Towards 2D Valleytronics

Johnson Goh

Institute of Materials Research and Engineering
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RPGR 2017 Sep

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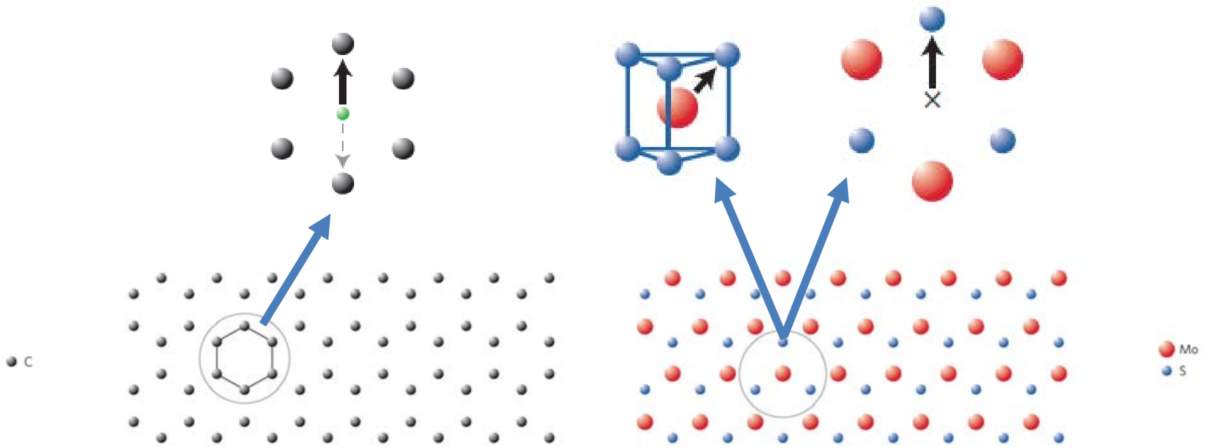
Inversion Symmetry

Broken in 2D Transition Metal Dichalcogenides (MX_2)



K. Behnia, *Nature Nanotech.* **7**, 488 (2012)

Valley Physics in 2D Materials

nature physics | REVIEW ARTICLE
PUBLISHED ONLINE: 30 APRIL 2014 | DOI: 10.1038/NPHYS2942

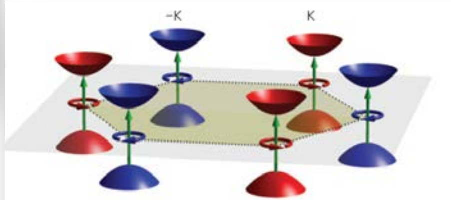
Spin and pseudospins in layered transition metal dichalcogenides

Xiaodong Xu[1]*, Wang Yao[2]*, Di Xiao[3] and Tony F. Heinz[4]

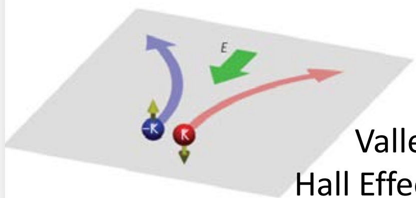
Broken Inversion Symmetry
$\Rightarrow$ Valley contrasting properties (spin texture, Berry curvature)

Table 1 | Internal degree of freedom of Bloch electrons in 2D hexagonal crystals and the associated physical phenomena.

	Spin	Valley pseudospin	Layer pseudospin
Magnetic moment	✓	✓	
Hall effect	✓	✓	
Optical selection rule	✓	✓	
Electrical polarization			✓



Optical Selection Rules



Valley Hall Effect

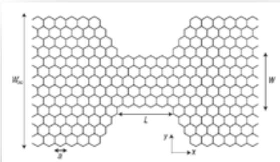
Opportunities in the Valley

PRL 99, 236809 (2007)		PHYSICAL REVIEW LETTERS		7 DECEM...

Valley-Contrasting Physics in Graphene: Magnetic Moment and Topological Transport

Di Xiao,* Wang Yao,* and Qian Niu
Department of Physics, The University of Texas, Austin, Texas 78712-0264, USA
(Received 11 September 2007; published 7 December 2007)

We investigate physical properties that can be used to distinguish the valley degree of freedom in systems where inversion symmetry is broken, using graphene systems as examples. We show that the pseudospin associated with the valley index of carriers has an intrinsic magnetic moment, in close analogy with the Bohr magneton for the electron spin. There is also a valley dependent Berry phase effect that can result in a valley contrasting Hall transport, with carriers in different valleys turning into opposite directions transverse to an in-plane electric field. These effects can be used to generate and detect valley polarization by magnetic and electric means, forming the basis for the valley-based electronics applications.



LETTERS

Valley filter and valley valve in graphene

A. RYCERZ[1,2], J. TWORZYDŁO[3] AND C. W. J. BEENAKKER[1]*
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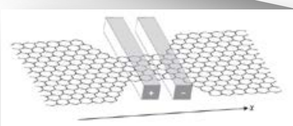
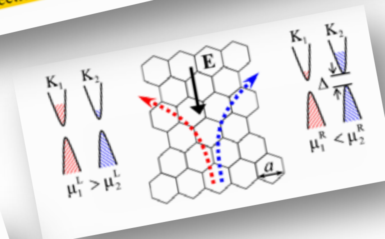
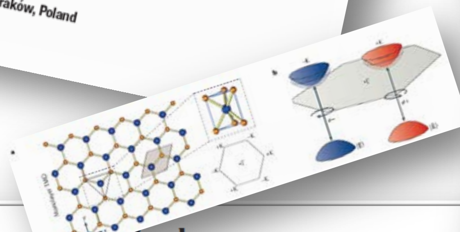
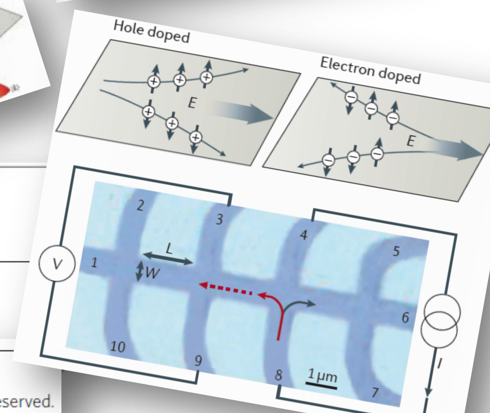
[3]Institute of Theoretical Physics, Warsaw University, Hoża 69, 00-681 Warsaw, Poland
*e-mail: beenakker@lorentz.leidenuniv.nl









Valleytronics in 2D materials

John R. Schaibley[1], Hongyi Yu[2], Genevieve Clark[3], Pasqual Rivera[1], Jason S. Ross[3], Kyle L. Seyler[1], Wang Yao[2] and Xiaodong Xu[1,3]

