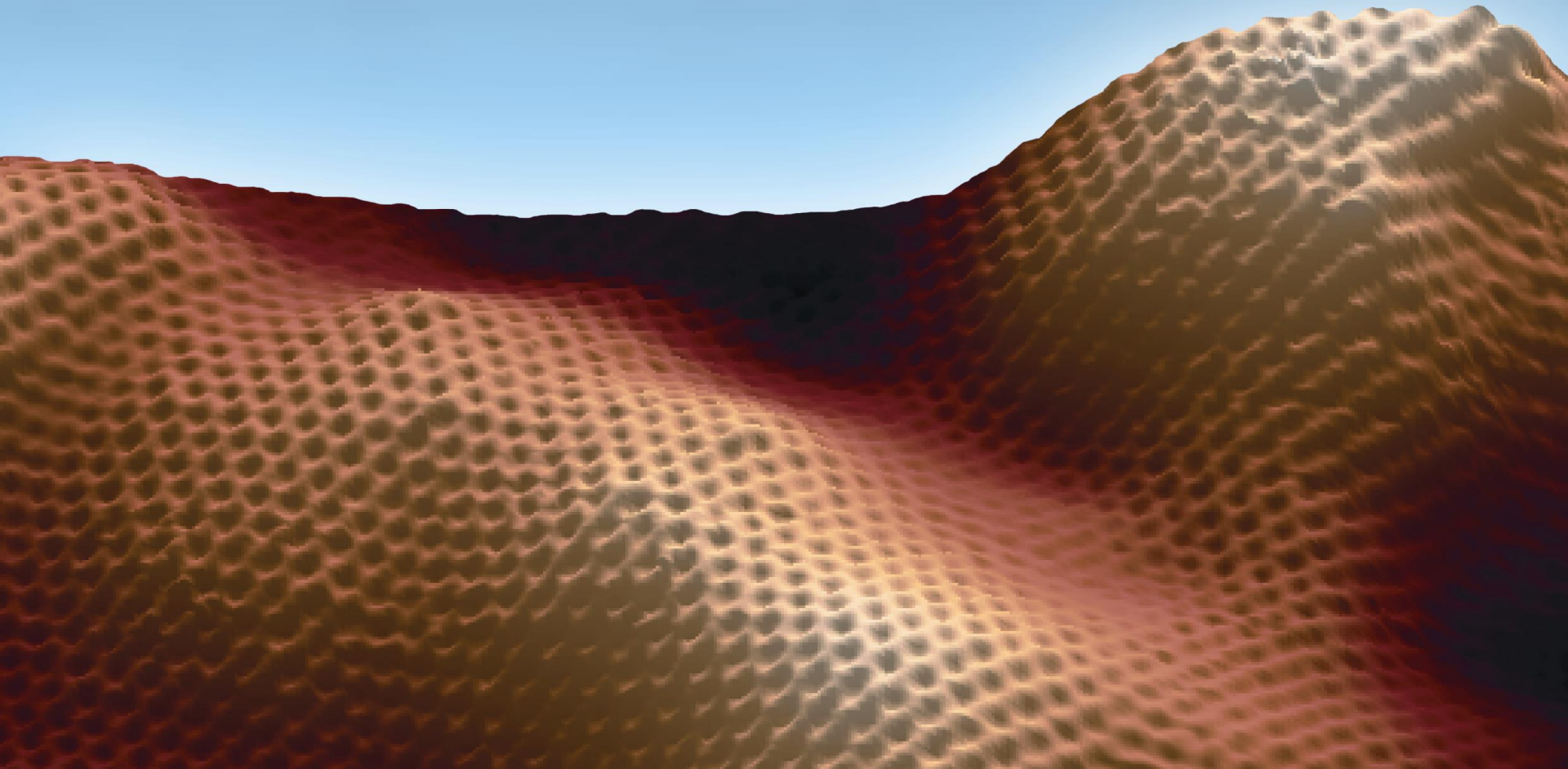


# Opportunities in Two-dimensional Material Research

Yuanbo Zhang (张远波)

Dept. of Physics, Fudan University, China

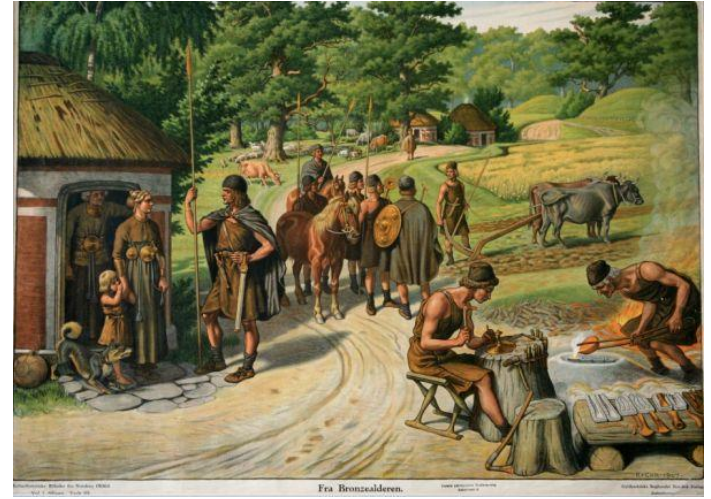


# A Brief History of Materials

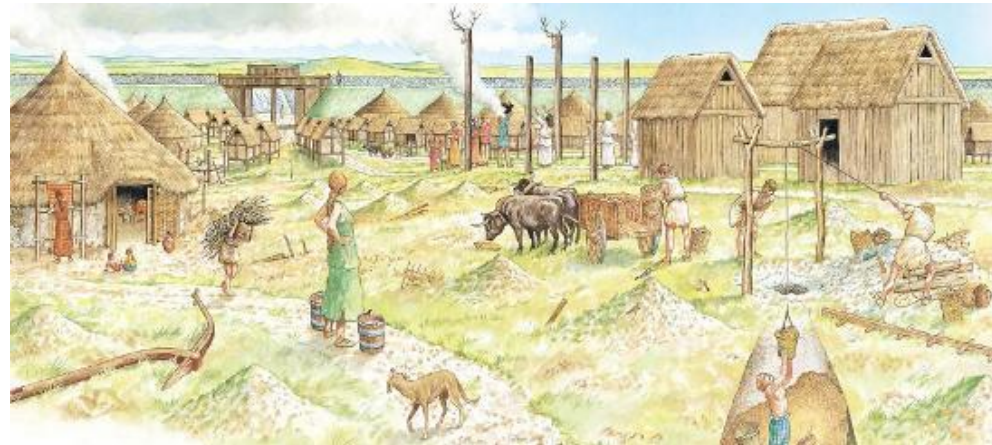
## The Stone Age



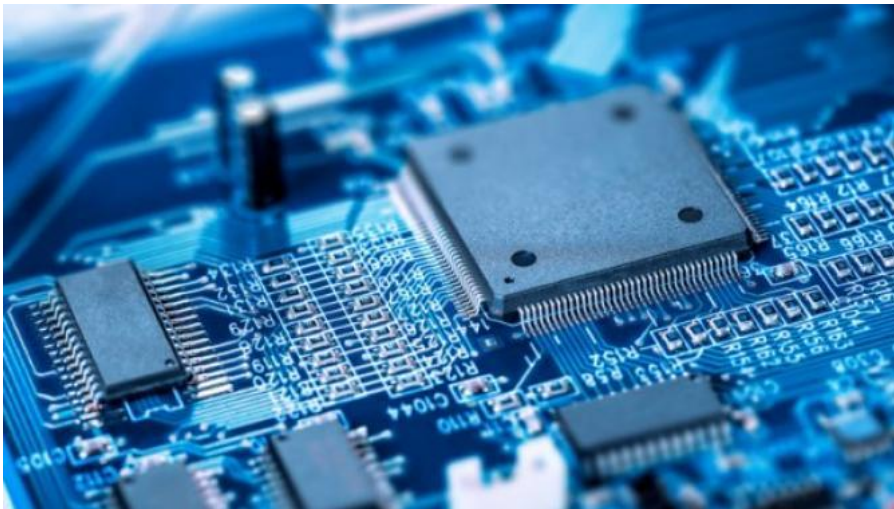
## The Bronze Age



## The Iron Age



# The Silicon Age



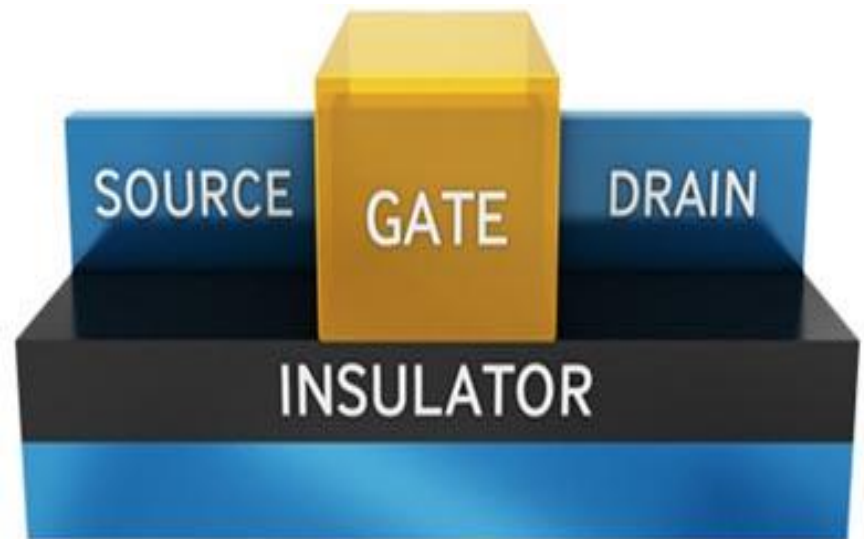
# “Interface is the Device”

The first transistor



Bell Lab, 1947

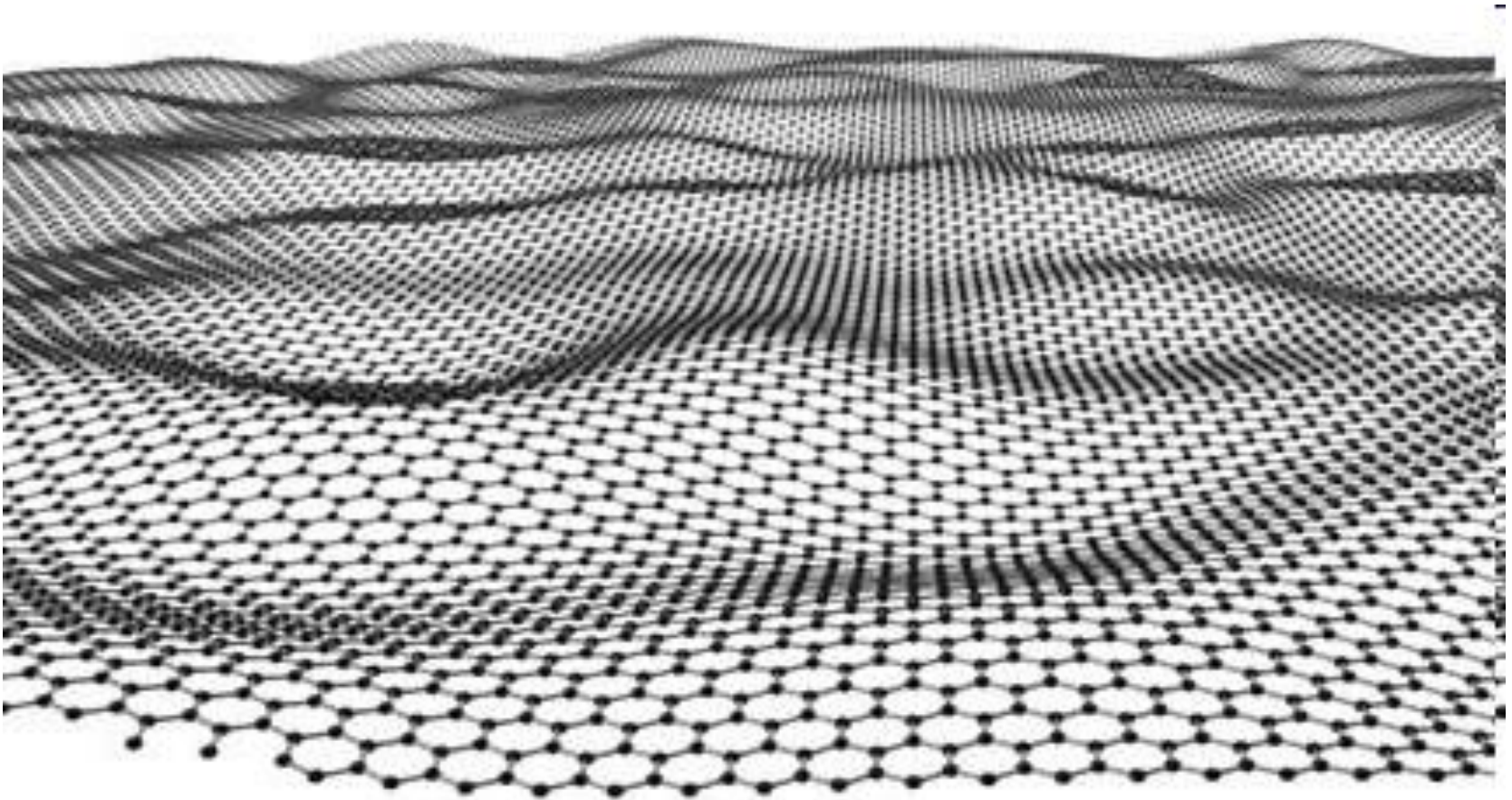
Modern FinFET



The key: **gate control** of a **thin** semiconductor

# How Thin Can It Be?

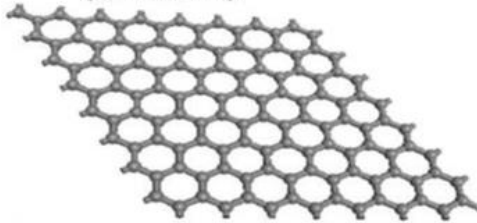
## Graphene



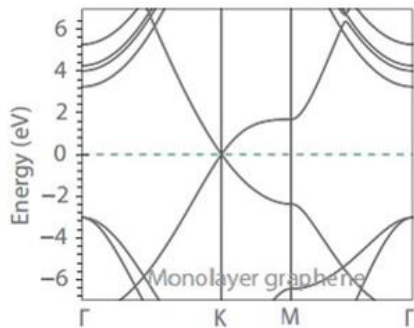
Geim group, 2004

# 2D Materials That Do Have a Gap

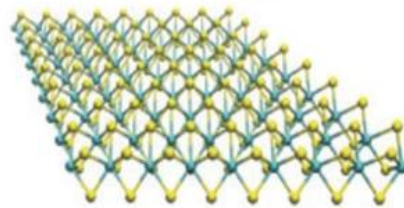
Graphene  
(semimetal)



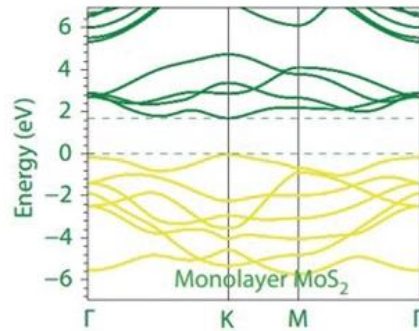
Graphene: zero-gap



MoS<sub>2</sub>  
(semiconductor)



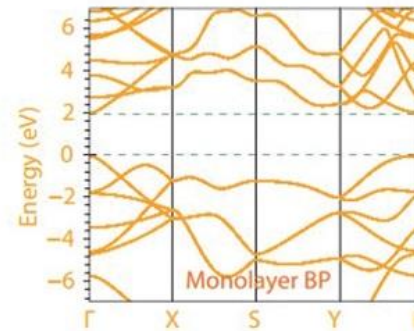
TMDC: ~1.0–2.5 eV



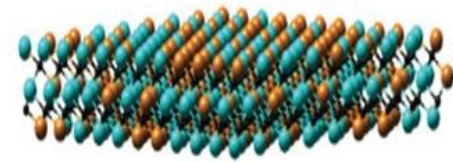
Black phosphorus  
(semiconductor)



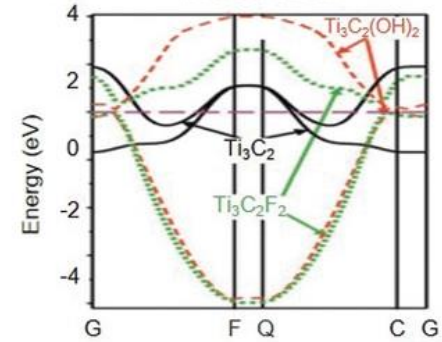
BP: 0.3–2 eV



Ti<sub>3</sub>C<sub>2</sub>  
(semiconductor)



MXenes: 0-2 eV



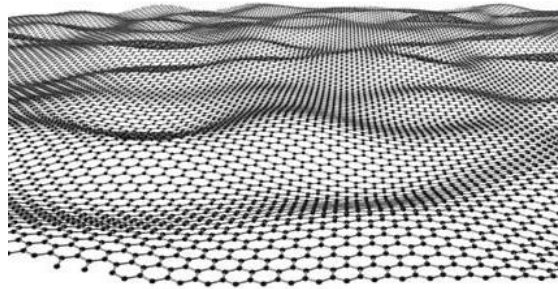
**Less is different**

# Less is Different

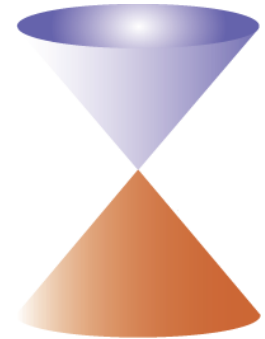
Graphite



Graphene



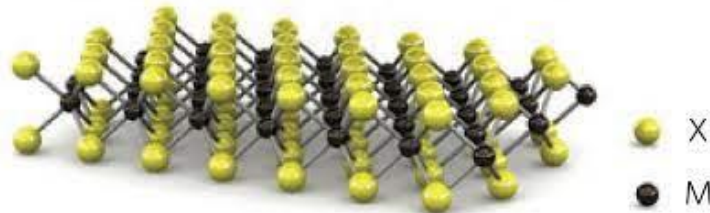
Dirac fermion in graphene



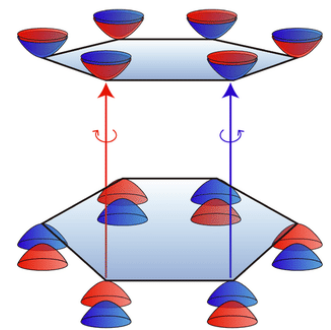
Bulk MoS2



Monolayer MoS2



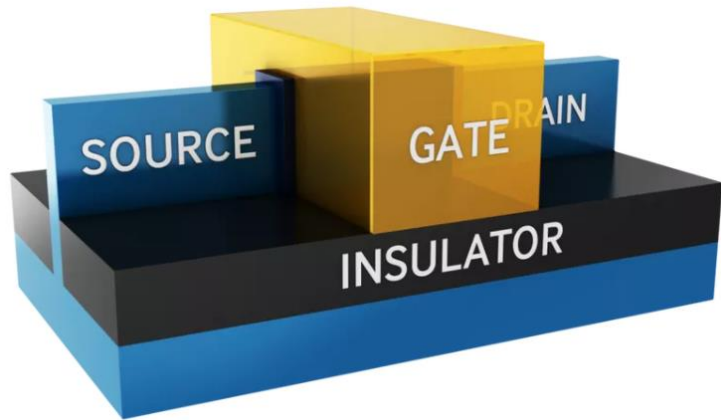
Valley physics in monolayer MoS2



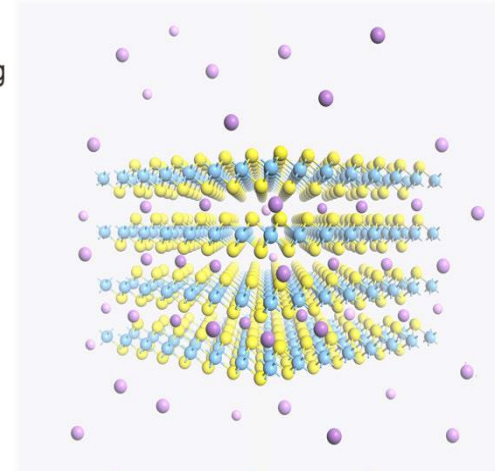
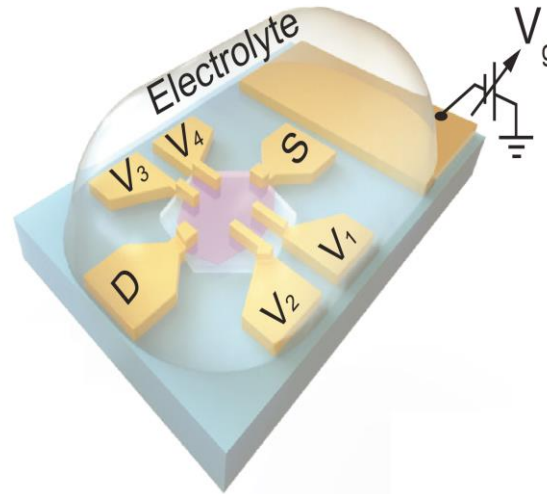
New physics often emerges in 2D

# Less is Different

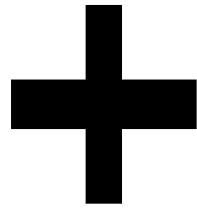
## Conventional FinFET



## Ionic gating of 2D materials

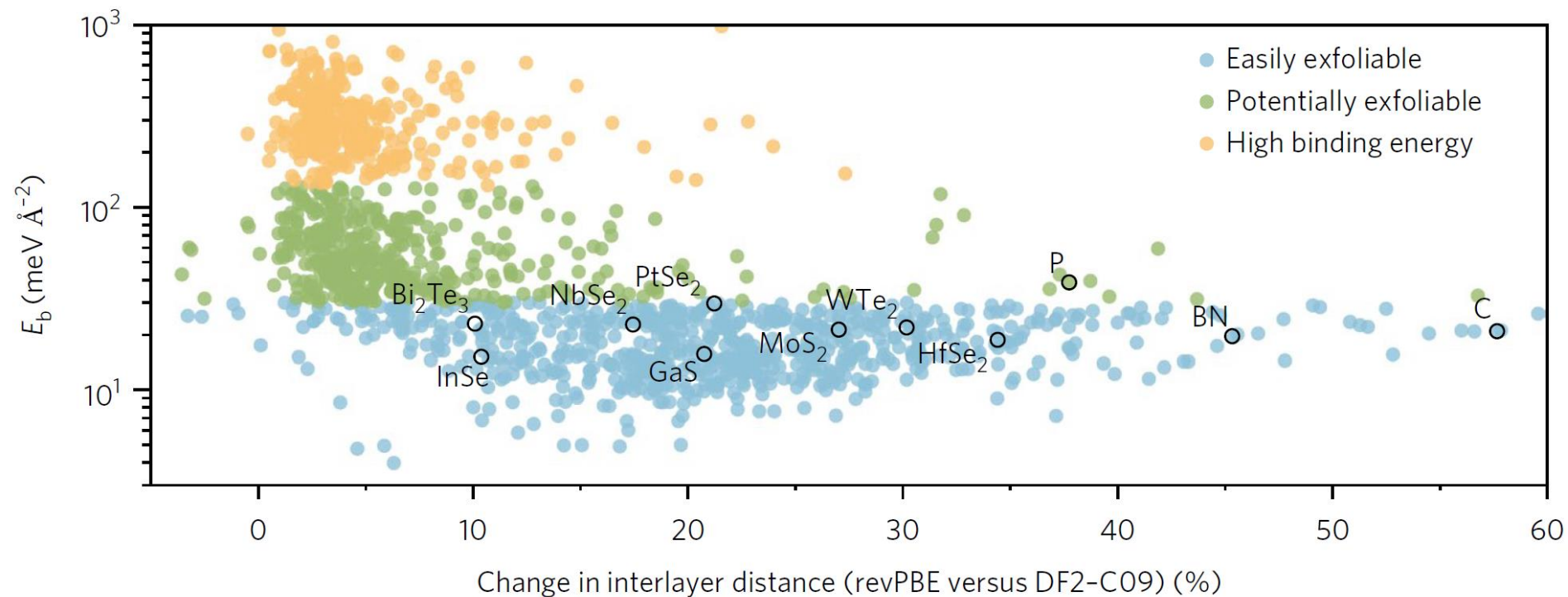


Extending “gating” capability beyond semiconductors



# Plenty of Room at the Bottom

Thousands of potential 2D materials  
waiting to be explored



# Opportunities in 2D Material Research

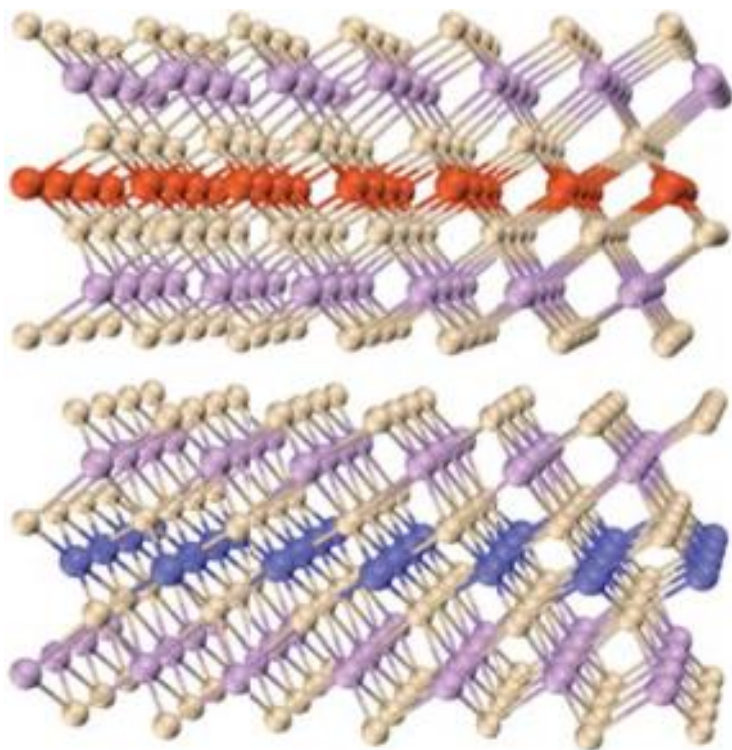
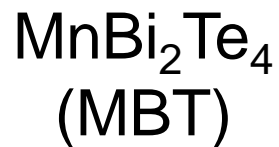
- ❑ **New 2D materials**

from thousands of layered materials

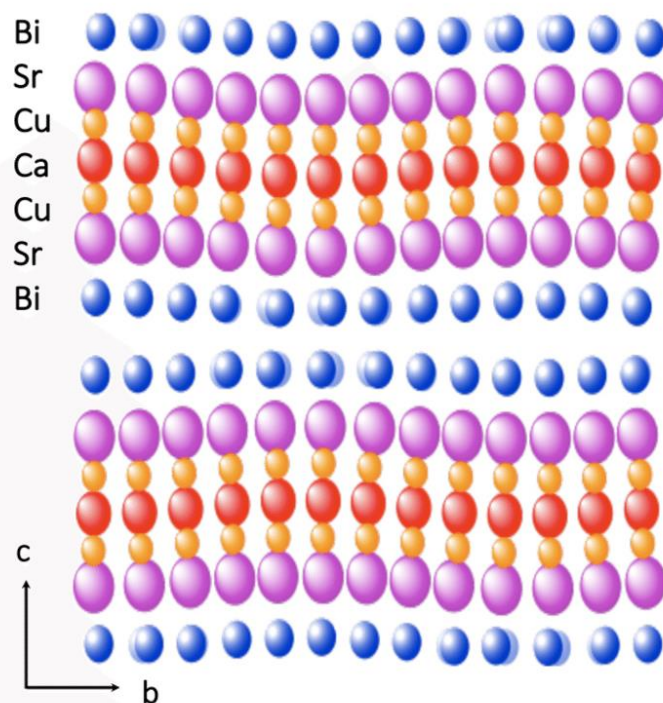
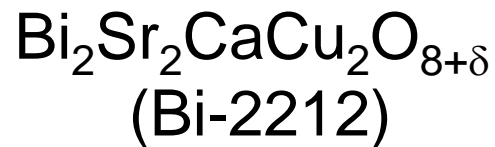
- ❑ **New gating methods**

such as ionic gating and oxygenation

# Exploring New 2D Materials



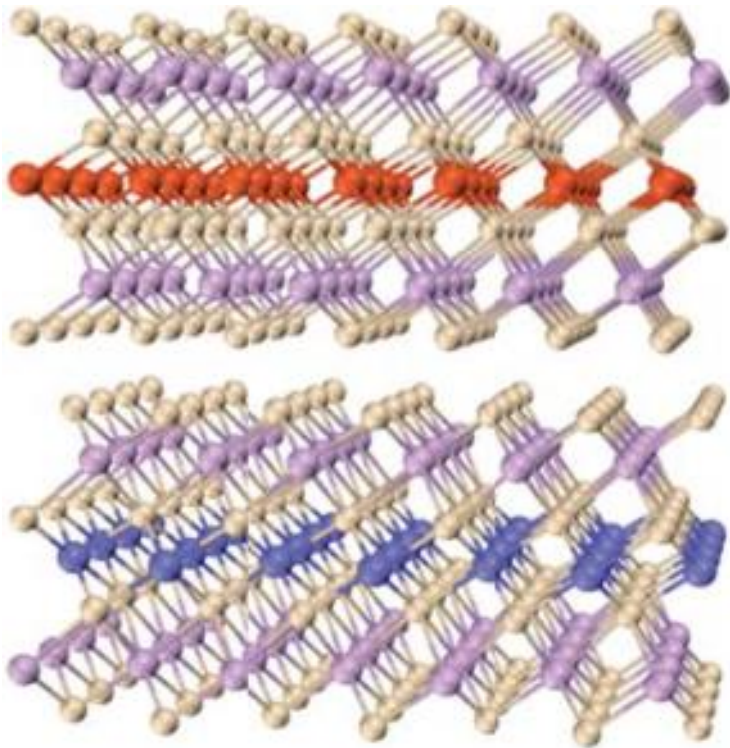
Quantum anomalous Hall effect in MBT



High  $T_c$  superconductivity  
in monolayer Bi-2212

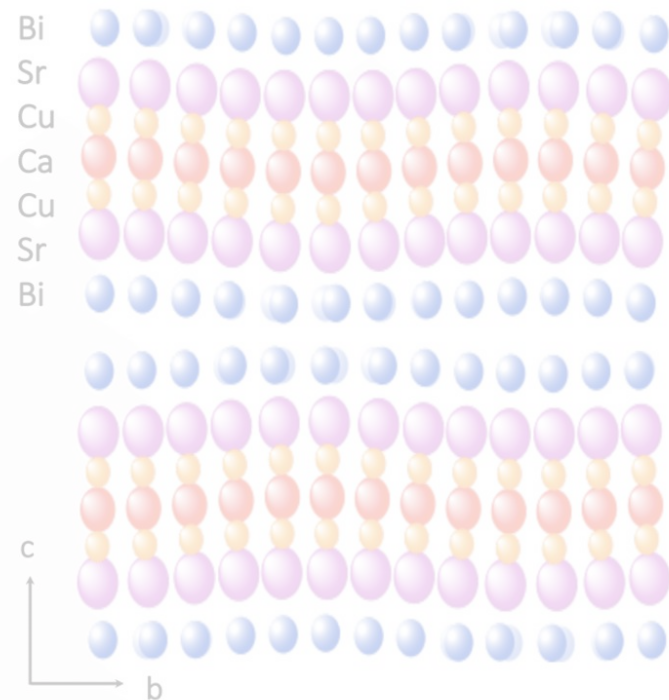
# Exploring New 2D Materials

$\text{MnBi}_2\text{Te}_4$   
(MBT)



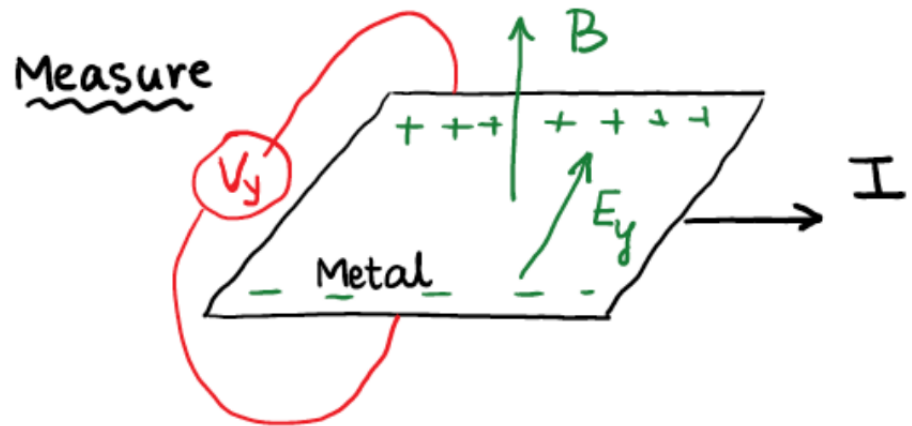
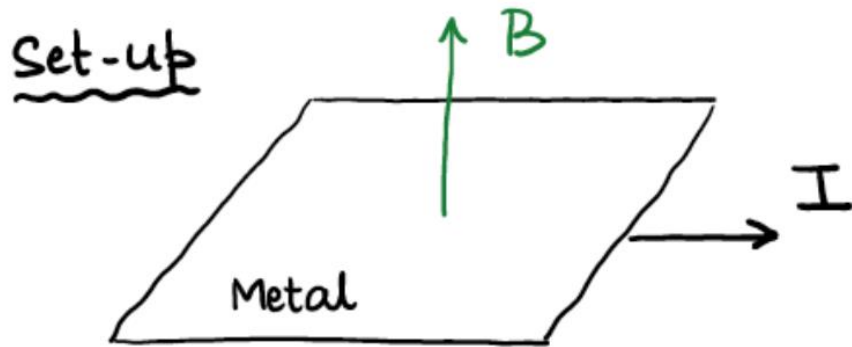
Quantum anomalous Hall effect in MBT

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$   
(Bi-2212)



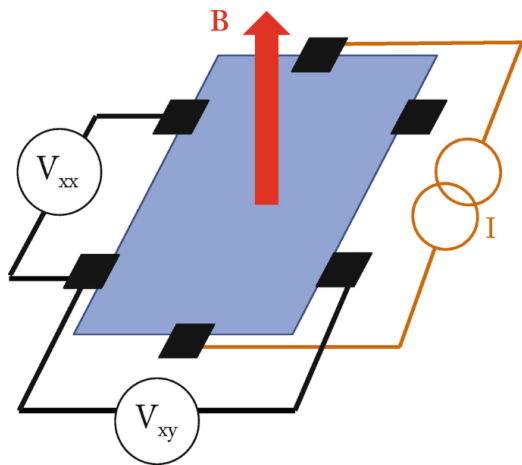
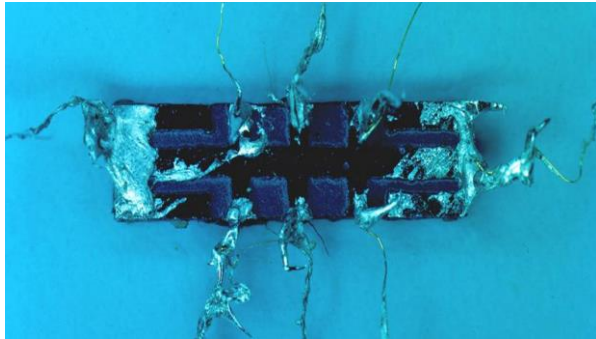
High  $T_c$  superconductivity  
in monolayer Bi-2212

