

Symmetry and nonlinear responses in van der Waals 2D materials

Yoshi Iwasa

RIKEN Center for Emergent Matter Science (CEMS)

1. Introduction
2. Bulk photovoltaic effect
3. Nonreciprocal transport
4. Superconducting diode effect

Introduction

Nonreciprocity in noncentrosymmetric systems

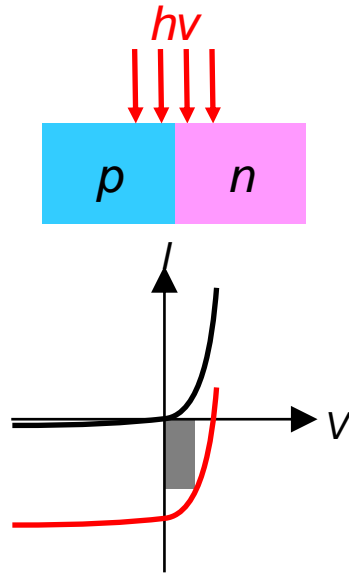
Nonreciprocal Response	Linear Response	Nonlinear Response
Time-reversal Unbroken	Forbidden (diagonal) Natural circular dichroism (off-diagonal)	Shift current Nonlinear Hall effect P-n junctions
Time-reversal Broken	Optical ME effect Magneto-chiral effect Nonreciprocal magnon	Nonreciprocal nonlinear optical effect Nonlinear electric magneto-chiral effect Inverse Edelstein effect Magneto-chiral anisotropy

OUTLINE

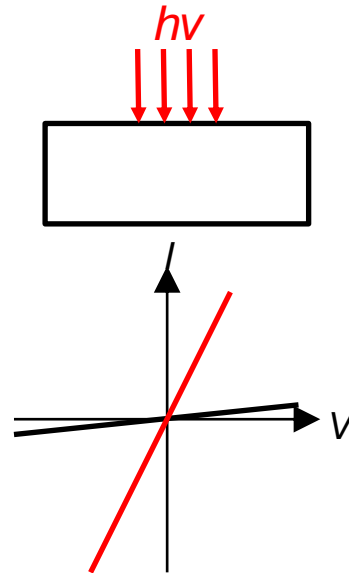
- Polar semiconductors
 - Bulk photovoltaic effect
- Polar semiconductors/metals
 - Nonreciprocal transport (2nd harmonic resistance)
 - Nonlinear Hall effect
- Noncentrosymmetric superconductors
 - Nonreciprocal transport/Nonlinear Hall effect
 - Superconducting diode effect
- Discussions on nonreciprocity in longitudinal response

1. Bulk photovoltaic effect in polar semiconductors

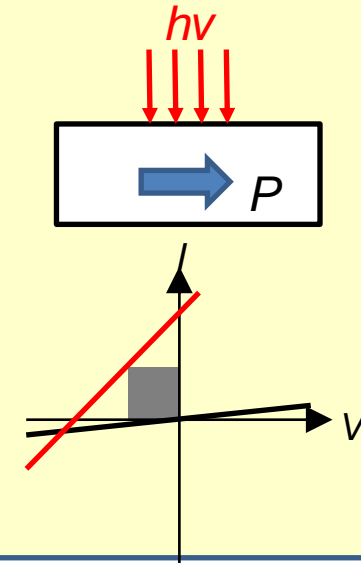
Photovoltaic effect



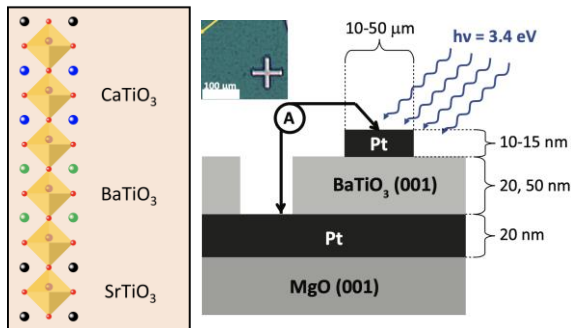
Photoconductivity



Bulk photovoltaic Effect (BPVE)



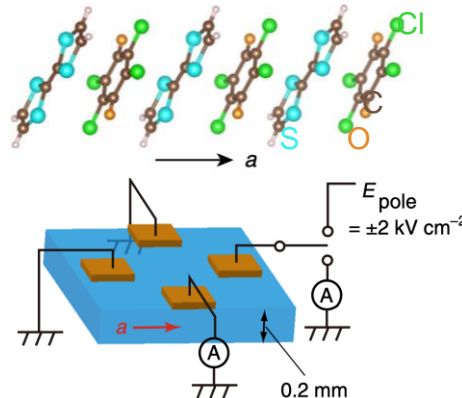
Perovskites (BaTiO_3 , etc)



A. Zenkevich, *et al.*, *PRB* (2014)

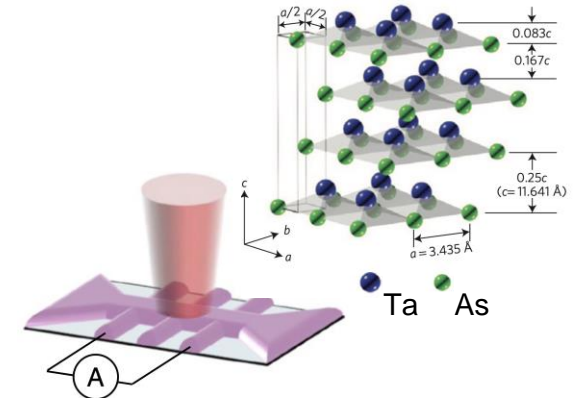
Y. Yun, *Sci. Adv.* (2021)

Organic crystal (TTF-CA)



M. Nakamura, *et al.*,
Nat. Commun. (2017)

Weyl semimetal (TaAs)

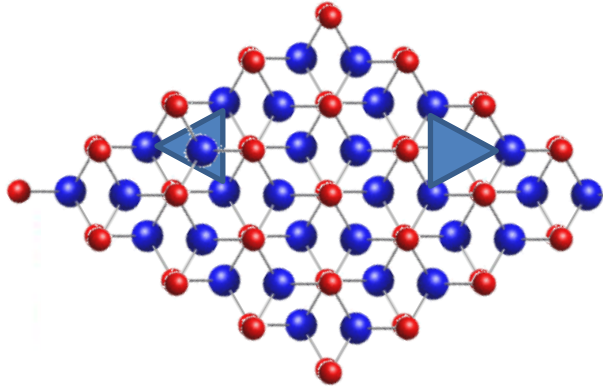


L. X. Yang, *Nat. Phys* (2015)

Osterhoudt, *Nat. Mater* (2019)

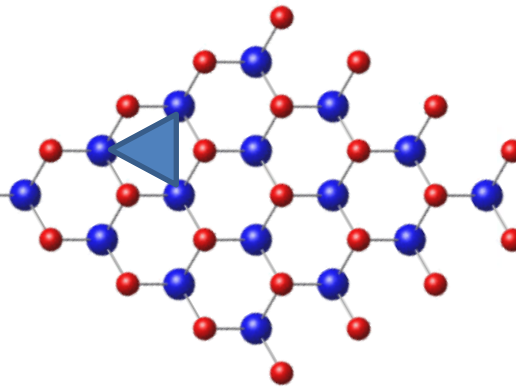
BPVE in TMD nanotubes

Bulk, bilayer
(D6h)



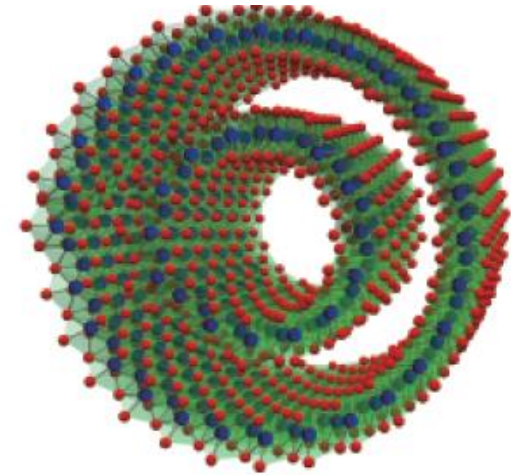
Centrosymmetric

Monolayer
(D3h)



Non-centrosymmetric

1D nanotube
(C3 x C2)



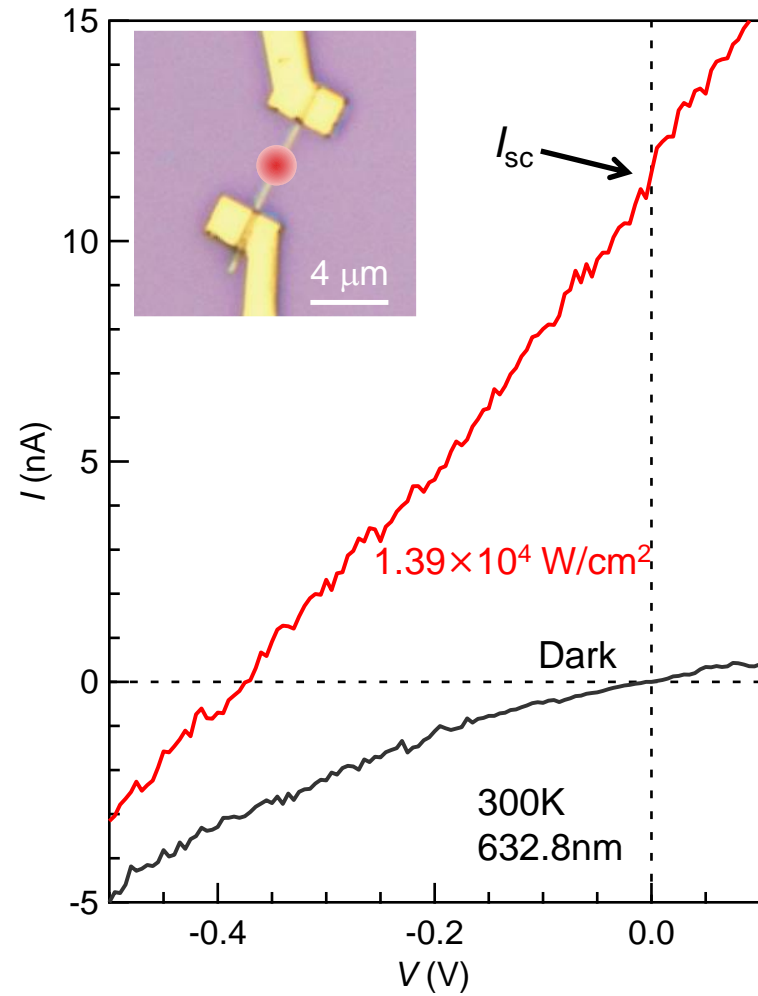
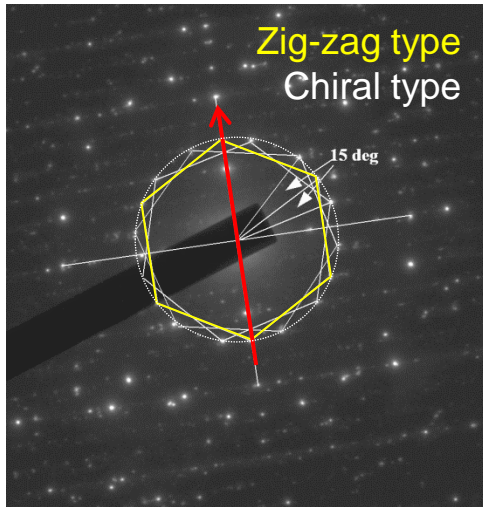
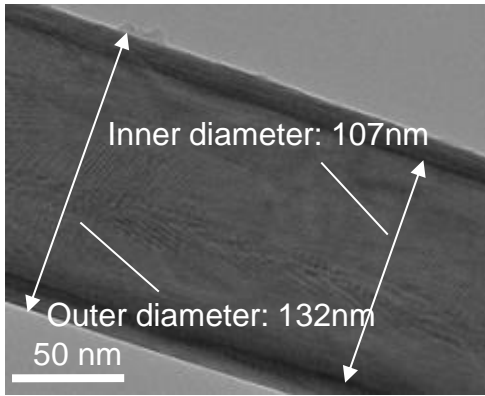
Non-centrosymmetric