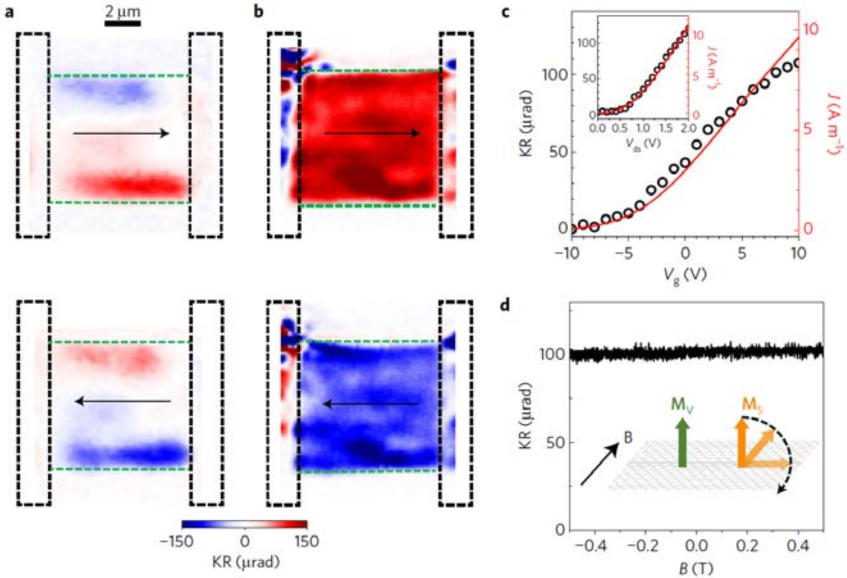
NATURE REVIEWS | MATERIALS

nature materials
LETTERS
PUBLISHED ONLINE: 10 JULY 2017 | DOI: 10.1038/NMAT4931

Valley magnetoelectricity in single-layer MoS_2

Jieun Lee[1,2], Zefang Wang[1], Hongchao Xie[1], Kin Fai Mak[1]* and Jie Shan[1]*

Unstrained   Strained



Electrical Generation (in-plane E)
+
Optical Detection (Kerr Rotation)

Valleytronics Materials, Architectures, and Devices Workshop

MIT Samberg Center, Cambridge, MA
August 22–23, 2017

<u>**Organizing Committee**</u>

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MIT Lincoln Laboratory
steven.vitale@ll.mit.edu
Philip Kim
Harvard University
philipkim@g.harvard.edu
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<u>**Confirmed Invited Speakers**</u>

- **Allan MacDonald, *UT Austin***
- **Artem Mishchenko, *U of Manchester***
- **Daniel Gunlycke, *NRL***
- **Feng Wang, *UC Berkeley***
- **George Yu-Shu Wu, *Nat .Tsing-Hua U***
- **Hongkun Park, *Harvard University***
- **Jie Shan, *Penn State University***
- **Kin Fai Mak, *Penn State University***
- **Nuh Gedik, *MIT***
- **Pablo Jarillo-Herrero, *MIT***
- **Philip Kim, *Harvard University***
- **Scott Crooker, *Los Alamos Nat. Lab***
- **Tony Heinz, *Stanford University***
- **Xiaodong Xu, *U of Washington***

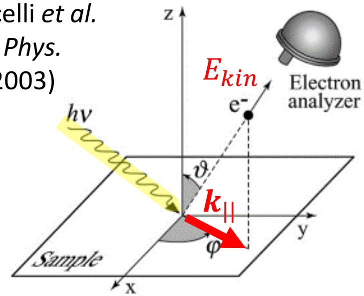
Key Challenges

Valley Polarization	Detection Control
Valley Current	Generation Detection

K. Behnia, *Nature Nanotech.* **7**, 488 (2012)
X. Xu *et. al. Nature Phys.* **10**, 343 (2014)

Spin- & Angle-resolved Photoemission Spectroscopy

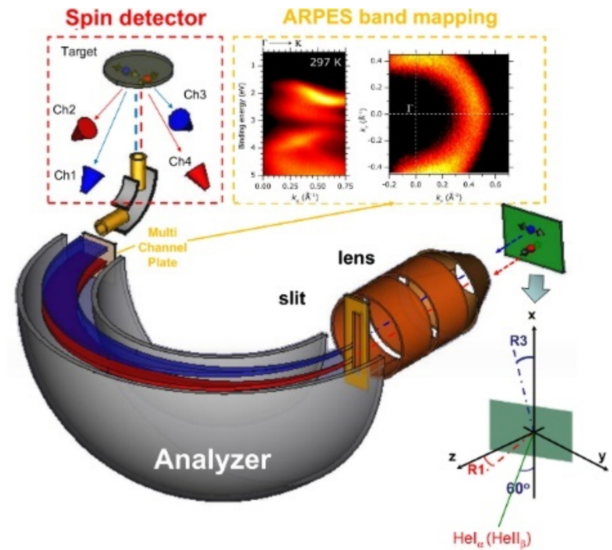
A. Damascelli *et al.*
Rev. Mod. Phys.
75, 473, (2003)



Photoemission geometry

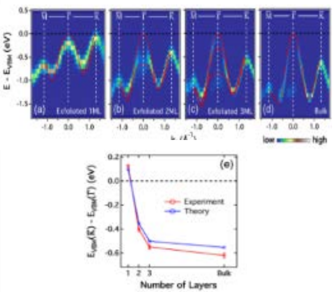
$$E_{kin} = h\nu - W - |E_B(k_{||})|$$

$$k_{||} = \frac{1}{\hbar}\sqrt{2mE_{kin}}\sin\theta$$



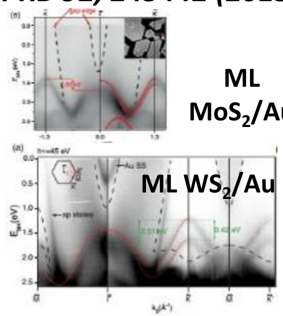
Band-structures - Synchrotron ARPES on TMDCs

W. Jin et al.
PRL 111, 106801 (2013)



Direct-to-indirect bandgap transition in **MoS_2**

J. Miwa et al.
PRL 114, 046802 (2015)
M. Dendzik et al.
PRB 92, 245442 (2015)

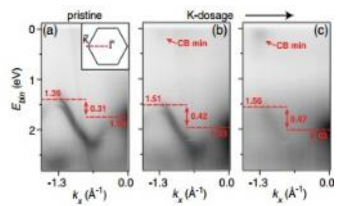


ML MoS_2/Au

ML WS_2/Au

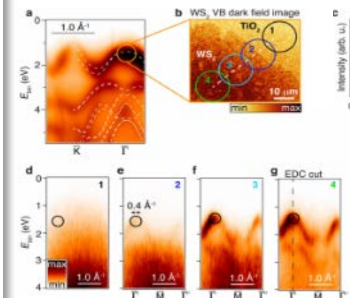
Spin-orbit split bands

J. Miwa et al.
PRL 114, 046802 (2015)



Tuning **ML MoS_2** by K **doping**

Ulstrup et al.
ACS Nano 10,10058 (2016)