# Conventional Hall Effect



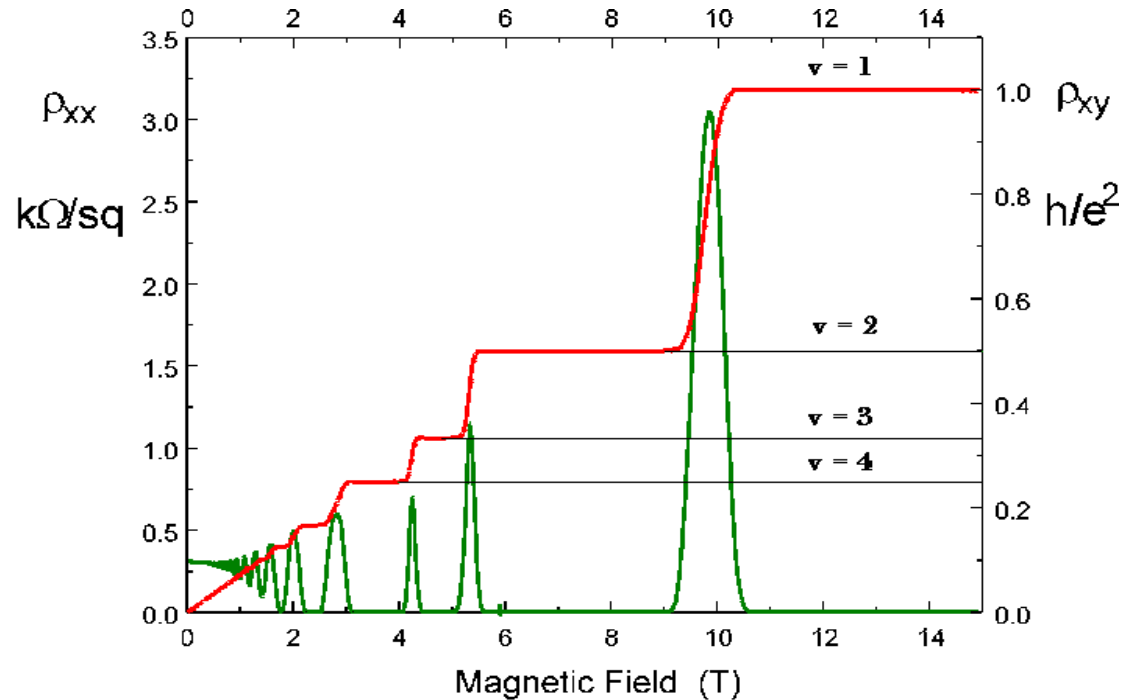
$$R_{xy} = \frac{V_y}{I} \propto B$$

# Quantum Hall Effect



$$R_{xy} = \frac{h}{e^2} \frac{1}{\nu}$$

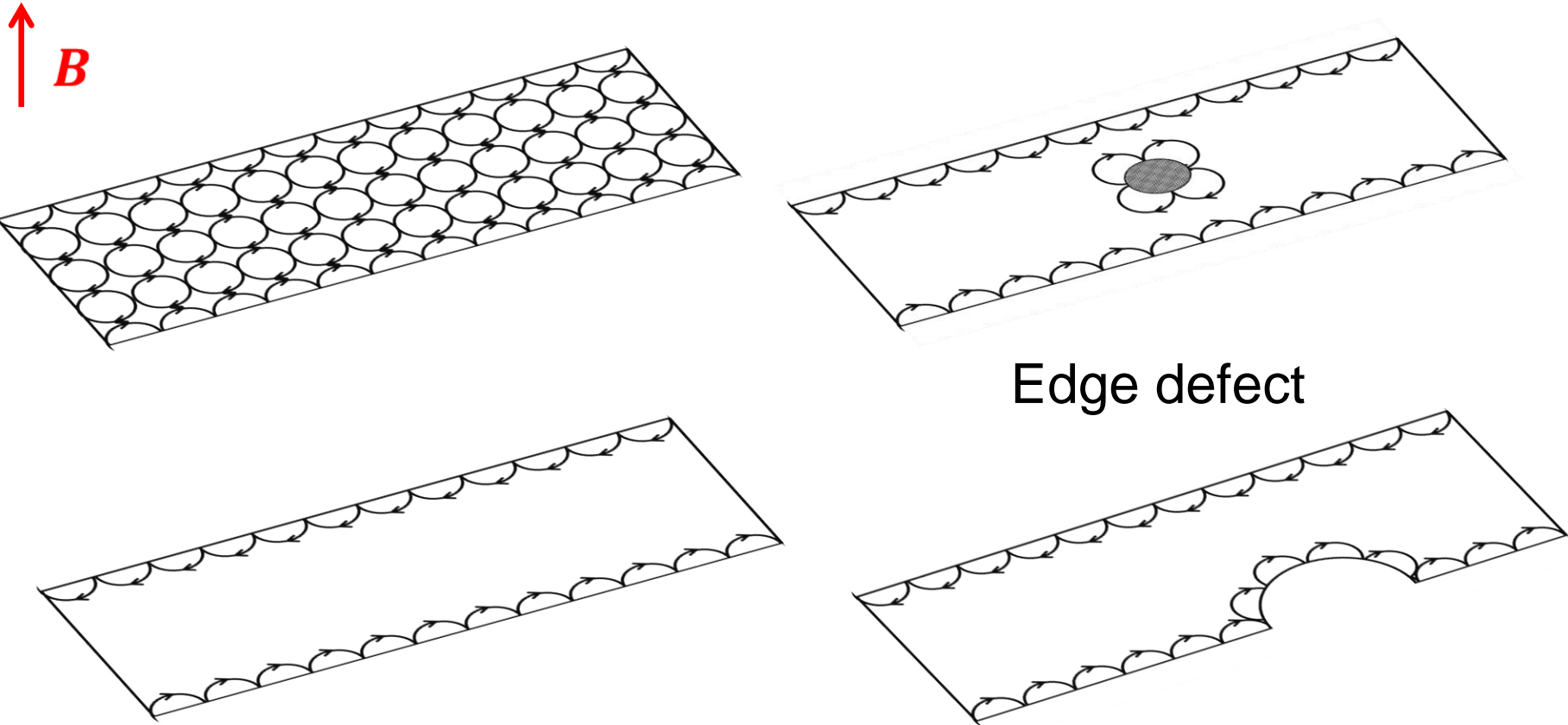
## Quantum Hall effect



K. von Klitzing et al. (1980)

$$R_K = \frac{h}{e^2} = 25812.80745... \Omega$$

# Quantum Hall Effect: Topological Edge States



Topological edge states in QHE that does not depend on local impurities

# Quantum Hall Effect

TKNN: Thouless, Kohmoto, Nightingale & Nijs 1982

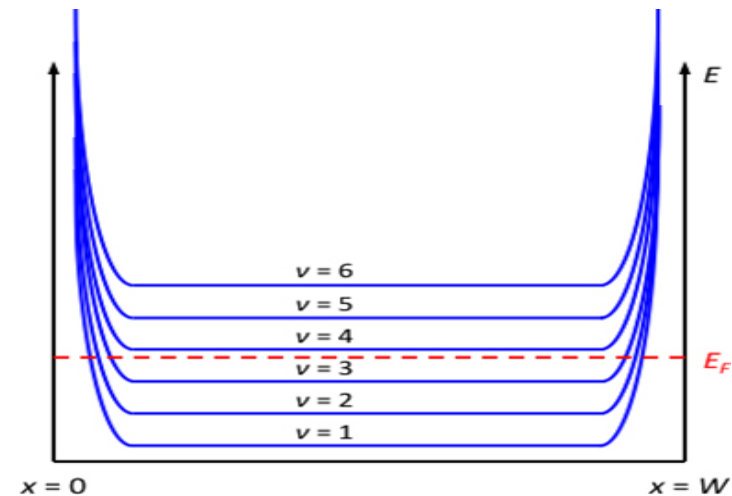
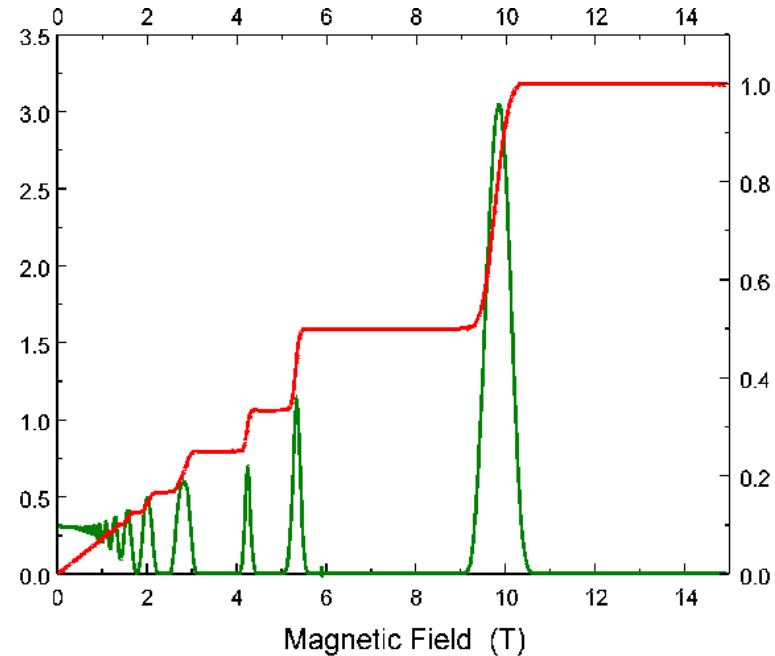
$$\sigma_{xy} = \frac{e^2}{h} C$$

$C$ : Chern number

$$C = \frac{1}{2\pi i} \int d^2 \nabla_{\mathbf{k}} \times \mathbf{A}$$

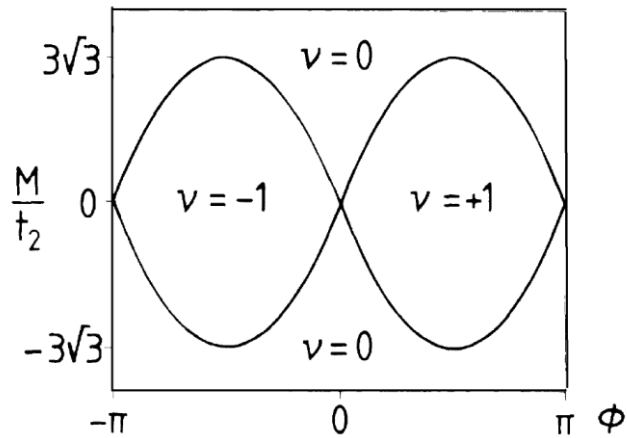
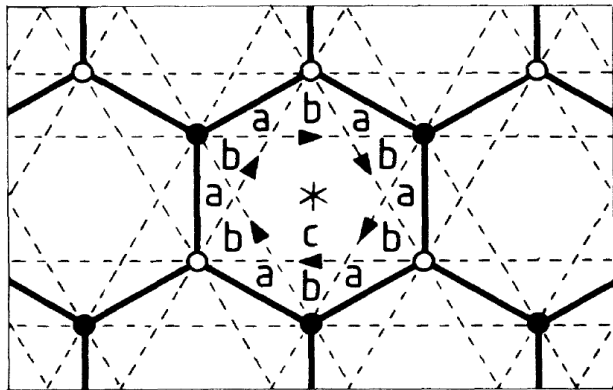
= number of edge modes crossing Fermi level

$\mathbf{A} = \langle \mathbf{k} | \nabla_{\mathbf{k}} | \mathbf{k} \rangle$ : Berry connection



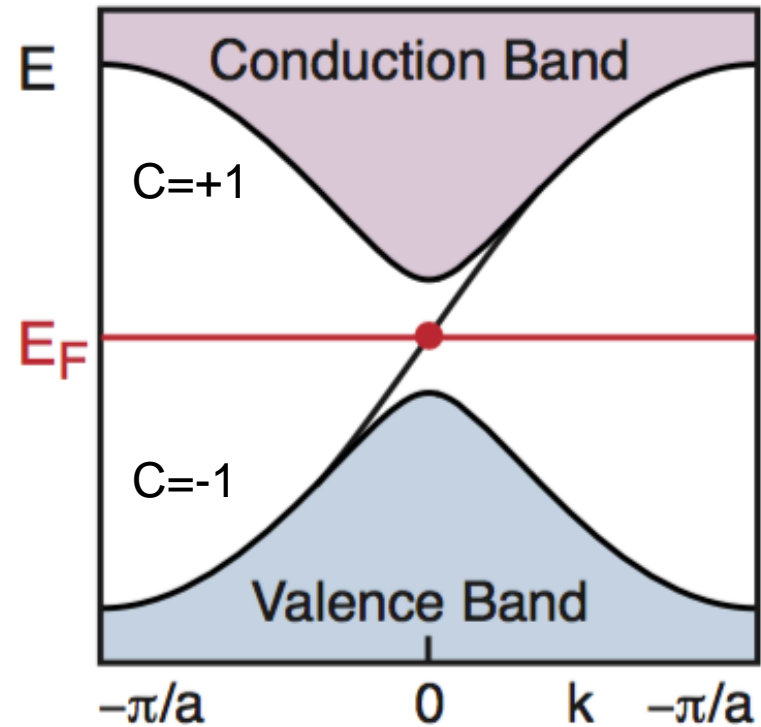
# Quantum Hall Effect at Zero Magnetic Field?

The Haldane model:  
graphene w/ NNN hopping in  
staggered field



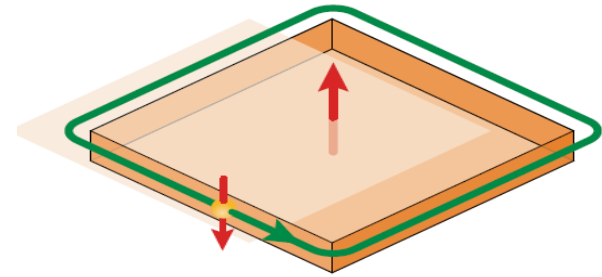
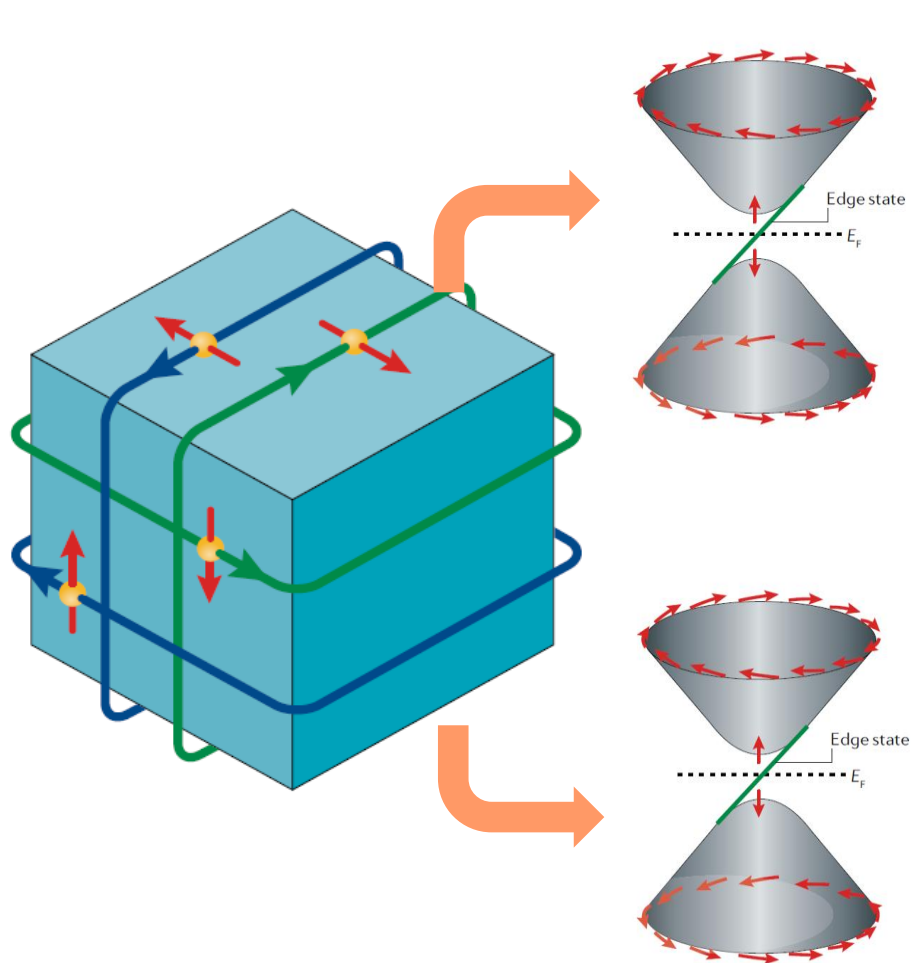
Haldane (1988)

Topological bands



# Quantum Hall Effect at ZERO Magnetic Field

## Making topological material magnetic



$$H = v_F(-k_y\sigma_x + k_x\sigma_y) + m\sigma_z = \mathbf{R} \cdot \boldsymbol{\sigma}$$

$$C = 2 \int_{\text{BZ}} \hat{\mathbf{R}} \cdot \left( \frac{\partial \hat{\mathbf{R}}}{\partial k_x} \times \frac{\partial \hat{\mathbf{R}}}{\partial k_y} \right) \frac{dk_x dk_y}{4\pi} = \text{sgn}(m)$$

$$\sigma_{xy} = \frac{e^2}{h} C$$

Haldane, PRL (1988).

Onoda & Nagaosa, PRL (2003).

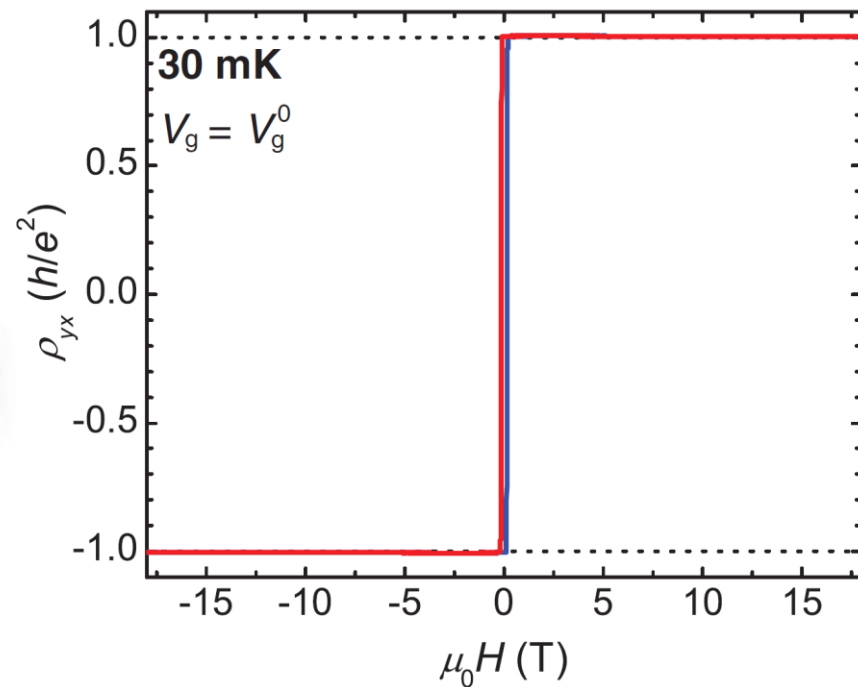
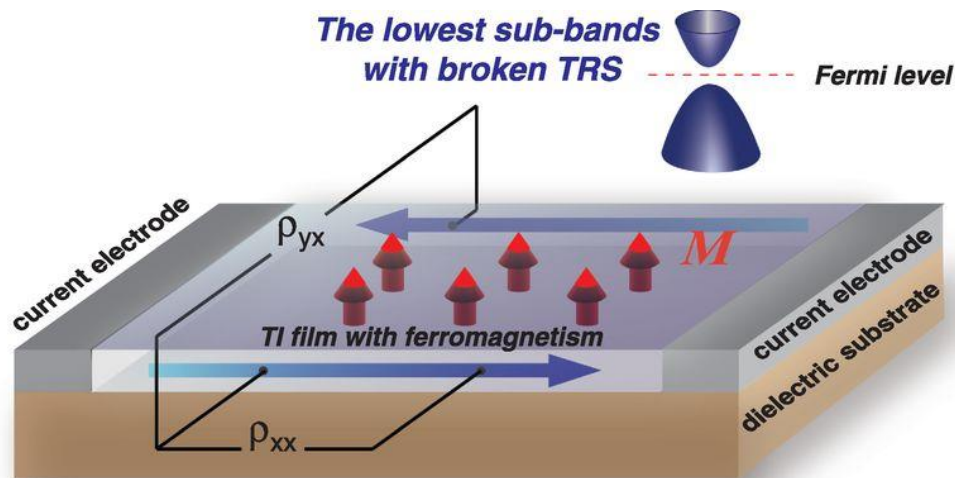
Kane & Mele, PRL (2005).

Qi, Hughes & Zhang, PRB (2008).

Fang & Dai, Science (2010).

# Quantum Anomalous Hall Effect in Magnetically Doped Topological Insulator

Cr-doped  $(\text{Bi,Sb})_2\text{Te}_3$  (CBST)

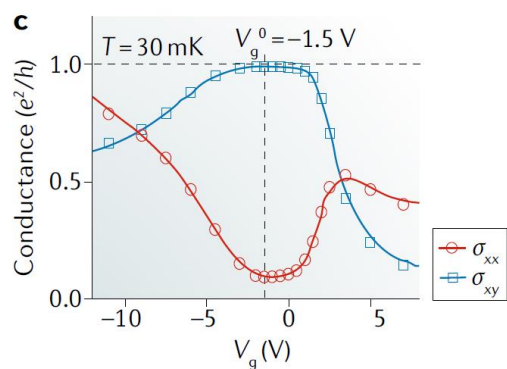
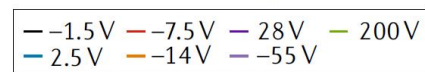
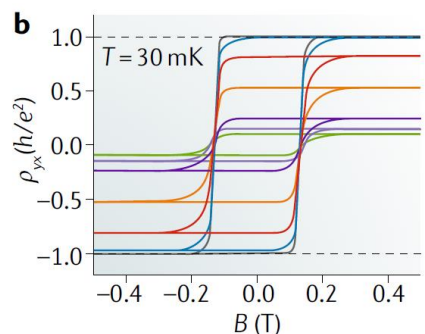
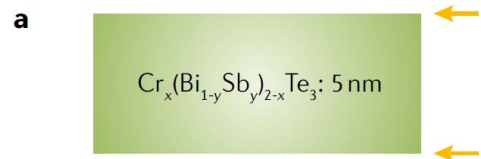


Chang, C.-Z. *et al. Science* **340** (2013).

Broken time-reversal symmetry leads to quantum anomalous Hall effect in ferromagnetic TI

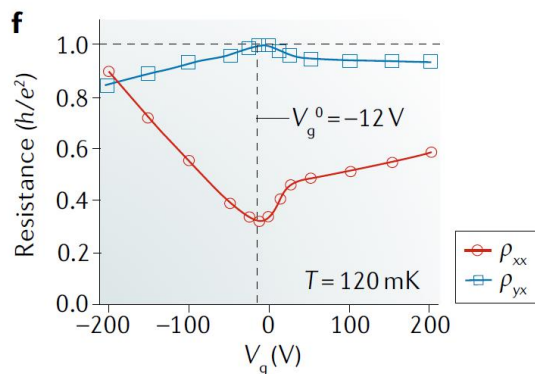
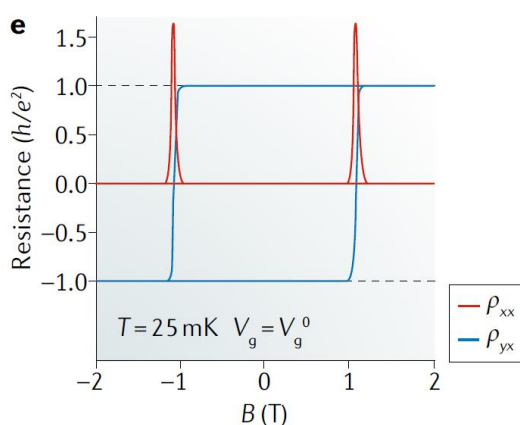
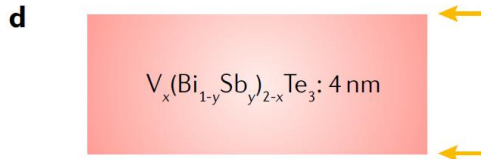
# Quantum Anomalous Hall Effect in Magnetically Doped Topological Insulator

CBST



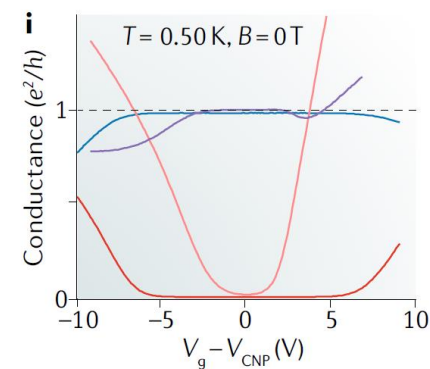
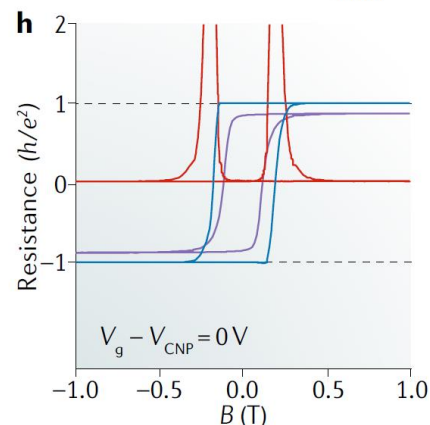
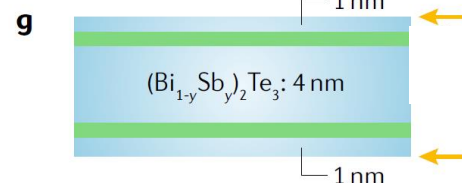
Qi-Kun Xue Group (2013)

VBST



Modera Group (2015)

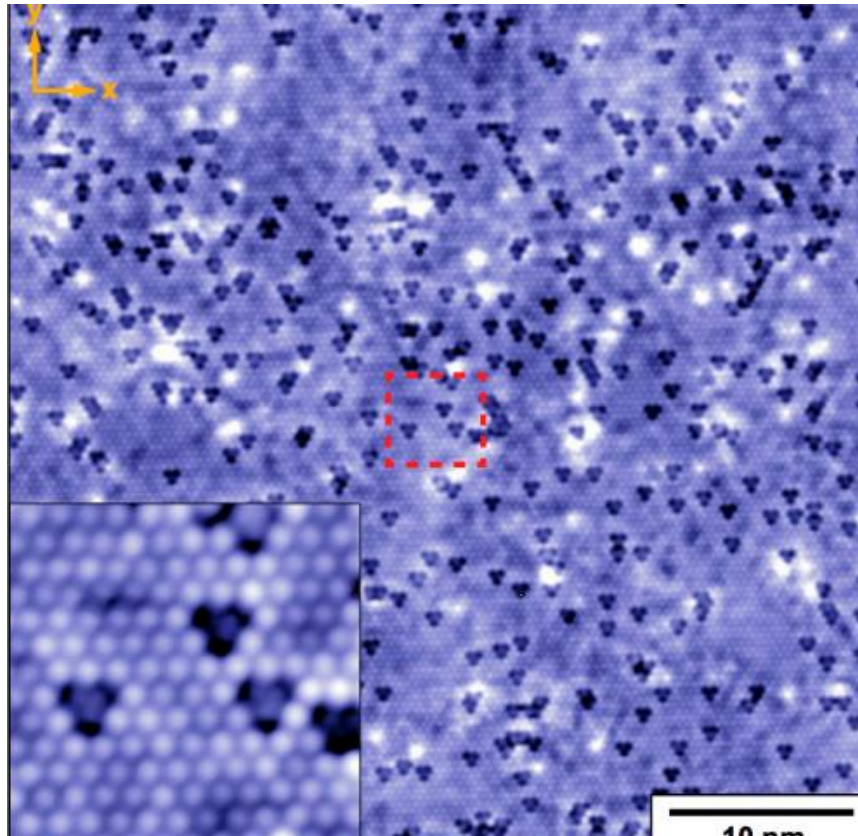
Modulation-doped CBST



Tokura Group (2015)

# Magnetic Dopants as Impurities

STM topography of  $\text{Cr}_x(\text{Bi}_{0.1}\text{Sb}_{0.9})_{2-x}\text{Te}_3$

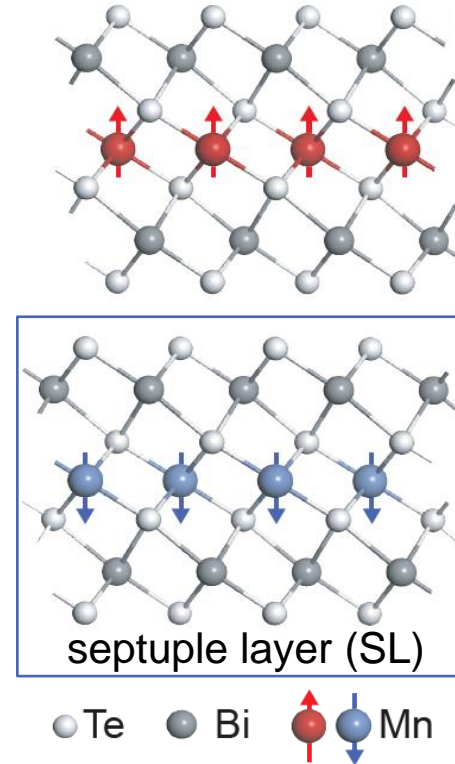


Inhee Lee et al., PNAS (2015)

**Problem: magnetic dopants at the same time acts as impurities**

# Intrinsic magnetic TI - $\text{MnBi}_2\text{Te}_4$

$\text{MnBi}_2\text{Te}_4$  (MBT)



**Bulk: AFM insulator**

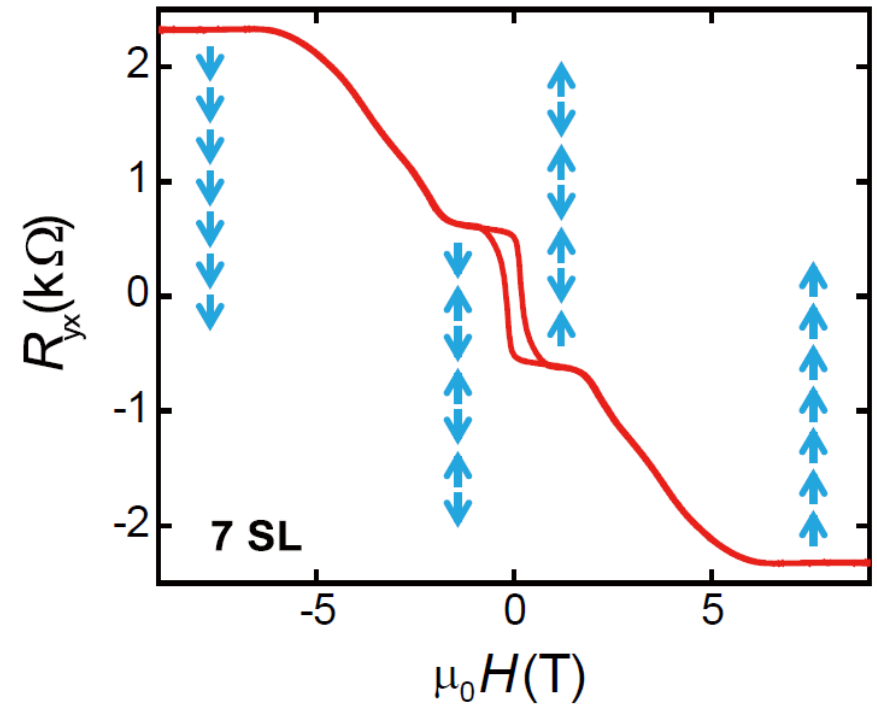
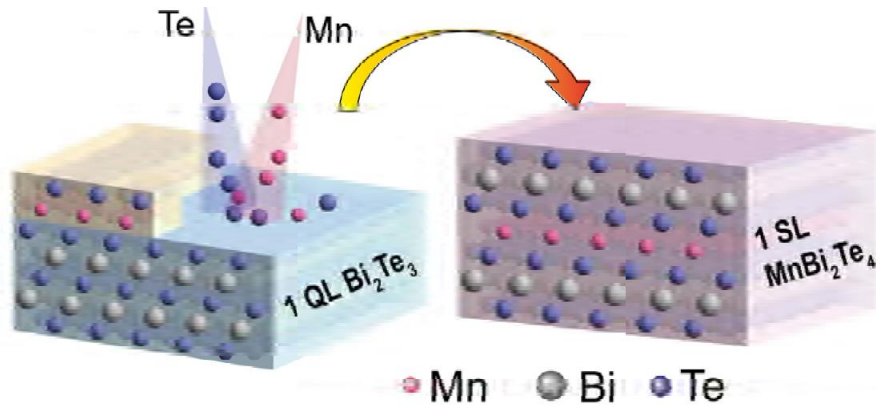
**Odd # of Layers: QAH insulator**

$\text{MnBi}_2\text{Te}_4$ :  $\text{Bi}_2\text{Te}_3$  intercalated by  $\text{MnTe}$

- Wang *et al.*, Phys. Rev. Lett. (2019)
- Li, J. *et al.*, Science Advances (2019)
- Gong, Y. *et al.*, Chinese Phys. Lett. (2019)
- Otrokov, M. M. *et al.*, Nature (2019)
- Chen, B. *et al.*, Nature Comm. (2019)

# MnBi<sub>2</sub>Te<sub>4</sub> Grown by MBE

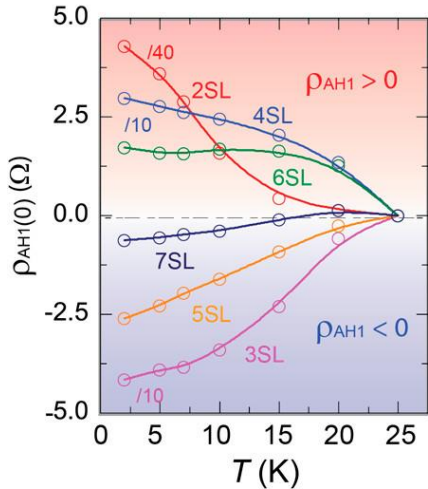
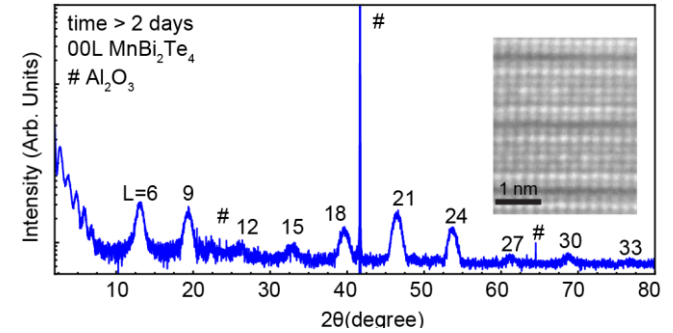
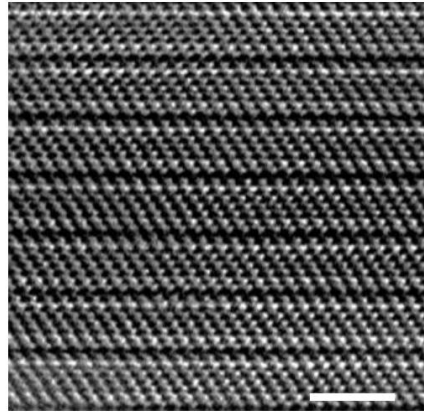
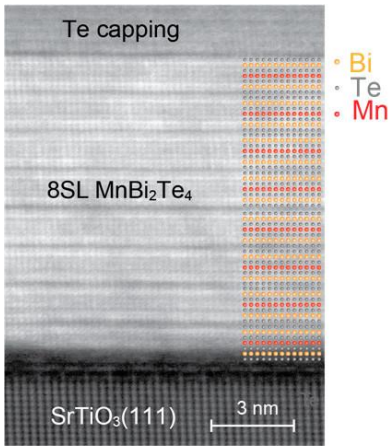
## MBE growth of MBT



