Towards 2D Valleytronics

Johnson Goh
Inversion Symmetry

Broken in 2D Transition Metal Dichalcogenides (MX$_2$)


Because materials matter
Because materials matter

**Valley Physics in 2D Materials**

**Spin and pseudospins in layered transition metal dichalcogenides**

Xiaodong Xu\(^1\)*, Wang Yao\(^2\)*, Di Xiao\(^3\) and Tony F. Heinz\(^4\)

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

<table>
<thead>
<tr>
<th></th>
<th>Spin</th>
<th>Valley pseudospin</th>
<th>Layer pseudospin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetic moment</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Hall effect</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Optical selection rule</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Electrical polarization</td>
<td>✗</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

Broken Inversion Symmetry ⇒ Valley contrasting properties (spin texture, Berry curvature)

Optical Selection Rules

Valley Hall Effect

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Opportunities in the Valley

Valley filter and valley valve in graphene

Valleytronics in 2D materials

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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  \hspace{2cm} Strained

Electrical Generation (in-plane E)  \hspace{2cm} +  \hspace{2cm} Optical Detection (Kerr Rotation)
Valleytronics Materials, Architectures, and Devices Workshop
MIT Samberg Center, Cambridge, MA
August 22–23, 2017

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Pablo Jarillo-Herrero, MIT
Philip Kim, Harvard University
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Tony Heinz, Stanford University
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Key Challenges

Valley Polarization

Detection
Control

Valley Current

Generation
Detection

Spin- & Angle-resolved Photoemission Spectroscopy

A. Damascelli et al. 
Rev. Mod. Phys. 

**Photoemission geometry**

\[ E_{\text{kin}} = h\nu - W - |E_B(k_\parallel)| \]

\[ k_\parallel = \frac{1}{\hbar} \sqrt{2mE_{\text{kin}} \sin \theta} \]
Band-structures - Synchrotron ARPES on TMDCs

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

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

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

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

Direct-to-indirect bandgap transition in MoS₂

Spin-orbit split bands

Tuning ML MoS₂ by K doping

ML WS₂ grown by CVD transferred onto TiO₂; Like free-standing WS₂

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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

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

M. Gehlmann et al.  

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

Spin-polarized bulk bands even with BL WSe$_2$ inversion-symmetry

SARPES reveals valley polarization in centrosymmetric bulk MoS$_2$

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)

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

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

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Spin-orbit Splitting at K

\[ \Delta_{s-o} \sim 0.15 \text{ eV} \]

MoS\(_2\):

CVD-growth

Theory

\[ \Gamma \rightarrow K \rightarrow \text{ML MoS}_2 \rightarrow 11 K \]

\[ k_r/(\text{Å}^{-1}) \]

\[ 0.0 \quad 0.5 \quad 1.0 \quad 1.5 \]

Layer dependence

WS\(_2\):

\[ \Delta_{s-o} \sim 0.45 \text{ eV} \]

Spin polarization at K, K'

Grown MoS\(_2\)

WS\(_2\) single crystal

**Bussolotti, in prep.**
Home-built CDPL System

- Home-built
- Continuous Wave laser (λ = 594 nm, 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.
Circular Dichoric PL

Layer 1
- S
- Mo

Layer 2

Inversion Symmetry Broken

Inversion Symmetry Restored

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

Valley polarization in MoS\(_2\) monolayers by optical pumping

Control of valley polarization in monolayer MoS\(_2\) by optical helicity
Anomalous WS$_2$

Anomalous 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$^{a,2}$

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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$_2$ $\sim$ 0.16 eV), which is significantly higher than the interlayer hopping energy ($\sim$0.1 eV); the interlayer coupling at K and K’ valleys in WS$_2$ is greatly suppressed as indicated in Fig. 1B (7, 9). Consequently,
Anomalous WS$_2$

*Nanoscale*, 2017, 9, 5148-5154

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CDPL on WS$_2$ @ IMRE

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

WS$_2$ Monolayer @120K

EX LHC $\rho = 0.29$

EX RHC $\rho = 0.26$

WS$_2$ Bilayer @120K

EX LHC $\rho = 0.45$

EX RHC $\rho = 0.47$

$\rho$ enhanced instead of quenched!