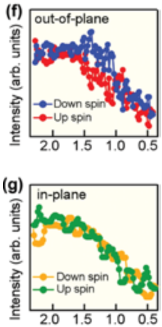


ML WS_2 grown by CVD **transferred** onto TiO_2; Like free-standing WS_2

Valley Polarization in 2D TMDCs

Lab SARPES

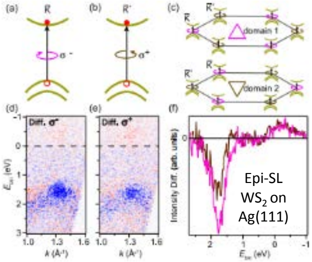
K. Sugawara et al.
APL 107, 071601 (2015)



Out-of-plane/In-plane spin components, epi-ML WSe_2 at 300K

Lab TR-ARPES

S. Ulstrup et al.
PRB 95 041405R (2017)

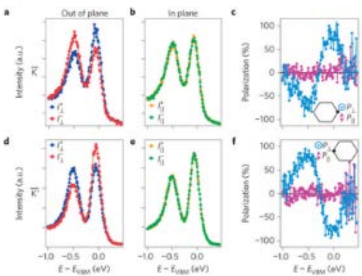


TR-ARPES with **CP laser source**; Selective valley polarization in **ML WS_2**

Valley Polarization in TMDCs

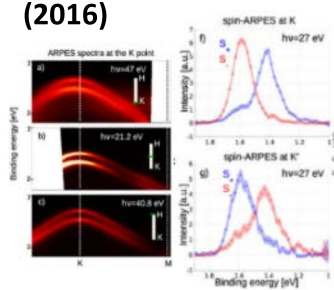
Synchrotron SARPES

J.M Riley et al.
Nat. Phys. 10, 835 (2014)



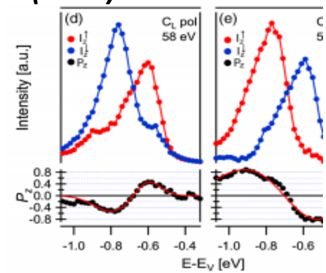
Spin-polarized bulk bands even with **BL WSe_2** inversion-symmetry

M. Gehlmann et al.
Sci. Rep. 6, 26197 (2016)



SARPES reveals **valley polarization** in centrosymmetric **bulk MoS_2**

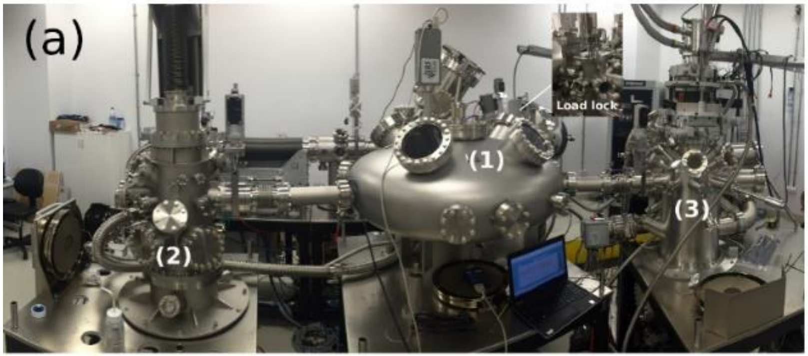
E. Razzoli et al.
PRL 118, 086402 (2017)



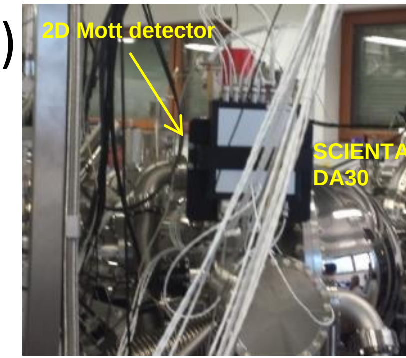
CP SARPES on **bulk MoS_2** reveals **valley- and layer-locked spins** in top 2 layers

Lab-based ARPES/SARPES in IMRE (A*STAR)

ADVANCED PHOTOELECTRON SPECTROSCOPY lab (B2-07 Synthesis Bld) (Since Sept 2016)



(b)