+ tubular+chiral
+ polar

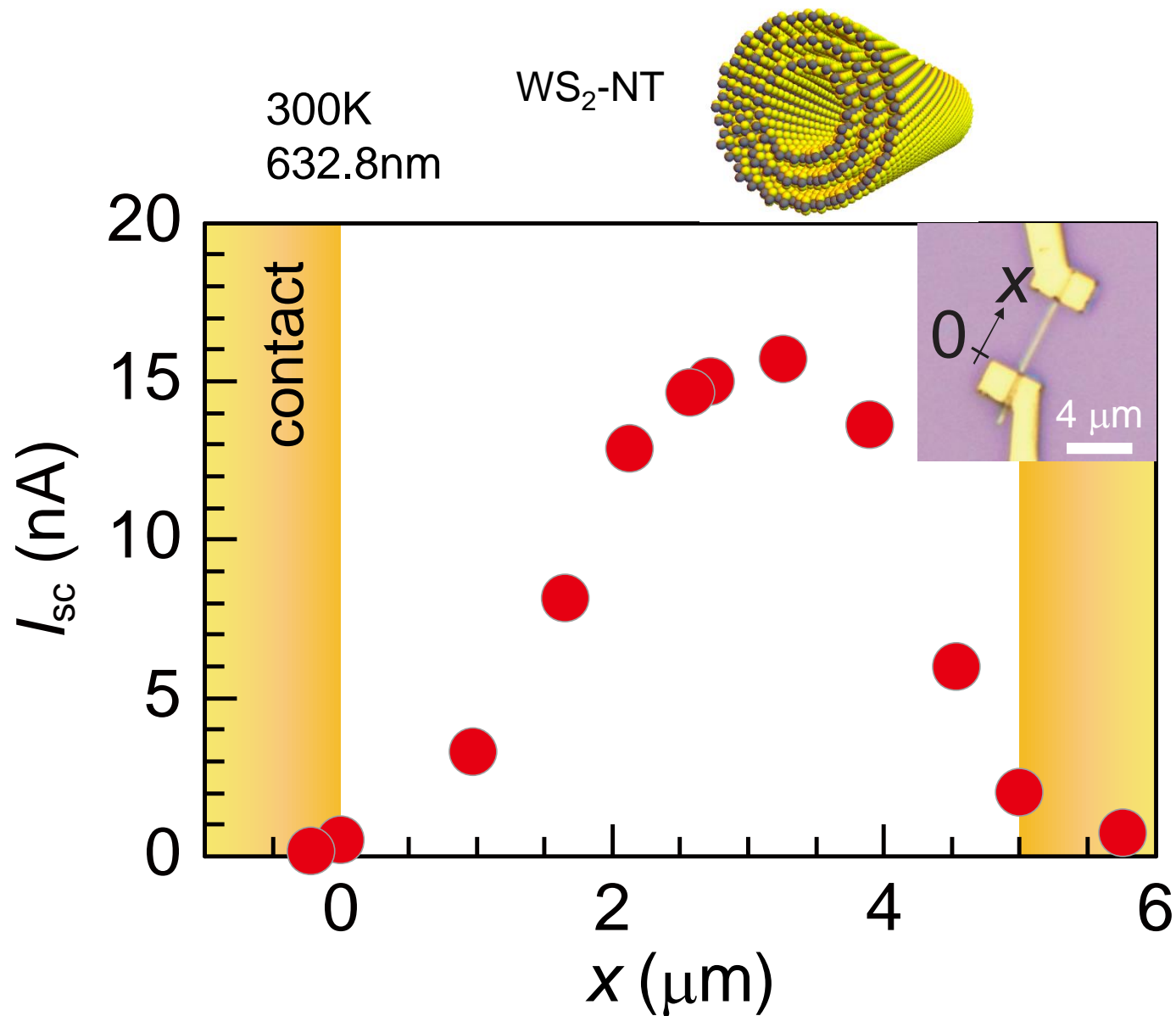


- **Valleytronics**
- Piezoelectric

Bulk photovoltaic effects in WS₂ nanotubes

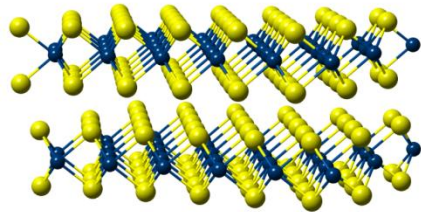


Laser position dependence of I_{sc}

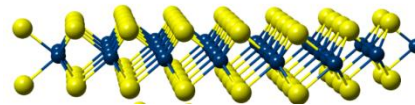


Bulk? or Schottky?

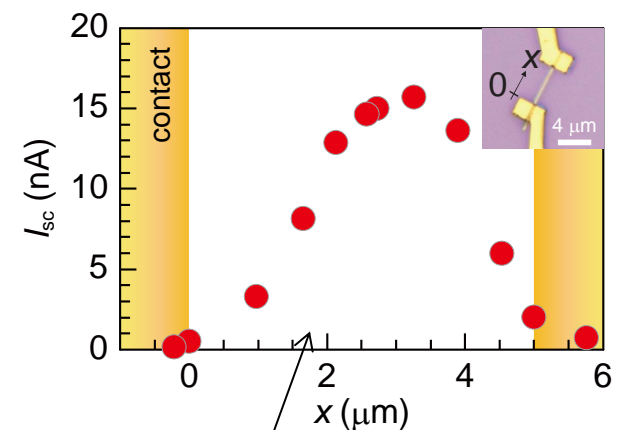
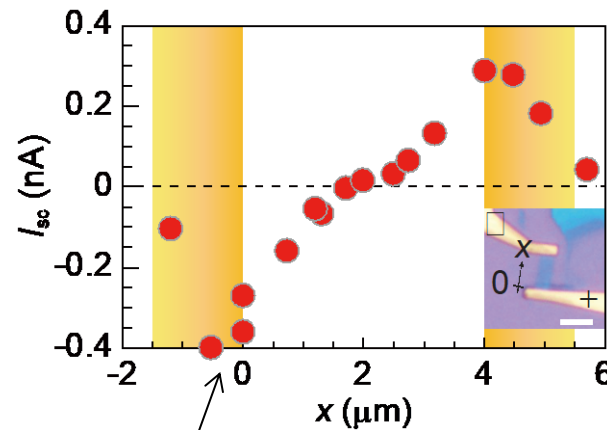
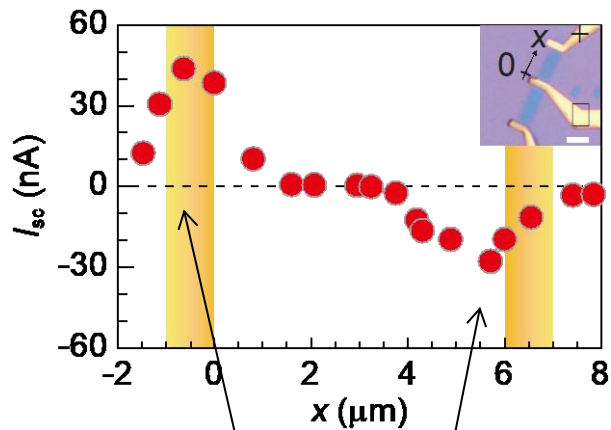
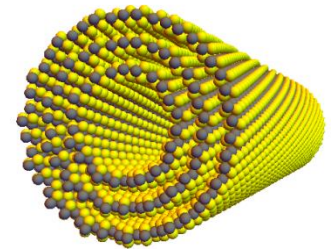
WS₂-bilayer



WS₂-monolayer



WS₂-NT



Photovoltaic effect due to Schottky barriers

Bulk photovoltaic effect

A shift current theory

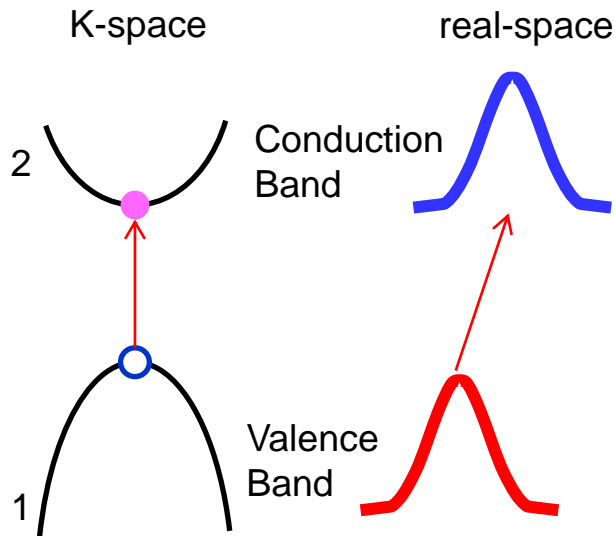
Shift current $\chi^{(2)}(0; \omega, -\omega)$ cf) SHG $\chi^{(2)}(2\omega; \omega, \omega)$

RESEARCH ARTICLE

OPTICS

Topological nature of nonlinear optical effects in solids

Takahiro Morimoto^{1*} and Naoto Nagaosa^{2,3}



$$\mathbf{r}_1 \neq \mathbf{r}_2$$

$$\mathbf{r}_n = i \frac{\partial}{\partial \mathbf{k}} + \mathbf{a}_n(\mathbf{k})$$

$$\mathbf{a}_n = -i \langle u_{n\mathbf{k}} | \nabla_{\mathbf{k}} | u_{n\mathbf{k}} \rangle$$

Berry connection

$$j_{\text{shift}} \propto \int d\mathbf{k} \dot{f}_{12} \left[\frac{\partial \varphi_{12}}{\partial \mathbf{k}} + \mathbf{a}_1 - \mathbf{a}_2 \right]$$

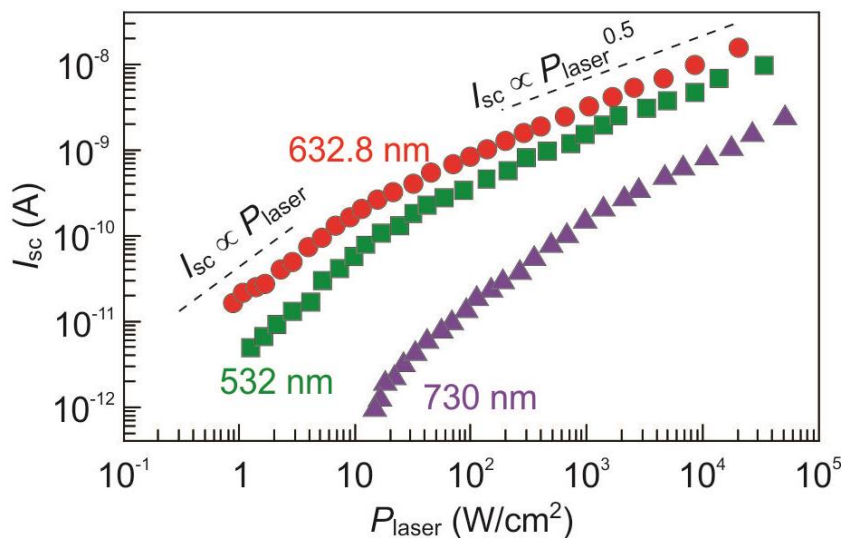
$$\dot{f}_{12} \propto \frac{|\mathbf{E}|^2}{\sqrt{A|\mathbf{E}|^2 + B}}$$

2nd order of E
(electric field of light)

Shift current $\propto E^2 \rightarrow E$

Laser power dependence

Bulk photovoltaic effect in
WS₂-NT



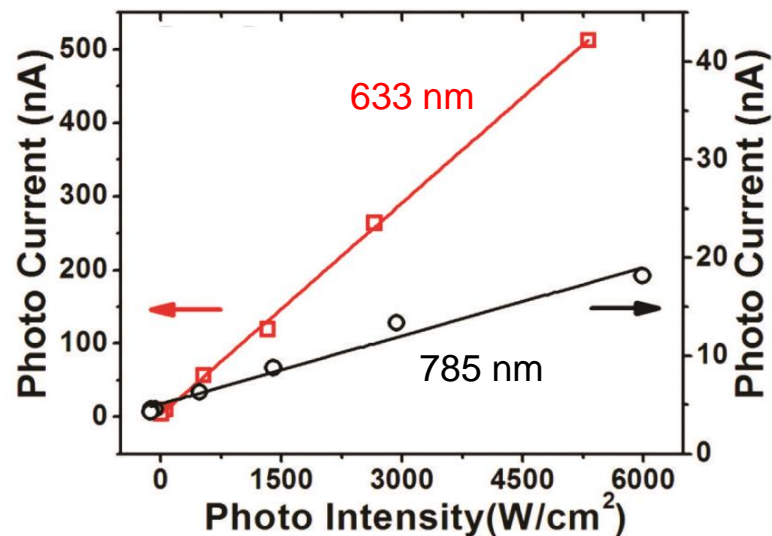
Crossover from linear to $\sqrt{}$ of P at 10 W/cm²

$$I \propto P^1 \rightarrow I \propto P^{0.5}$$

$$I \propto E^2 \rightarrow E$$

➔ Shift current mechanism is likely

Photovoltaic effect at
WS₂-NT/metal Schottky barrier



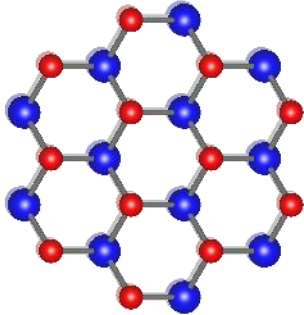
Linear up to 6×10^3 W/cm²

C. Zhang *et al.*, APL 100 243101 (2012)

In-plane polar vdW heterostructures

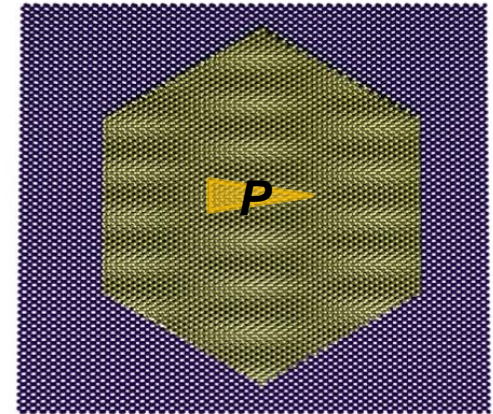
Heterostructure of different crystal symmetry

WSe₂ (C₃ rotational symmetry)

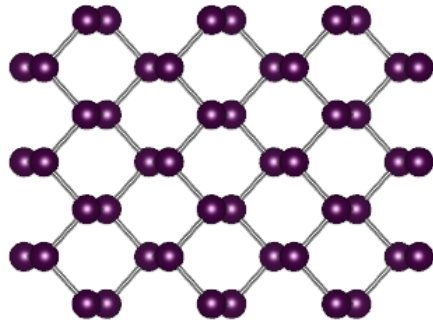


WSe₂/BP

————— *m*



BP (C₂ rotational symmetry)