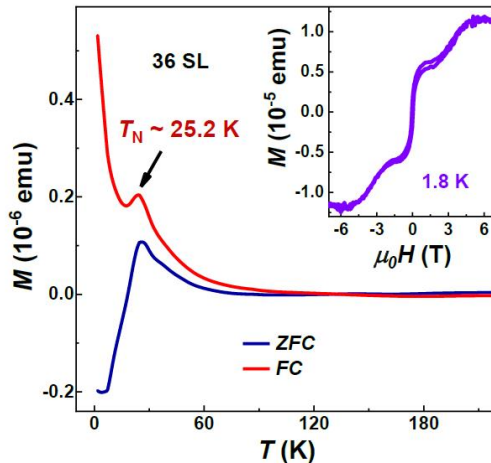
Gong, Y. et al. Chinese Phys. Lett. 36, 076801 (2019)

MBT thin film are magnetic, but QAH is not observed

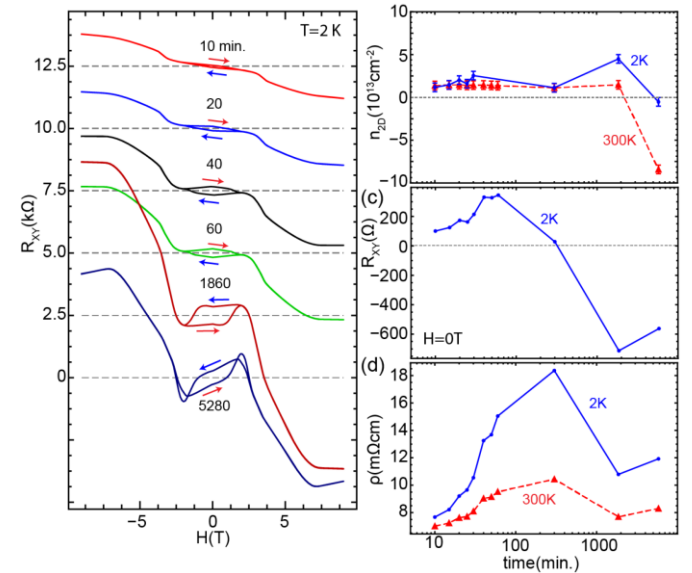
# MnBi<sub>2</sub>Te<sub>4</sub> Grown by MBE



Cui-Zu Chang group (2021)



Faxian Xiu group (2021)

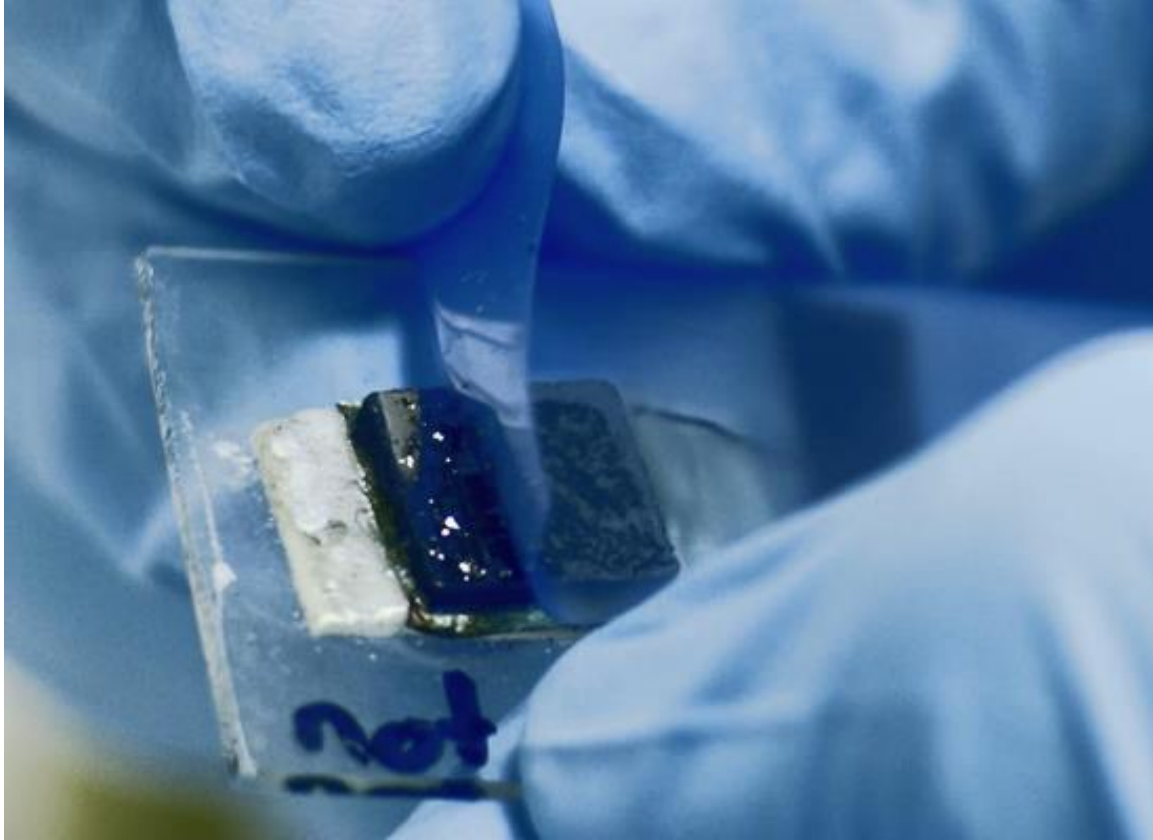


Matthew Brahlek group (2022)

Common problem: difficult to grow high-quality film w/ MBE



# Limitations of Conventional “Scotch Tape” Method



Picture from [graphene.manchester.ac.uk](http://graphene.manchester.ac.uk)

MBT is difficult to exfoliate

# The Trick: Making the Substrate More Sticky

SCIENTIFIC REPORTS

OPEN **Exfoliation of large-area transition metal chalcogenide single layers**

Gábor Zsolt Magda<sup>1</sup>, János Pető<sup>2</sup>, Gergely Dobrik<sup>2</sup>, Chanyong Hwang<sup>2</sup>, László P. Biró<sup>3</sup> & Levente Tapasztó<sup>2</sup>

Received: 08 April 2015

Materials Views

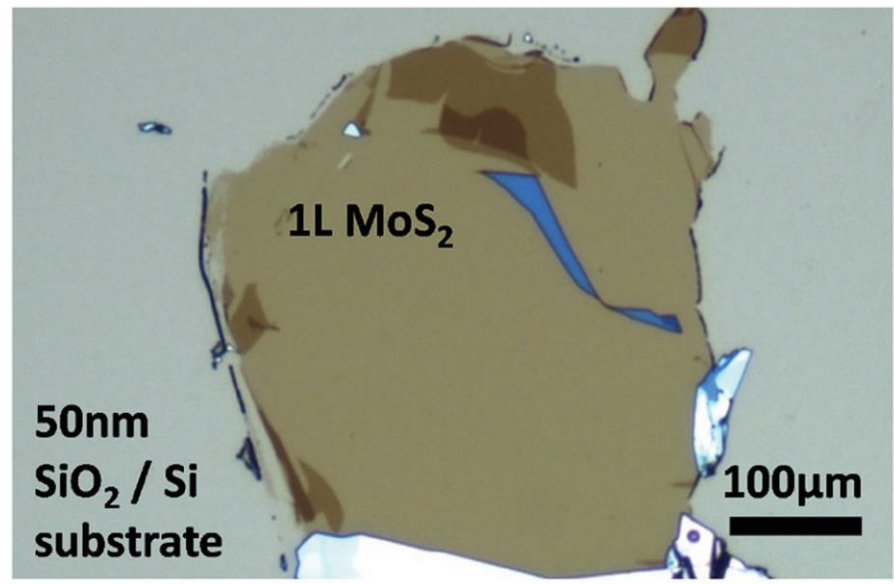
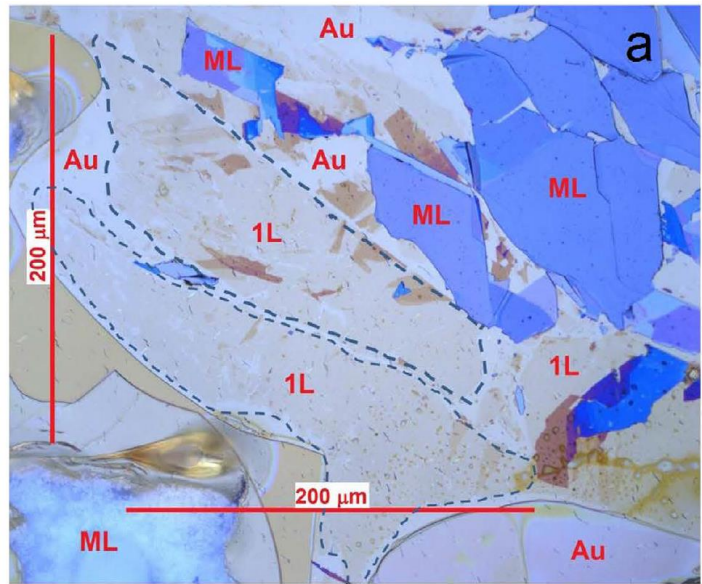
www.MaterialsViews.com

ADVANCED MATERIALS

www.advmat.de

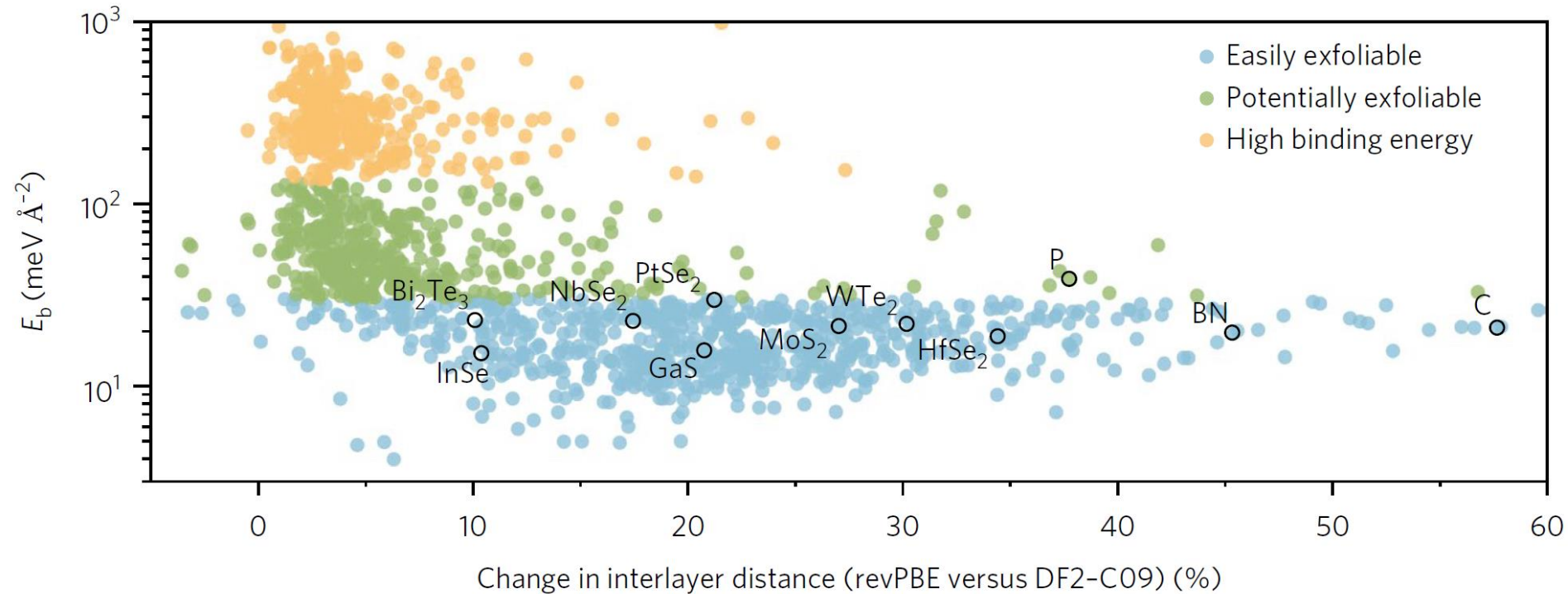
## Gold-Mediated Exfoliation of Ultralarge Optoelectronically-Perfect Monolayers

Sujay B. Desai, Surabhi R. Madhvapathy, Matin Amani, Daisuke Kiriya, Mark Hettick, Mahmut Tosun, Yuzhi Zhou, Madan Dubey, Joel W. Ager III, Daryl Chrzan, and Ali Javey\*



Au (or metal in general) is much more sticky than SiO<sub>2</sub> substrate

# Thousands of Potential 2D Materials



So far, only a **handful out of thousands** of known layered materials are cleaved to few atomic layers

# Using $\text{Al}_2\text{O}_3$ Thin Film to Exfoliate Layered Materials



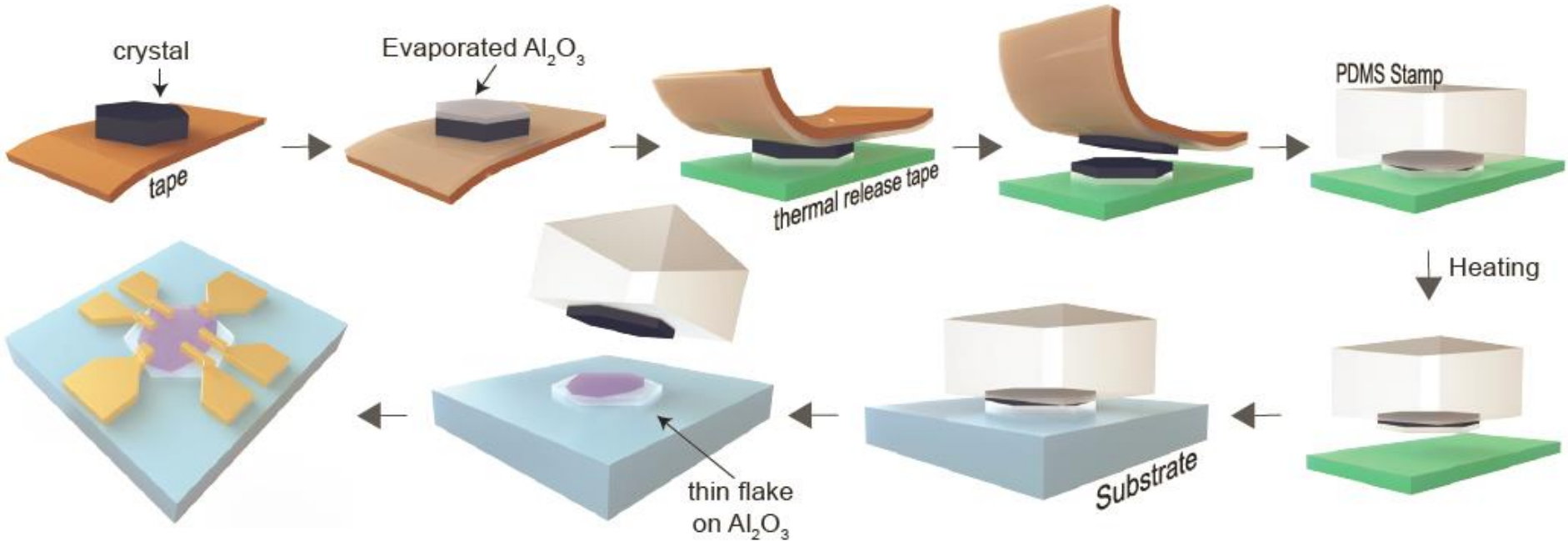
Yujun Deng



Yijun Yu

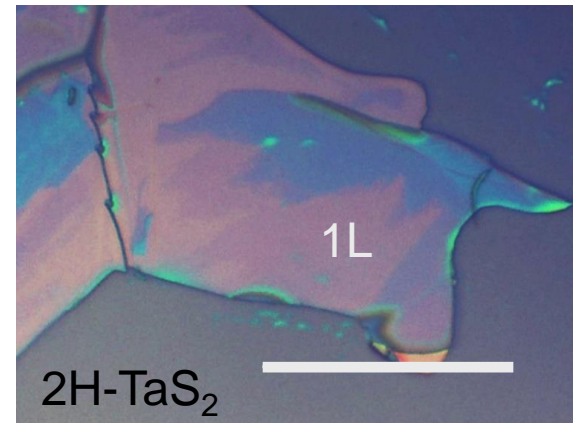
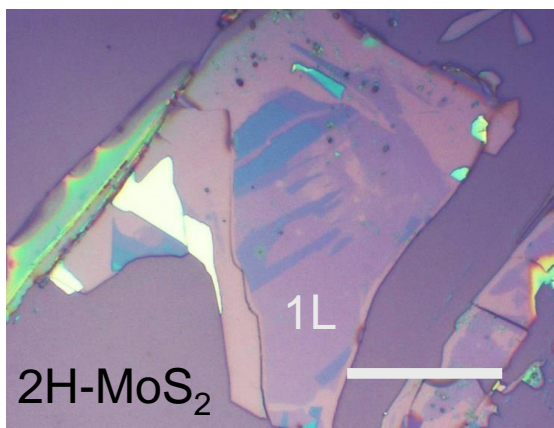
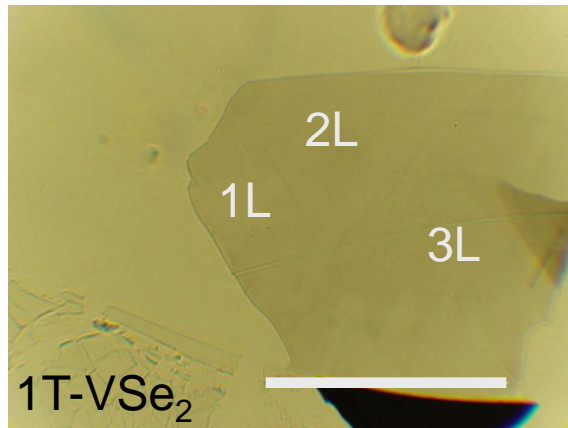
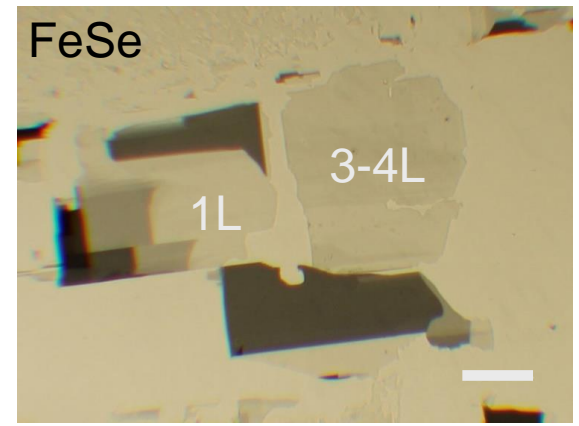
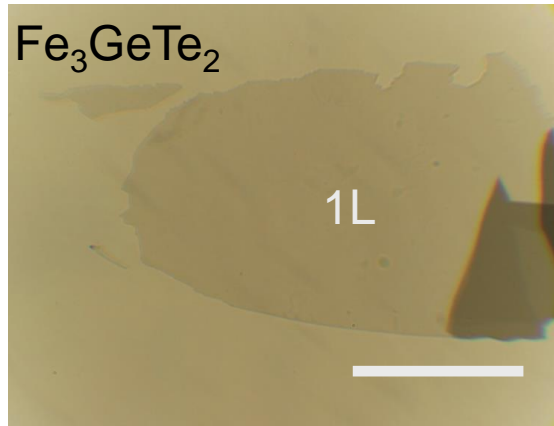
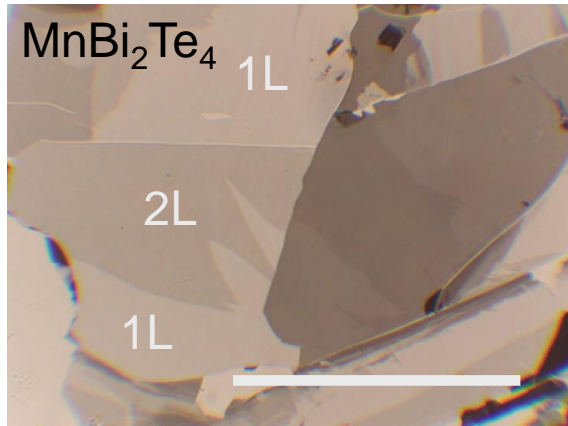


Yichen Song



A new method for exfoliating “difficult” 2D materials

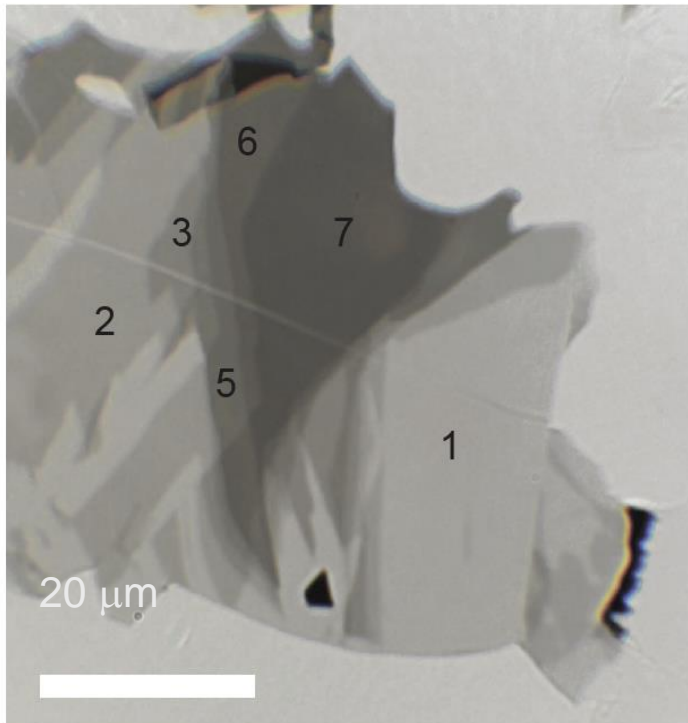
# Monolayer Flakes Exfoliated from Various Crystals



Scale bar: 50  $\mu$ m

# Al<sub>2</sub>O<sub>3</sub>-assisted Exfoliation of MBT Down to Monolayer

Few-layer MnBi<sub>2</sub>Te<sub>4</sub>  
under microscope



Yujun Deng

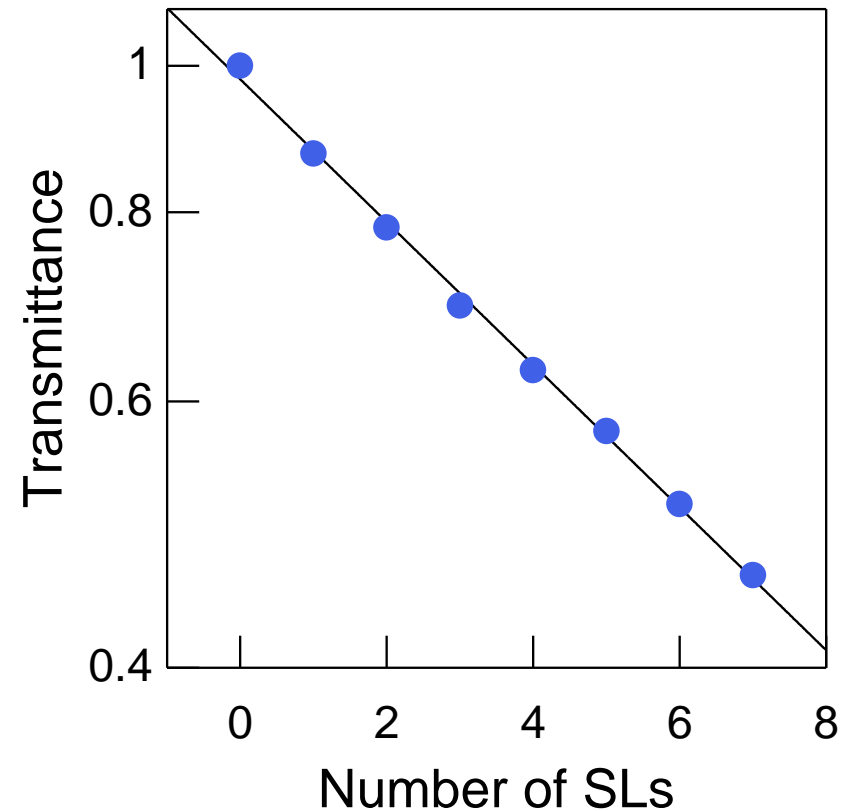


Yijun Yu

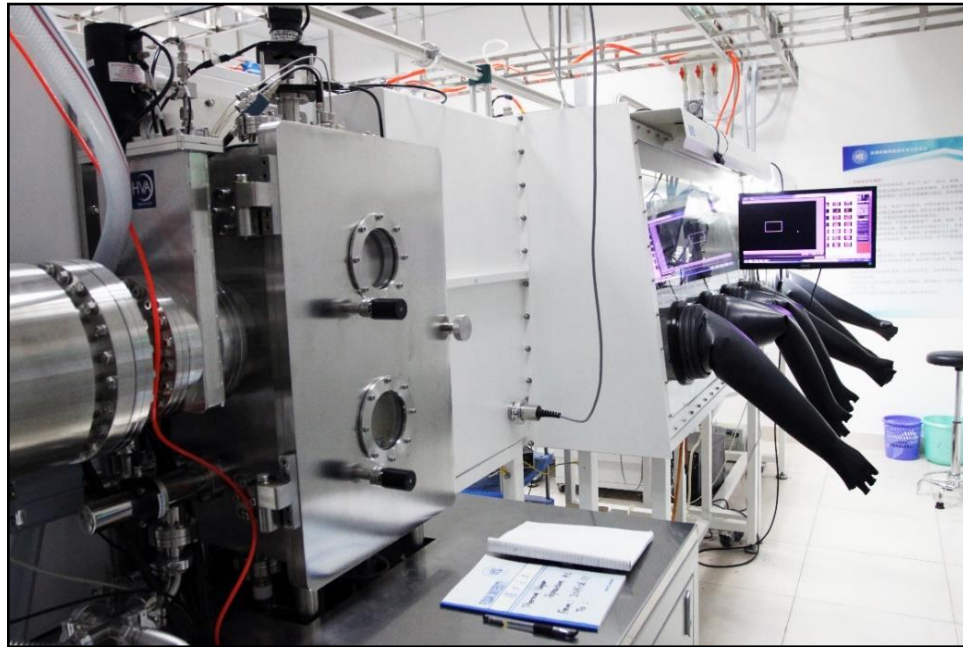


Zhongxun Guo

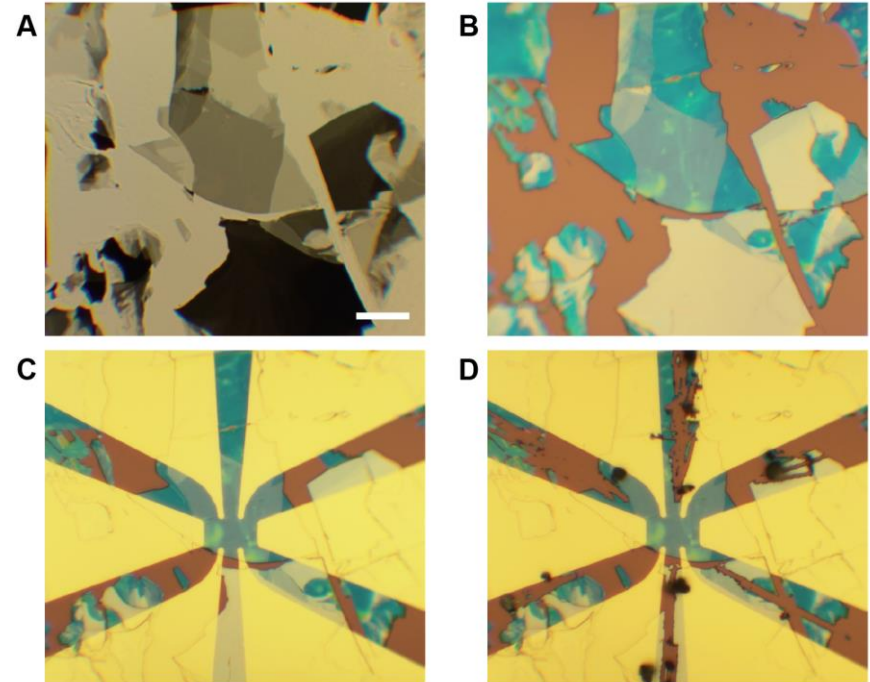
Transmittance of few-layer MnBi<sub>2</sub>Te<sub>4</sub>



# 2D Material Device Fabrication



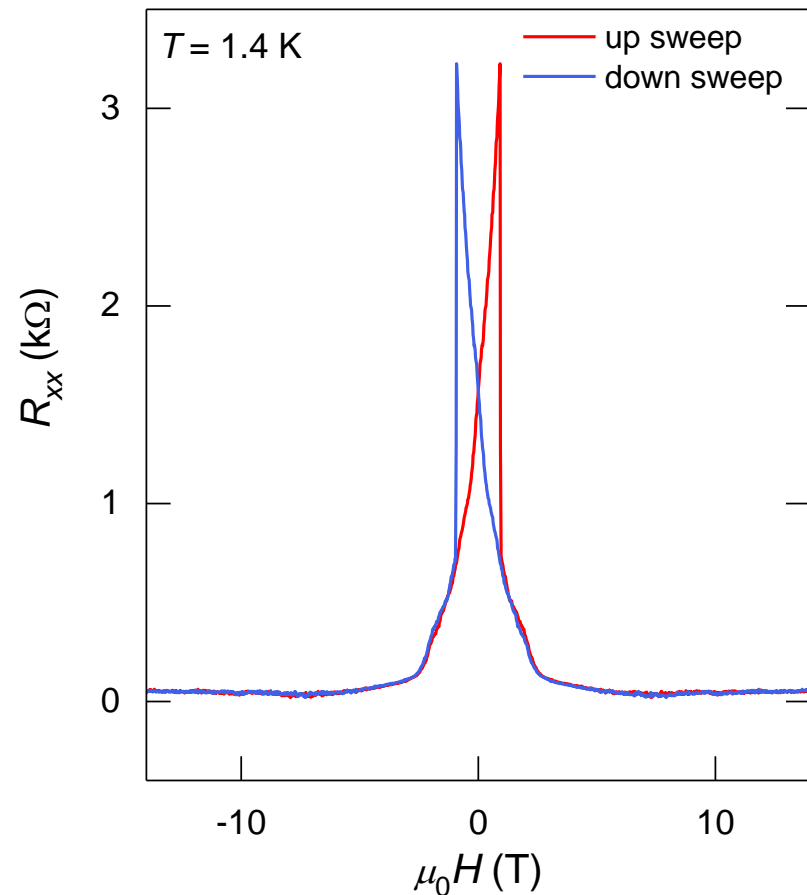
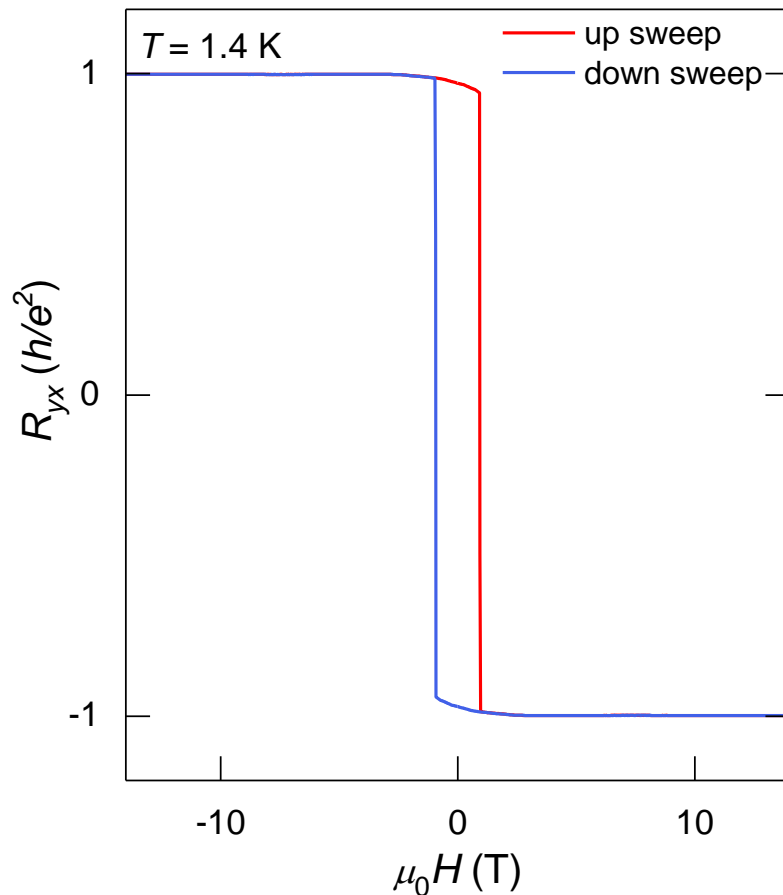
Entire fabrication process done in Ar-filled glove box ( $O_2$  and  $H_2O$  level  $< 0.5$  ppm, partial pressure  $< 10^{-3}$  mbar)