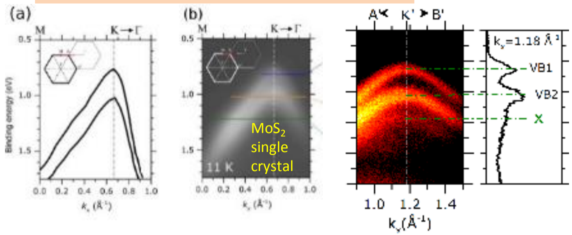


1. UFO transfer chamber
2. Preparation chamber
3. Analysis chamber

- UHV
- 11 – 300 K
- ARPES: 20 meV resolution
- SARPES: 150 meV resolution

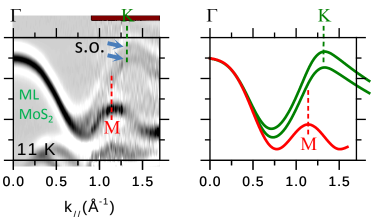
ARPES/SARPES Capabilities in IMRE

Spin-orbit Splitting at K

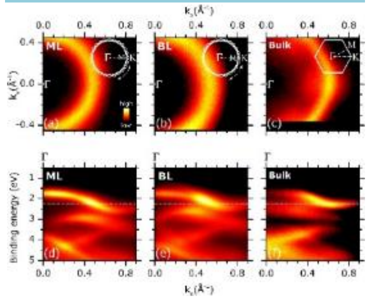


MoS_2: $\Delta_{s\text{-}o}$ ~0.15 eV WS_2: $\Delta_{s\text{-}o}$ ~0.45 eV

CVD-growth Theory

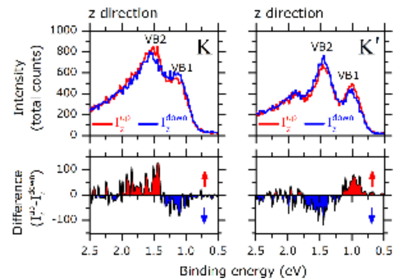


Layer dependence



Grown MoS_2

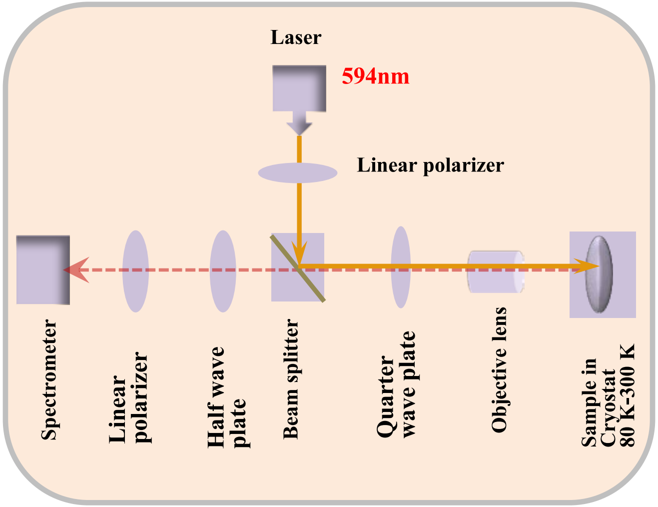
Spin polarization at K, K'



WS_2 single crystal

Bussolotti, in prep.

Home-built CDPL System



- Home-built
- Continuous Wave laser (λ= 594nm, 2.087 eV)
- Spot size 4 μm
- Power: 30 μW-100 μW

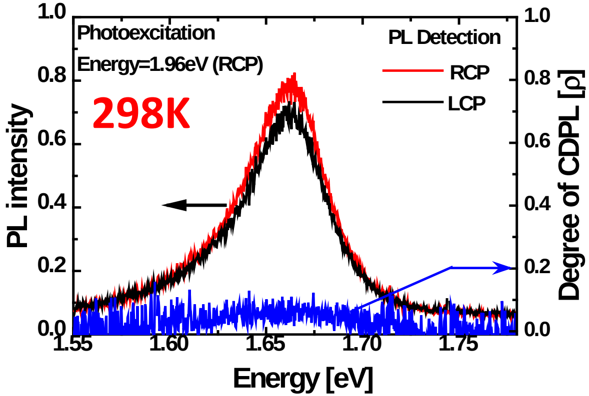
Degree of Circular Polarization (DOCP, ρ)

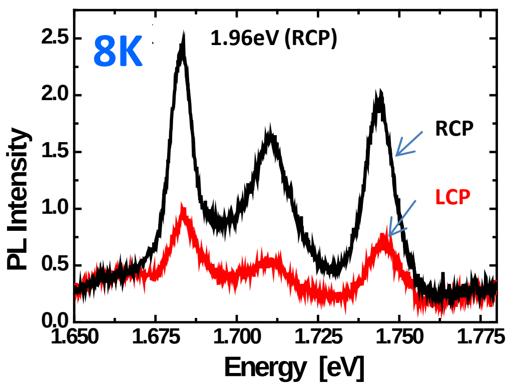
$$\rho = \frac{I(\sigma^+) - I(\sigma^-)}{I(\sigma^+) + I(\sigma^-)}$$

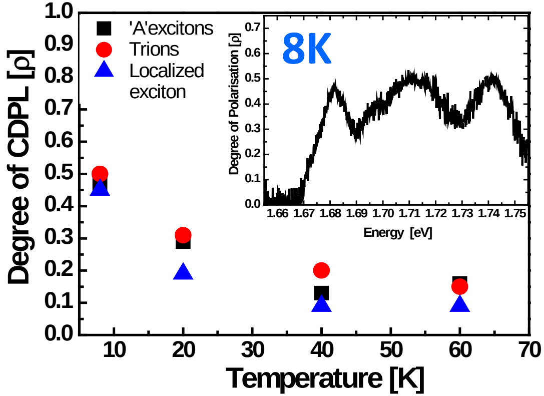
$I(\sigma^+)$: Intensity of co-polarized emission

$I(\sigma^-)$: Intensity of counter-polarized emission

PL and CDPL in Monolayer WSe_2







Chellappan, in prep.

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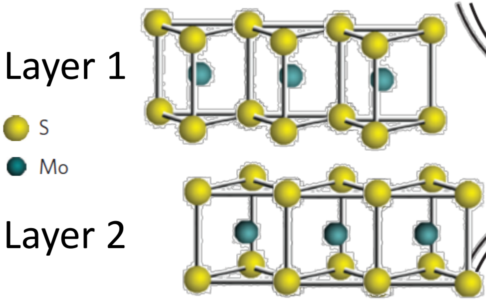
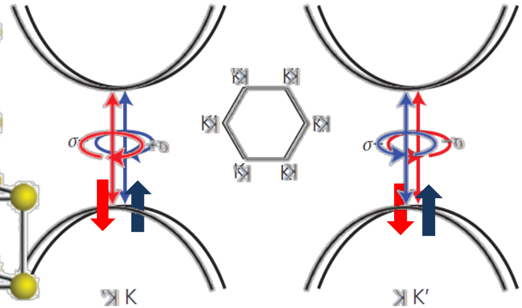
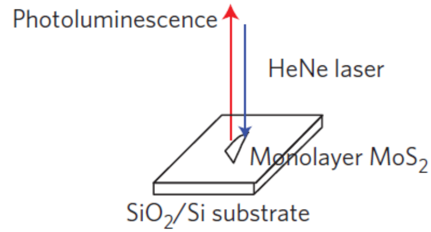
Circular Dichoric PL

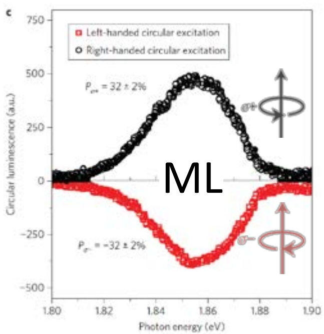


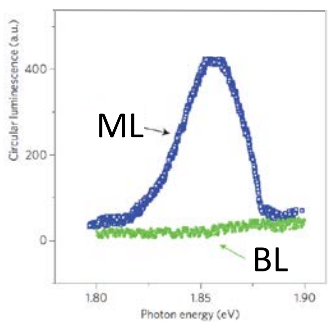


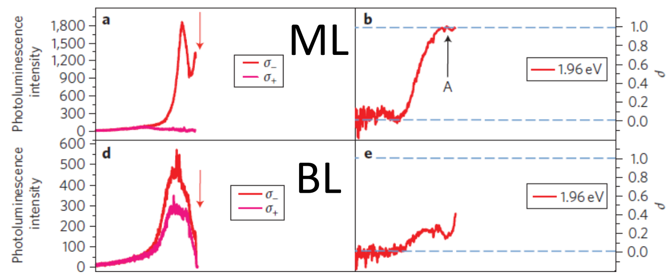


$$\rho = \frac{I(\sigma +) - I(\sigma -)}{I(\sigma +) + I(\sigma -)}$$

Inversion Symmetry Restored







LETTERS
PUBLISHED ONLINE: 17 JUNE 2012 | DOI: 10.1038/NNANO.2012.95
nature nanotechnology