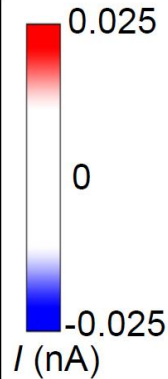
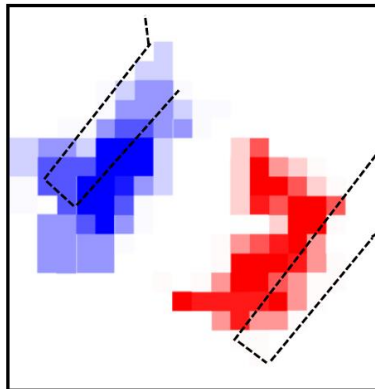
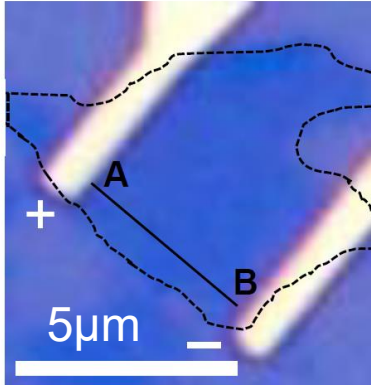
Rotational symmetry broken
One mirror plane remains

In-plane
polarization

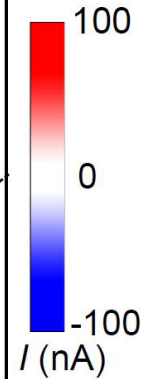
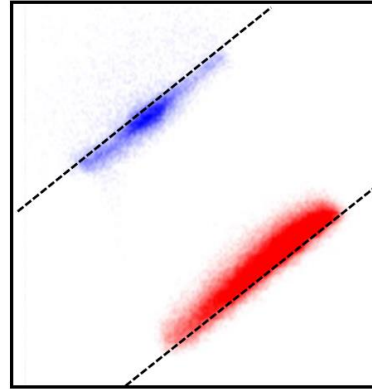
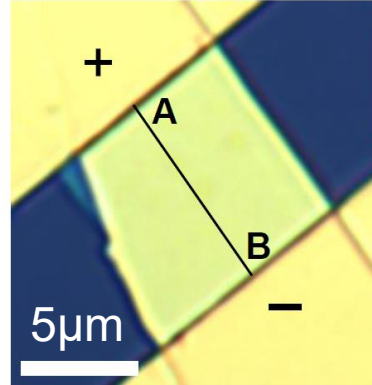
Nonpolar (WSe₂) + Nonpolar (BP) ⇒ Polar

Photocurrent in van der Waals heterostructures

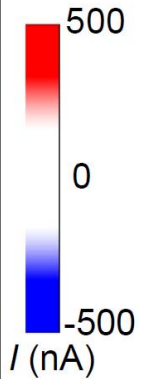
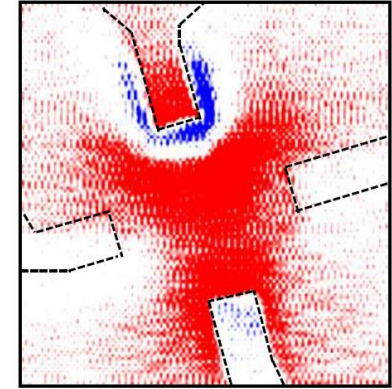
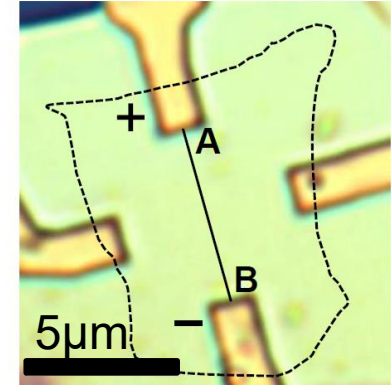
1L- WSe₂



Black Phosphorus

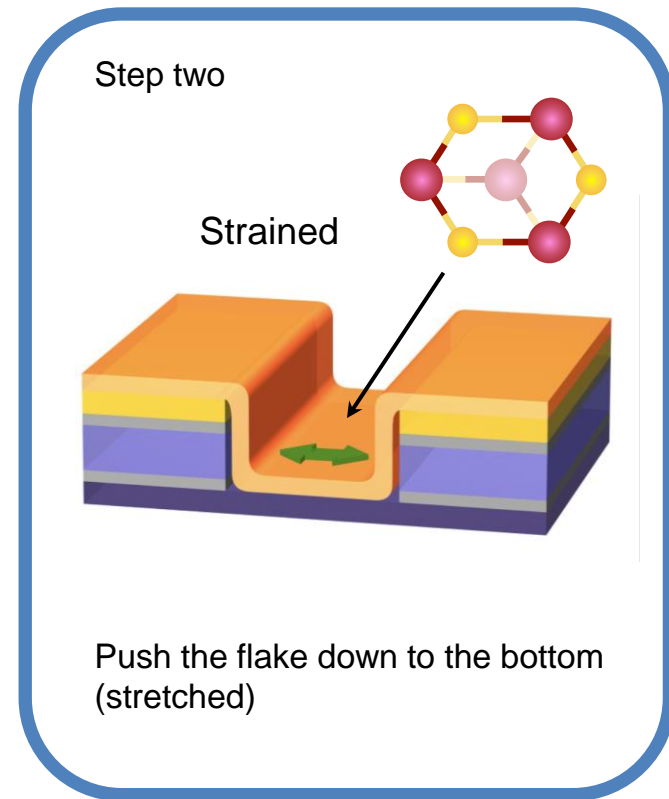
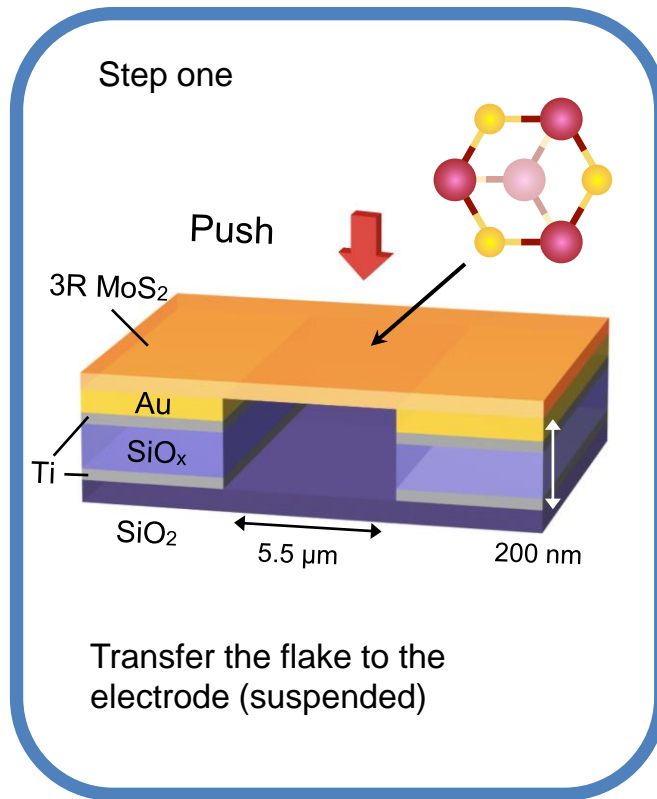


WSe₂ / Black Phosphorus



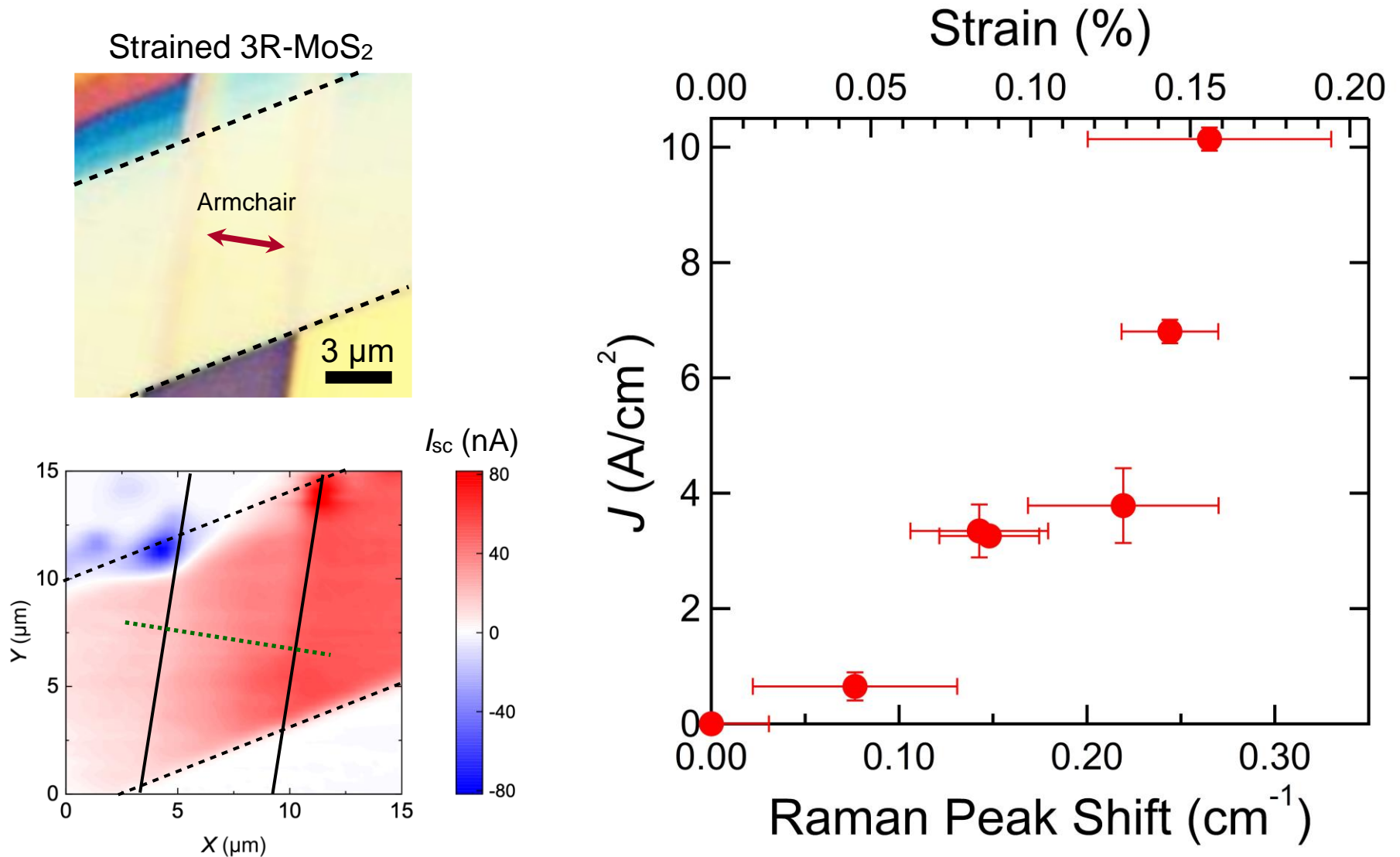
Anomalous photovoltaic effect in WSe₂ / Black Phosphorus interface

Method for applying strain to 3R MoS₂

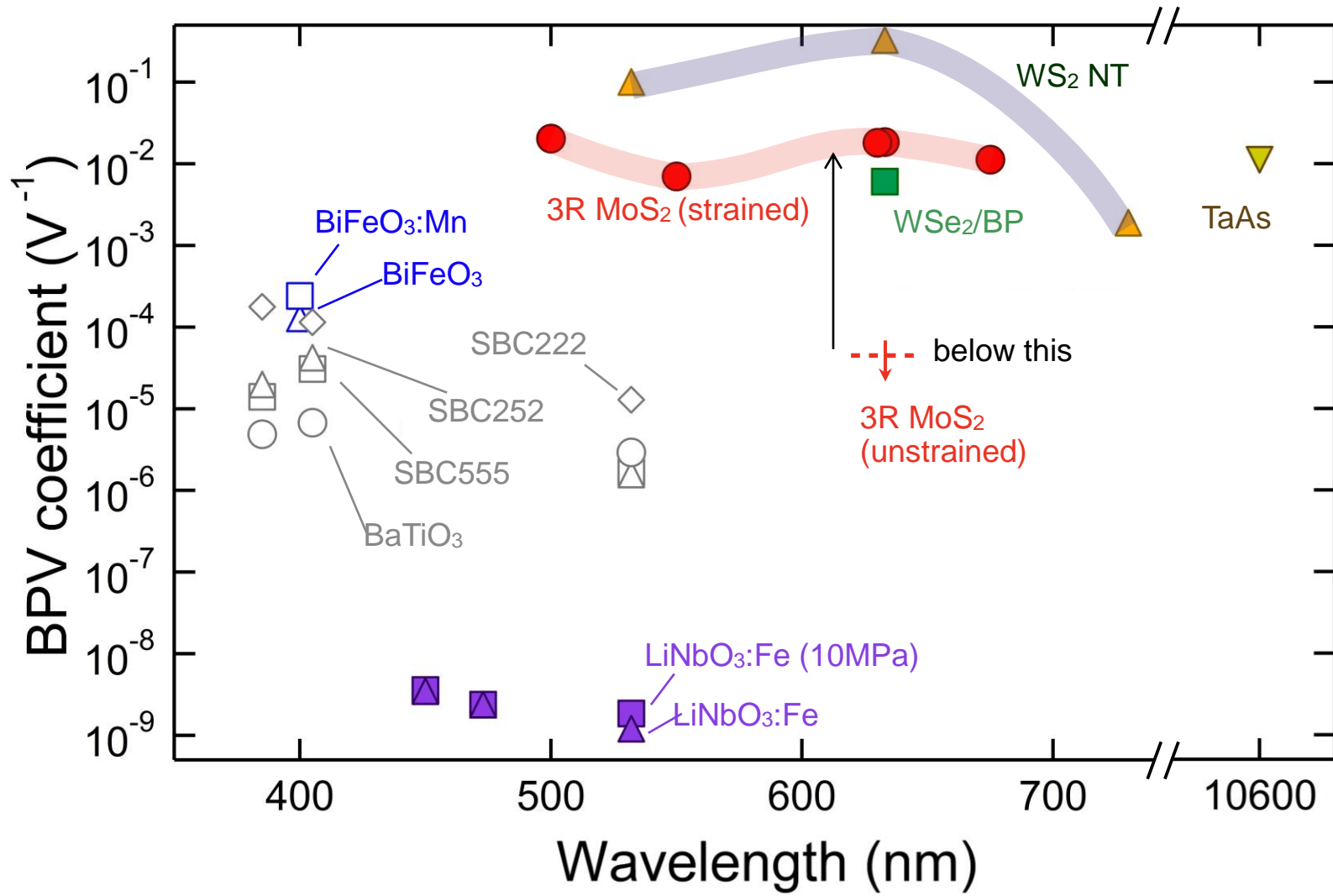


By adjusting the height of bottom electrode, the strain intensity can be controlled.