Use shadow mask instead of EBL to make electrical contacts

# Quantum Anomalous Hall Effect in MBT

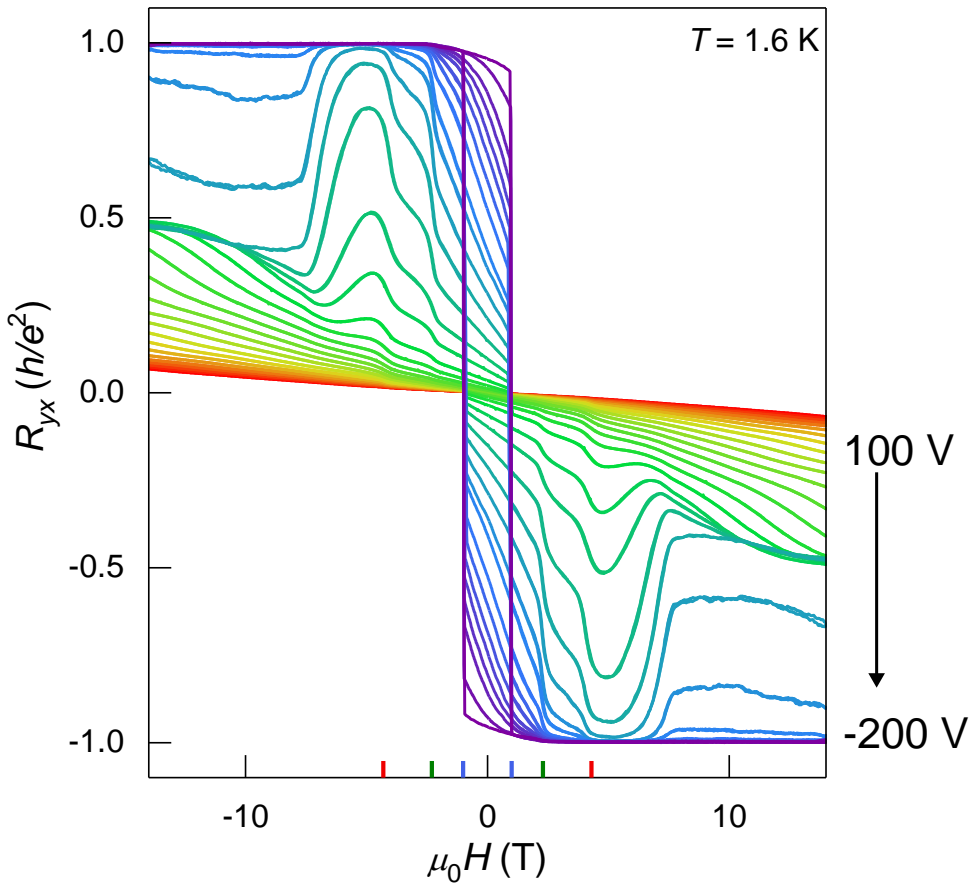
## QAH in a five-layer MBT



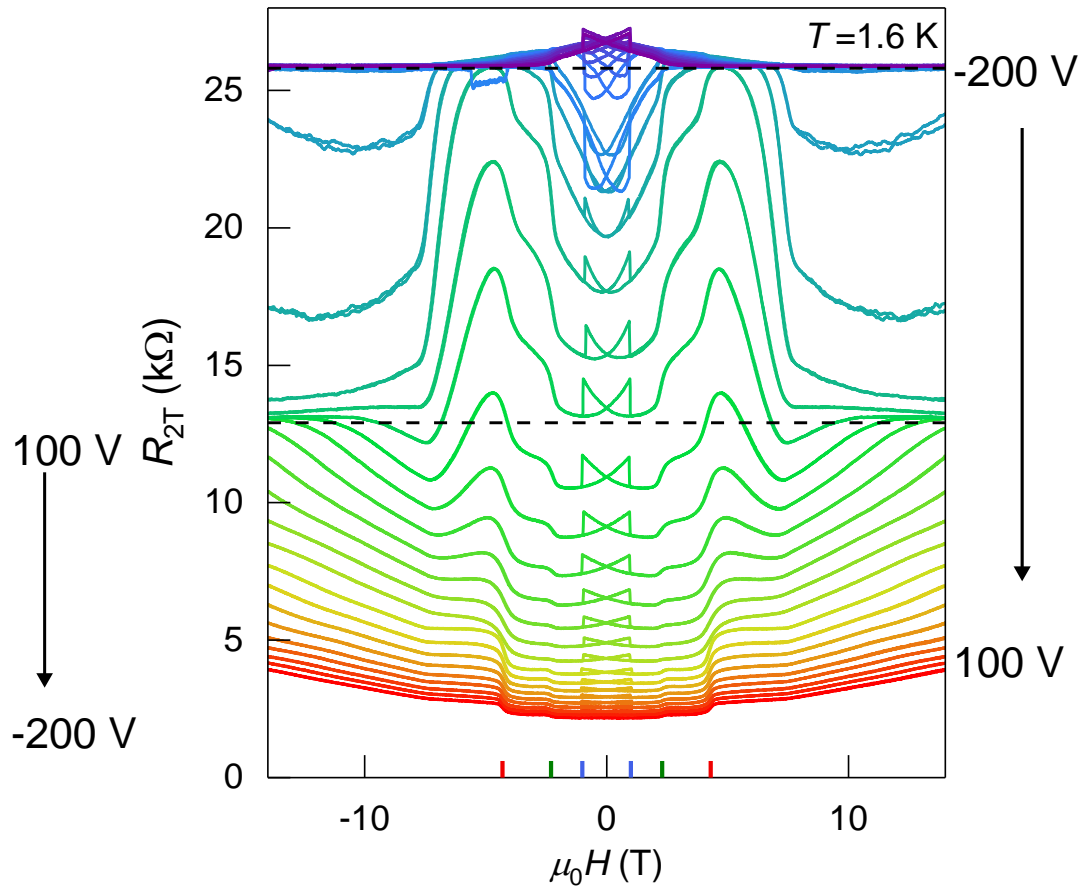
$R_{yx}$  reaches 97%  $h/e^2$  at  $T = 1.4$  K under zero magnetic field

# QAHE in MBT Tuned by Backgate

$R_{yx}$  at various gate voltages



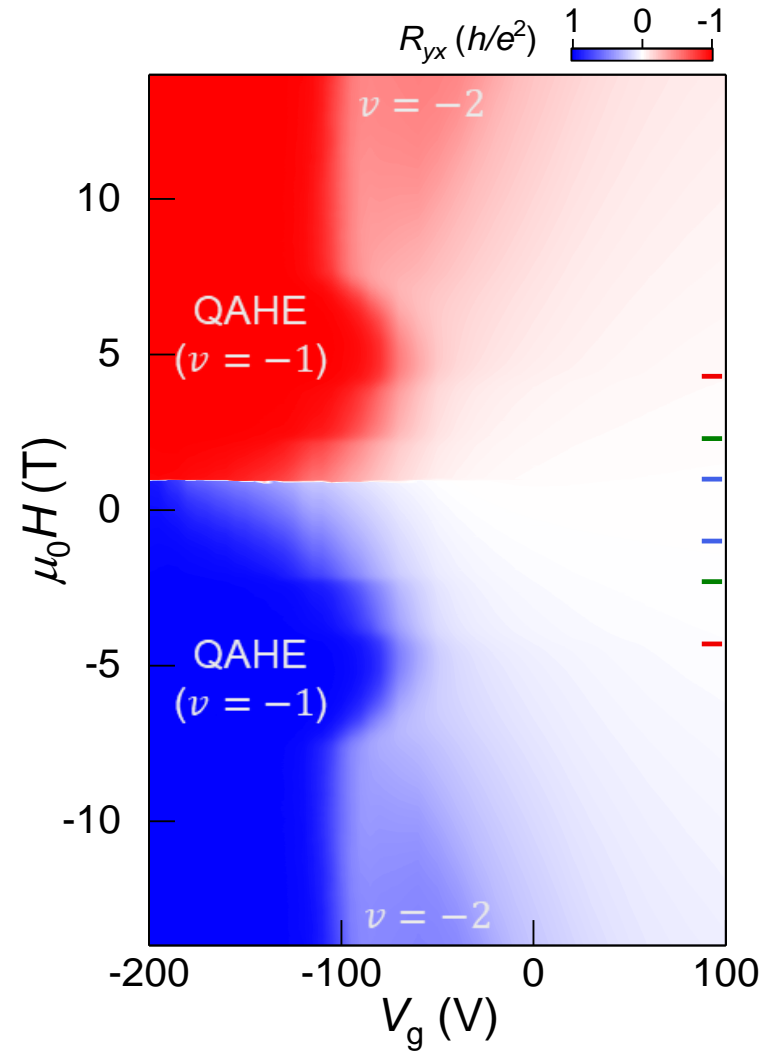
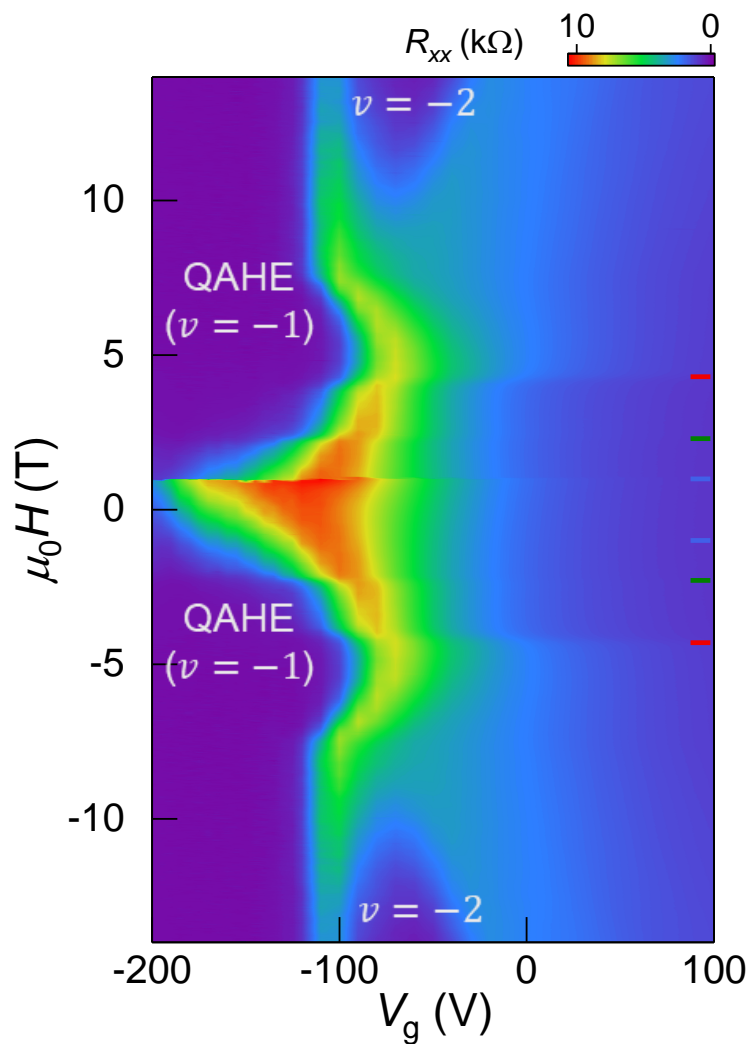
Two-terminal  $R_{xx}$  at various gate voltages



Additional quantization plateau at  $h/(2e^2)$

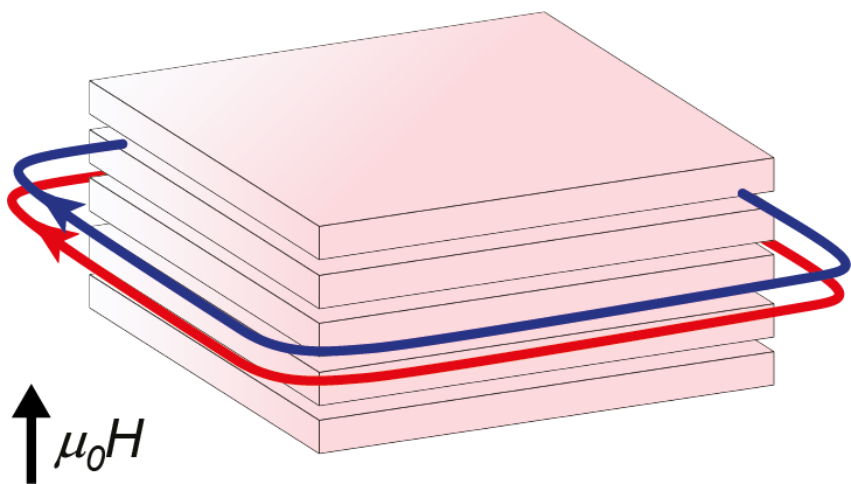
# Additional Quantization at $\nu = 2$ at Finite Doping

2D plots of  $R_{xx}$  and  $R_{yx}$



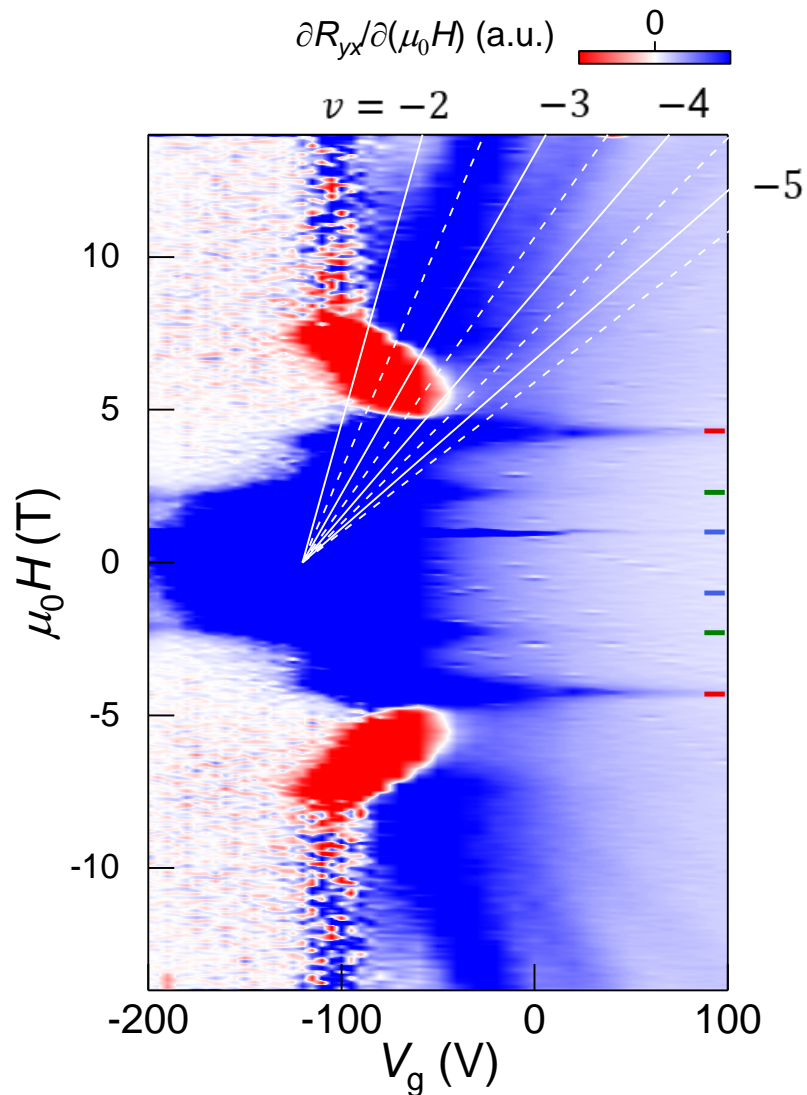
# Coexistence of QAH and QH Effects in MBT

QAH + QH edge states  
( $\nu = \nu_{QAH} + \nu_{QH} = 2$ )



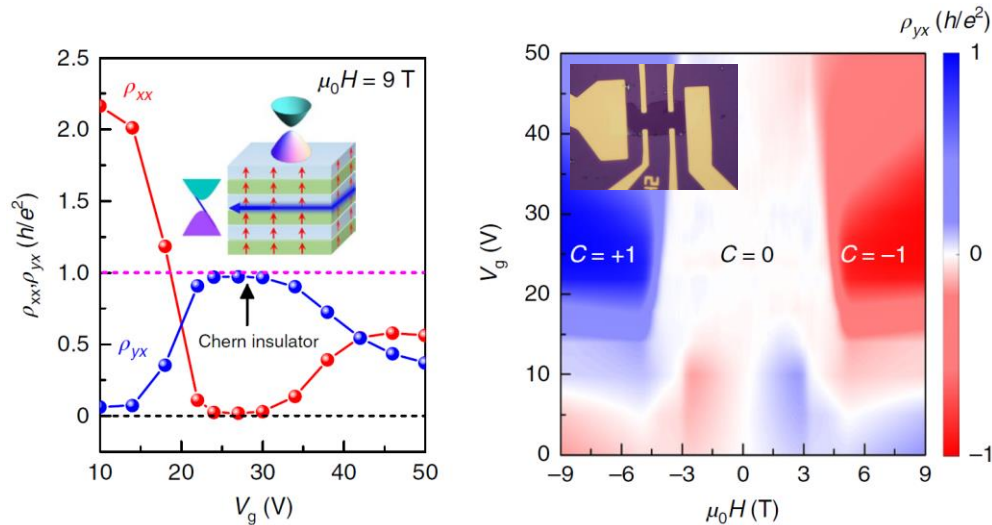
— QAH edge state  
 $\nu_{QAH} = 1$

— QH edge state  
 $\nu_{QH} = 1$



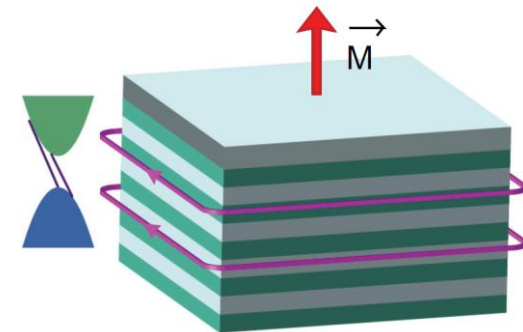
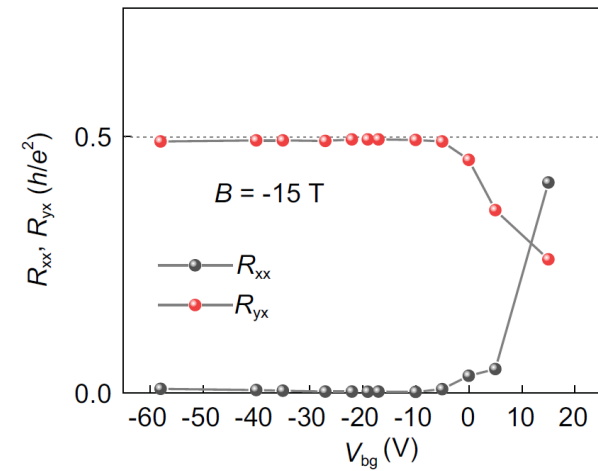
# QAH Effect in Even-layer MBT Under High Magnetic Field

QAH in a 6-SL sample



Yayu Wang group, Tsinghua University (2020)

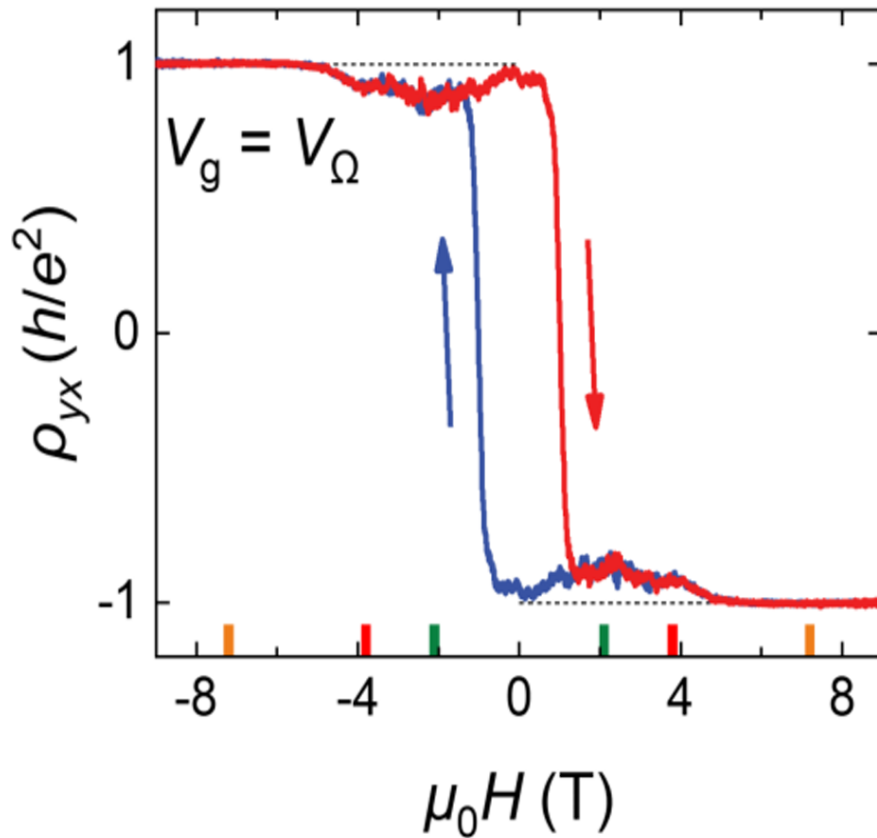
High Chern number QAH state in a 10-SL sample



Jian Wang group, Peking University (2020)

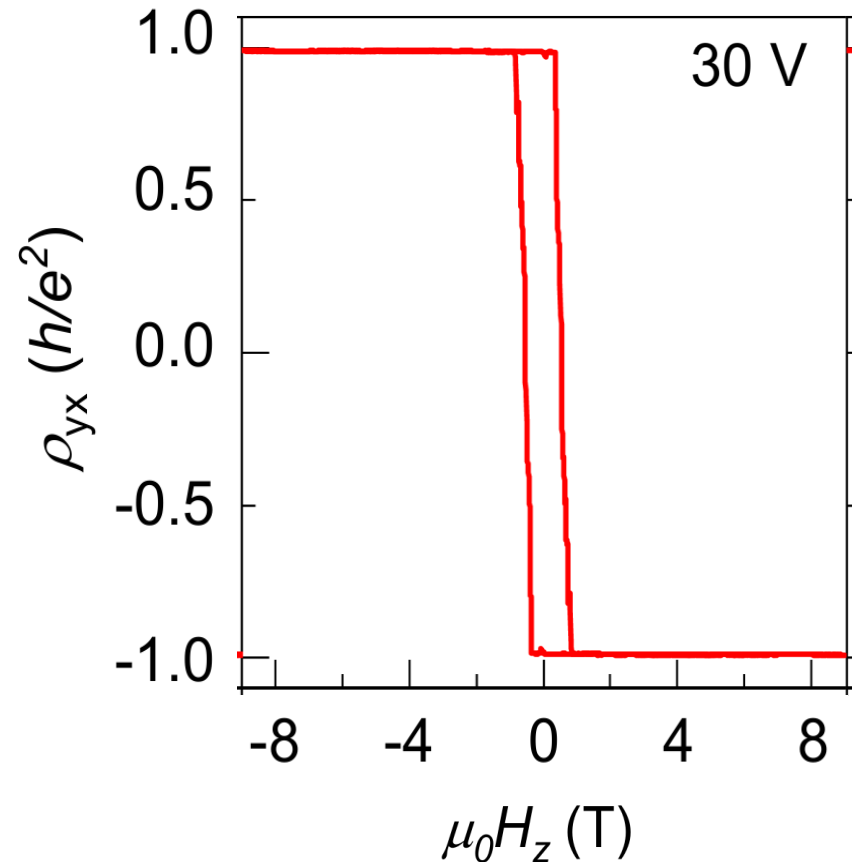
# Progresses on Reproducing QAHE in $\text{MnBi}_2\text{Te}_4$

## MBE thin film



Li et al, arXiv:2401.11450(2024)

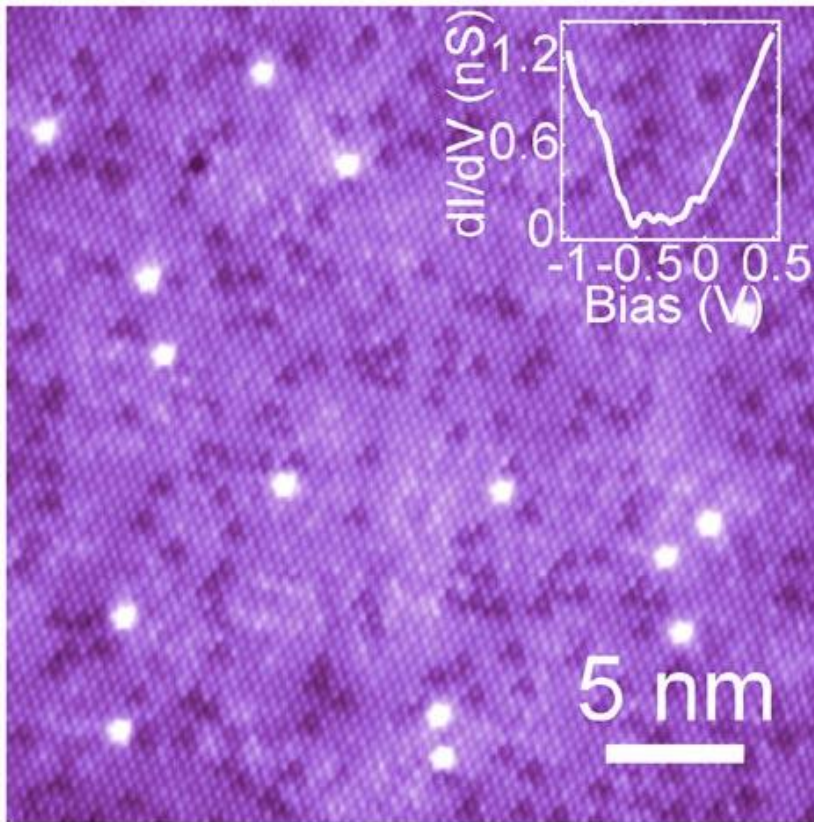
## 7-SL thin flake



Lian et al, arXiv:2405.08686(2024)

# The Sample Quality Issue

## Defects in MBT bulk crystal



Qi-Kun Xue group (2020)

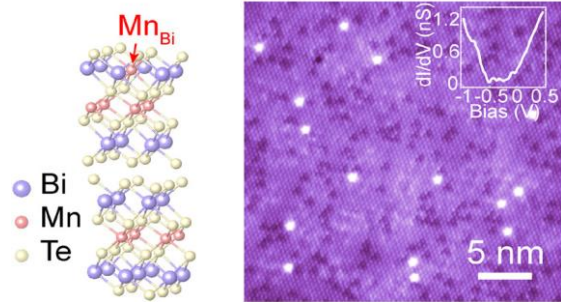
Bright spots:  
Mn or Bi substitution of Te

Dark triangles:  
Mn-on-Bi antisite defects  
(~ 5%)

**These defects may  
compromise QAH effect,  
and alter magnetic phases**

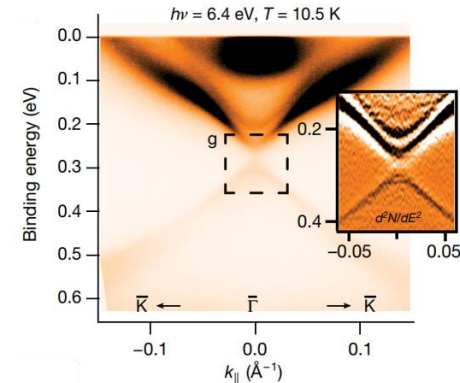
# Spectroscopy Measurements: Gap or No Gap

No gap observed on bulk surface w/ STS



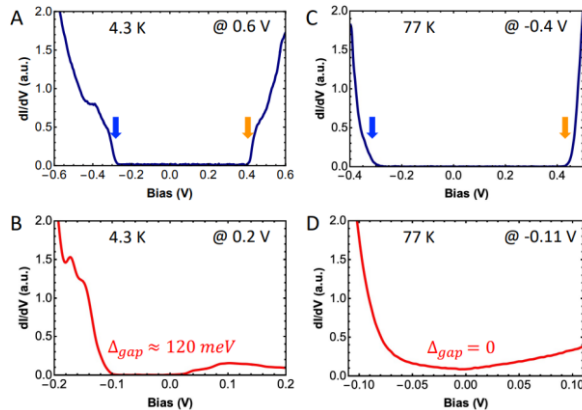
Qi-Kun Xue group (2020)

$E_g \sim 200$  meV observed in ARPES



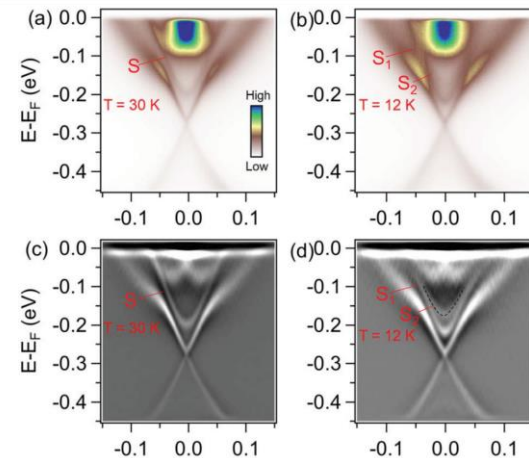
M. Otkov et al. (2019)

Large STS gap observed on MBE thin film



Chih-Kang Shih group (2022)

No gap observed in ARPES

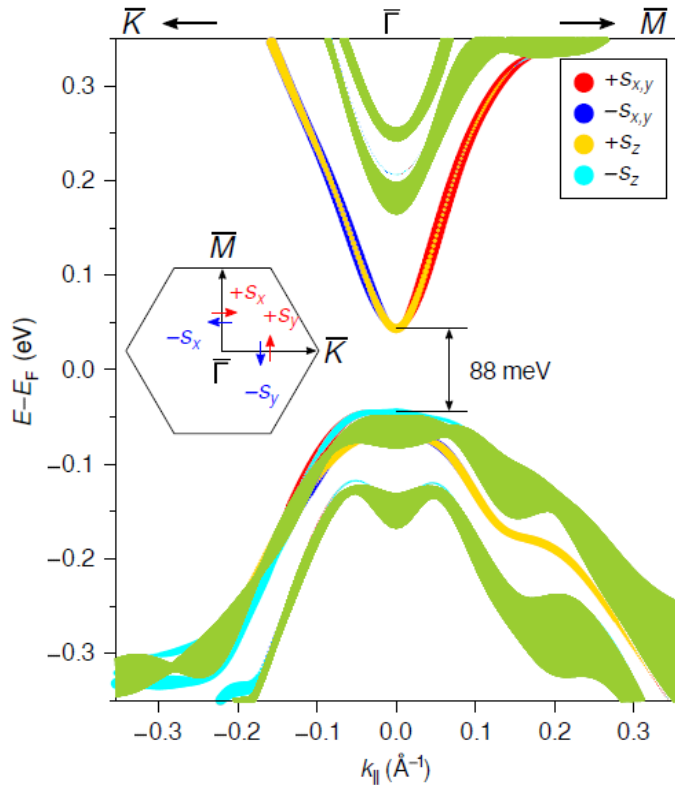


Zhiqiang Mao group and Shuolong Yang group (2021)

ARPES/STS gave inconsistent results on different samples

# Energy Scale of the QAHE in MBT

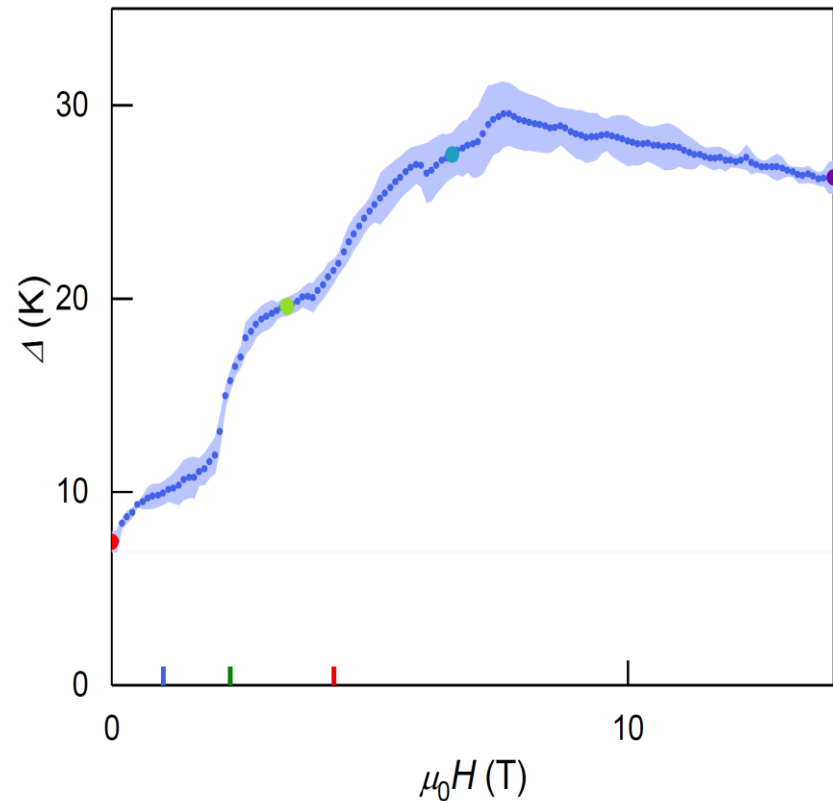
Calculated surface bands of MBT



Calculated exchange gap  
~ 88 meV (1000 K)

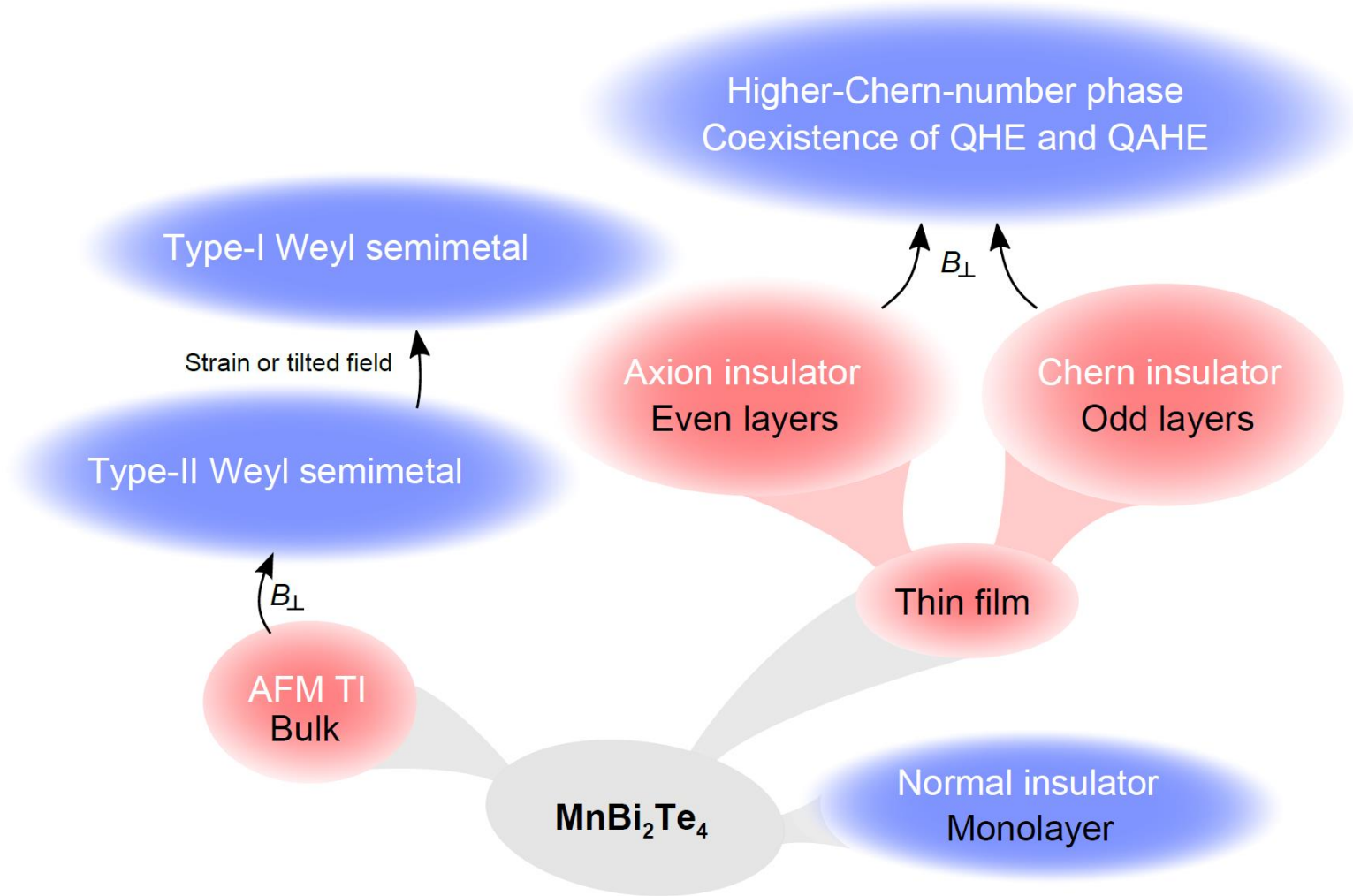
See, for example, Otrokov, M. M. *et al.*, Nature (2019)

