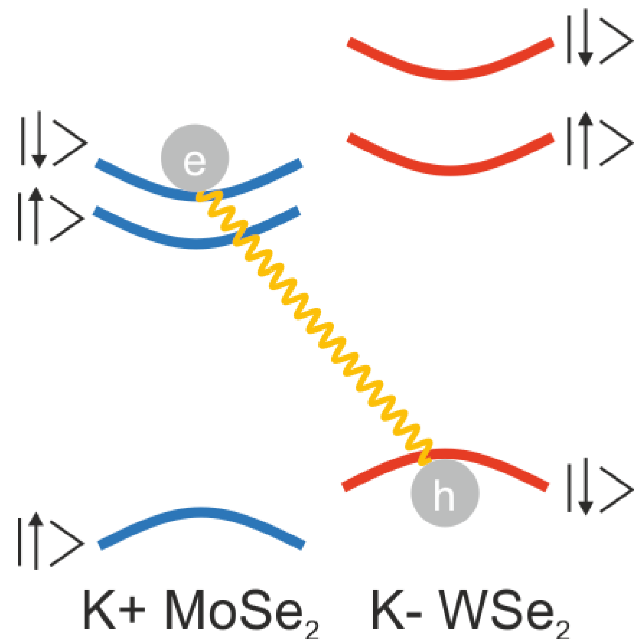
P. Nagler, TK et al., Nature Comms 2017

- Giant Zeeman splitting of interlayer exciton PL emission
- g factor about 4x larger than for monolayer excitons

➢ Near-unity valley polarization in sufficiently large fields

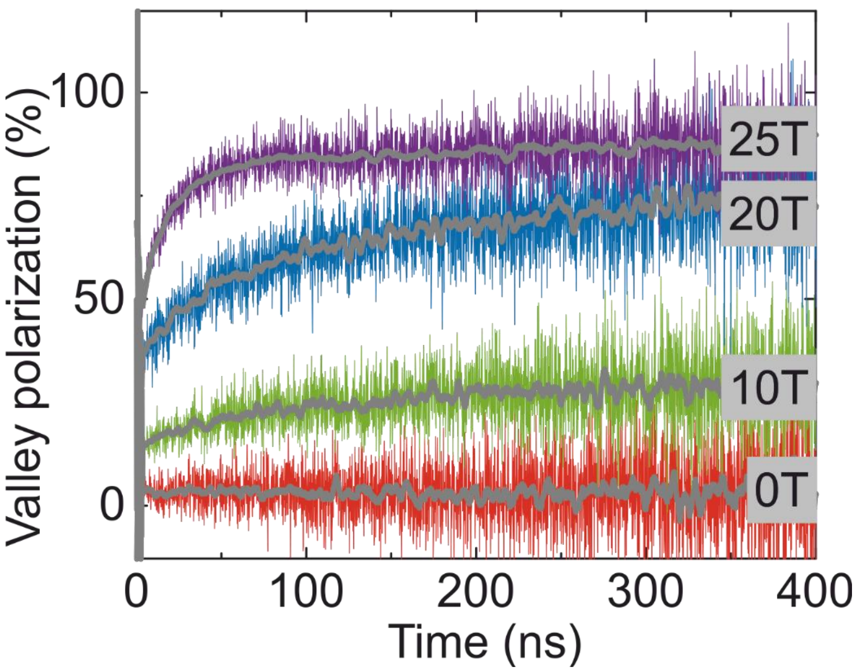
g factor engineering in heterostructures

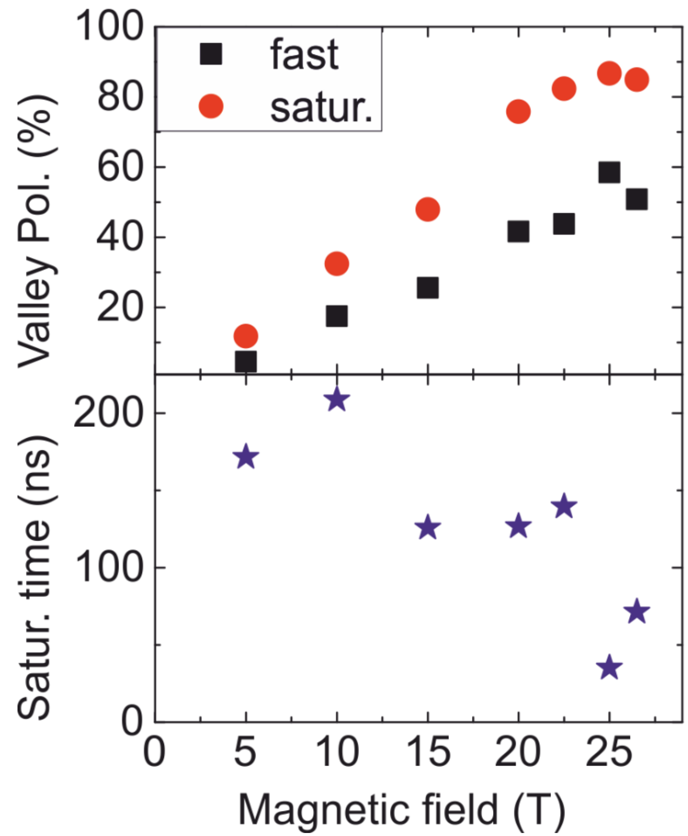




- Anti-alignment: transitions between $MoSe_2$ K+ and WSe_2 K- valleys (almost) direct in *k* space
- ILE transition between **opposite** K valleys
- CB and VB shift in opposite directions with B
- **sum** of CB and VB valley magnetic moments yields giant splitting