Strain induced photocurrent

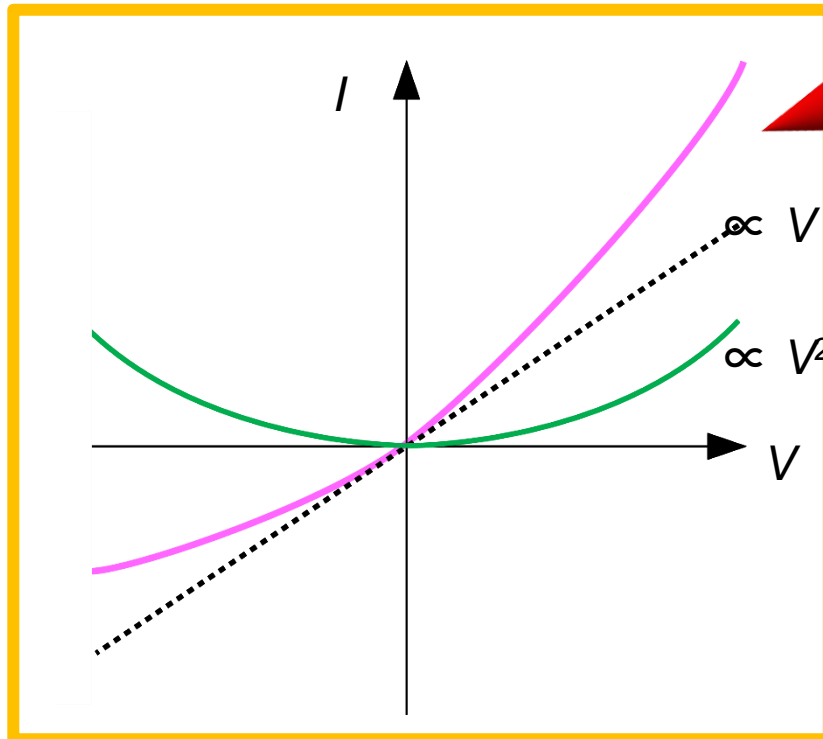
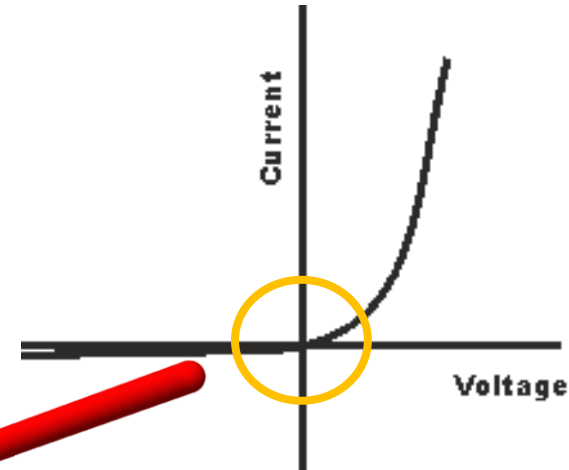
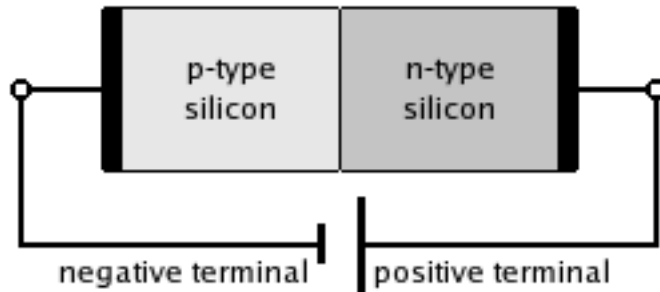


BPV coefficient



2. Nonreciprocal resistance in polar conductors

- Diode (broken inversion and translational symmetry)

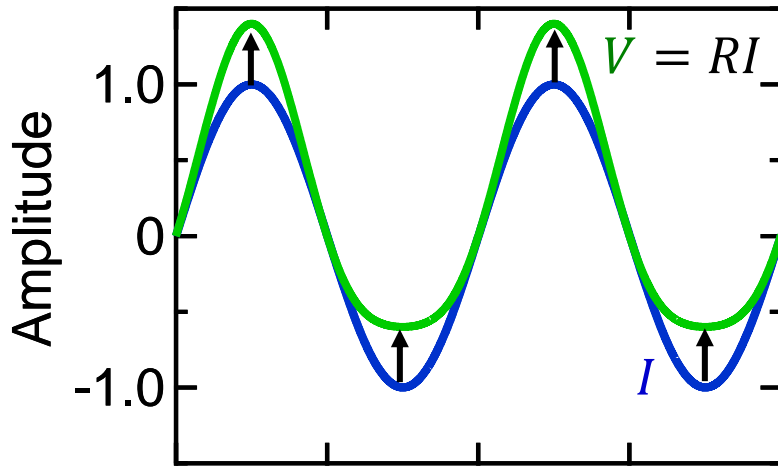


$$I = G^{(1)}V + G^{(2)}V^2 + \dots$$

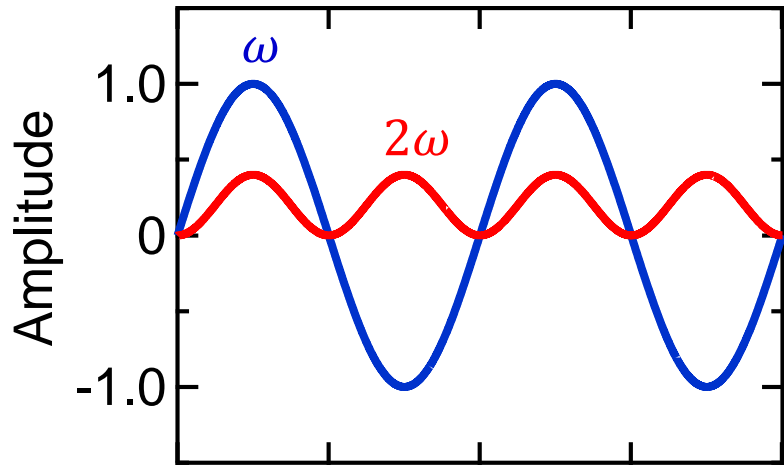
$$V = R^{(1)}I + \underline{R^{(2)}I^2} + \dots$$

Detection of rectification/ratchet motions

■ Second harmonic resistance



time



time

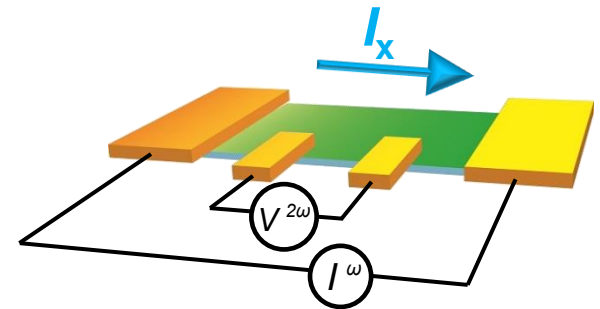
Output: $V = R_0 I (1 + \gamma B I)$



Input: $I = I_0 \sin \omega t$

$$V = R^\omega I_0 \sin \omega t + \gamma \frac{R^\omega B I_0^2}{2} \sin(2\omega t - \frac{\pi}{2})$$

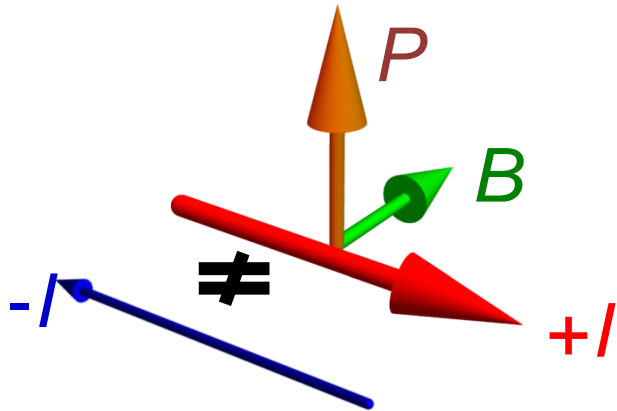
III
 $V^{2\omega}$



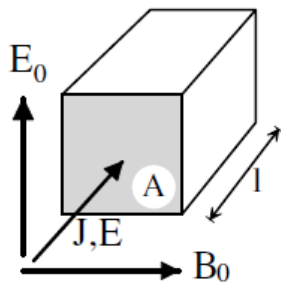
Extract 2ω signals with 90° phase delay

Nonreciprocal electric transport in polar & chiral systems

■ Polar systems



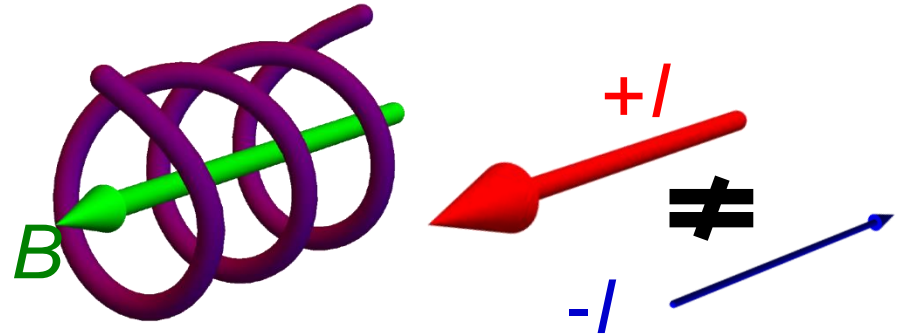
● *n*-channel Si FET



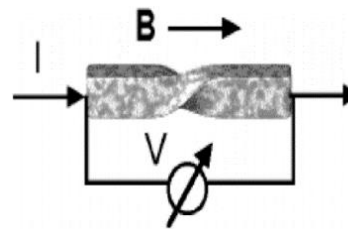
G. L. J. A. Rikken *et al.*,
Phys. Rev. Lett. **94**,
016601 (2005).

- $\Delta R \propto I \cdot (E \times B)$
- Polarity \Leftrightarrow Sign of nonreciprocity

■ Chiral systems

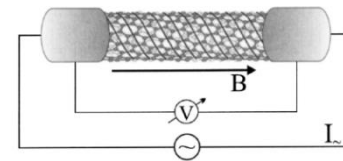


● Bi helix



G. L. J. A. Rikken *et al.*
Phys. Rev. Lett. **87**,
236602 (2001).

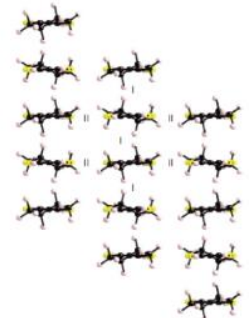
● Carbon nanotube



Krstić, V. *et al.*
J. Chem. Phys. **117**, 11315
(2002).

- $\Delta R \propto B \cdot I$
- Chirality \Leftrightarrow Sign of nonreciprocity

● Organic materials

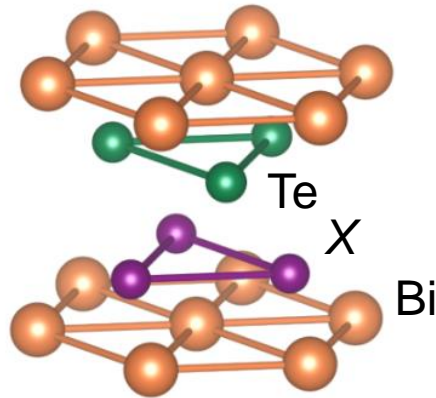


F. Pop *et al.*
Nat. Commun. **5**,
3757 (2014).

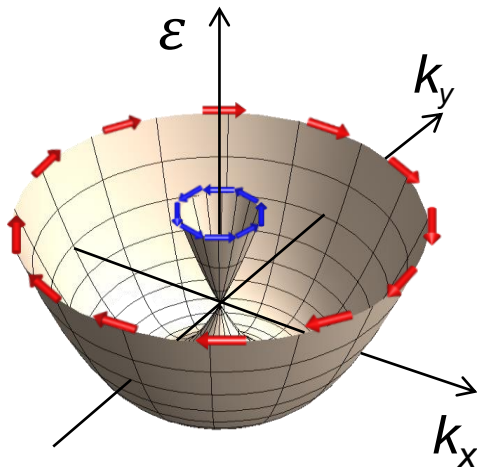
Polar semiconductor BiTeBr

■ BiTeX (X = I, Br)

● ABCABC... (natural tricolor stacking)