Magnetic field-dependent  
QAH energy gap

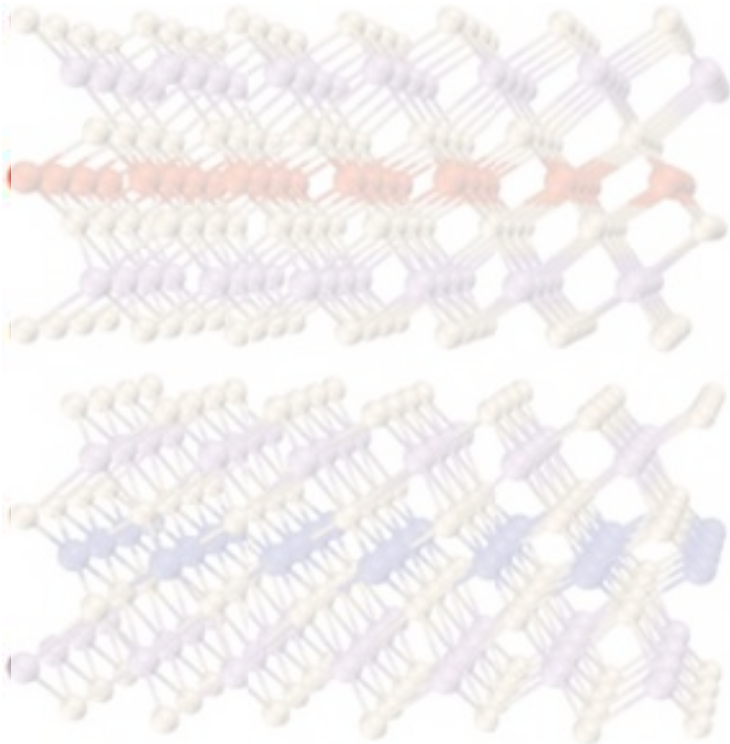


- Zero-field gap  $\Delta = 7.4$  K
- Highest gap value  $\Delta \sim 30$  K

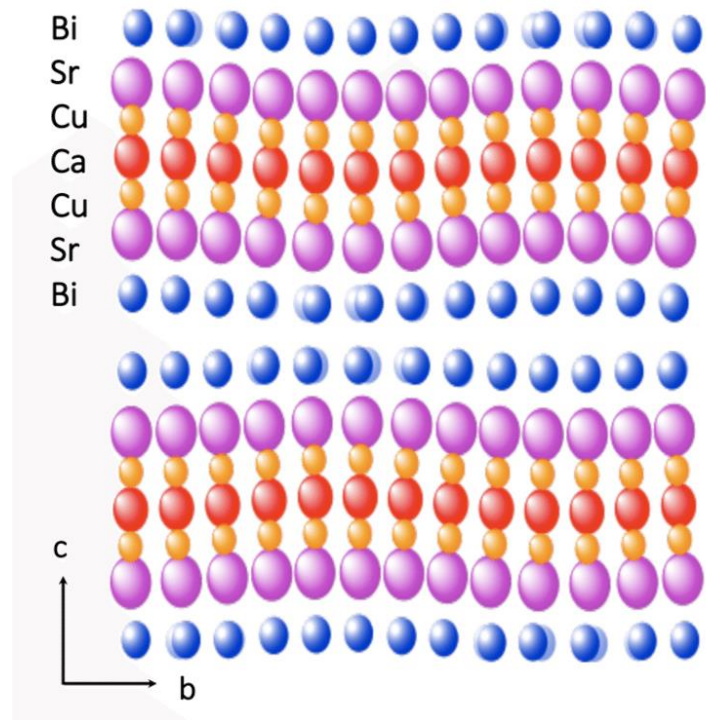
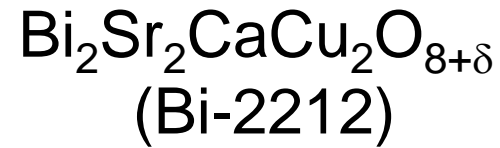
# Rich Topological Phases in MBT



# Exploring New 2D Materials



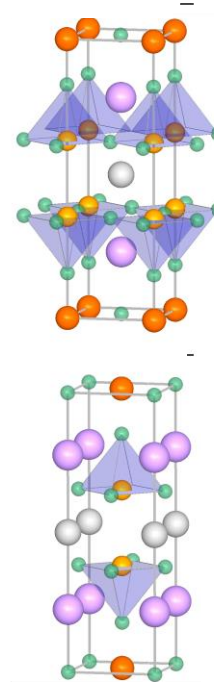
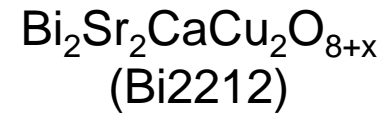
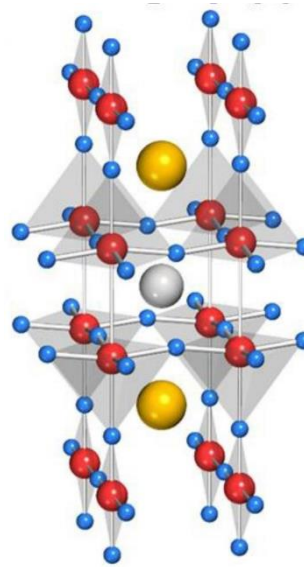
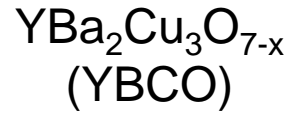
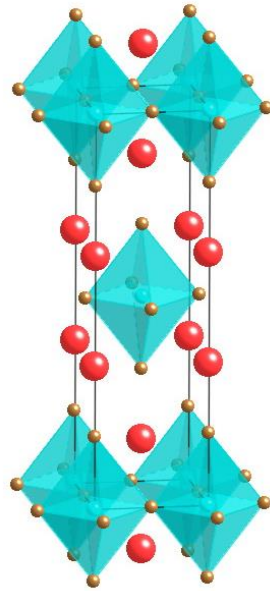
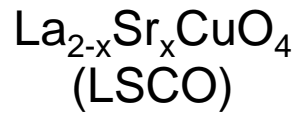
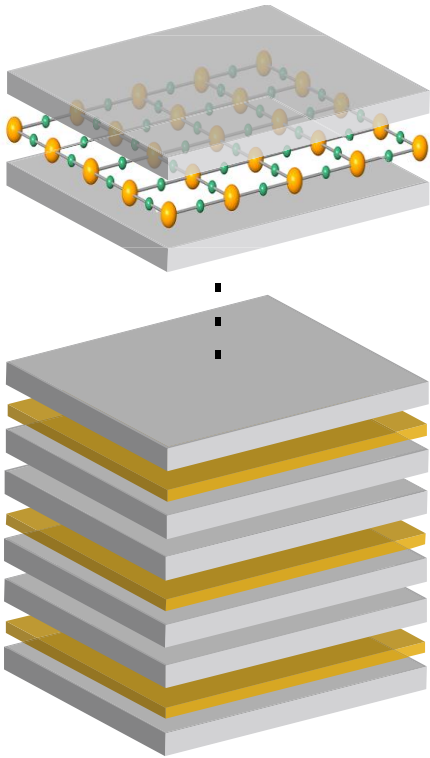
Magnetic topological insulator



High  $T_c$  superconductor

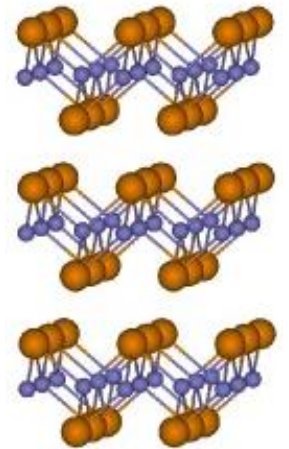
# Layered Structure of High $T_c$ Superconductors

Layered structure  
of high  $T_c$   
superconductors



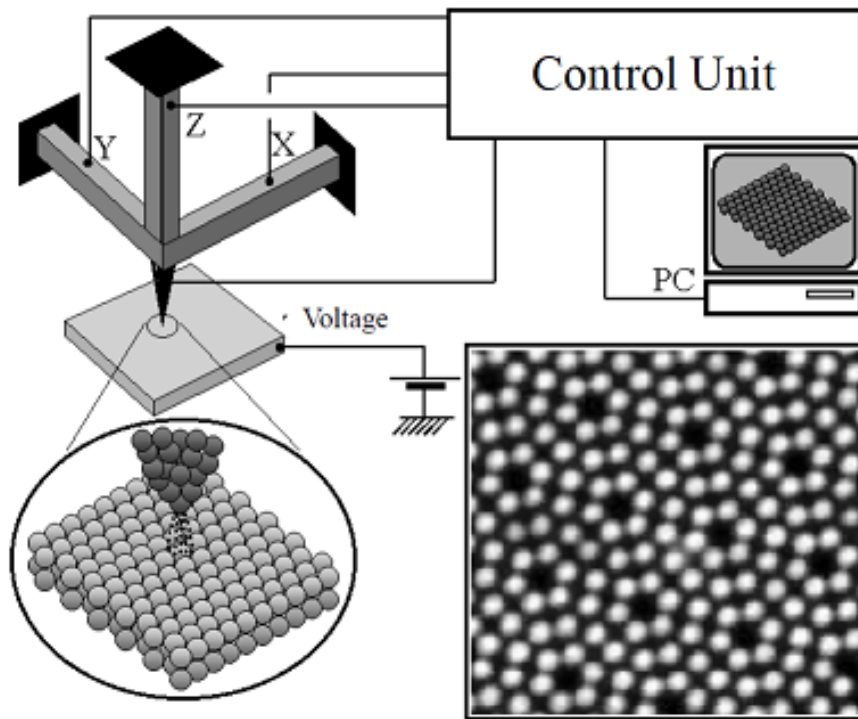
Bi  
Sr  
Ca  
Cu  
O

FeSe

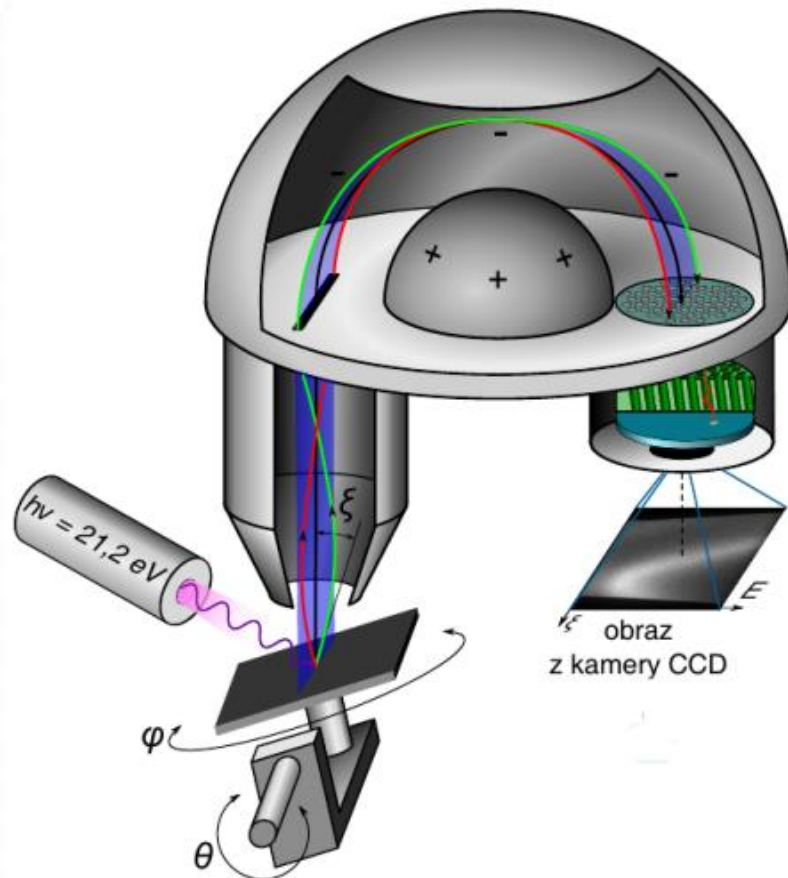


# STM & ARPES as Surface Probes for High $T_c$

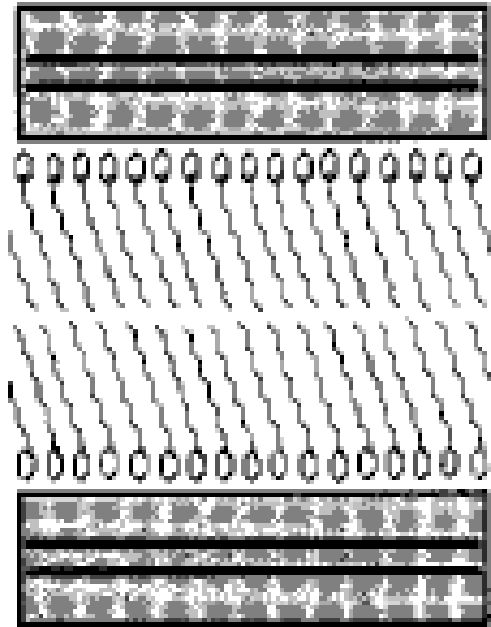
Scanning Tunneling Microscopy  
(STM)



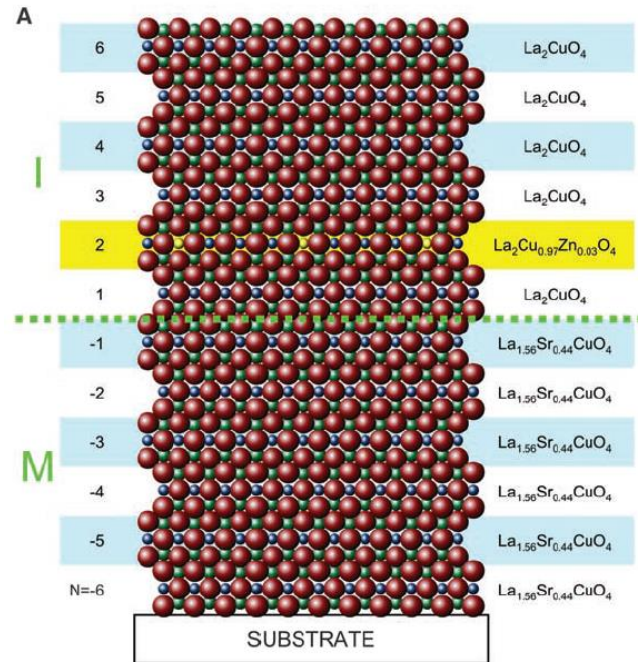
Angle-resolved Photoemission Spectroscopy  
(ARPES)



# Previous Studies on the Role of Dimensionality



Choy, J.-H. *et al*, *Science* 280, 1589 (1998)



Bozovic, I. *et al*. *J. Supercond.* 5, 19 (1992).  
Logvenov, G. *et al*, *Science* 326, 699 (2009)



**Scotch™**

**810D Scotch™ Magic Tape 3M 3M**

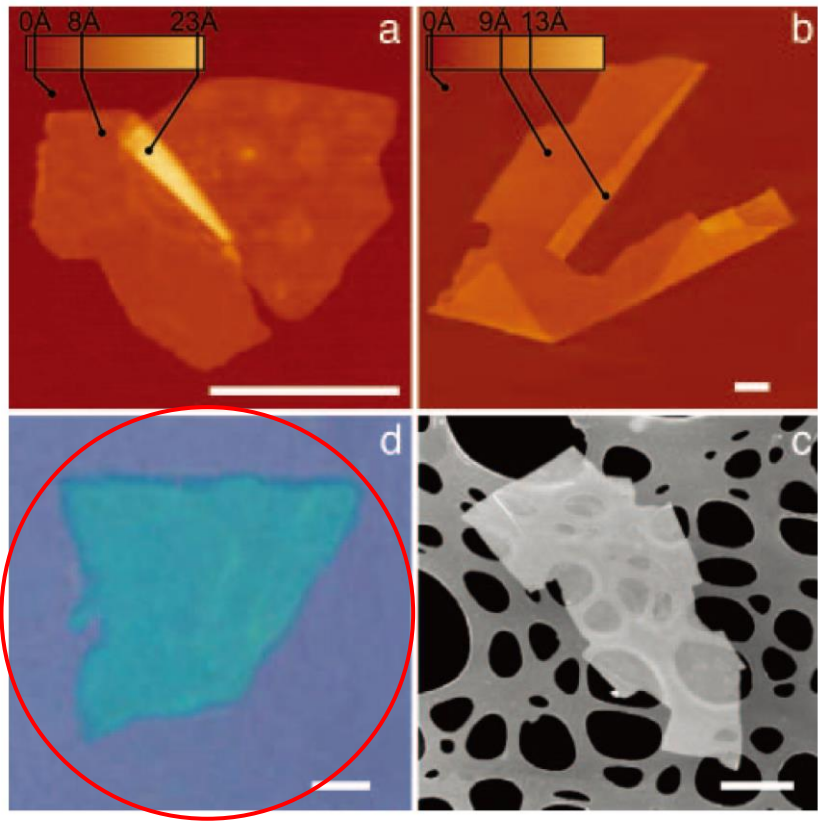
**3/4" x 1296"**

**Refillable Dispenser**

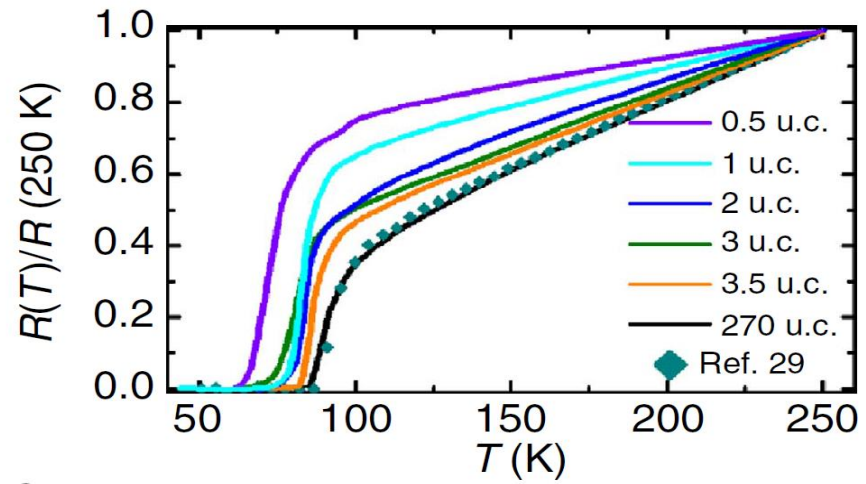
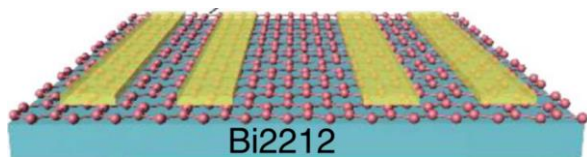
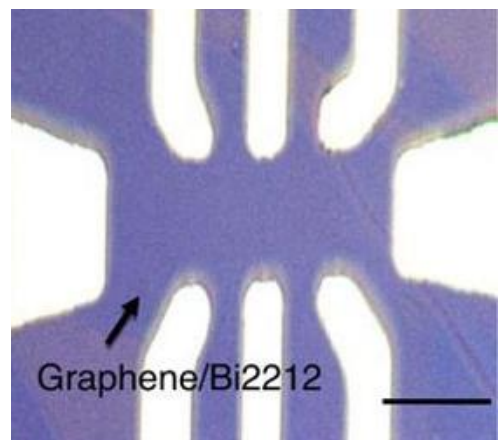
St. Paul, MN 55144-1000 Made in U.S.A.

# Some of the Previous Studies on Bi2212 Few Layer

## Bi2212 thin flake

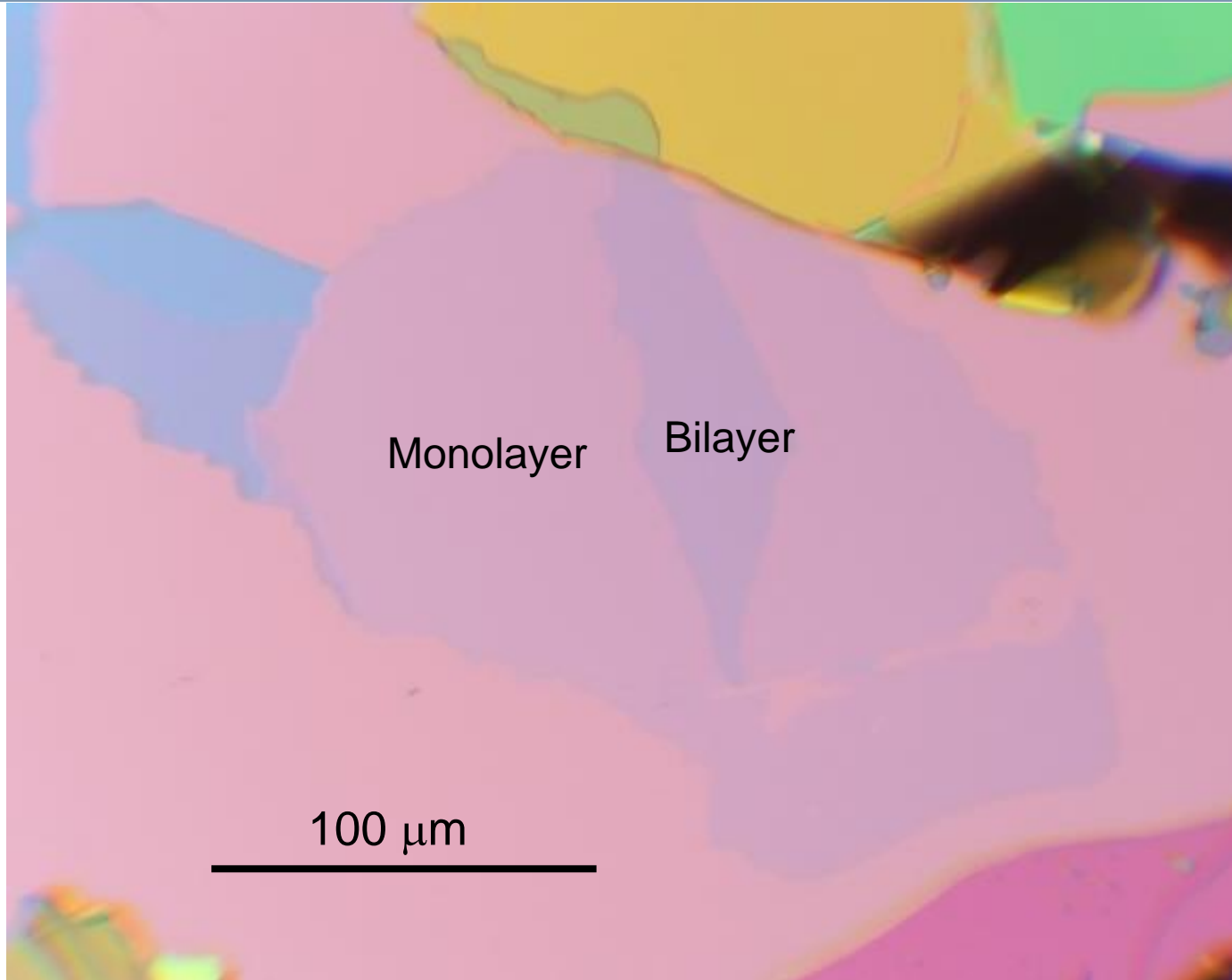


Novoselov, K. S. *et al.* PNAS (2005)



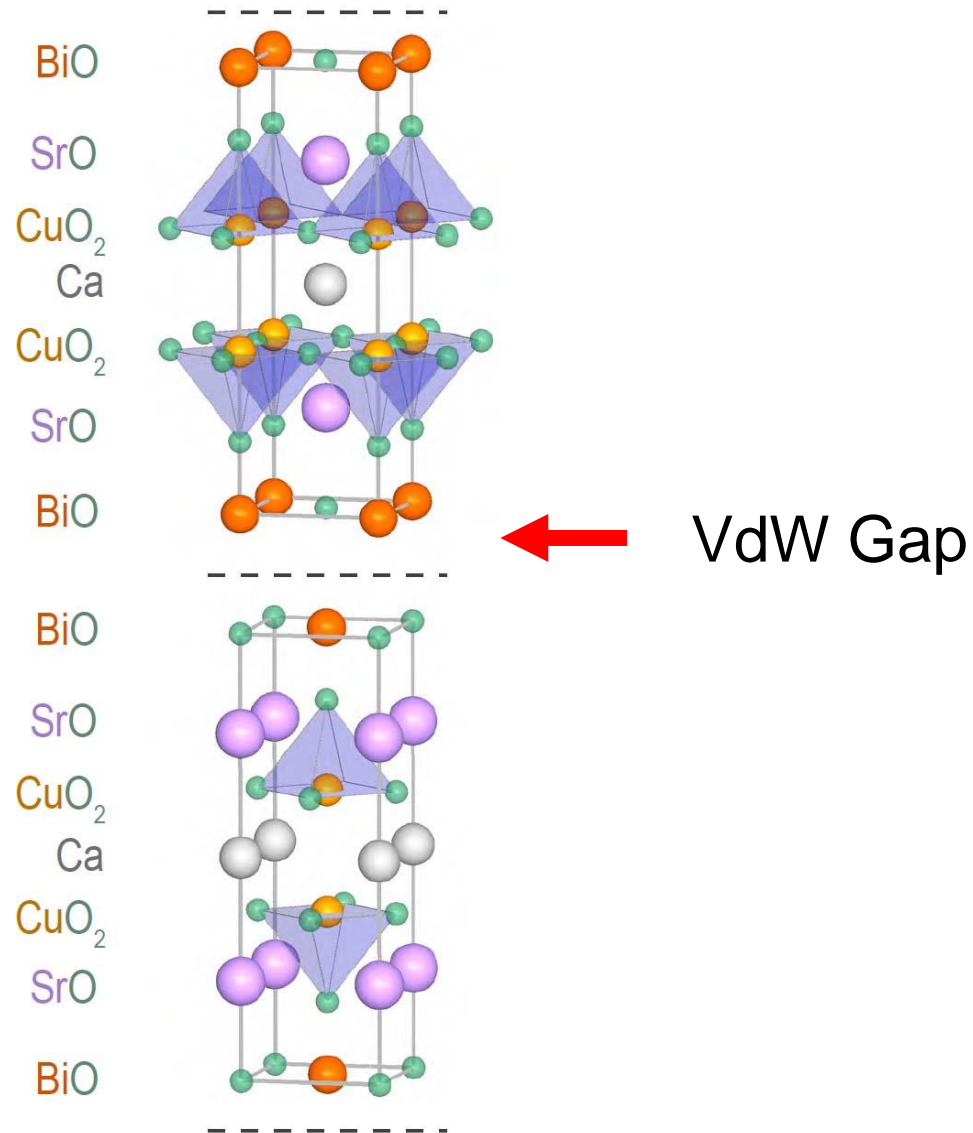
Jiang, D. *et al.*, *Nat. Commun.* 5, 5708 (2014)