Valley polarization in MoS_2 monolayers by optical pumping

Hualing Zeng[1†], Junfeng Dai[2,1†], Wang Yao[1,3], Di Xiao[4] and Xiaodong Cui[1]*

LETTERS
PUBLISHED ONLINE: 17 JUNE 2012 | DOI: 10.1038/NNANO.2012.96
nature nanotechnology

Control of valley polarization in monolayer MoS_2 by optical helicity

Kin Fai Mak[1], Keliang He[2], Jie Shan[2] and Tony F. Heinz[1]*

Anomalous WS_2

Anomalously robust valley polarization and valley coherence in bilayer WS_2

Bairen Zhu[a,1], Hualing Zeng[b,1,2], Junfeng Dai[c], Zhirui Gong[a], and Xiaodong Cui[a,2]

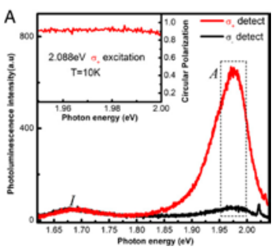
[a]Physics Department, University of Hong Kong, Hong Kong 999077, China; [b]Physics Department, Chinese University of Hong Kong, Hong Kong 999077, China; and [c]Physics Department, South University of Science and Technology of China, Shenzhen 518055, China

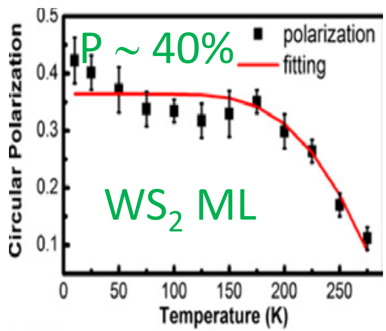
Edited by Paul L. McEuen, Cornell University, Ithaca, NY, and approved July 3, 2014 (received for review April 16, 2014)

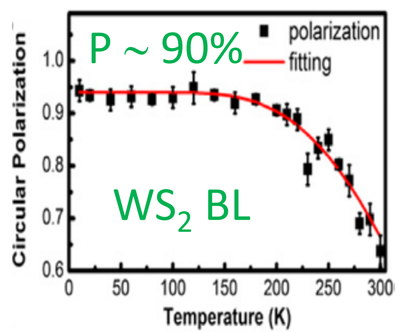
We report the observation of anomalously robust valley polarization and valley coherence in bilayer WS_2. The polarization of the photoluminescence from bilayer WS_2 follows that of the excitation source with both circular and linear polarization, and remains even at room temperature. The near-unity circular polarization of the

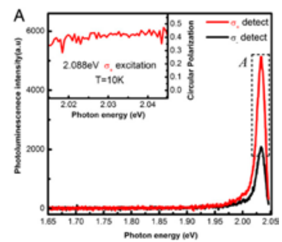
indices is taken into account. Note that the spin–valley coupling strength in WS_2 is around 0.4 eV (the counterpart in MoS_2 ~ 0.16 eV), which is significantly higher than the interlayer hopping energy (~0.1 eV); the interlayer coupling at K and K′ valleys in WS_2 is greatly suppressed as indicated in Fig. 1*B* (7, 9). Consequently,

$\rho_{BL} > \rho_{ML}$!!!









Anomalous WS_2

$\rho_{BL} > \rho_{ML}$!!!

Nanoscale, 2017,**9**, 5148-5154

Huimin Su,[a] Chengrong Wei,[ab] Aiying Deng,[a] Dongmei Deng,[a] Chunlei Yang[c] and Jun-Feng Dai*[a]
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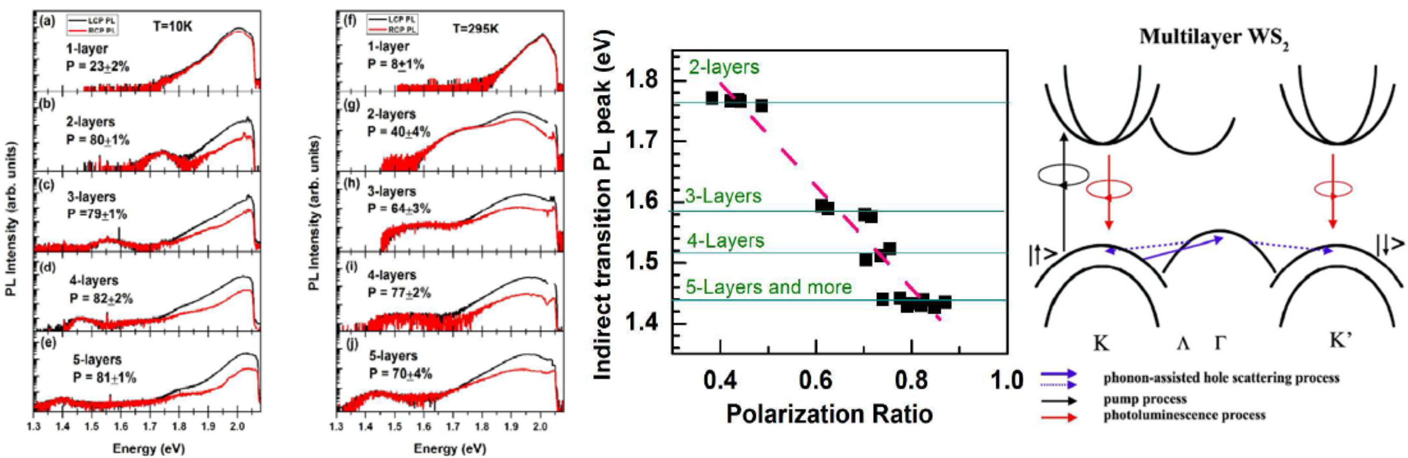
[a] Department of Physics, South University of Science and Technology of China, Shenzhen 518055, China
[b] Physics Department, The University of Hong Kong, Pokfulam road, China
[c] Center for Photovoltaic and Solar Energy, Shenzhen Institutes of Advanced Technology, CAS, Shenzhen 518055, China