● Rashba-type spin splitting w/o B

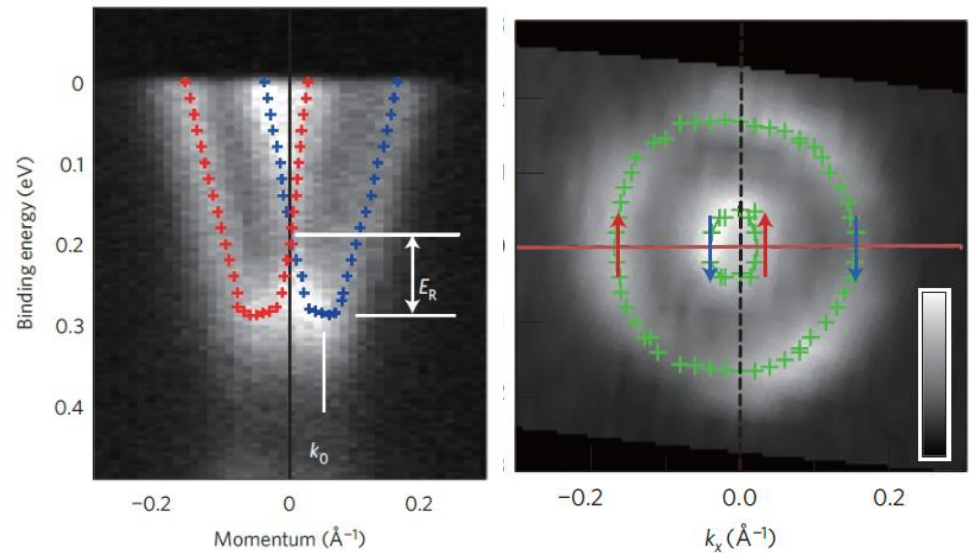


Polar structure



Rashba -type spin-orbit coupling

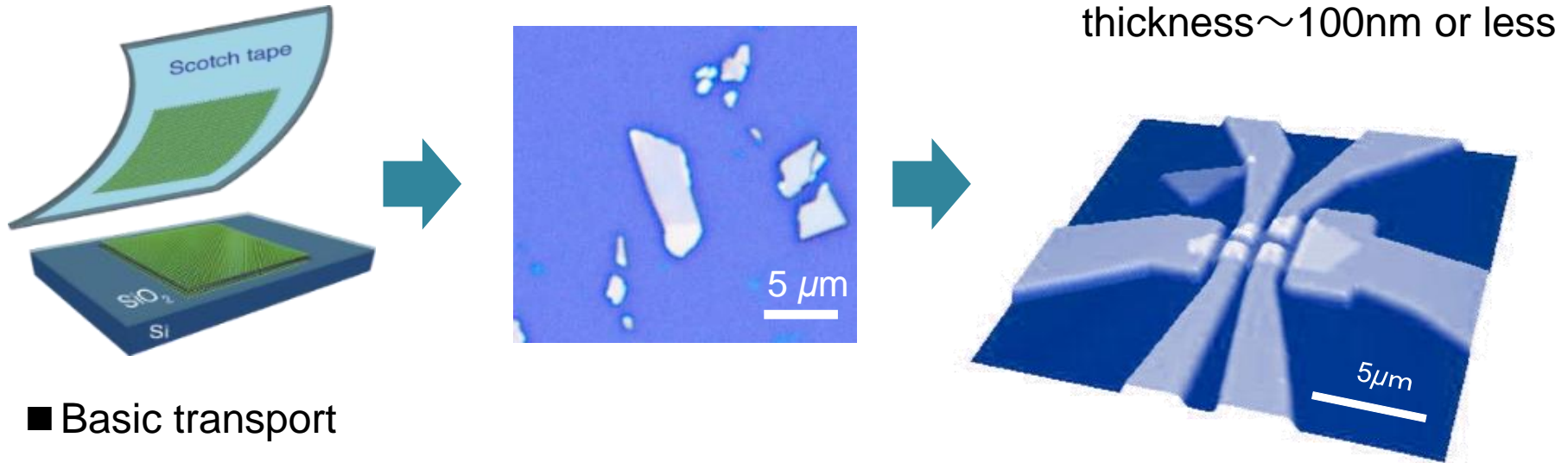
$$H_{\text{SOI}} = \alpha \hbar v_{\text{F}} (k_y \sigma_x - k_x \sigma_y)$$



K. Ishizaka *et al.*, Nat. Mater., **10**, 521 (2011)

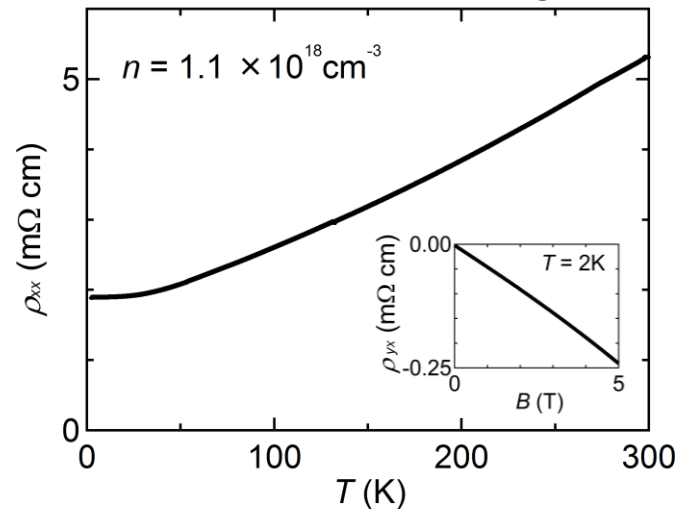
Device fabrication in BiTeBr

■ Exfoliation and Electron Beam Lithography



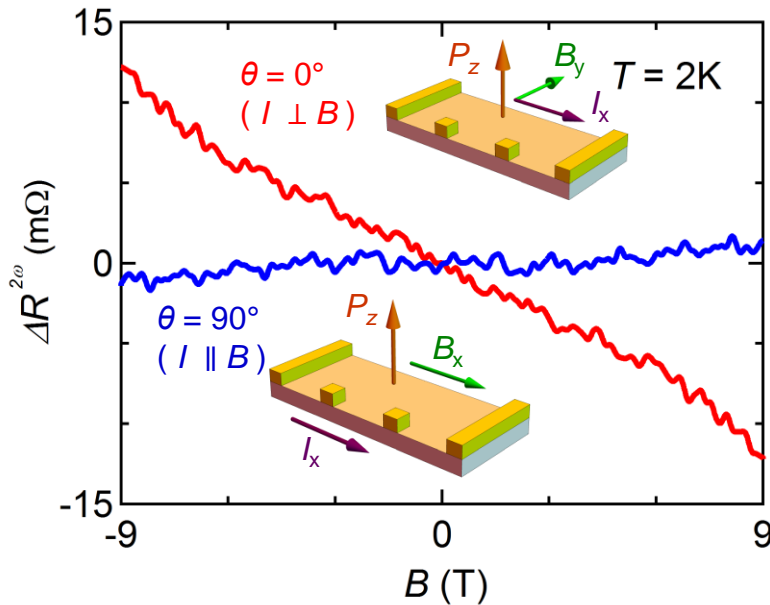
■ Basic transport

Metallic down to low T due to the electron doping

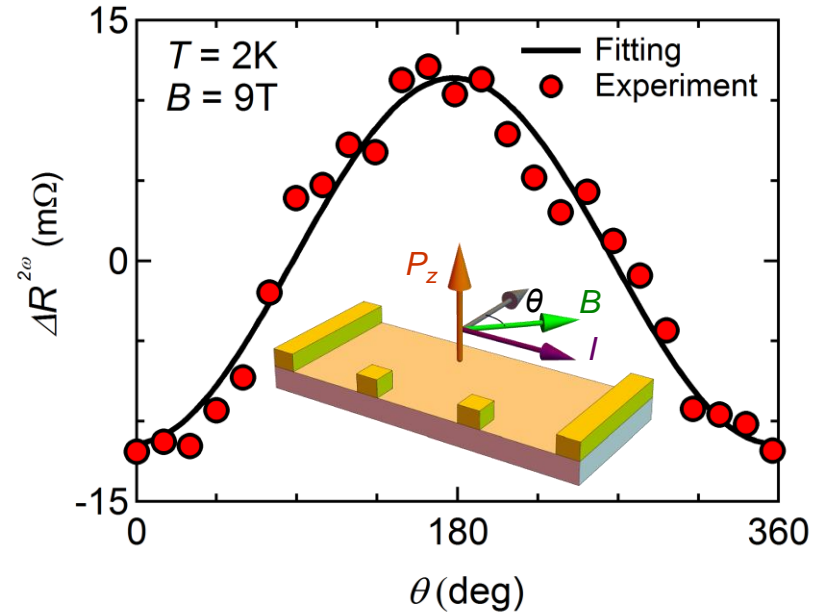


Nonreciprocal transport in BiTeBr

■ B dependence



■ Angle dependence

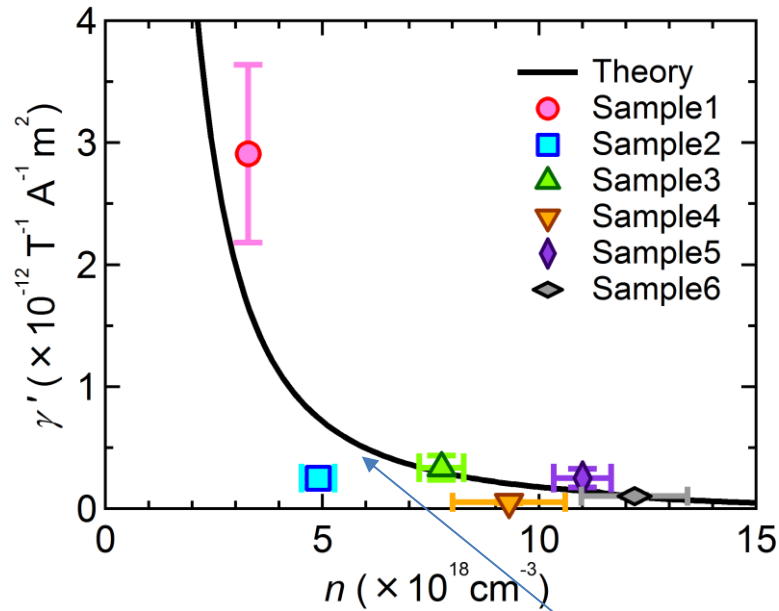


Selection rules characteristic of polar materials

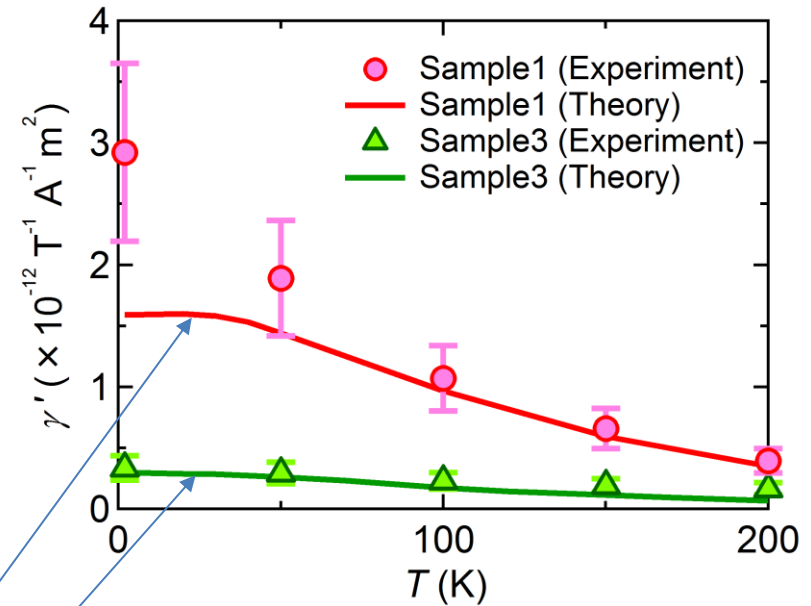
$$R^{2\omega} \equiv \frac{V^{2\omega}}{I\omega} \propto I \cdot P \times B$$

Comparison with theory

- Carrier density dependence at 2 K



- Temperature dependence for $n = 3.2 \times 10^{18} \text{ cm}^{-3}$
 $n = 7.8 \times 10^{18} \text{ cm}^{-3}$



Theoretical calculation from Boltzmann equation without fitting parameters assuming the simple Rashba band

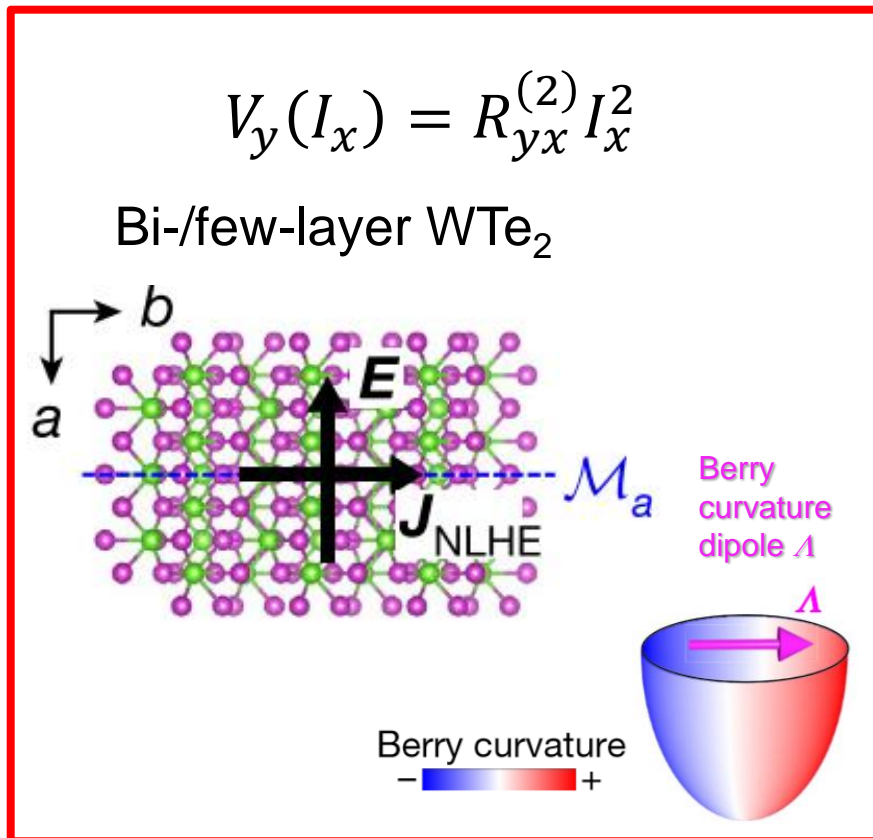
Independent from sample size or scattering time