# Mechanical Exfoliation of Monolayer Bi2212

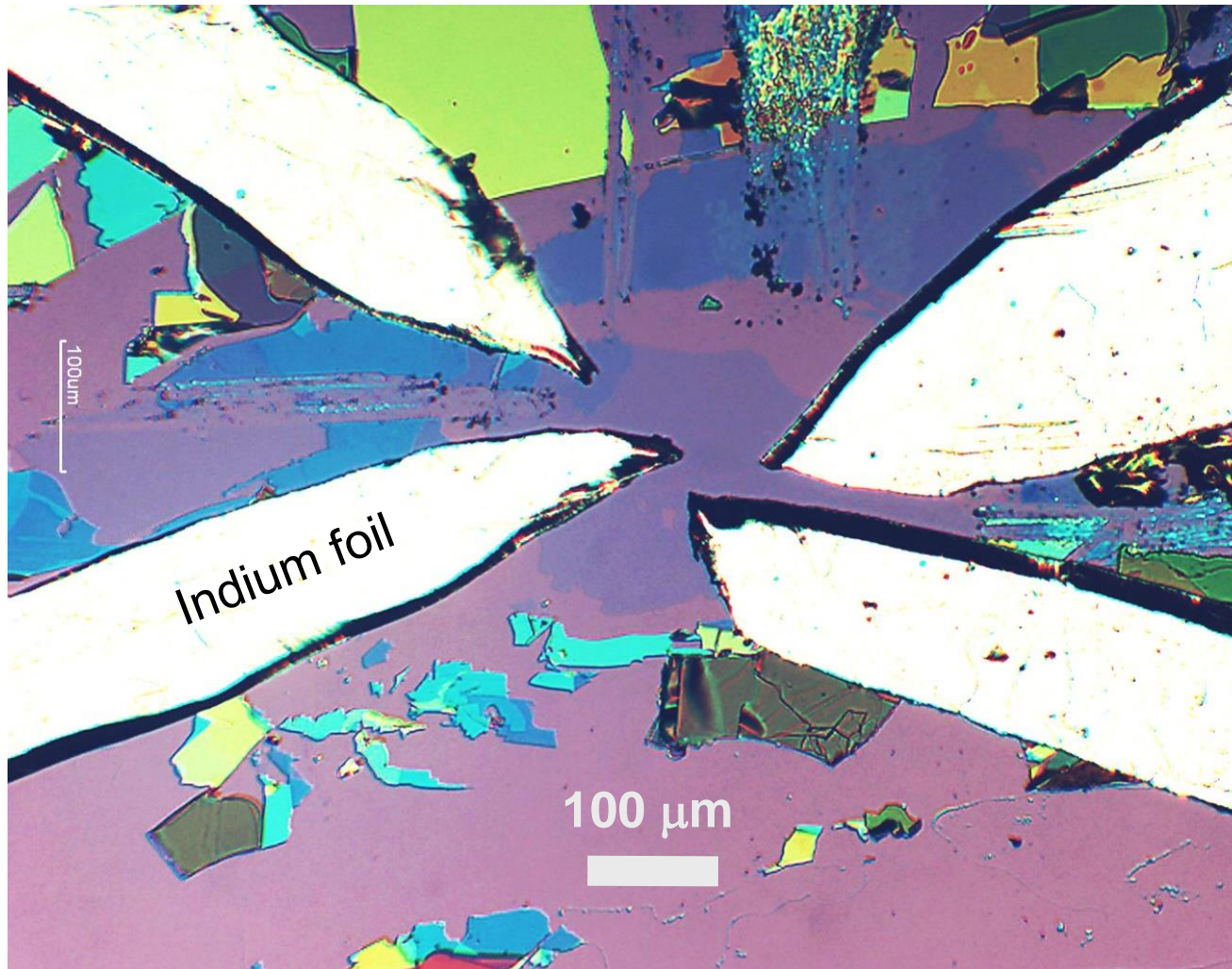


The trick: low temperature (-40C) fabrication in Ar atmosphere

# Layered Structure of Bi2212



# Device Fabrication for Transport Measurements



Yijun Yu



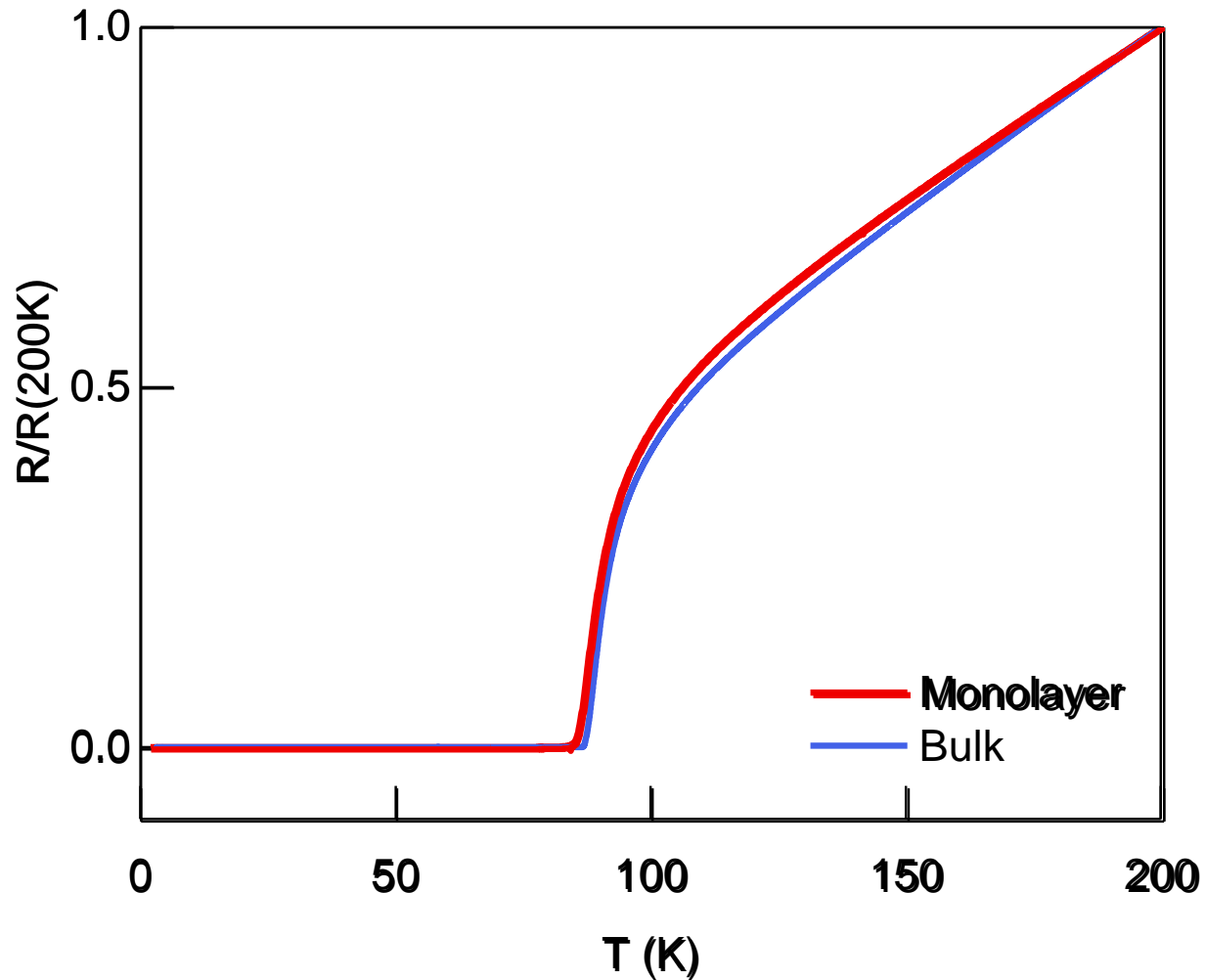
Ligu Ma



Peng Cai

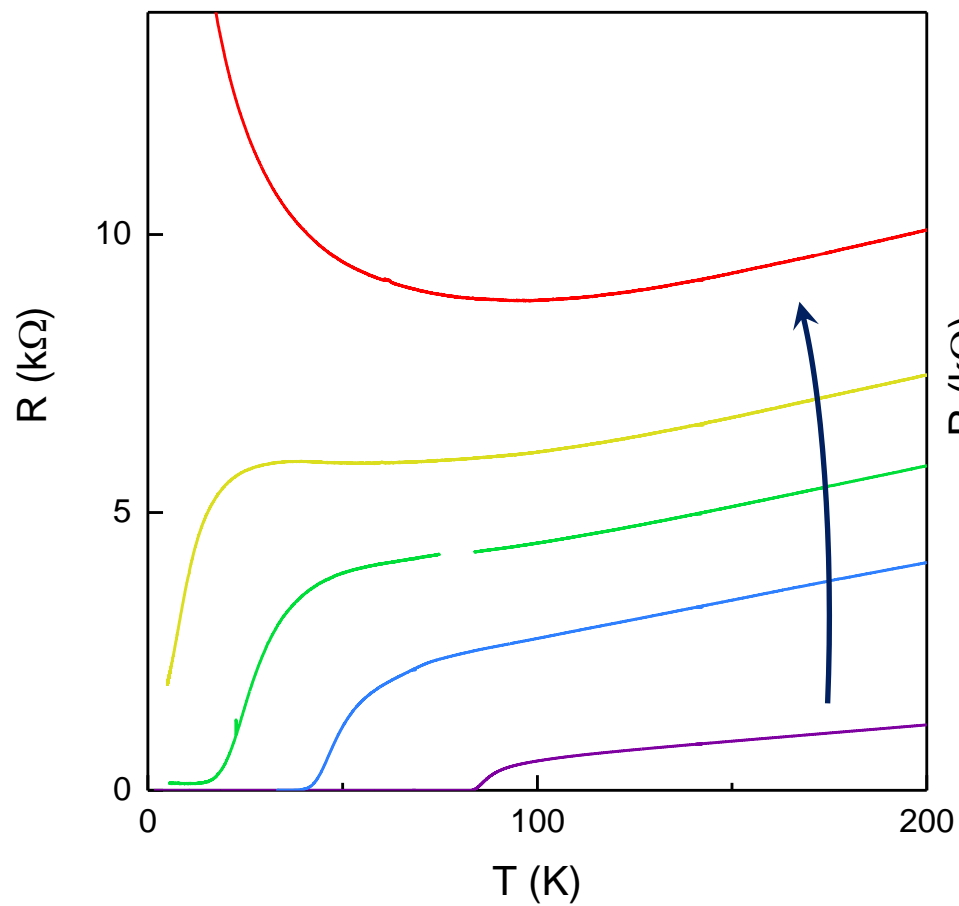
# Monolayer Bi2212 is a Superconductor

R vs. T of optimal doped monolayer Bi2212

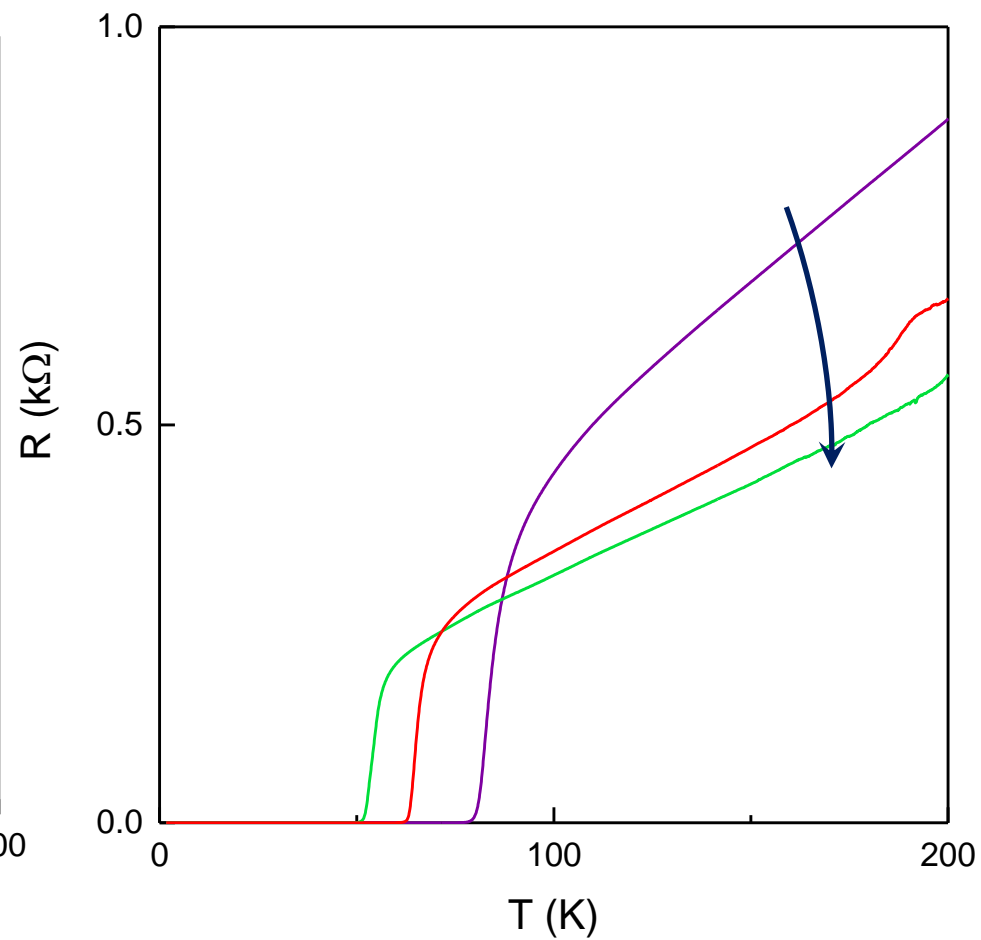


# *In situ* Tuning of Doping Level

## Annealing in vacuum

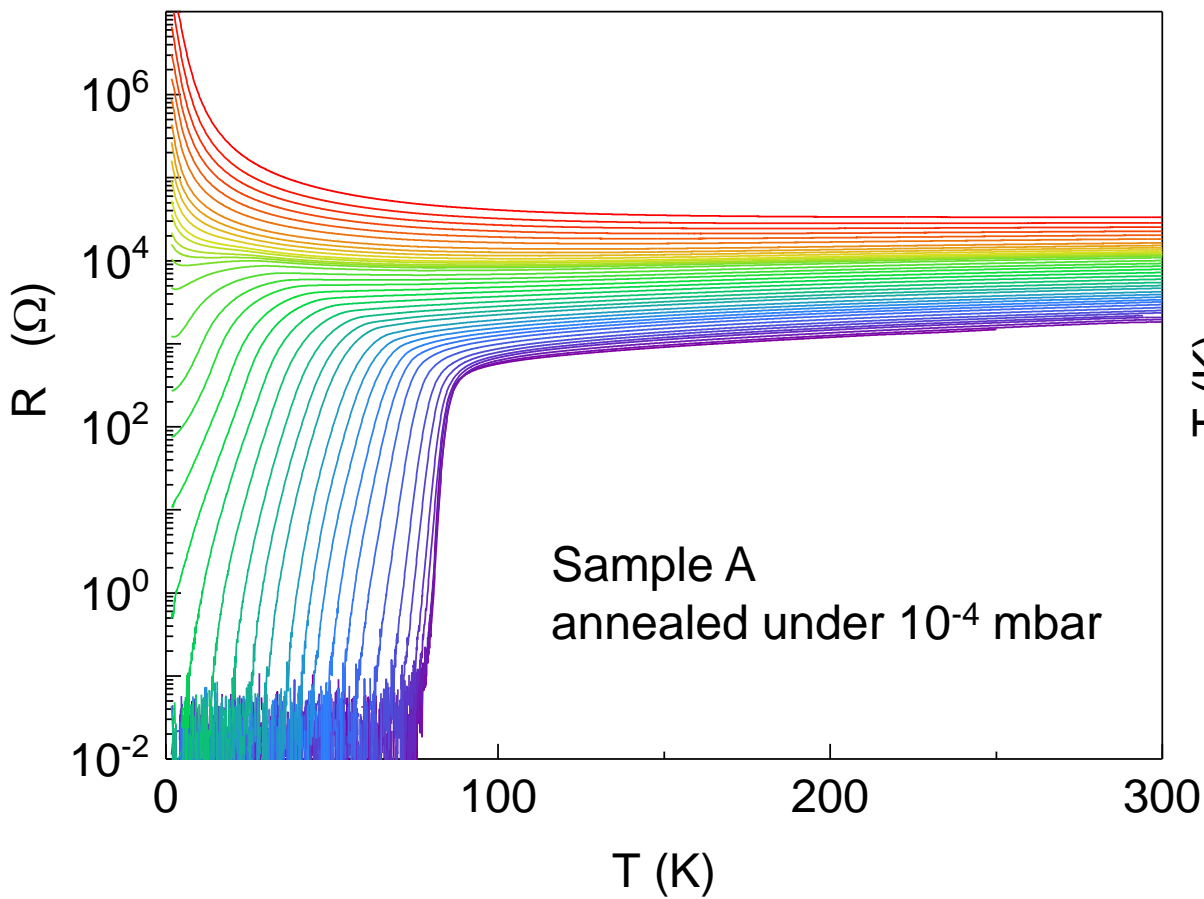


## Annealing in ozone

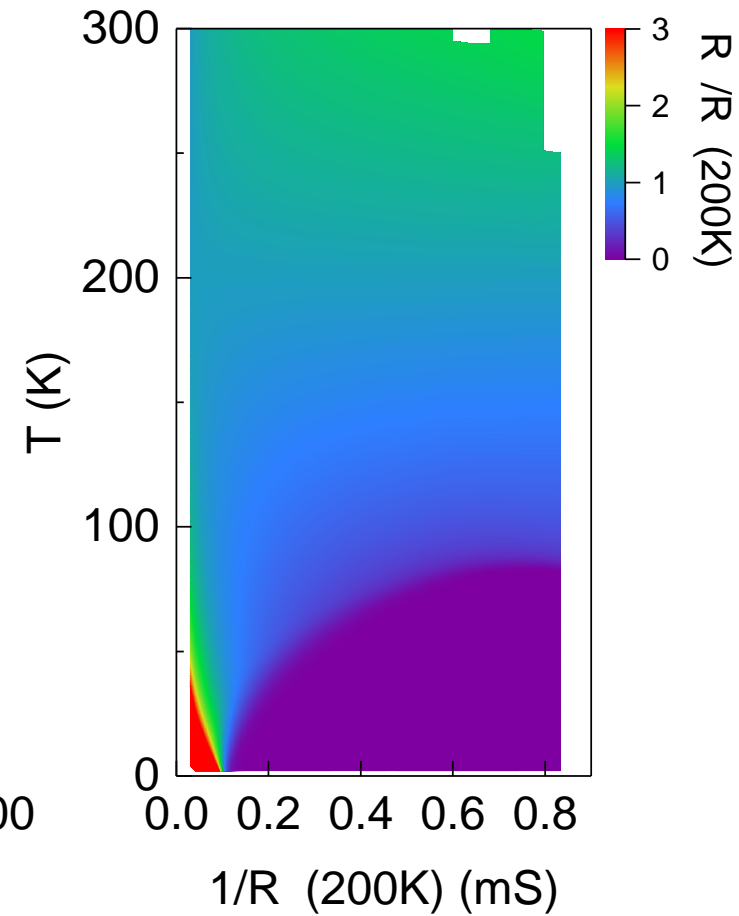


# *In-situ* Tuning of Doping Level – Mapping Phase Diagram

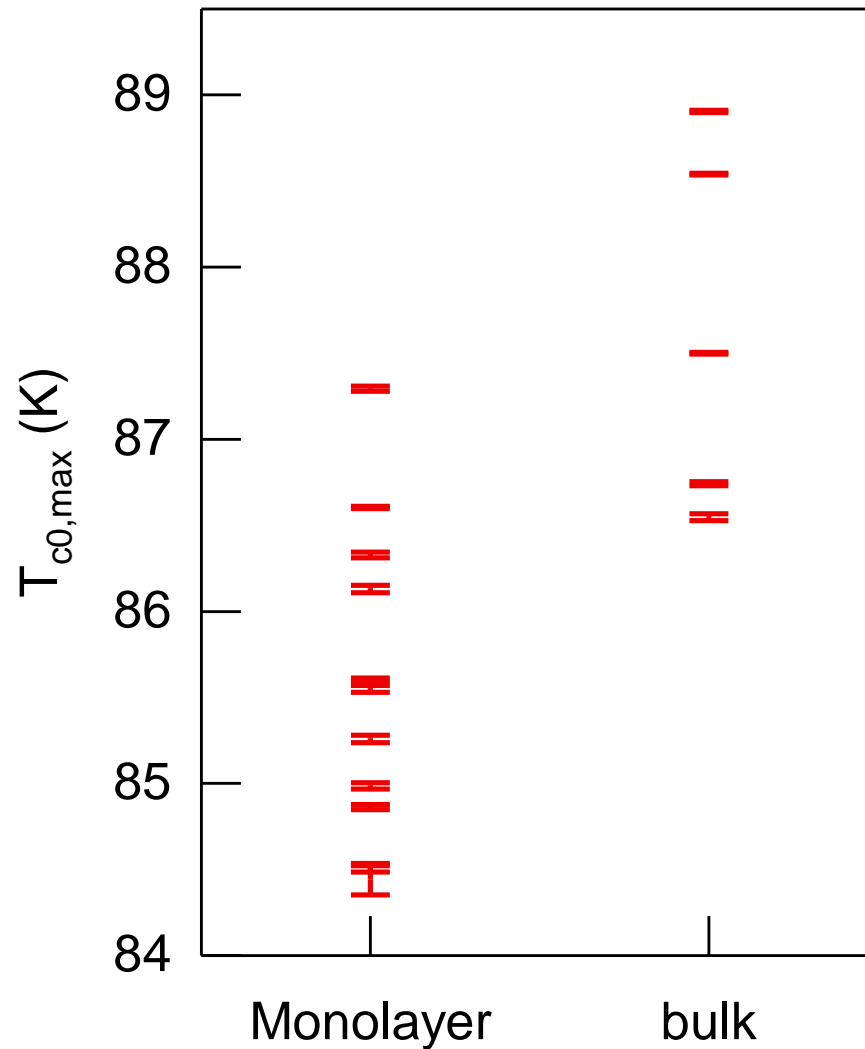
R vs. T curves of monolayer Bi2212



Phase diagram



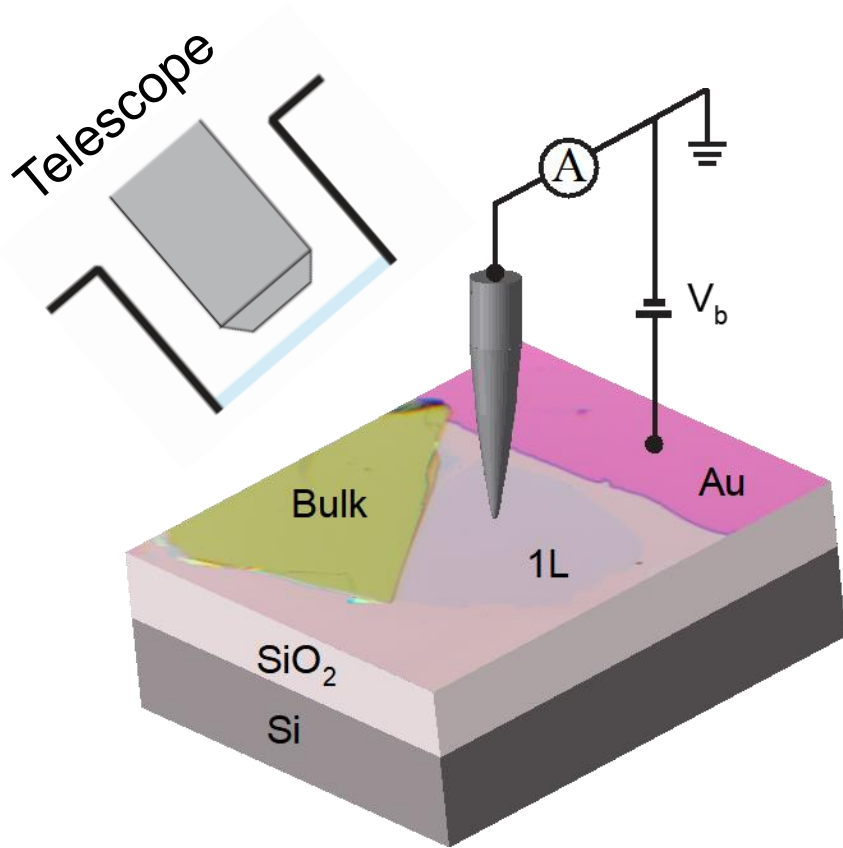
# Comparing Highest $T_c$ in Monolayer to That in Bulk



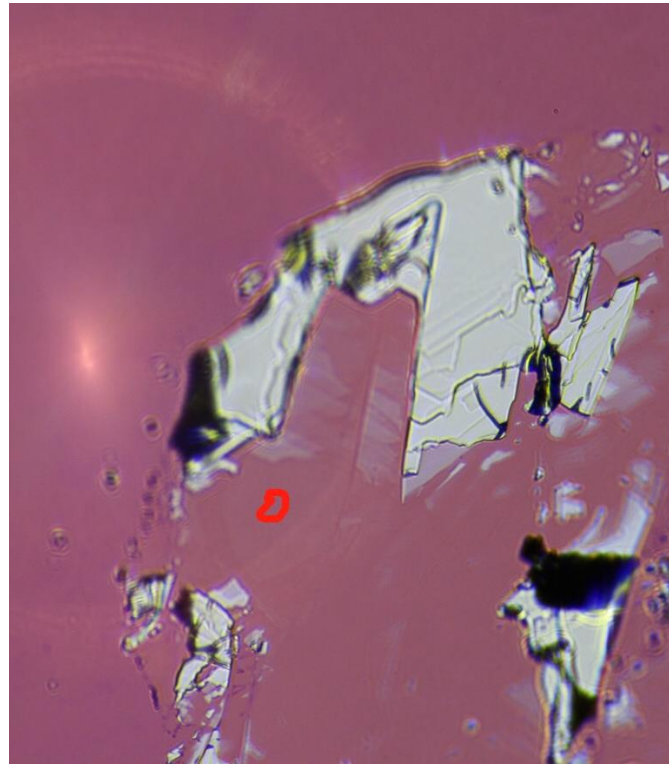
Highest  $T_c$  in monolayer almost the same with bulk

# Finding Monolayer Crystals in STM

## Experimental setup



## Monolayer flake inside STM



Ligu Ma



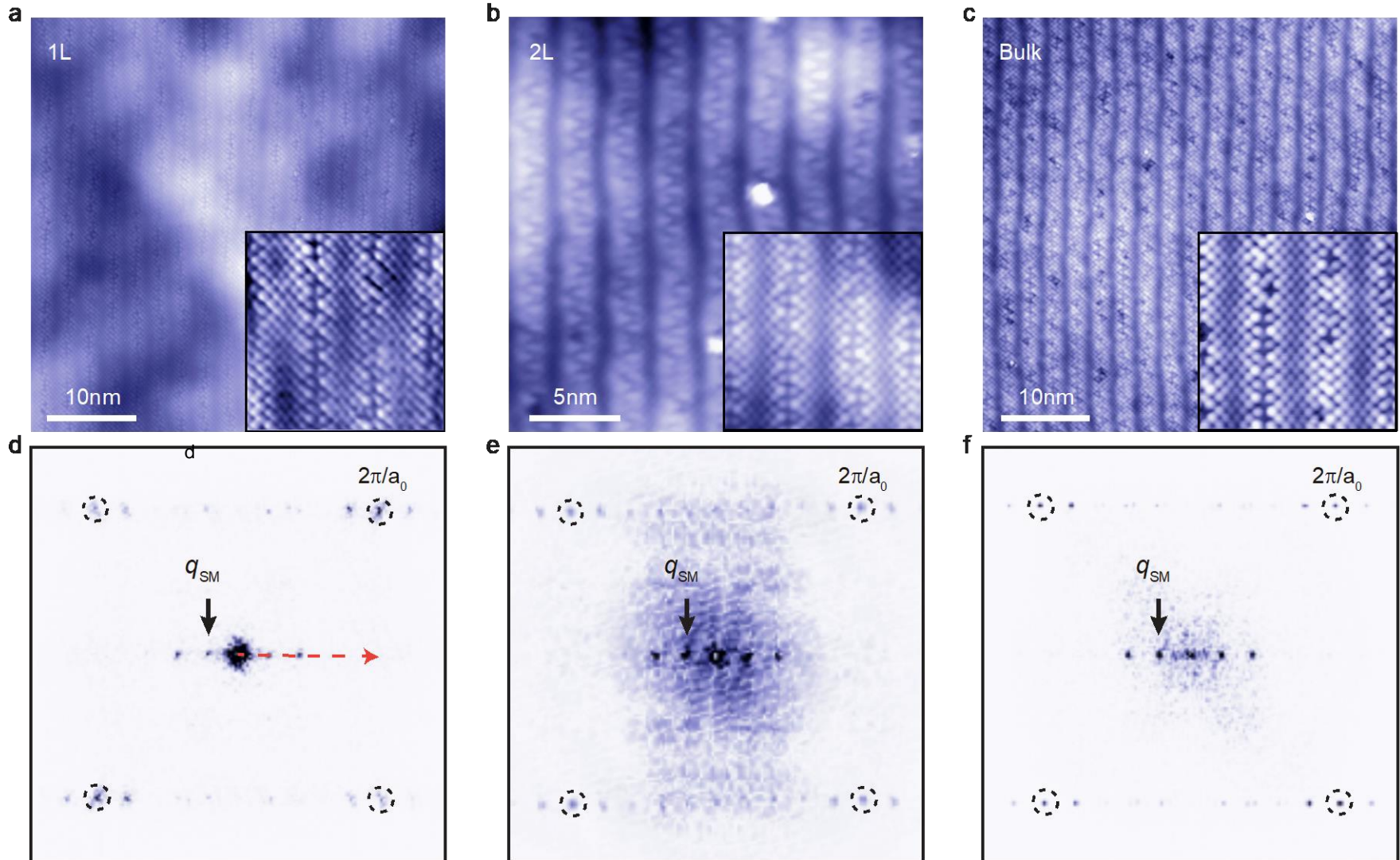
Yijun Yu



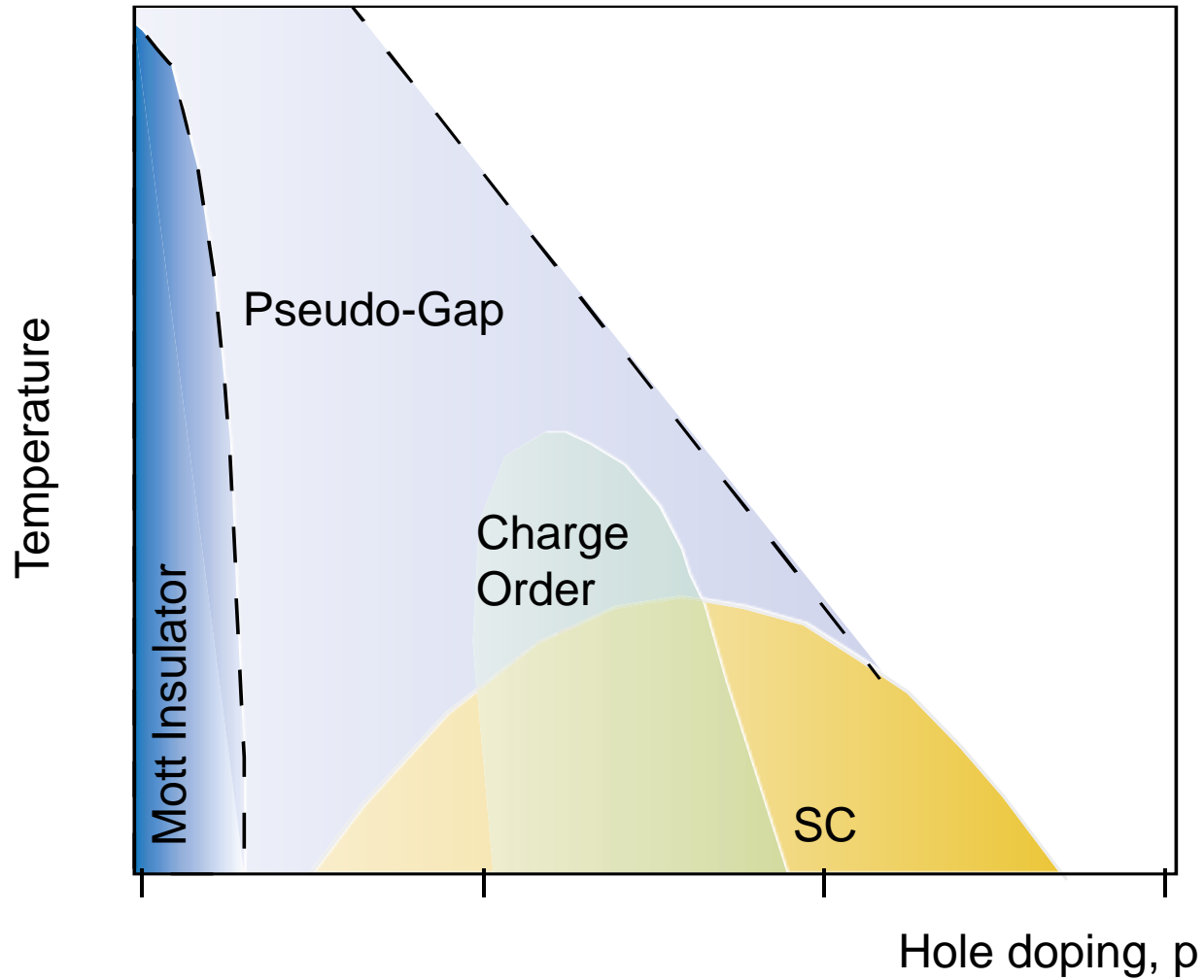
Peng Cai

# STM Topography of Monolayer Bi2212

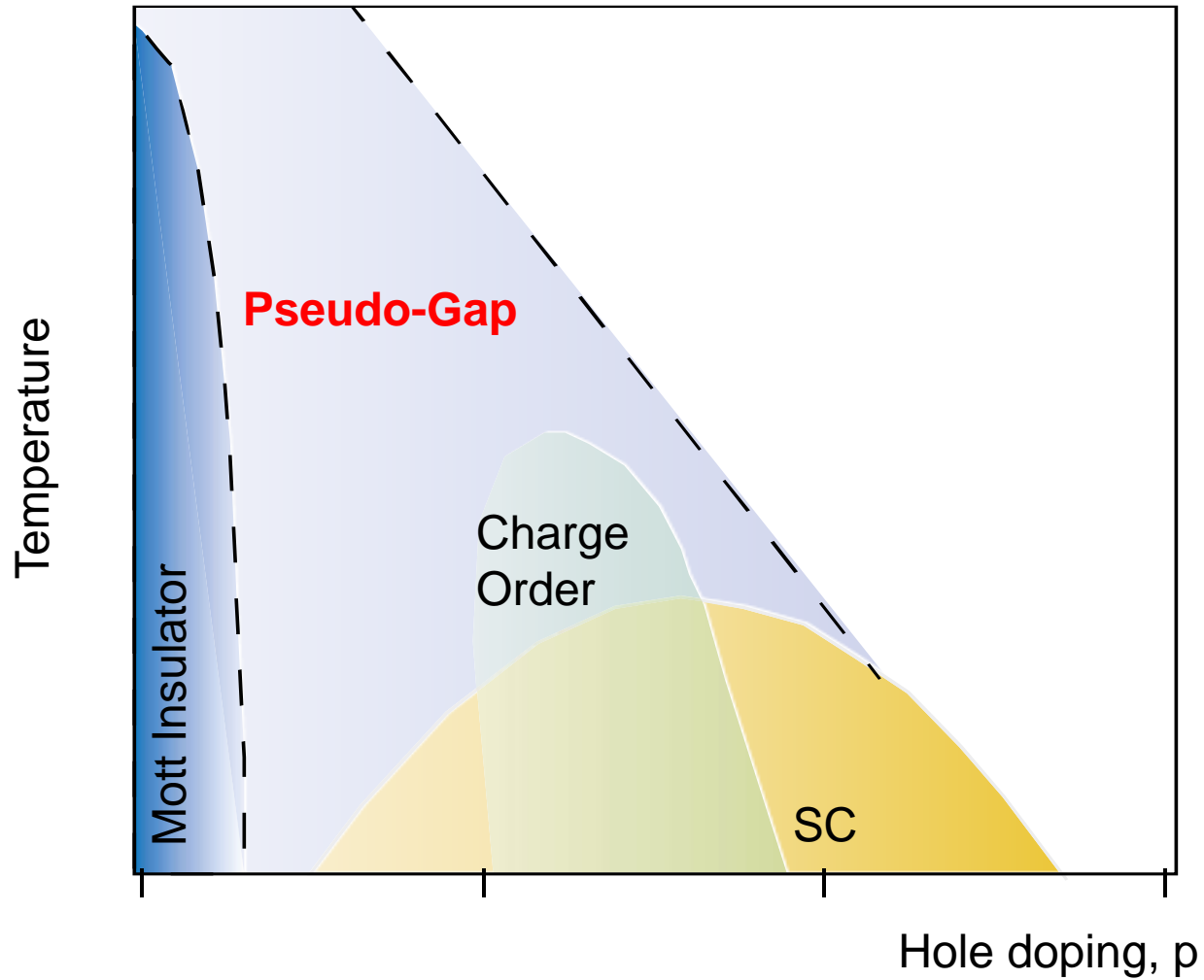
## Crystal structure and lattice supermodulation



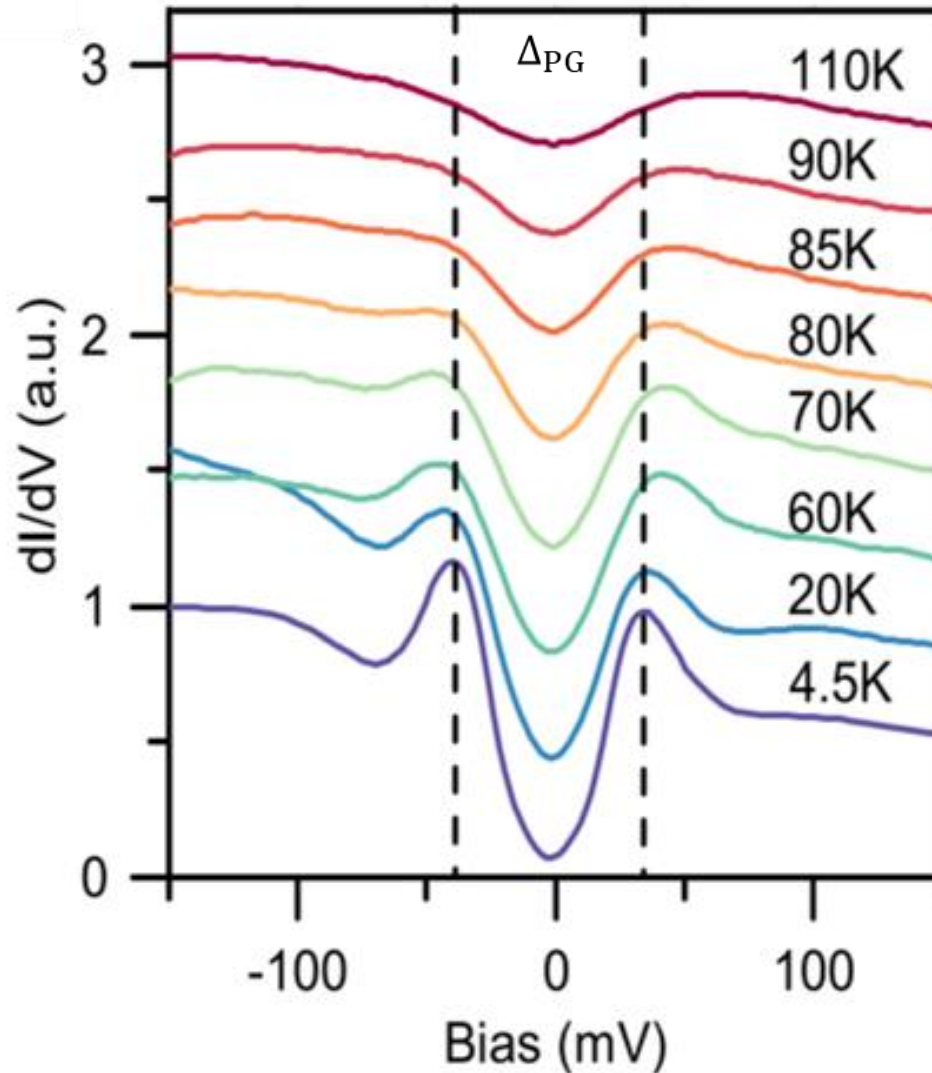
# Phase Diagram of Bulk Bi2212



# Phase Diagram of Bulk Bi2212

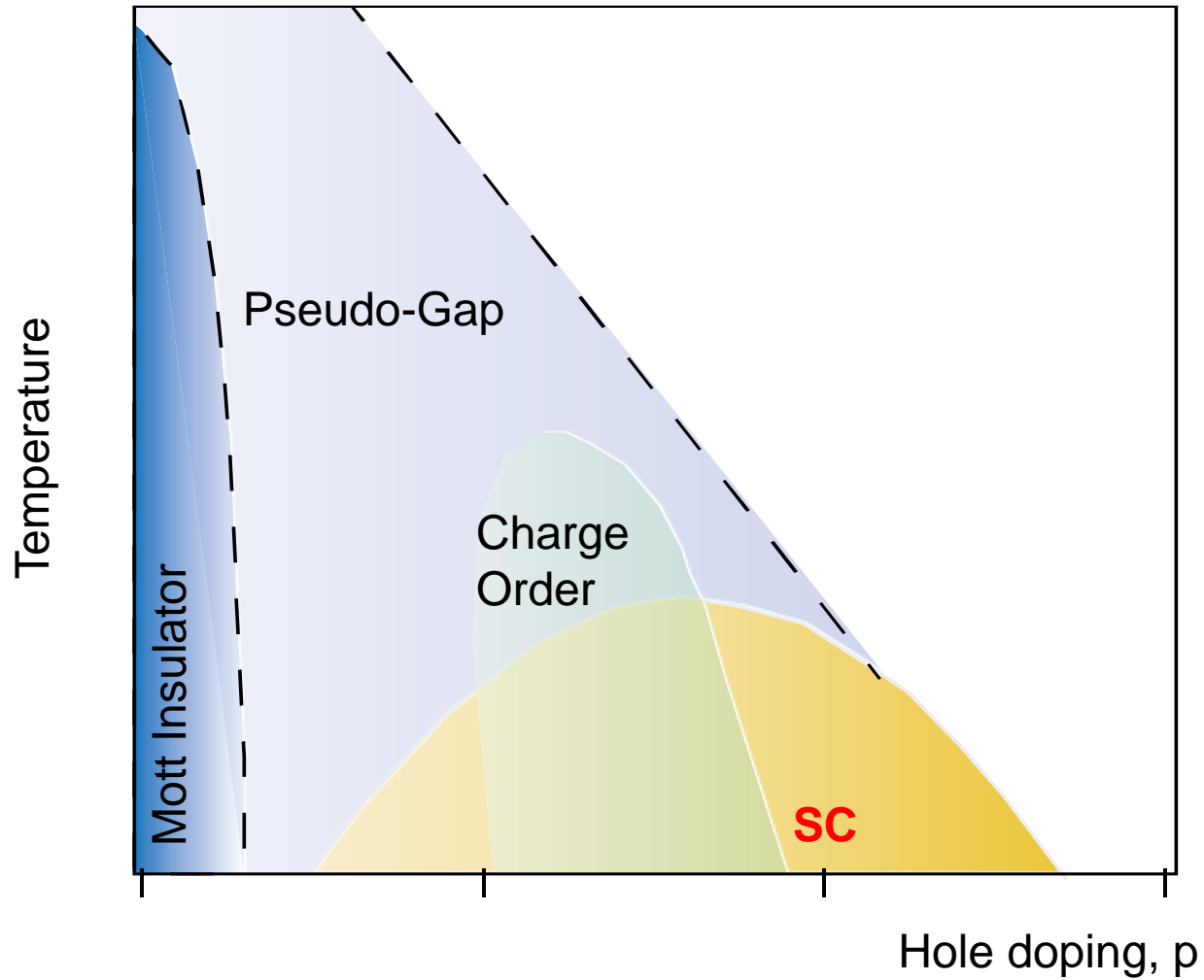


# Tunneling Spectroscopy of Monolayer Bi2212



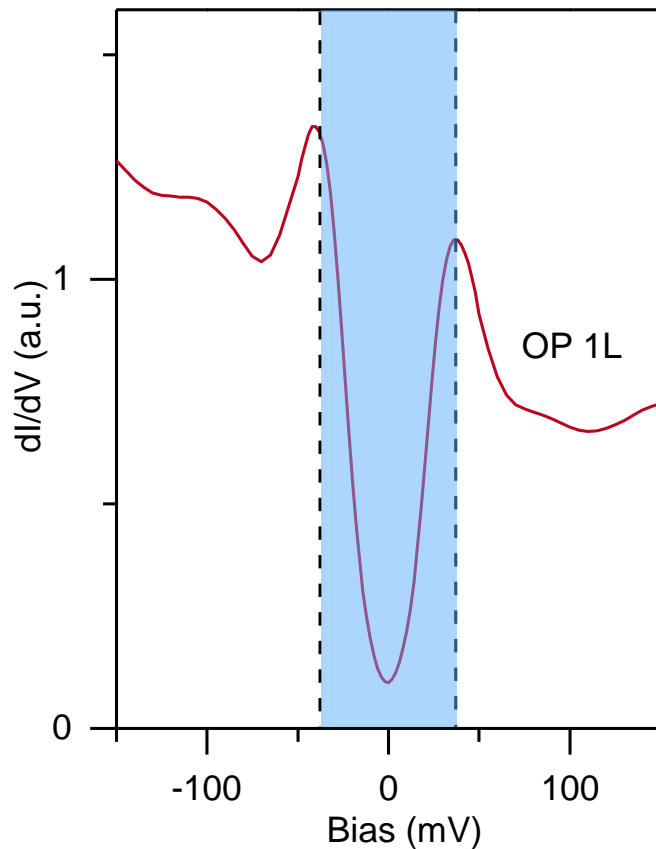
Pseudo-gap seen in optimally doped monolayer above  $T_c$