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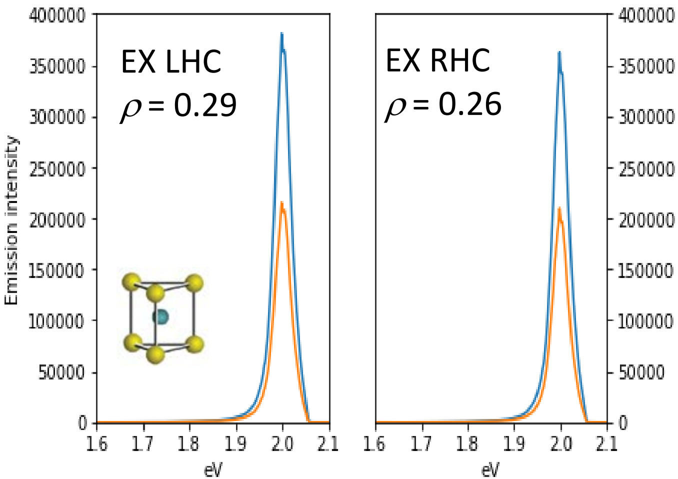
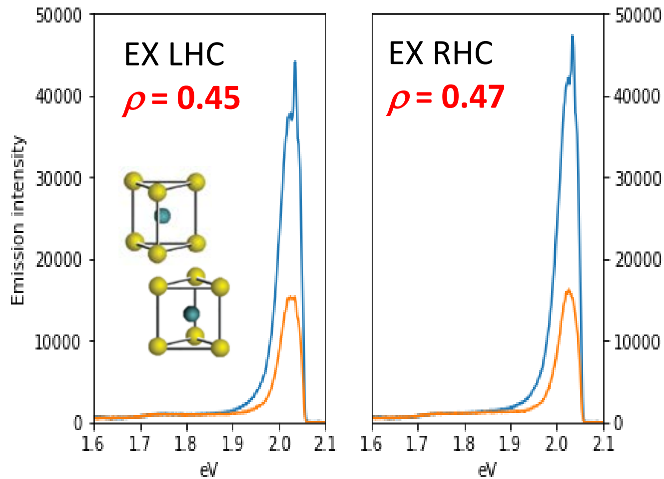
CDPL on WS_2 @ IMRE

$\rho_{BL} > \rho_{ML}$!!!

WS_2 Monolayer @120K



WS_2 Bilayer @120K



ρ enhanced instead of quenched!

Chellappan, Ooi, in prep.

nature physics

ARTICLES

PUBLISHED ONLINE: 13 APRIL 2014 | DOI: 10.1038/NPHYS2933

Hidden spin polarization in inversion-symmetric bulk crystals

Xiuwen Zhang[1,2,3†], Qihang Liu[1,4†], Jun-Wei Luo[3*], Arthur J. Freeman[4] and Alex Zunger[1*]

Compensated (hidden) spin polarization: R-2 and D-2 effects (Fig. 1c). These can arise in crystal structures where inversion symmetry is present in the bulk space group, but not in the site point groups (Fig. 1c). This is the case when the individual sites carry either a local dipole field (for R-2) or a site inversion asymmetric crystal field (for D-2). A combination of a bulk centrosymmetric

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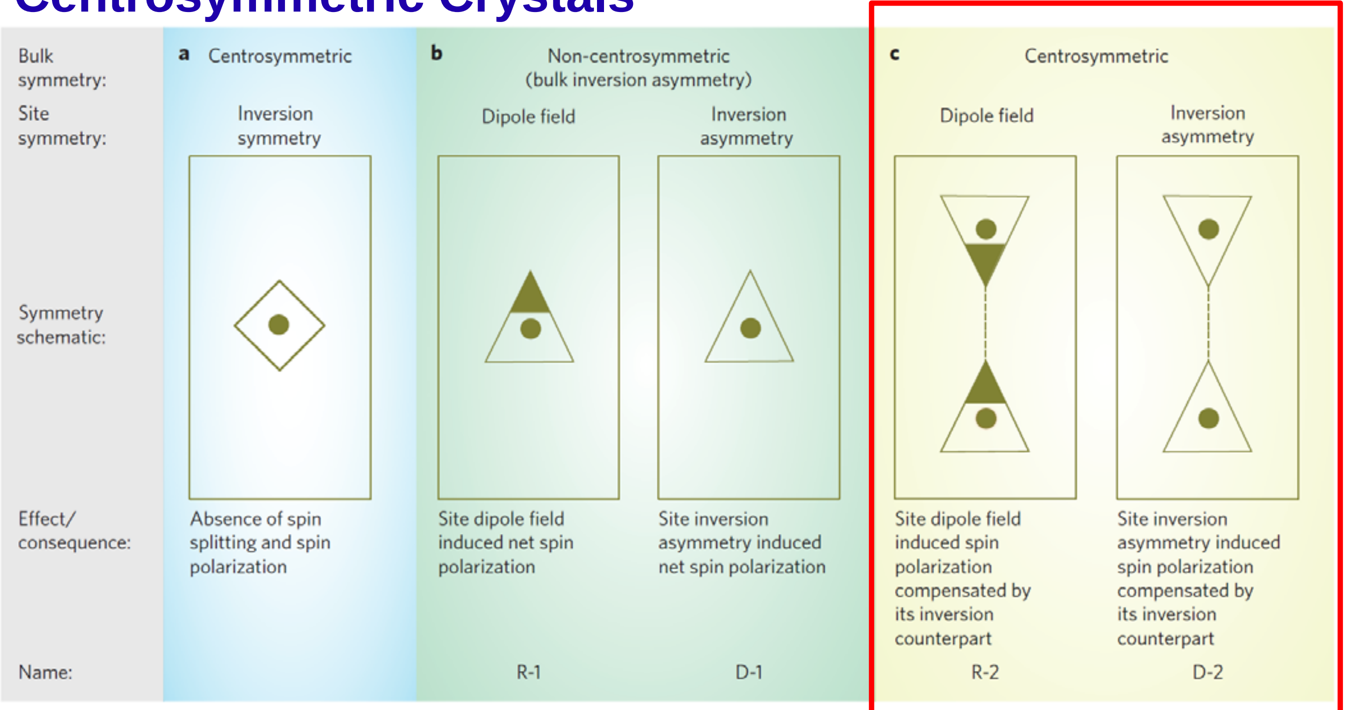
R2-D2 “Hidden” Local Spin Polarizations in Bulk Centrosymmetric Crystals



gure 1 | The three classes of spin polarization in nonmagnetic bulk crystals. a, Absence of spin polarization in centrosymmetric crystals if all atomic sites e inversion symmetric. As the local environment (crystal field) of centrosymmetric atomic sites does not produce spin–orbit coupling induced spin larization, the total (bulk) spin polarization is absent as well. **b**, Net bulk spin polarization (R-1 and D-1 effects): a local site dipole field or the site version asymmetry leads to local Rashba or Dresselhaus effects, respectively. In combination with a non-centrosymmetric space group, these local fects produce bulk R-1 (Rashba) and D-1 (Dresselhaus) effects, respectively. **c**, Compensated (hidden) bulk spin polarization (R-2 and D-2 effects): a local te dipole field or the site inversion asymmetry leads to local Rashba or local Dresselhaus effects, respectively, as in **b**. In combination with a entrosymmetric space group, these local effects produce bulk R-2 (Rashba) and D-2 (Dresselhaus) effects, respectively. Here the spin polarization from ach sector is concealed by compensation from their inversion partners, but is readily visible when the results from individual sectors are observed.