Rashba splitting can be estimated from nonreciprocal transport

Band-driven nonlinear Hall transport

Nonlinear Hall effect at $B = 0$ (under Time Reversal Symmetry)



1) Polar system Td- WTe_2

Berry curvature dipole

Q. Ma *et al.*, *Nature* **565**, 337 (2019)
K. Kang *et al.*, *Nat. Mater.* **18**, 324 (2019).

2) AFM interface: even layer even layered $MnBi_2Te_4$ /Black phosphorous interface

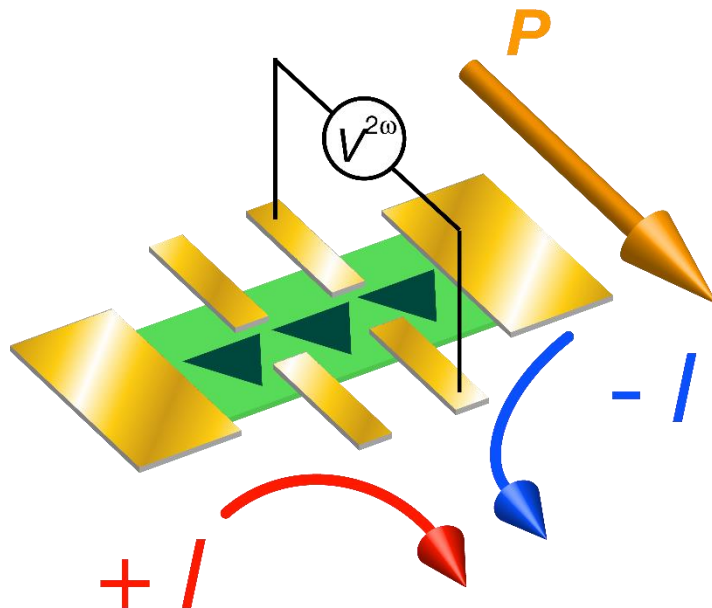
Quantum Metric

A. Gao *et al.*, *Science* **381**, 181 (2023)

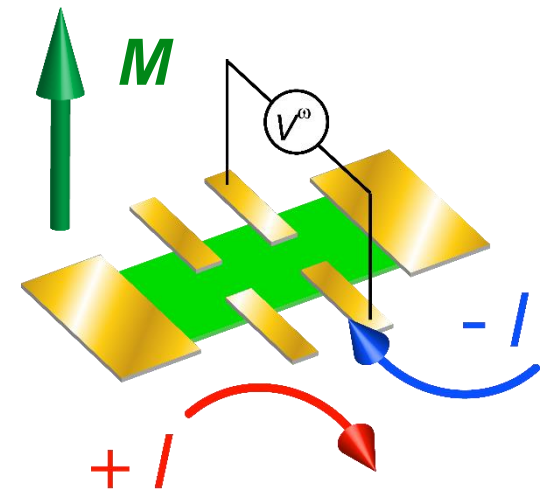
Real space picture of NHE

Nonlinear (anomalous) Hall effect

Q. Ma *et al.*, *Nature* **565**, 337 (2019).
K. Kang *et al.*, *Nat. Mater.* **18**, 324 (2019).



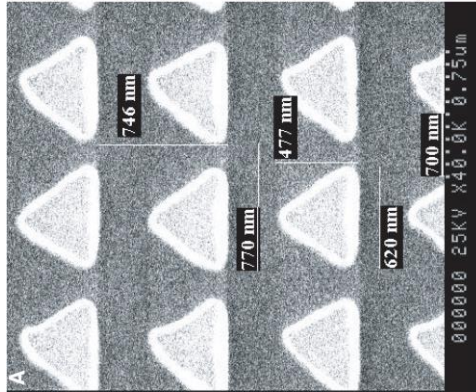
cf) Anomalous Hall effect (AHE)



Electron trajectory is bent by polarization P

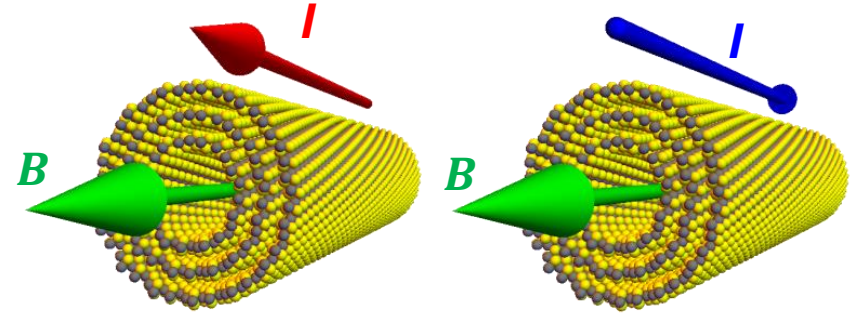
3. Superconducting rectifiers

Device architecture



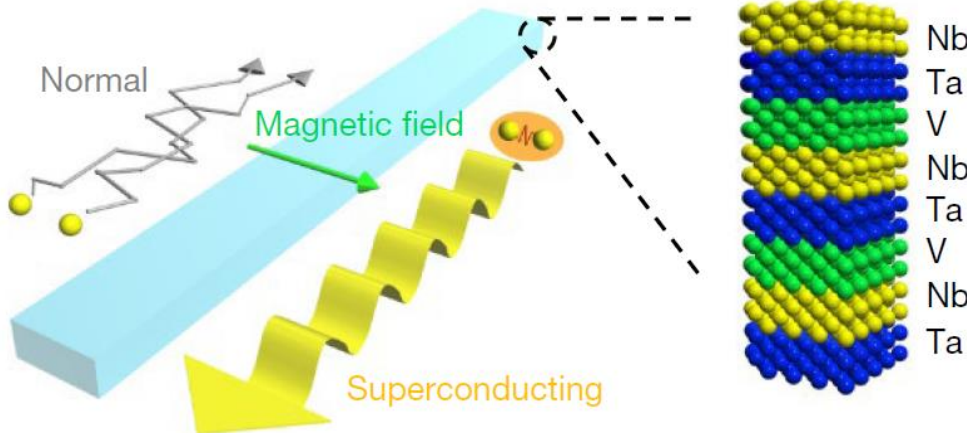
J. E. Villegas *et al.* *Science* (2003).

Crystal structure (Intrinsic)

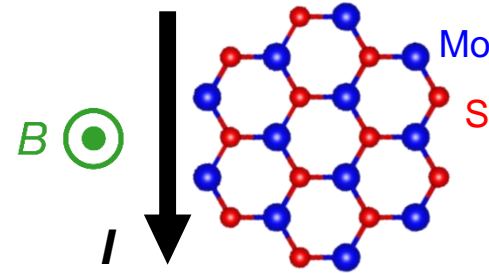


Chiral SC F. Qin *et al.* *Nat Comm* (2017).

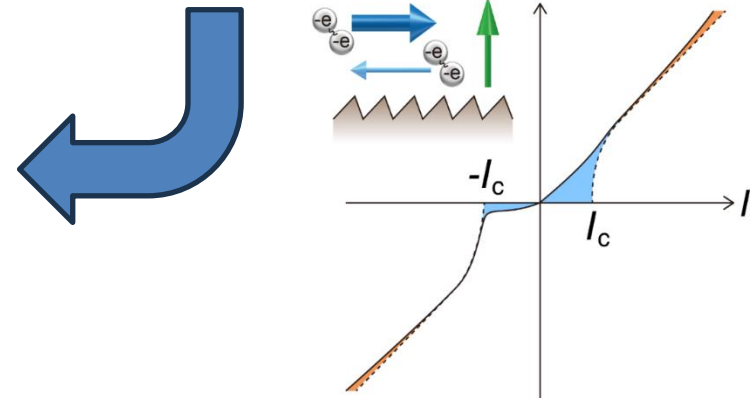
Diode effect ($I_{C+} \neq I_{C-}$)



F. Ando *et al.*, *Nature* **584**, 373 (2020)

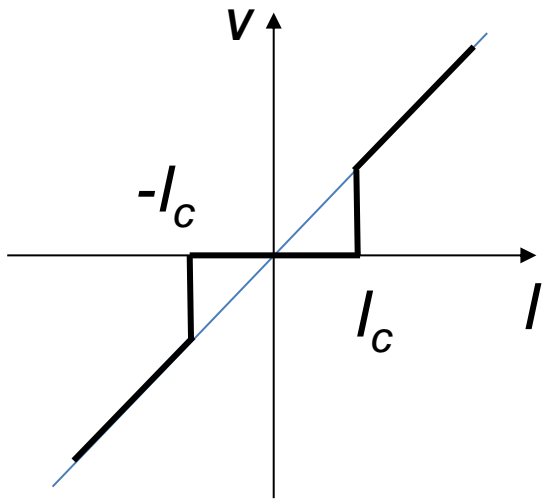


Trigonal SC
Wakatsuki/Saito *et al.*
Sci. Adv (2017).



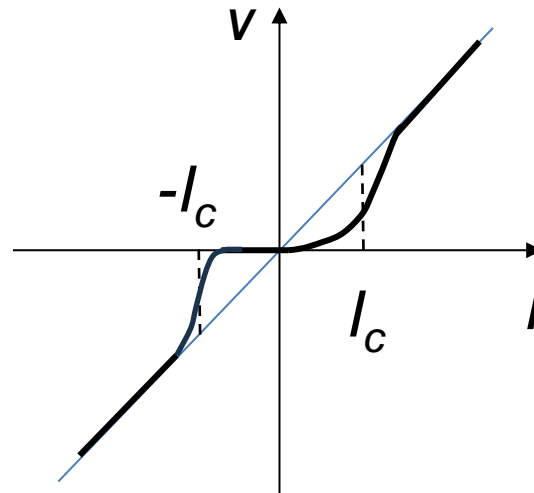
Rectification in noncentrosymmetric superconductors

Centrosymmetric

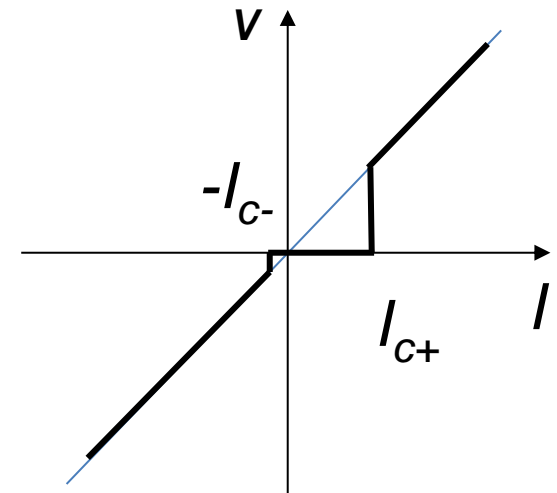


Noncentrosymmetric

Nonreciprocal transport



Superconducting diode effect (SDE)



$$I_{c+} \neq I_{c-}$$

Extrinsic

J. E. Villegas *et al.* *Science* (2003).

Intrinsic

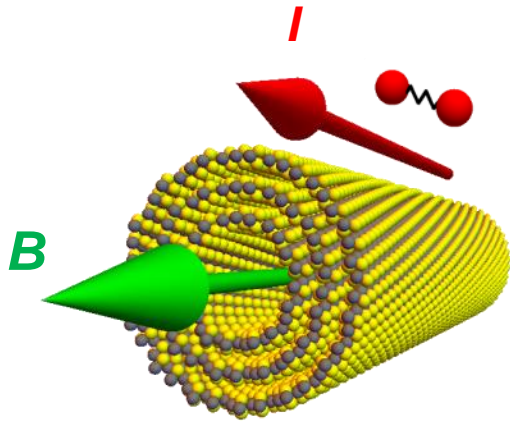
Iwasa group, *Nat Comm* (2017)

Sci. Adv (2017)