# Phase Diagram of Bulk Bi2212

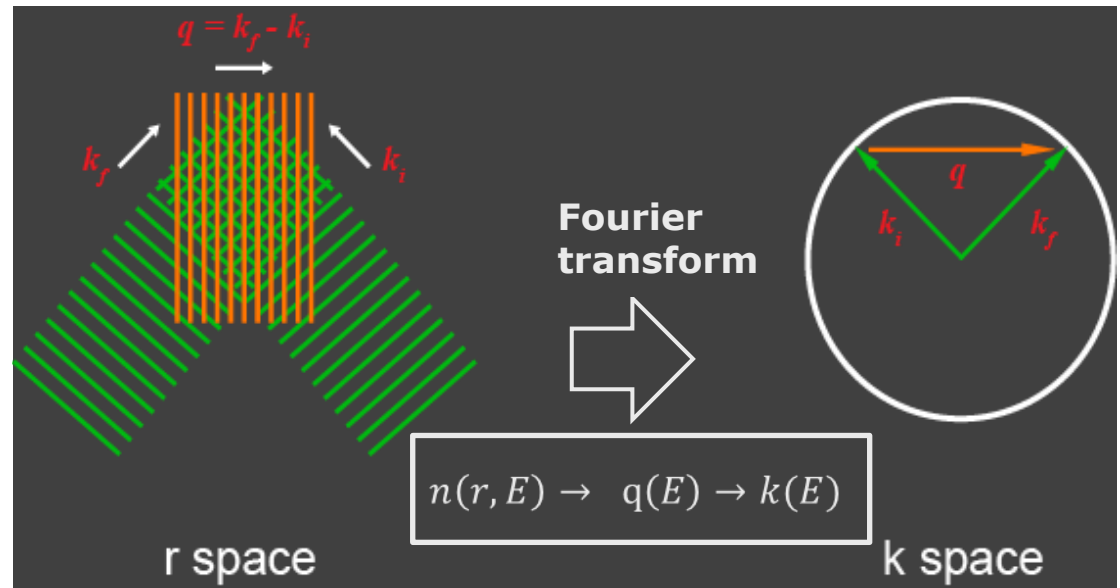


# Bogoliubov Quasi-particle Scattering Inside SC Gap

Bogoliubov quasi-particle  
State inside of the gap



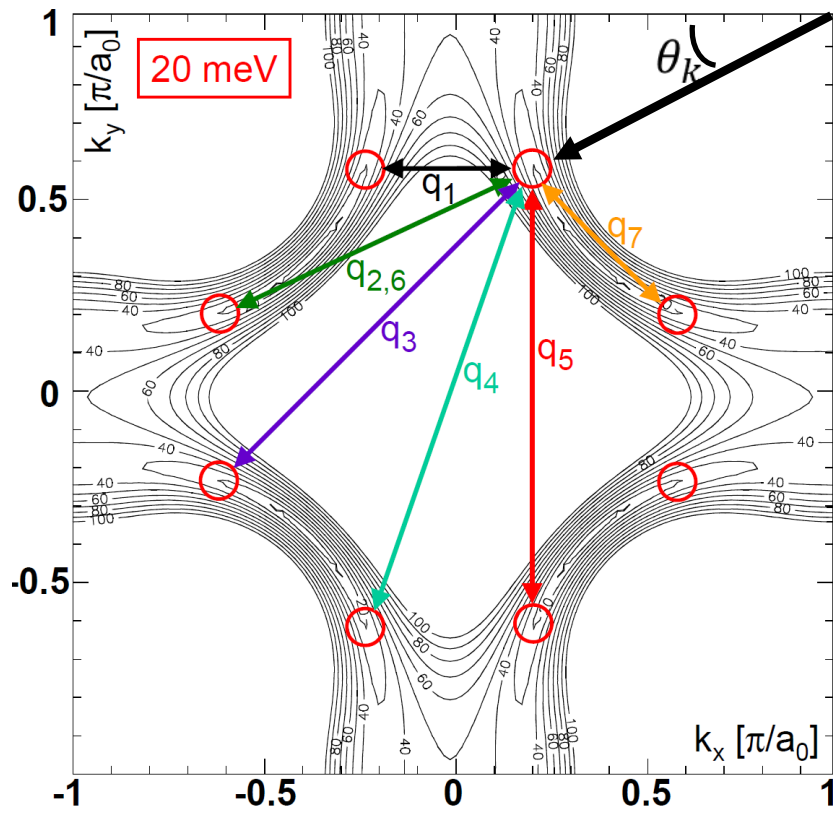
Quasiparticle interference (QPI)



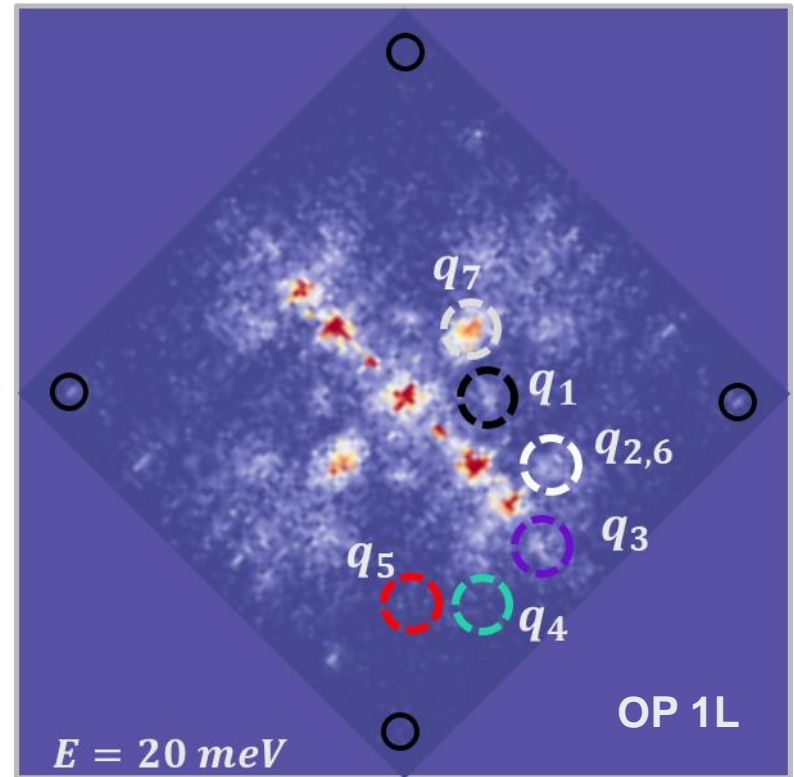
1. Hasegawa *et al.* *Phys. Rev. Lett.* 71, 10711074 (1993)
2. Crommie *et al.* *Nature* 363, 524 (1993)
3. Hoffman *et al.* *Science* 297, 1148 (2002)
4. McElroy *et al.* *Nature* 422, 592 (2003)

# Bogoliubov Quasiparticle Interference

Octet model for d-wave SC  
 $\Delta = \Delta_0 \cos(2\theta_k)$



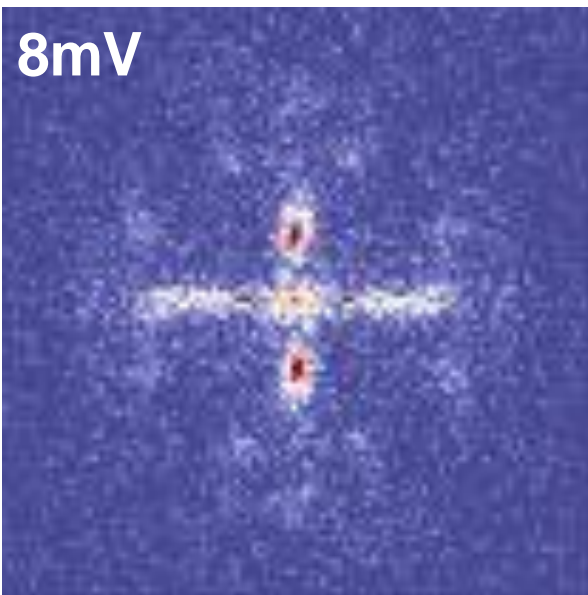
QP interference on monolayer  
FFT of  $dI/dV(\mathbf{r}, E)$



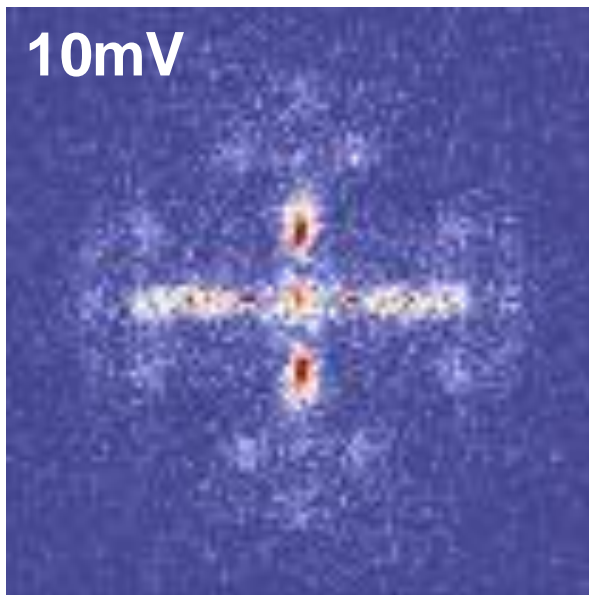
Crommie, M. F. *et al.* (1993); Hasegawa, Y. *et al.* (1993); Hoffman, J. E. *et al.* (2002); McElroy, K. *et al.* (2003)

# Dispersion of Quasiparticle Interference

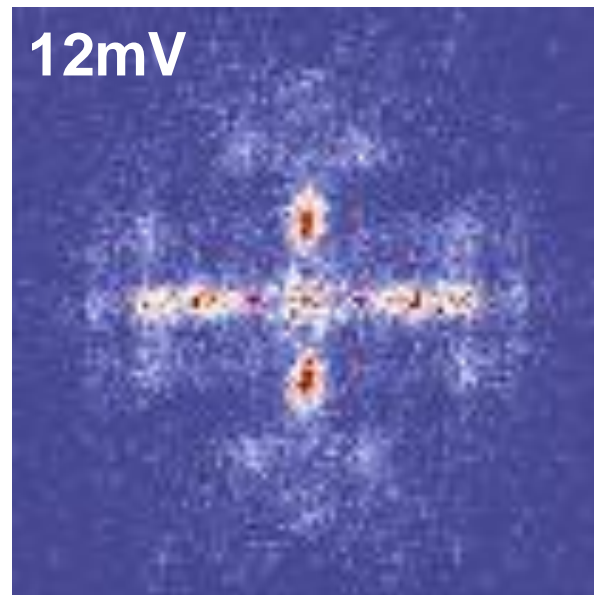
8mV



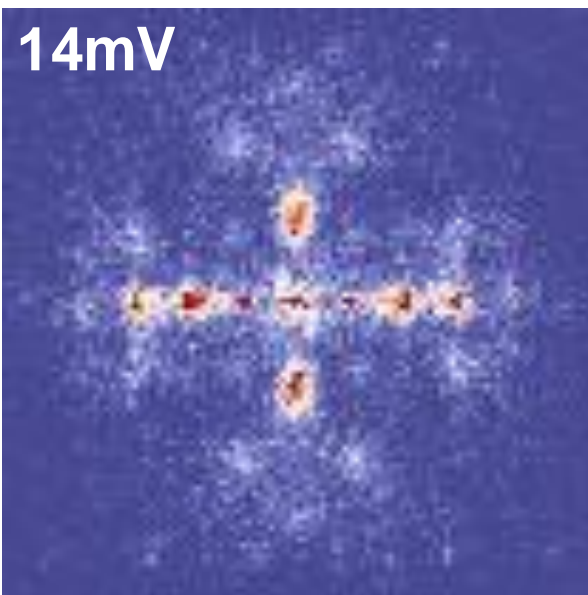
10mV



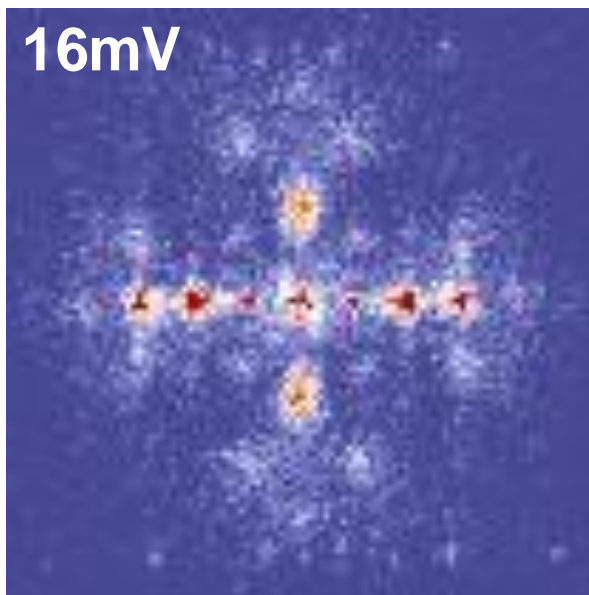
12mV



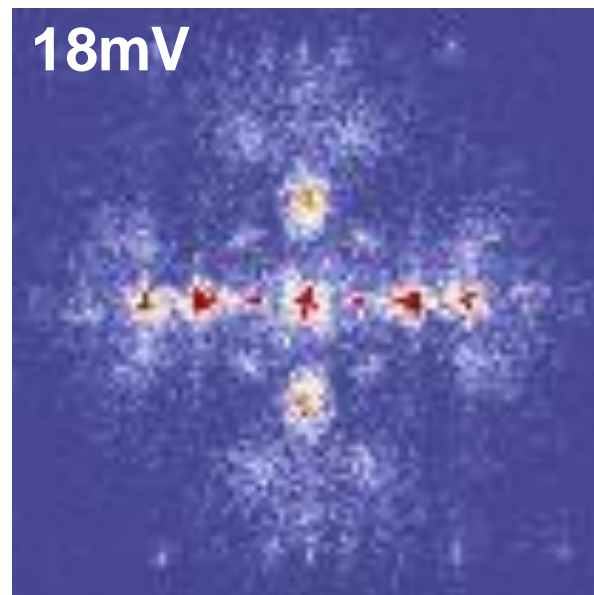
14mV



16mV

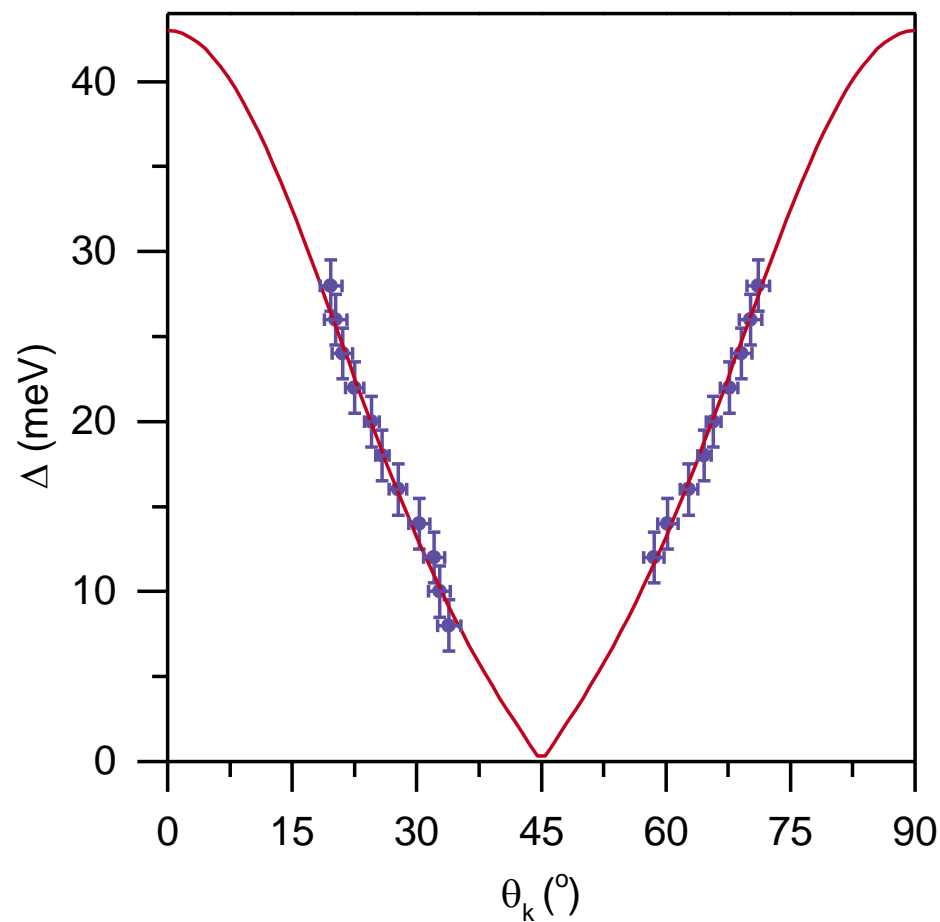
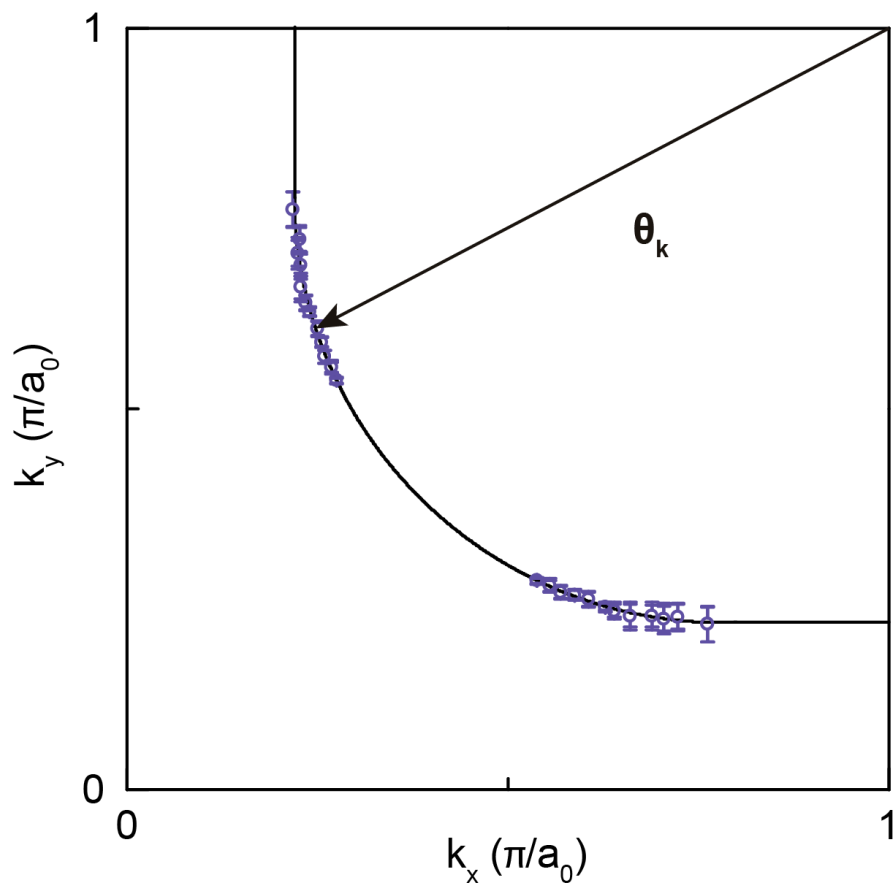


18mV

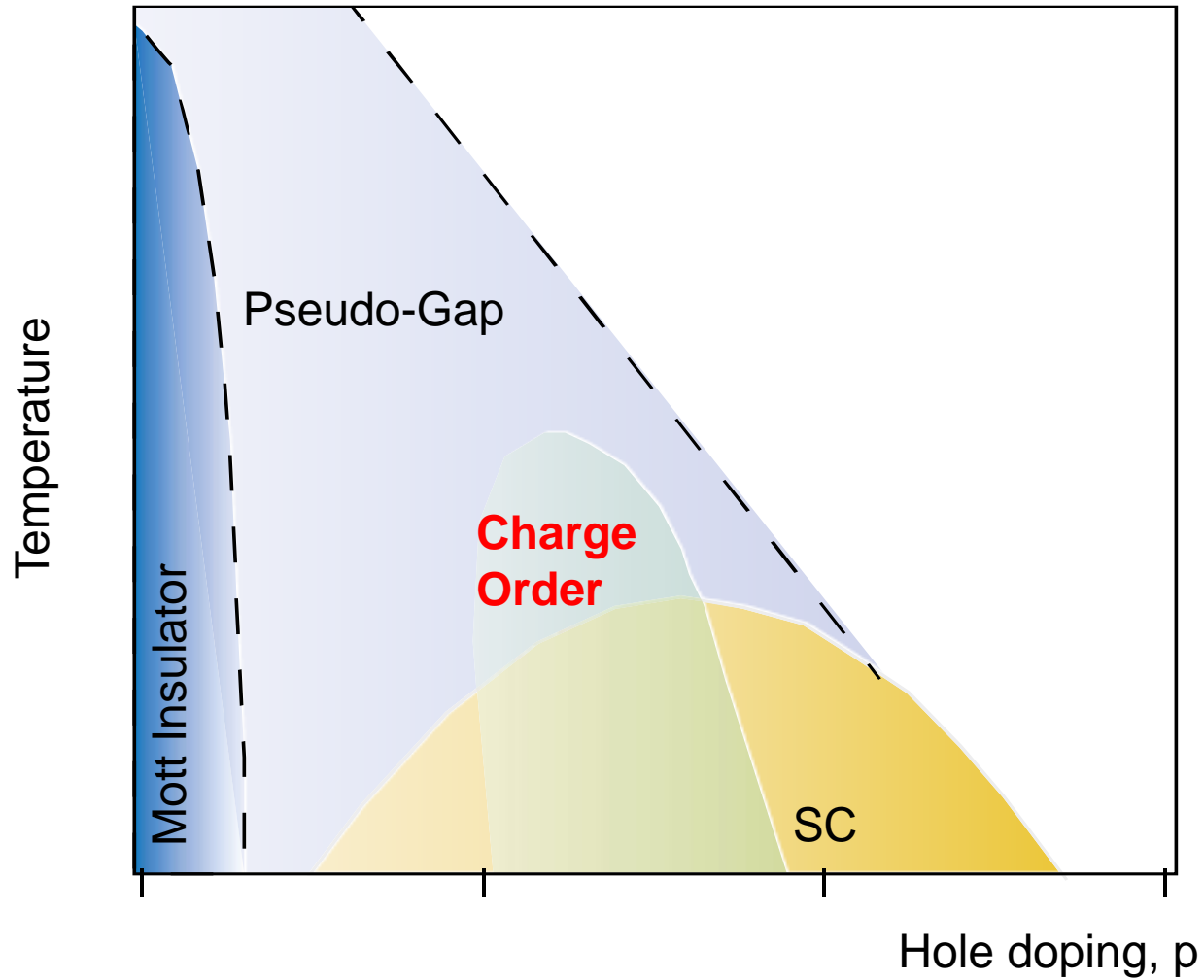


# Dispersion of Quasiparticle Interference

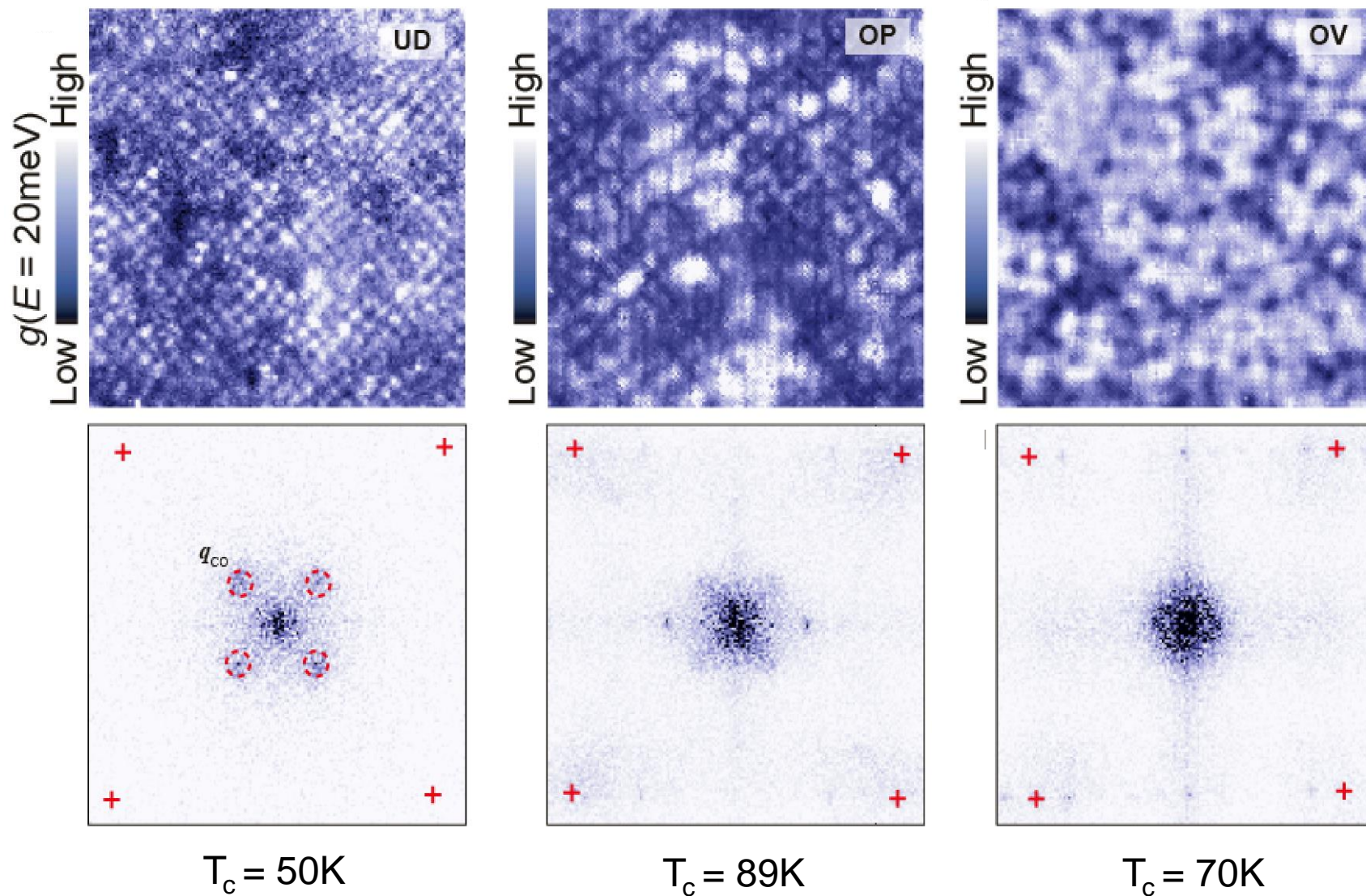
## D-wave gap structure of monolayer Bi2212



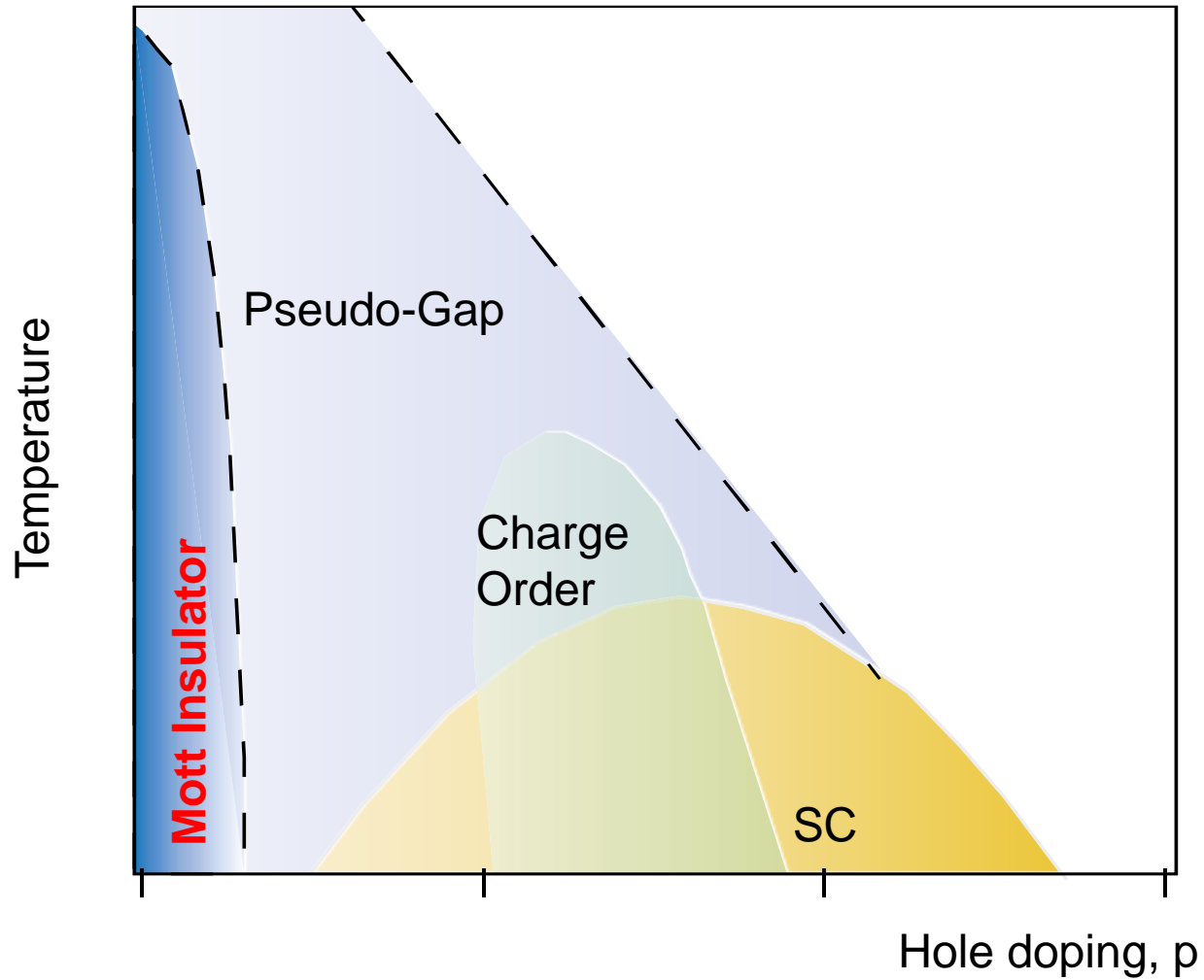
# Phase Diagram of Bulk Bi2212



# Charge Order in Monolayer Bi2212



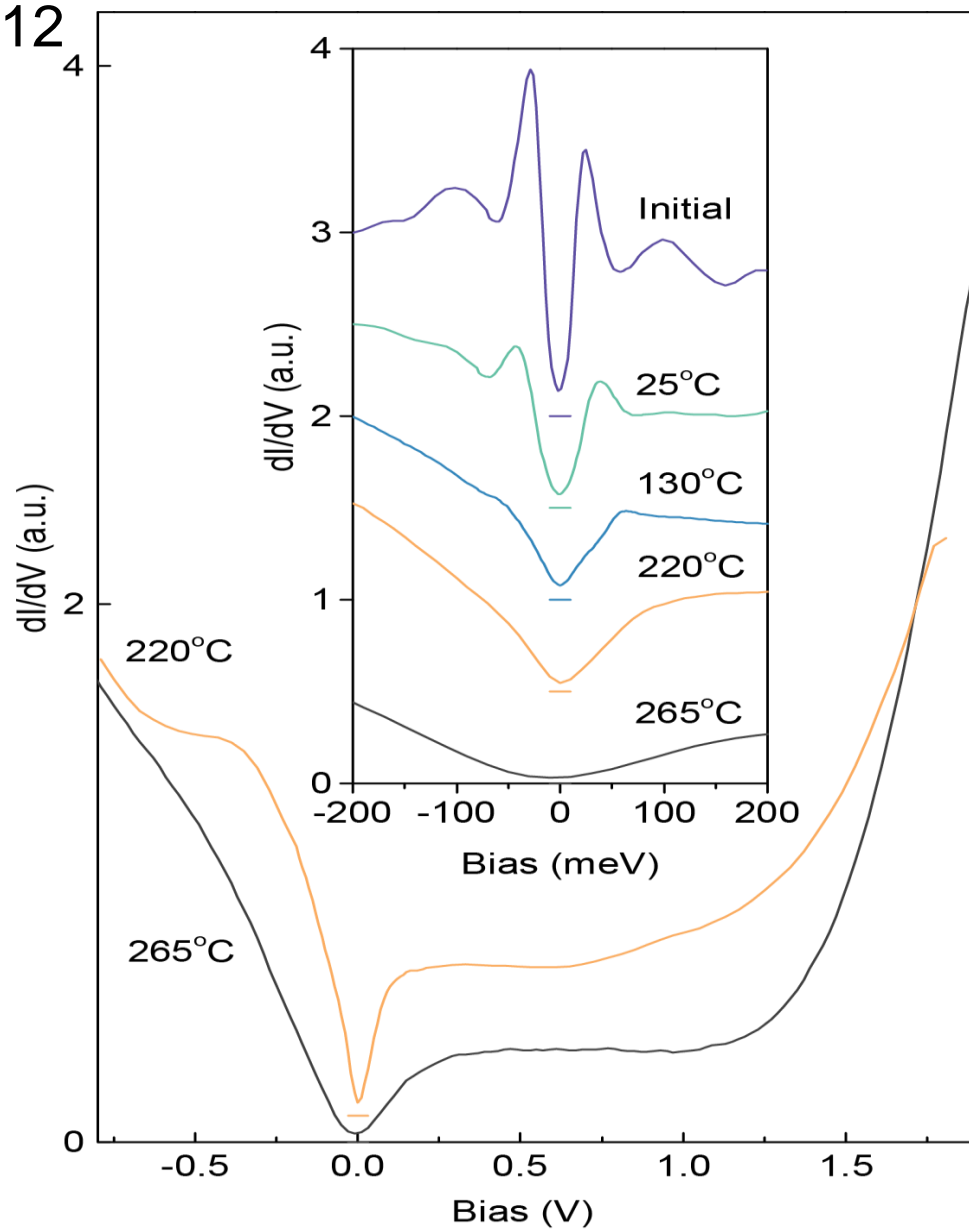
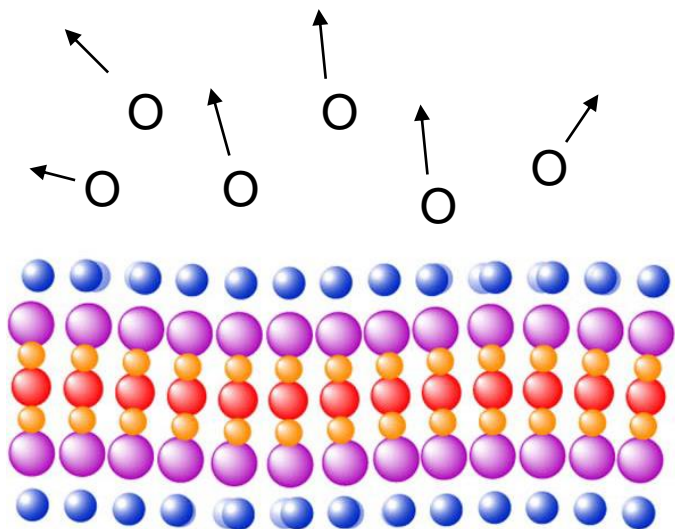
# Phase Diagram of Bulk Bi2212