Don’t ignore local Rashba and Dresselhaus SOC effects!

"Hidden" Spin Polarizations in Bulk TMDCs

Site point group / Bulk space group	Non-centrosymmetric (at least one site)			Centrosymmetric (all sites) (C_i, C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{6h}, D_{6h}, T_h, O_h)
	Non-polar (all sites) (D_2, D_3, D_4, D_6, S_4, D_{2d}, C_{3h}, D_{3h}, T, T_d, O)	Polar (at least one site) (C_1, C_2, C_3, C_4, C_6, C_{1v}, C_{2v}, C_{3v}, C_{4v}, C_{6v})		
		Dipoles add up to zero	Dipoles add up to non-zero	
Non-centrosymmetric (for example, $F\bar{4}3m$)	**a** D-1 Example: GaAs, ZrCoBi	**b** D-1 Example: γ-$LiAlO_2$	**c** R-1 & D-1 Example: BiTeI, α-SnTe	*Not possible* (*Site point group* cannot be centrosymmetric *if space group is non*-centrosymmetric)
Centrosymmetric (for example, $R\bar{3}m$)	**d** D-2 Example: Si, NaCaBi	**e** R-2 & D-2 Example: MoS_2, Bi_2Se_3, $LaOBiS_2$ **MoS_2**		**f** Absence of spin polarization Example: β-SnTe

Light in the valley?

PRL **114,** 087402 (2015) PHYSICAL REVIEW LETTERS week ending 27 FEBRUARY 2015

Intrinsic Circular Polarization in Centrosymmetric Stacks of Transition-Metal Dichalcogenide Compounds

Qihang Liu,[*] Xiuwen Zhang, and Alex Zunger[†]
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(Received 21 June 2014; revised manuscript received 28 January 2015; published 27 February 2015)

The circular polarization (CP) that the photoluminescence inherits from the excitation source in n monolayers of transition-metal dichalcogenides $(MX_2)_n$ has been previously explained as a special feature of *odd* values of n, where the inversion symmetry is absent. This "valley polarization" effect results from the fact that, in the absence of inversion symmetry, charge carriers in different band valleys could be selectively excited by different circular polarized light. Although several experiments observed CP in centrosymmetric MX_2 systems, e.g., for bilayer MX_2, they were dismissed as being due to some extrinsic sample irregularities. Here we show that also for $n =$ even, where inversion symmetry is present and valley polarization physics is strictly absent, such intrinsic selectivity in CP is to be expected on the basis of fundamental spin-orbit physics. First-principles calculations of CP predict significant polarization for $n = 2$ bilayers: from 69% in MoS_2 to 93% in WS_2. This realization could broaden the range of materials to be considered as CP sources.

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Re-Learning Valley Polarization in TMDCs

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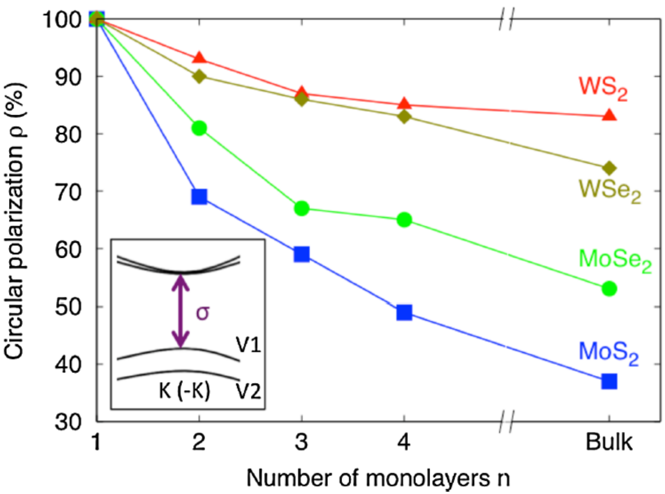

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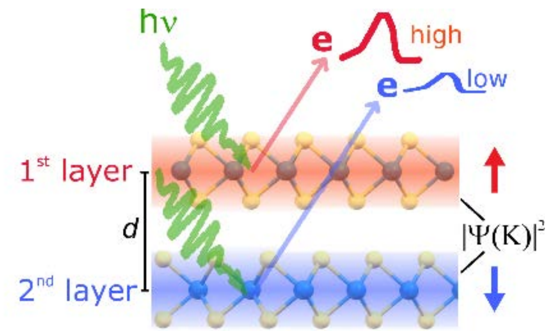
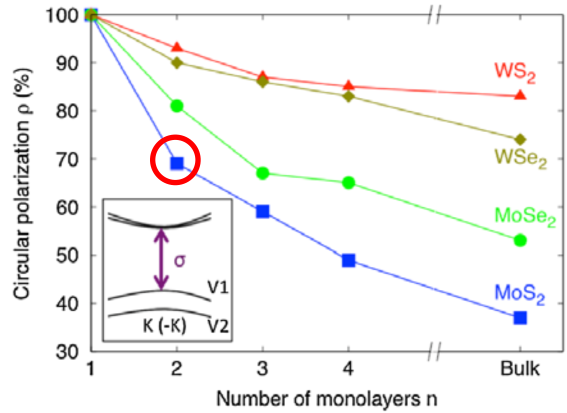
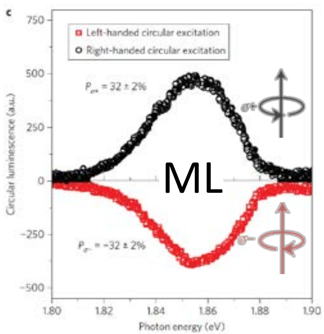
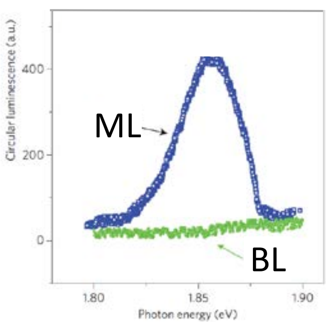
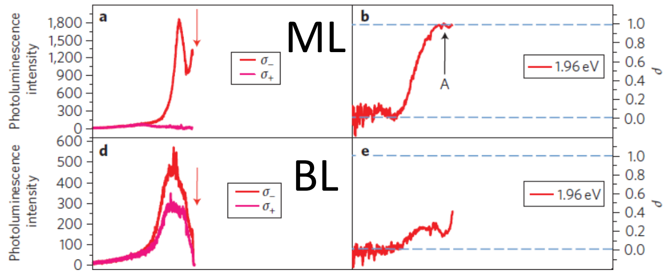
Circular Dichoric PL in MoS_2 due to R2-D2?