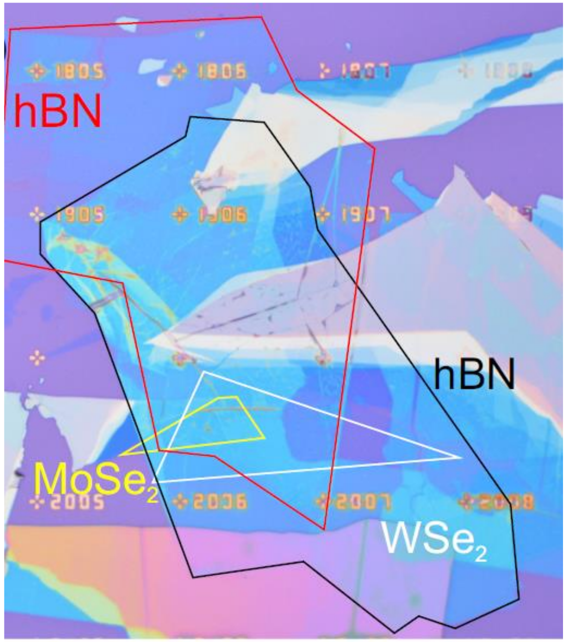
Valley dynamics in large magnetic fields

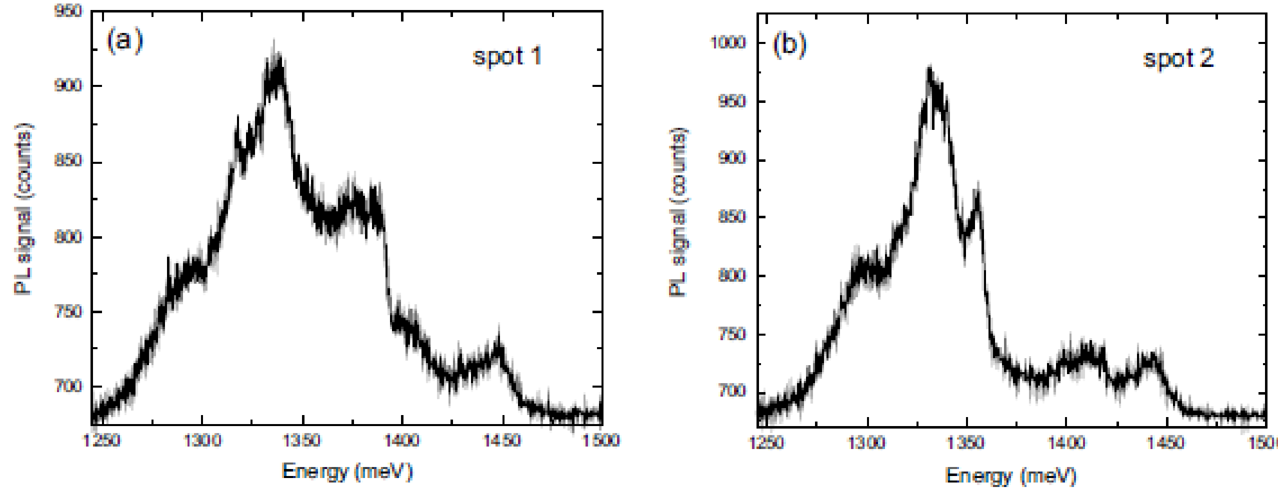




- Valley polarization shows complex dynamics
- Fast process yields initial, finite value
- Slow saturation process on 100 ns timescale, speeds up with B field

Outlook: signatures of moiré effects





c.f. Tran et al., Nature 2019

$MoSe_2$-WSe_2 HS encapsulated in hBN

- Multiple peaks observable in interlayer exciton energy range

➢ Interlayer excitons trapped in moiré potential?

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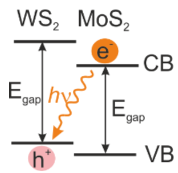
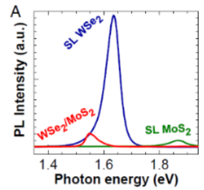
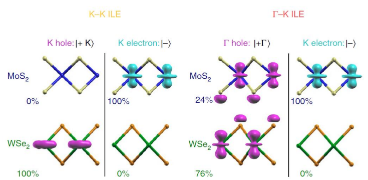
Summary

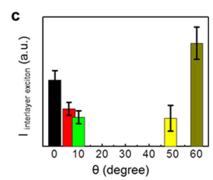
✓ TDMC heterostructures host interlayer excitons



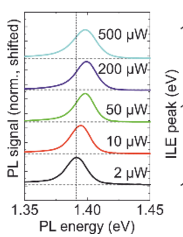


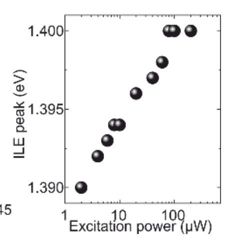
✓ ILE character depends on specific material combination

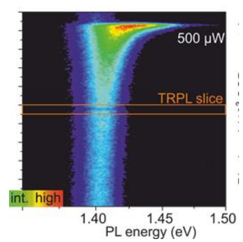




• ILE show interactions and complex dynamics







✓ Interlayer twist allows to control energy and valley-related properties