# Driving Monolayer to Extremely Under-doped Regime

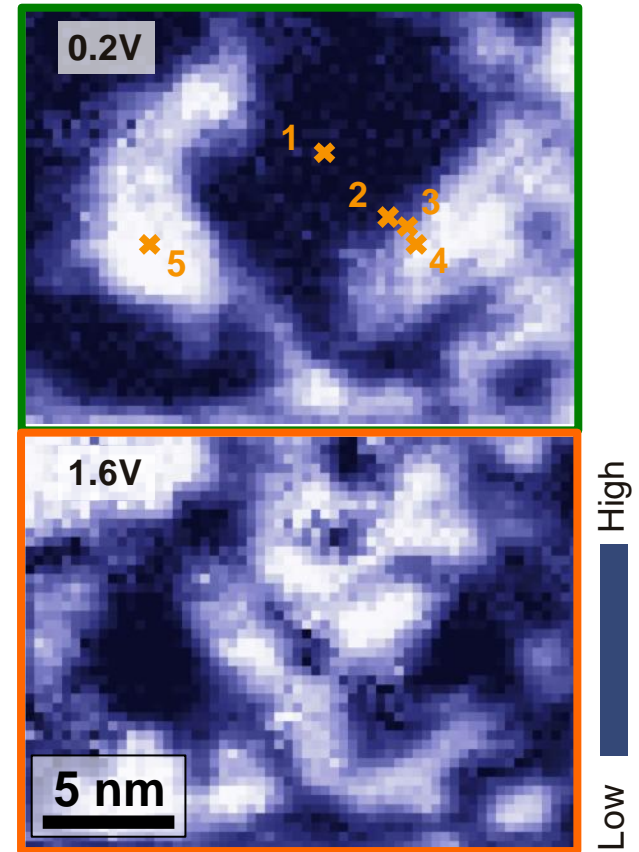
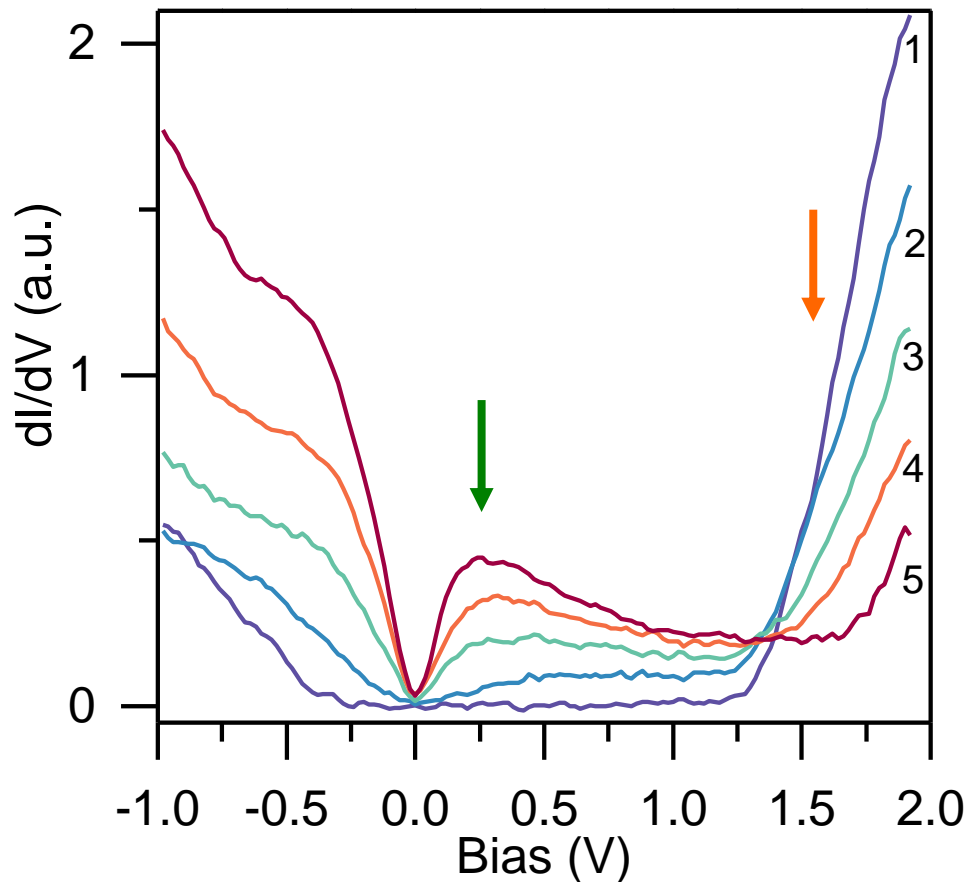
## Spectra of monolayer Bi2212

Annealing in vacuum



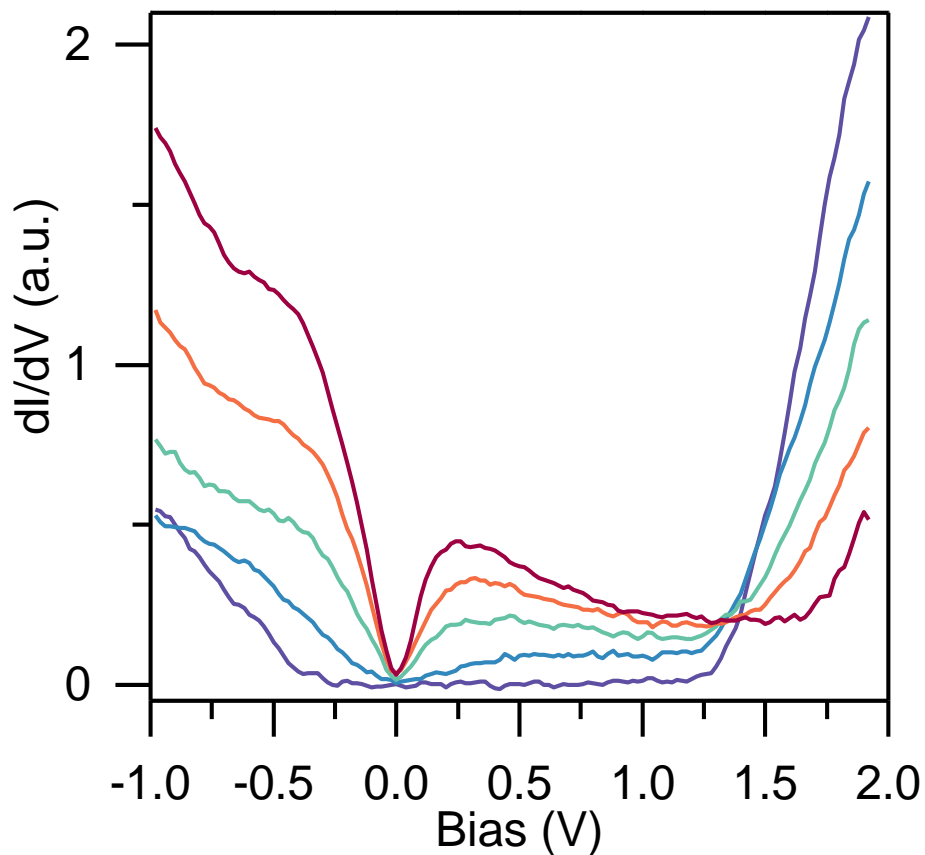
# Mott Insulating State in Monolayer Bi2212

Spectra of extremely under-doped monolayer Bi2212

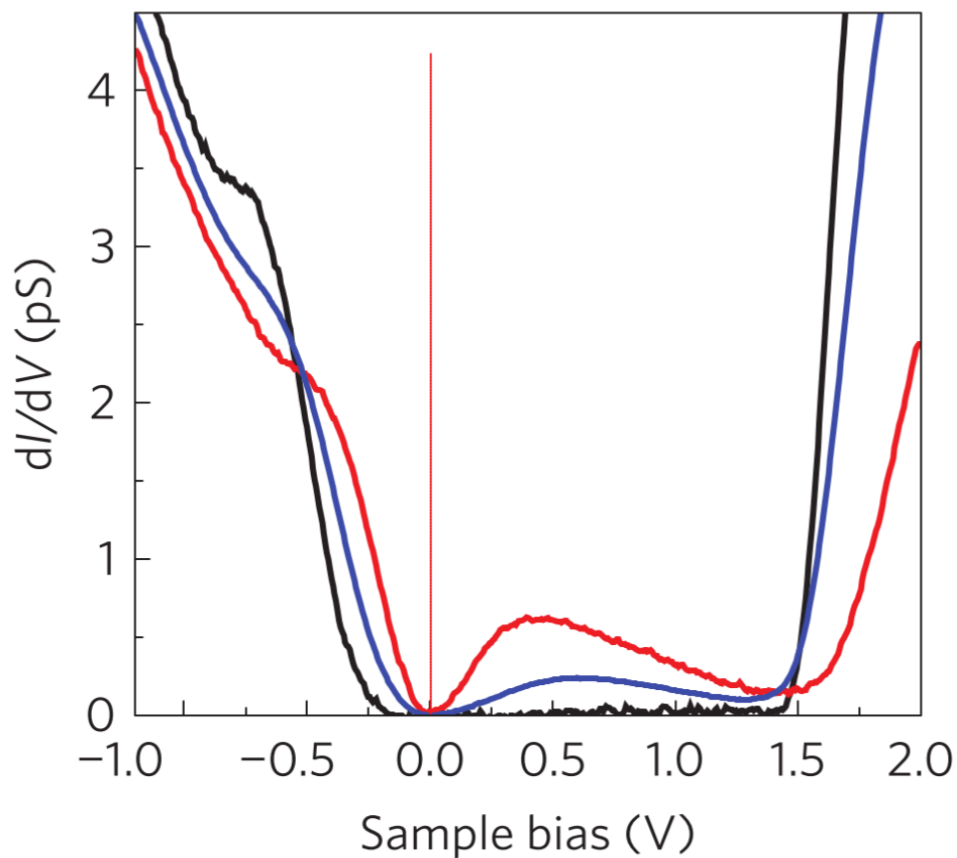


# Mott Insulating State in Monolayer Bi2212

Extremely under-doped  
**monolayer Bi2212**



Extremely under-doped  
**bulk Bi2201**

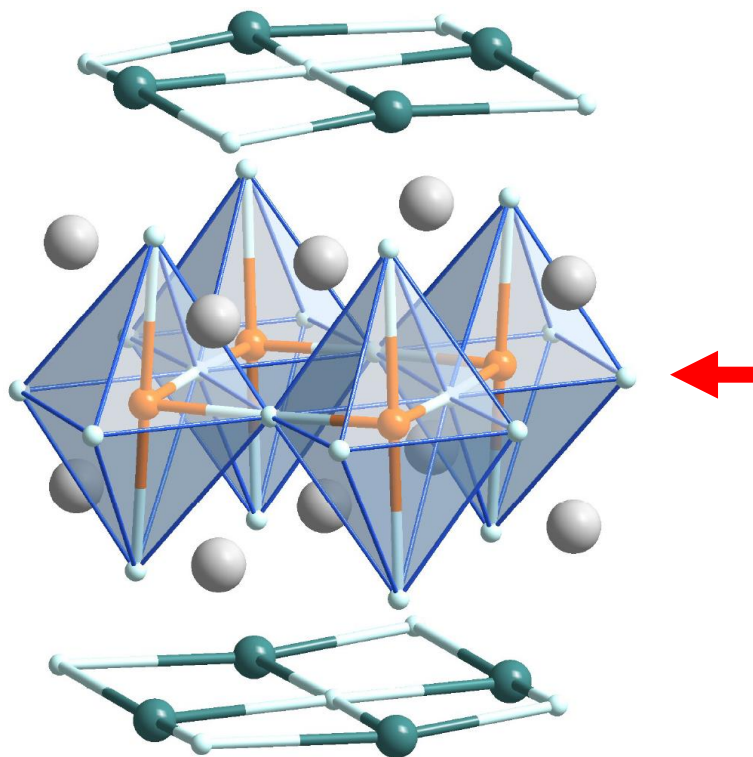


All essential physics in Bi2212  
is contained in its monolayer

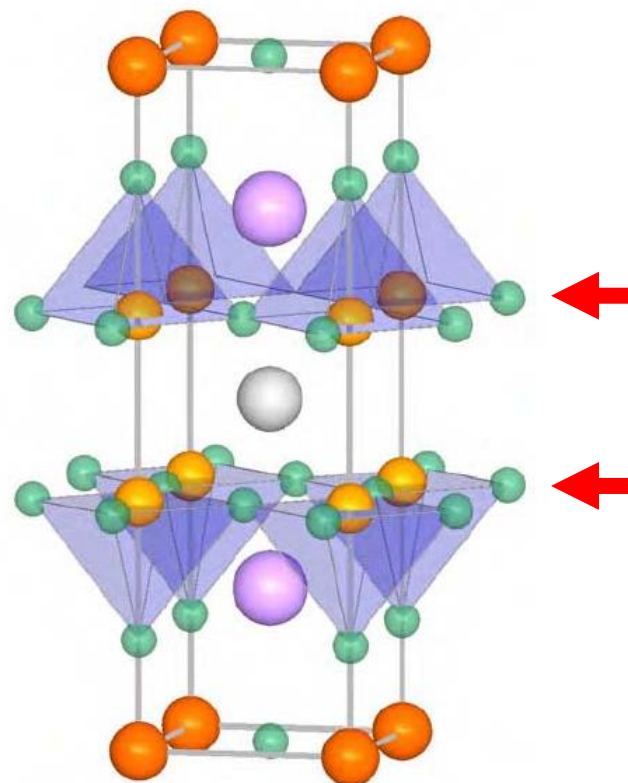
Yijun Yu, Liguo Ma, Peng Cai *et al.*, *Nature* 575, 156 (2019)

# Monolayer Bi2201

Bi2201

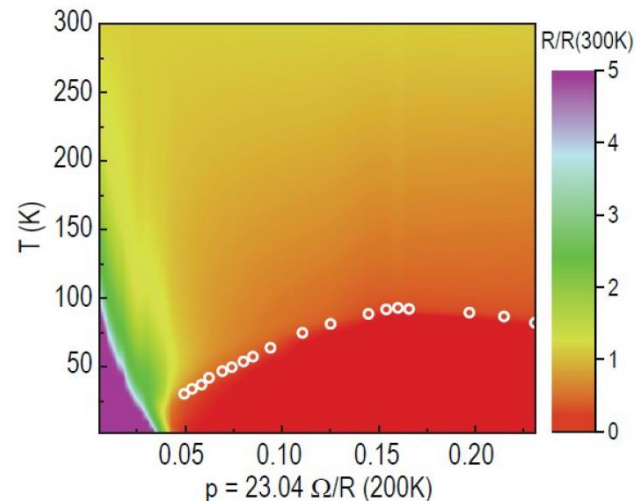
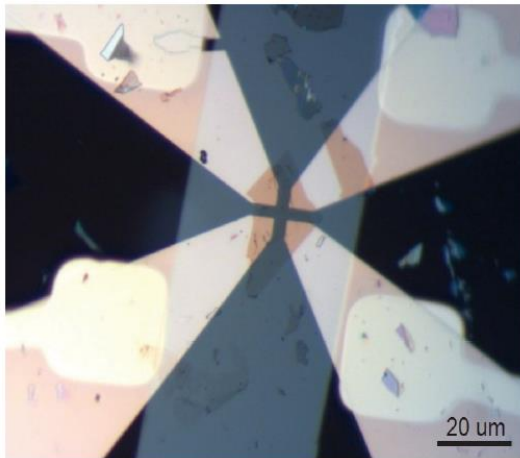
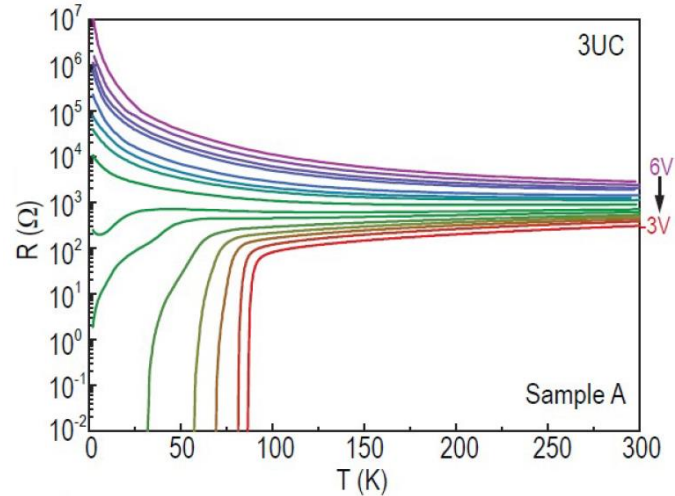
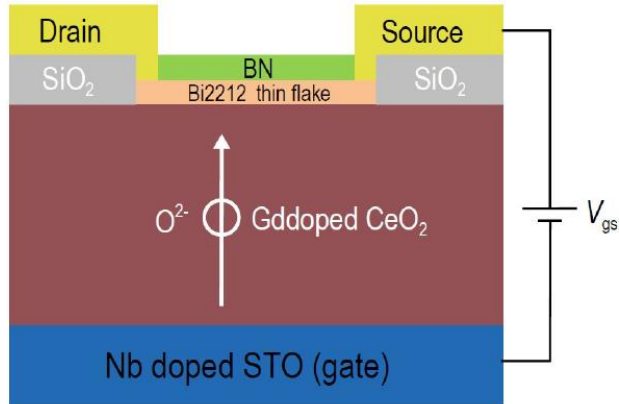


Bi2212

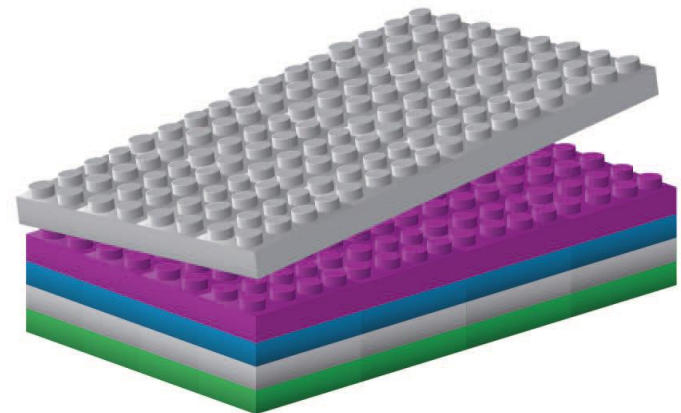
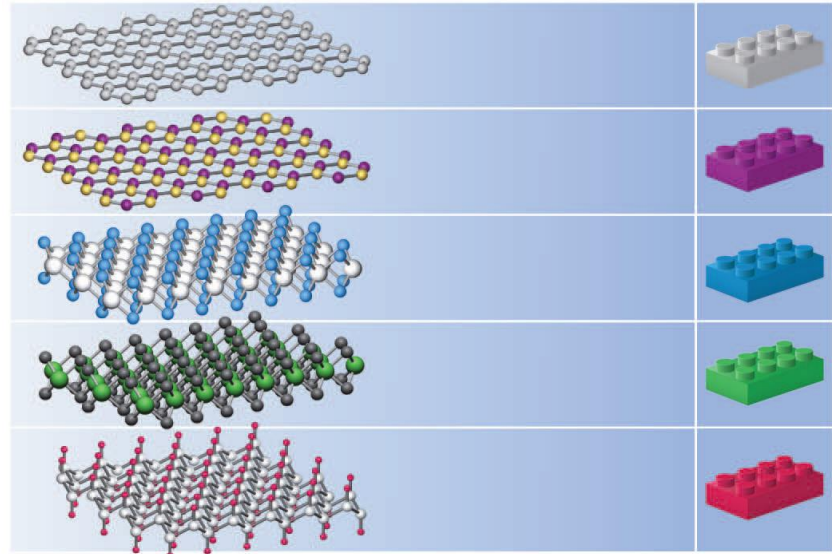
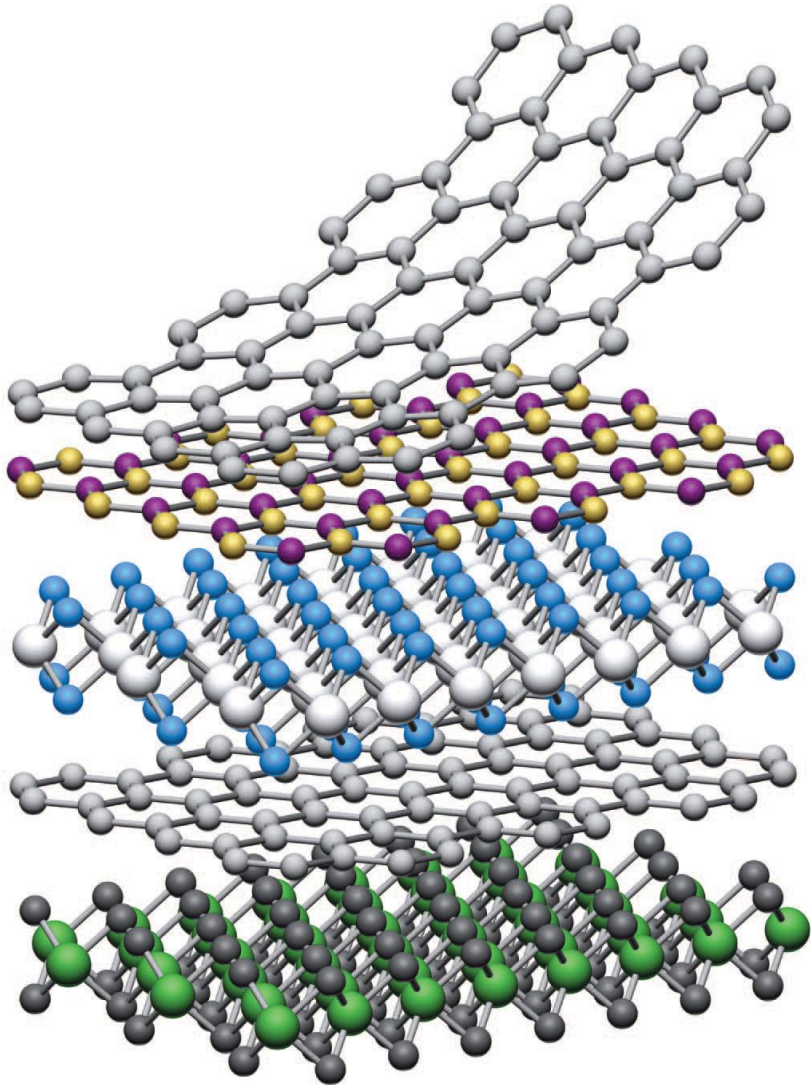


Monolayer Bi2201 contains only a single CuO plane

# Bi2212 Device with a Solid-state Gate

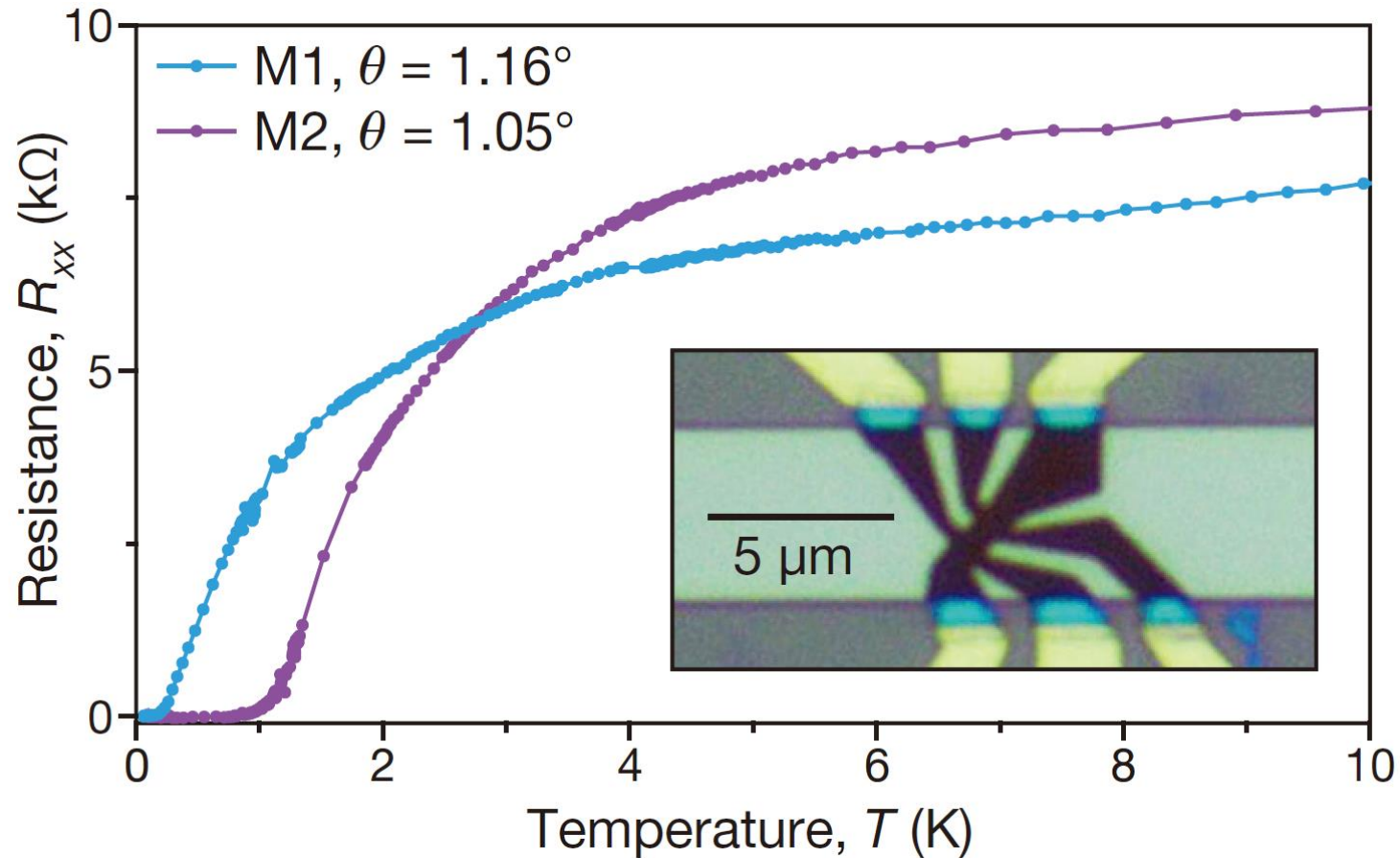


# Stacking of Different 2D Materials



Geim et al., Nature Materials (2016)

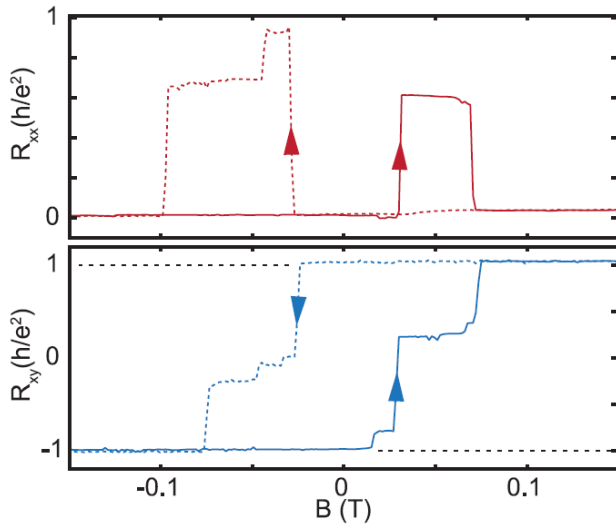
# Superconductivity in Twisted Magic-angle Bilayer Graphene



Cao et al., Nature (2019)

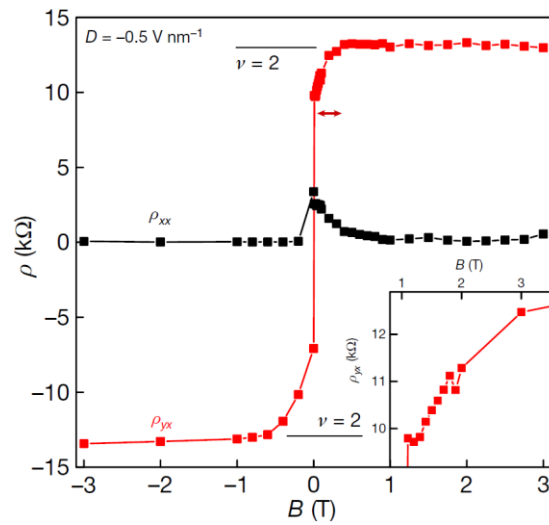
# Quantum Anomalous Hall Effect in Twisted Systems

Twisted bilayer graphene



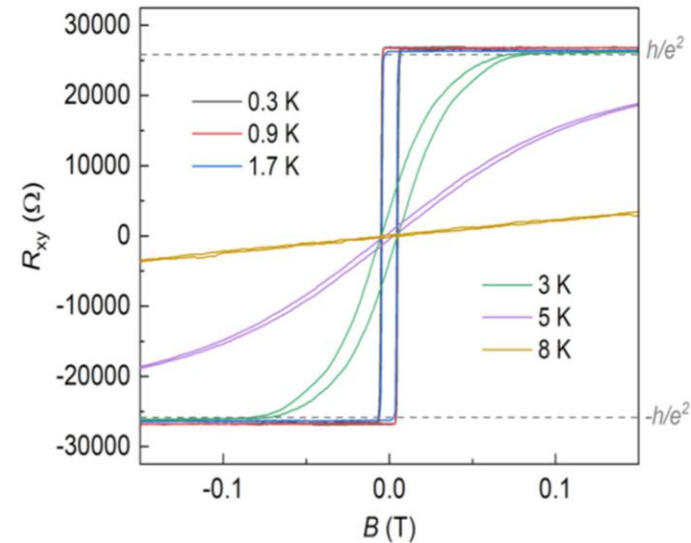
Andrea Young group (2020)

ABC trilayer graphene on hBN



Feng Wang group, Yuanbo Zhang group and David Goldhaber-Gordon group (2020)

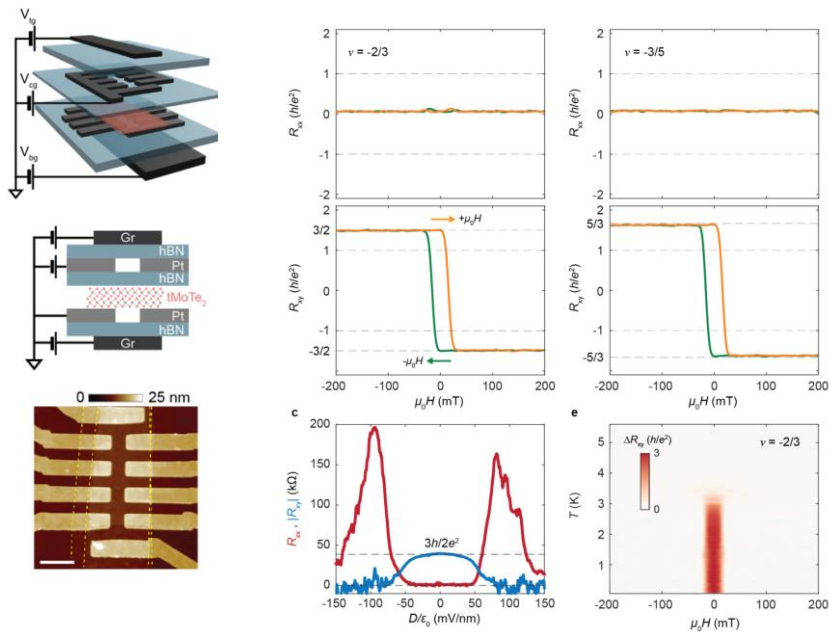
Twisted MoTe<sub>2</sub>/WSe<sub>2</sub>



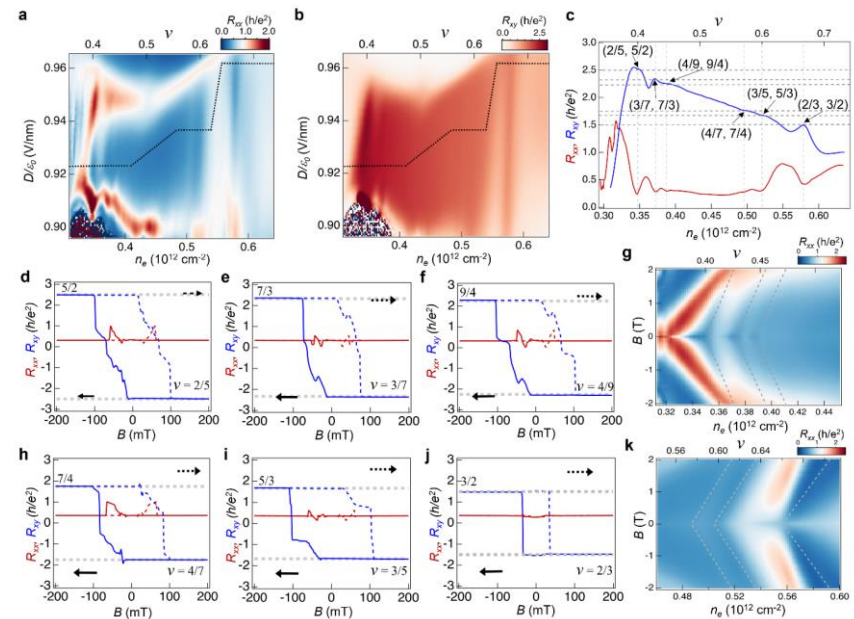
Kin Fai Mak group, Jie Shan group (2021)

# Fractional Quantum Anomalous Hall Effect in Twisted 2D Materials

## Twisted MoTe<sub>2</sub>



## Multilayer graphene Moire superlattice



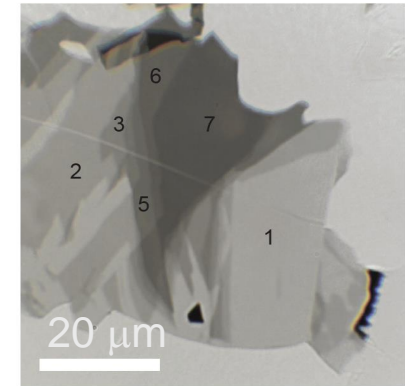
Xiaodong Xu group, Nature (2023)  
Tingxin Li group, PRL (2023)

Long Ju group (2023)

The possibilities are practically endless

# Summary

- Monolayer Bi2212 retains high  $T_c$  superconductivity and is “gate” tunable
- Quantized anomalous Hall effect in magnetic TI  $\text{MnBi}_2\text{Te}_4$



Enormous opportunities in exploring new 2D materials and in developing new gating capabilities

# Collaborators

**Transport:** Yujun Deng, Yijun Yu, Hengsheng Luo, Zhongxun Guo, Jingjing Gao, Mingyan Luo, Yichen Song, Wei Ruan

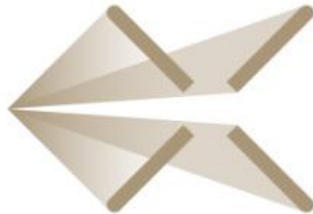
**STM:** Liguo Ma, Peng Cai, Hengsheng Luo, Zhiwei Huang, Cun Ye, Jian Shen

**High field measurement:** Chuanying Xi, Guangli Kuang

**MnBi<sub>2</sub>Te<sub>4</sub> crystal:** Xianhui Chen, Mengzhu Shi, Naizhou Wang, Zihan Xu, Yuping Sun

**BSCCO crystal:** Genda Gu, Ruidan Zhong, Hiroshi Eisaki, Dongjoon Song

**Theory:** Jing Wang, Zhaochen Liu, Hua Jiang, Xincheng Xie



科学探索奖  
XPLORER PRIZE



新基石研究员项目  
NEW CORNERSTONE  
INVESTIGATOR PROGRAM

**Thank you for your attention!**