T. Ono group., *Nature* (2020)

Nonreciprocal superconducting transport

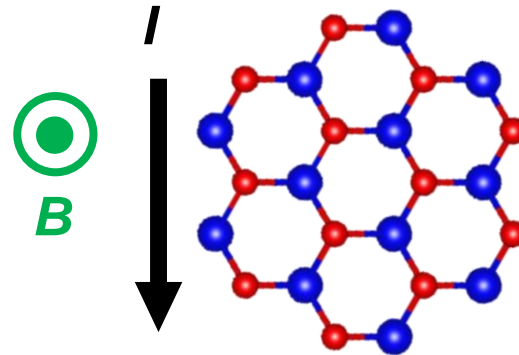
Chiral



WS₂ nanotube

F. Qin et al.,
Nat Comm. **8**, 14465 (2017).

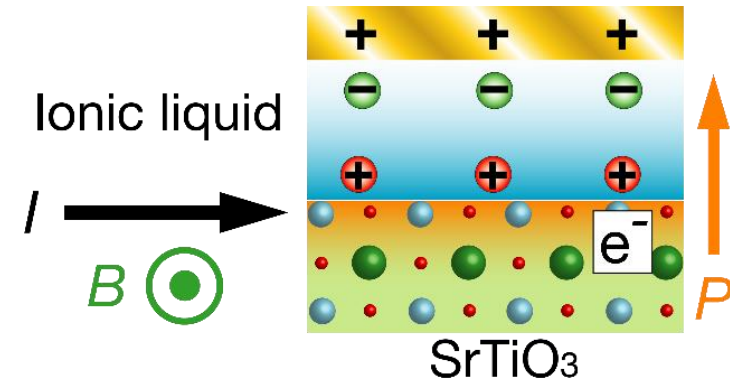
Trigonal



MoS₂

R. Wakatsuki et al.,
Sci. Adv. **3**, e1602390 (2017).

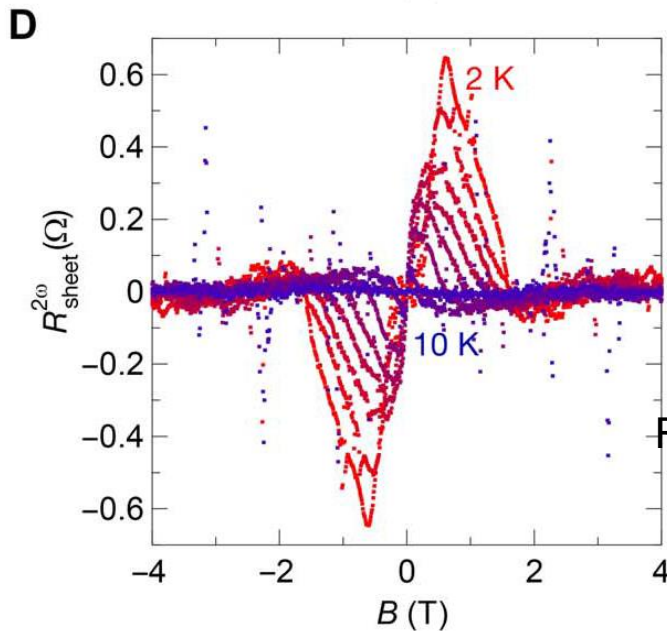
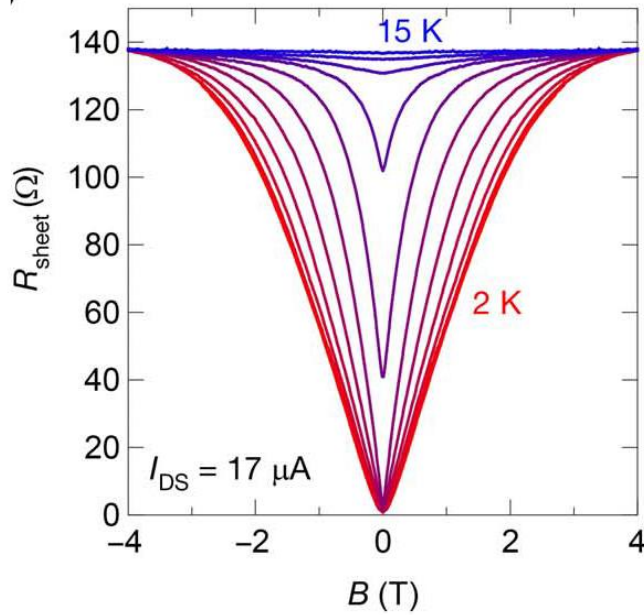
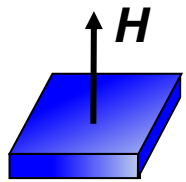
Rashba



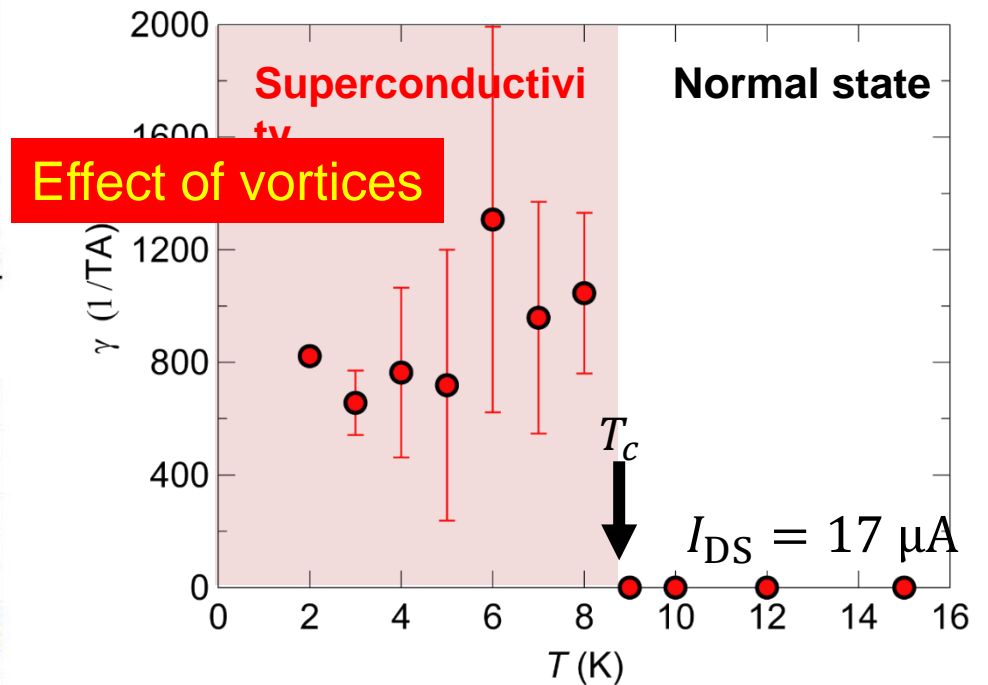
SrTiO₃

Y. M. Itahashi et al.,
Sci. Adv. **6**, eaay9120
(2020).

Second harmonic resistance $R^{2\omega}$

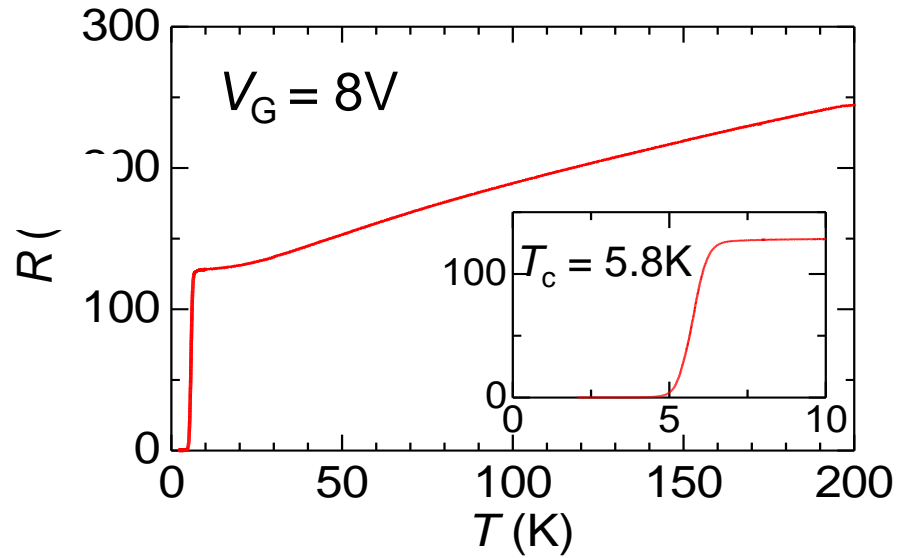
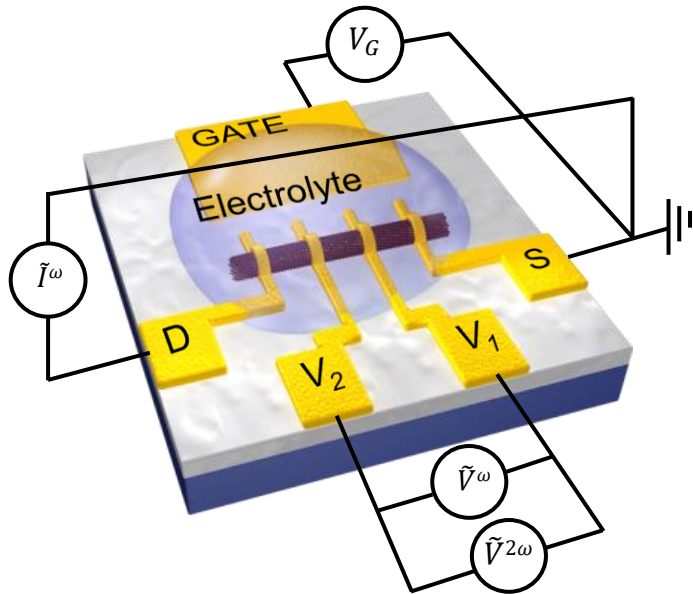
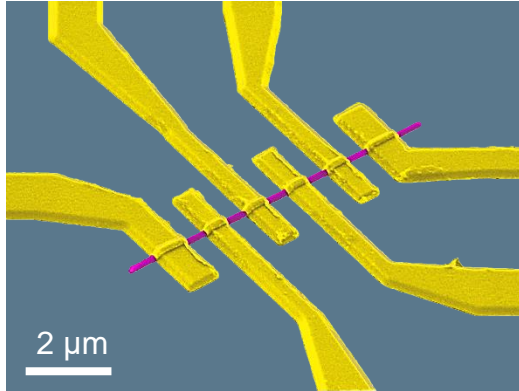


$$\gamma \equiv \frac{2R^{2\omega}}{IBR^\omega} \sim 1000 \text{ T}^{-1}\text{A}^{-1} \text{ below } T_c$$

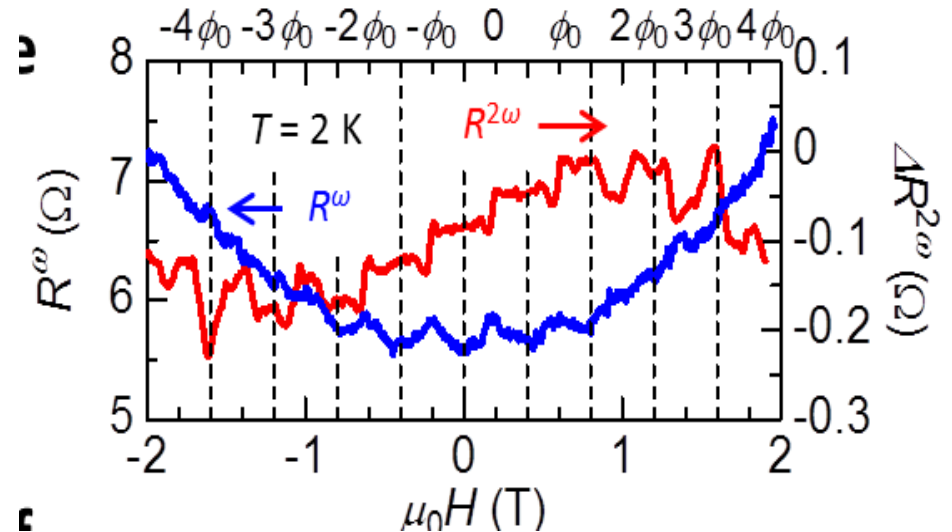


R. Wakatsuki, Y. Saito, *et al.* Sci. Adv. 3: e1602390 (2017)

Gate-induced superconductivity in WS₂ nanotube

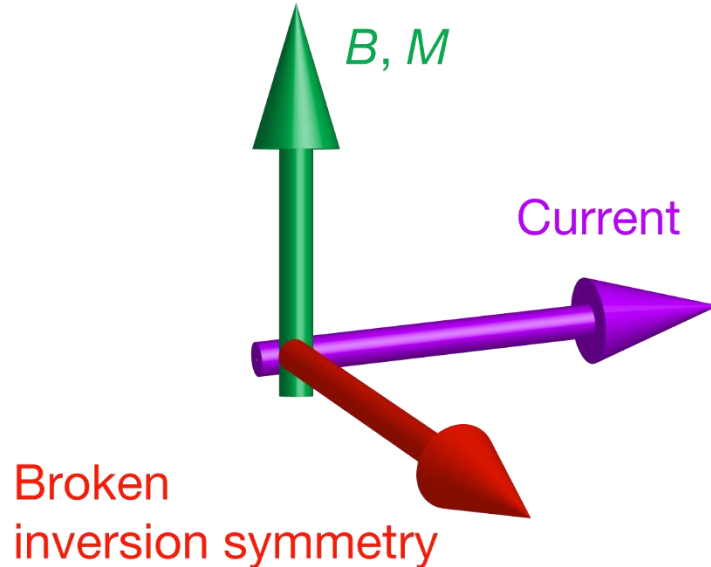


Nonreciprocal Little-Parks oscillation



Superconducting diode effects (SDE)

Broken time reversal symmetry (TRS)

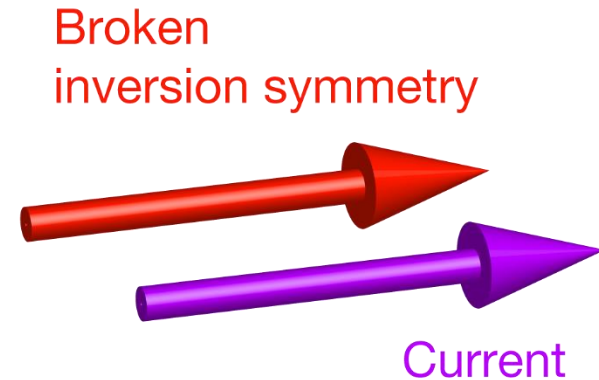


at $B \neq 0$ or with ferromagnet

- F. Ando, *et al.*, *Nature* **584**, 373 (2020).
- B. Pal *et al.*, *Nat. Phys.* **18**, 1228 (2022).
- Y. Y. Lyu *et al.*, *Nat. Commun.* **12**, 2703 (2021).
- K. R. Jeon *et al.*, *Nat. Mater.* **21**, 1008 (2022).
- A. Mizuno *et al.*, *IEEE Trans. Appl. Supercond.* **32**, 6601005 (2022).
- H. Narita *et al.*, *Nat. Nanotechnol.* **17**, 823 (2022).
- L. Bauriedl *et al.*, *Nat. Commun.* **13**, 4266 (2022).
- R. Kealhofer *et al.*, *PRL* **107**, L100504 (2023).

etc...