Chellappan, Ooi, in prep.
Hidden spin polarization in inversion-symmetric bulk crystals

Xiuwen Zhang\textsuperscript{1,2,3*}, Qiang Liu\textsuperscript{1,4*}, Jun-Wei Luo\textsuperscript{3*}, Arthur J. Freeman\textsuperscript{4} and Alex Zunger\textsuperscript{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...
R2-D2 “Hidden” Local Spin Polarizations in Bulk Centrosymmetric Crystals

Don’t ignore local Rashba and Dresselhaus SOC effects!
### “Hidden” Spin Polarizations in Bulk TMDCs

<table>
<thead>
<tr>
<th>Site point group</th>
<th>Bulk space group</th>
<th>Non-centrosymmetric (at least one site)</th>
<th>Centrosymmetric (all sites)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Non-polar (all sites)</td>
<td>Polar (at least one site)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(D_2', D_3', D_4', D_6', S_4', D_{2d}, C_{3h}', D_{3h}', T, T_d', O)</td>
<td>(C_1', C_2', C_3', C_4', C_6', C_{1V}', C_{2V}', C_{3V}', C_{4V}', C_{6V}')</td>
<td>(C_{i}, C_{2h}, D_{2h}, C_{4h}, D_{4h}, S_6, D_{3d}, C_{6h}, D_{6h}, T_h, O_h)</td>
</tr>
<tr>
<td></td>
<td>Dipoles add up to zero</td>
<td>Dipoles add up to non-zero</td>
<td></td>
</tr>
<tr>
<td>Non-centrosymmetric (for example, (F\overline{4}3m))</td>
<td>a (D-1) Example: GaAs, ZrCoBi</td>
<td>b (D-1) Example: (\gamma)-LiAlO(_2)</td>
<td>c (R-1 &amp; D-1) Example: BiTeI, (\alpha)-SnTe</td>
</tr>
<tr>
<td>Centrosymmetric (for example, (R\overline{5}m))</td>
<td>d (D-2) Example: Si, NaCaBi</td>
<td>e (R-2 &amp; D-2) Example: MoS(_2), Bi(_2)Se(_3), LaOBiS(_2)</td>
<td>f Absence of spin polarization Example: (\beta)-SnTe</td>
</tr>
</tbody>
</table>

**MoS\(_2\)**
Intrinsic Circular Polarization in Centrosymmetric Stacks of Transition-Metal Dichalcogenide Compounds

Qihang Liu, Xiwen Zhang, and Alex Zunger

University of Colorado, Boulder, Colorado 80309, USA

(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 \( n = \text{even} \), 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.
Intrinsic Circular Polarization in Centrosymmetric Stacks of Transition-Metal Dichalcogenide Compounds

Qihang Liu, Xiwen Zhang, and Alex Zunger
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(Received 21 June 2014; revised manuscript received 28 January 2015; published 27 February 2015)
Circular Dichoric PL in MoS$_2$ due to R2-D2?

Valley polarization in MoS$_2$ monolayers by optical pumping

Control of valley polarization in monolayer MoS$_2$ by optical helicity
Layer spin polarization in centrosymmetric TMDC single crystal: The case of bulk WS$_2$

Detecting 1$^\text{st}$ Layer Spin Polarization

Bussolotti, in prep.
CDPL: Valley Polarization in WS$_2$ mono- & multi-layers

- $\rho$ increases with $T$, highest observed at $\sim$150 K
- $\rho$ decreases for $T > 150$ K, but up to $\sim$40% remains at 300 K

Chellappan, Ooi, in prep.
## Expectations vs Observations

<table>
<thead>
<tr>
<th>Expectation for Valley Polarization</th>
<th>Observation/New understanding</th>
</tr>
</thead>
<tbody>
<tr>
<td>ONLY if inversion symmetry broken</td>
<td>YES for MoS$_2$ (CDPL: 2012)</td>
</tr>
<tr>
<td></td>
<td>NO for WS$_2$ (CDPL: 2015, 2017)</td>
</tr>
<tr>
<td></td>
<td>NO, local SOC dominates (Theory: 2015)</td>
</tr>
<tr>
<td>Quenched at high T</td>
<td>YES for MoS$_2$ and WSe$_2$ in most studies</td>
</tr>
<tr>
<td>(inter-valley scattering)</td>
<td>NO for WS$_2$, in fact &gt;70% for 4ML or more at 300K (2017)</td>
</tr>
<tr>
<td>Reduced as number of layers increases</td>
<td>YES for MoS$_2$ (CDPL: 2012)</td>
</tr>
<tr>
<td></td>
<td>NO for WS$_2$, apparent correlation with bandgap decrease with number of layers (CDPL 2017)</td>
</tr>
</tbody>
</table>
Valleytronics Team

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Thank you