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PUBLISHED ONLINE: 17 JUNE 2012 | DOI: 10.1038/NNANO.2012.95
nature nanotechnology

Valley polarization in MoS_2 monolayers by optical pumping

Hualing Zeng[1†], Junfeng Dai[2,1†], Wang Yao[1,3], Di Xiao[4] and Xiaodong Cui[1*]

LETTERS
PUBLISHED ONLINE: 17 JUNE 2012 | DOI: 10.1038/NNANO.2012.96
nature nanotechnology

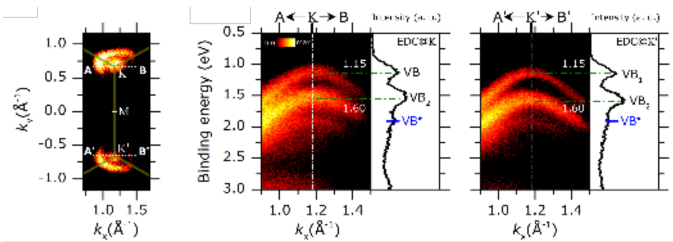
Control of valley polarization in monolayer MoS_2 by optical helicity

Kin Fai Mak[1], Keliang He[2], Jie Shan[2] and Tony F. Heinz[1*]

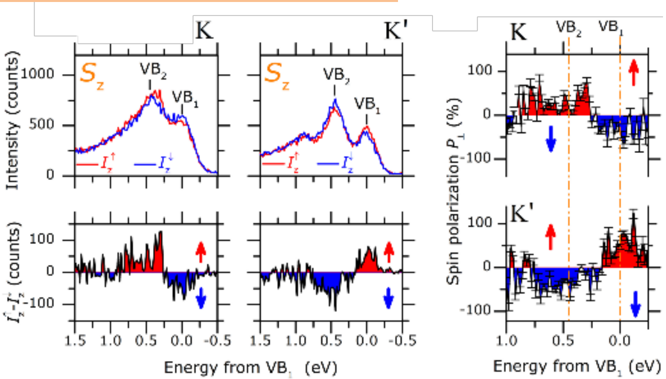
Layer spin polarization in centrosymmetric TMDC single crystal: The case of bulk WS_2

Detecting 1st Layer Spin Polarization

WS_2 ARPES @ 300K

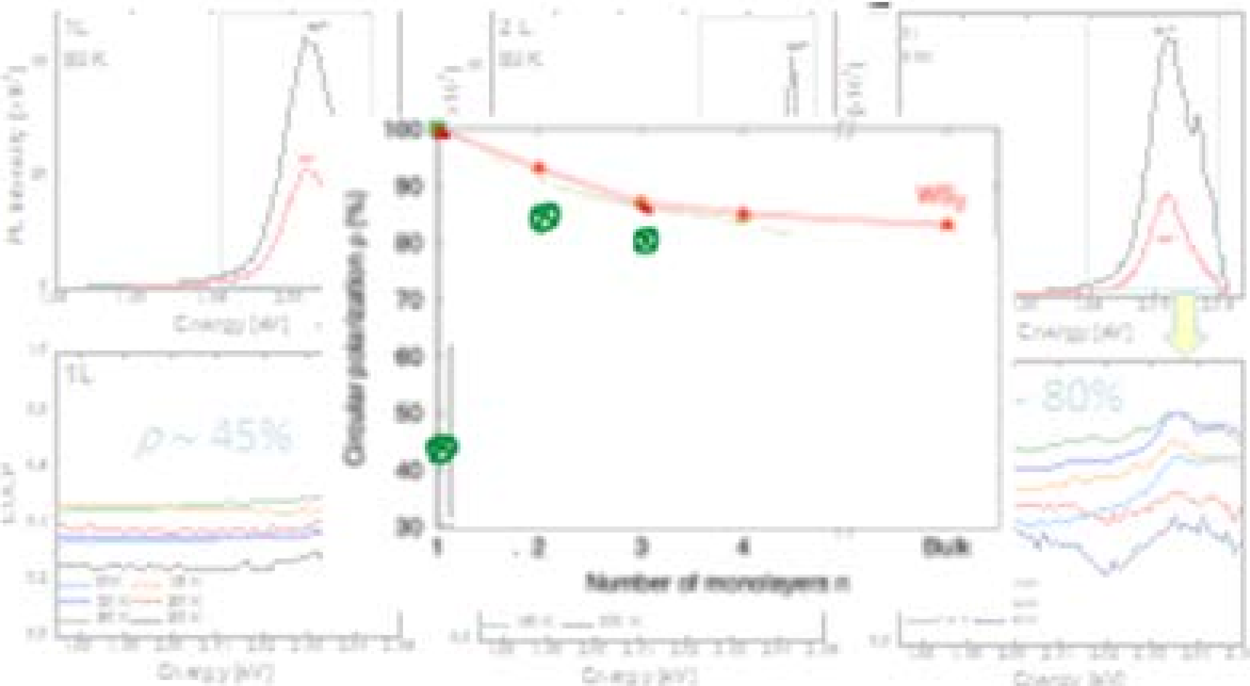


WS_2 SARPES @ 300K



Bussolotti, in prep.

CDPL: Valley Polarization in WS_2 mono- & multi-layers

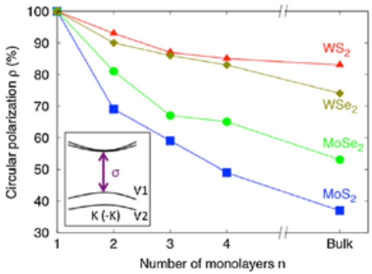


- ρ increases with T, highest observed at ~150 K
- ρ decreases for T > 150 K, but up to ~40% remains at 300 K

Chellappan, Ooi, in prep.

Expectations vs Observations

Expectation for Valley Polarization	Observation/New understanding
ONLY if inversion symmetry broken	**YES** for MoS_2 (CDPL: 2012) **NO** for WS_2 (CDPL: 2015, 2017) **NO** for MoS_2, WSe_2 (SARPES: 2014, 2016, 2017) **NO**, local SOC dominates (Theory: 2015)
Quenched at high T (inter-valley scattering)	**YES** for MoS_2 and WSe_2 in most studies **NO** for WS_2, in fact >70% for 4ML or more at 300K (2017)
Reduced as number of layers increases (inter-layer scattering)	**YES** for MoS_2 (CDPL: 2012) **NO** for MoS_2, WSe_2 (SARPES: 2014, 2016, 2017) **NO** for WS_2, apparent correlation with bandgap decrease with number of layers (CDPL 2017)



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Thank you