Without explicit TRS breaking



at $B = 0$

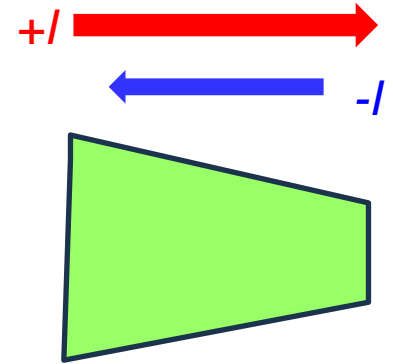
- H. Wu *et al.*, *Nature* **604**, 653 (2022)
- J.-X. Lin *et al.*: *Nat. Phys.* **18**, 1221 (2022)
- Frank Zhao *et al.*; *Science* **382**, 1422 (2023)
- T. Le *et al.*, *Nature* **630**, 64 (2024)
- Z. Wan, *Nature* **632**, 69 (2024)

Purpose of this research

To observe “intrinsic” 2nd harmonic transport and SDE with TRS



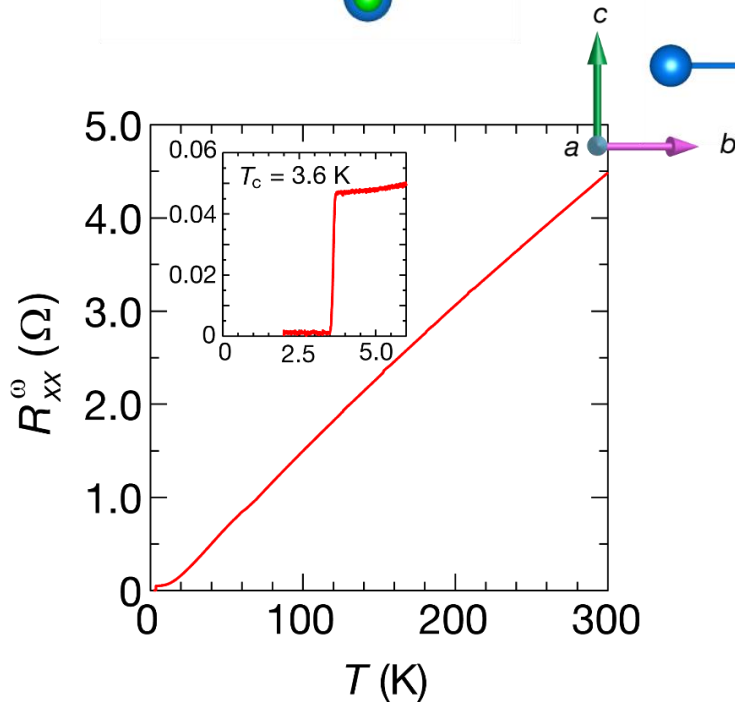
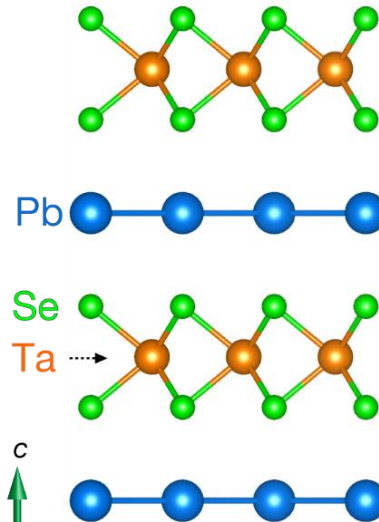
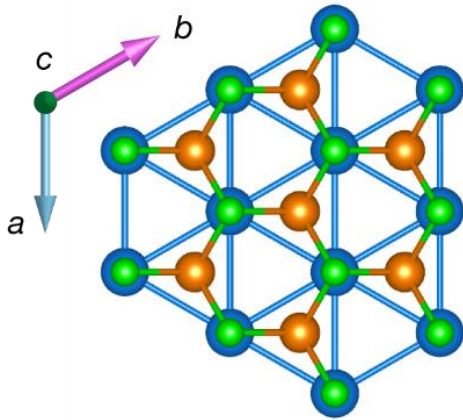
- Experimental difficulty of zero-field SDE : to distinguish from extrinsic effect
- Experimentally, broken time reversal symmetry (TRS) seems to be required for zero-field superconducting diode effect (SDE).



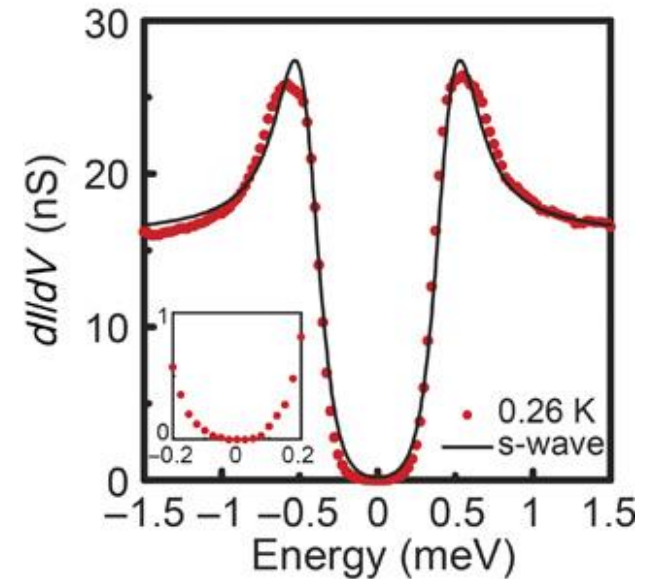
Following papers claim that SDE occurs because TRS is broken in superconducting states

- Twisted Graphene: J.-X. Lin et al. *Nat. Phys.* **18**, 1221 (2022)
- Twisted BISCO; Frank Zhao et al., *Science* **382**, 1422 (2023)
- Kagome: T. Le et al., *Nature* **630**, 64 (2024)
- Chiral Molecule/TaS₂:Z. Wan, *Nature* **632**, 69 (2024)

PbTaSe₂



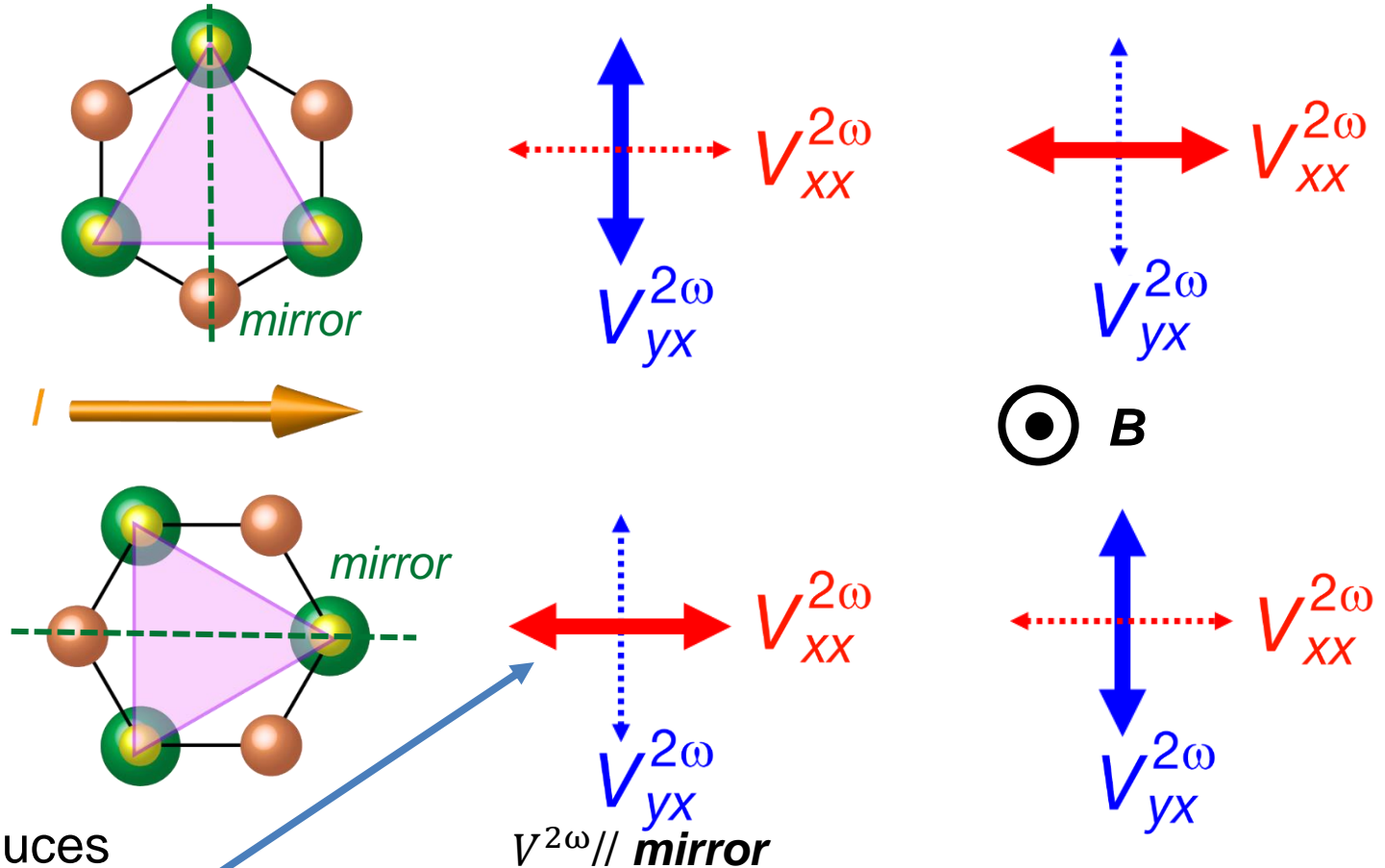
- 1H-TaSe₂ + intercalated Pb
- Noncentrosymmetric structure (D_{3h})
- **Trigonal** superconductor ($T_c \sim 3.8$ K)
- s-wave is highly likely



Nonlinear Transport in Trigonal PbTaSe₂

B = 0

B ≠ 0



Scattering induces nonreciprocity under TRS predicted by

H. Isobe and L. Fu
Sci. Adv. 6, eaay2497 (2020).

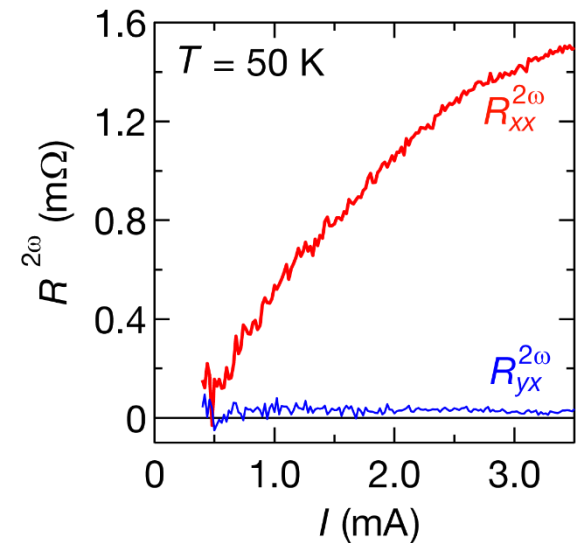
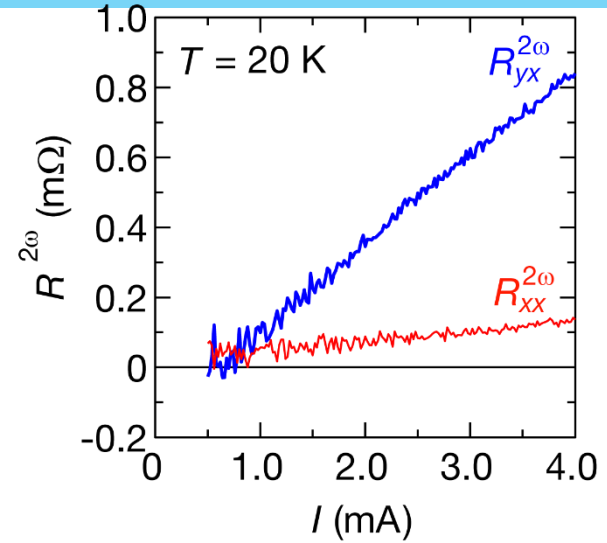
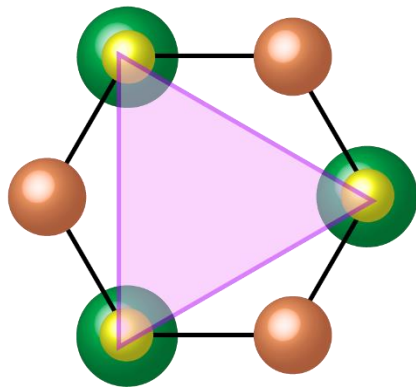
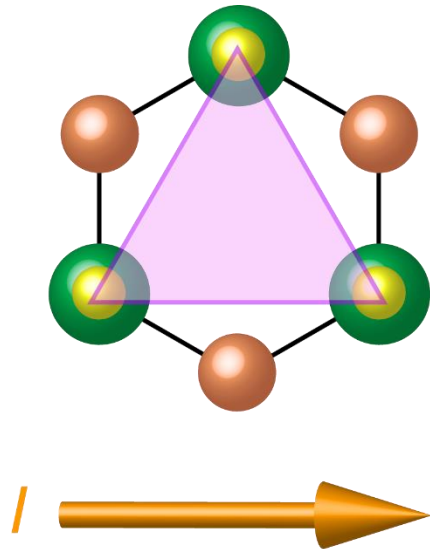
$$R_{ix}^{2\omega} = \frac{V_i^{2\omega}}{I_x} \propto I_x \quad (i = x, y)$$

Y. M. Itahashi et al.,
Nat Comm 13, 1659 (2022)

90° rotated

T. Ideue et al.,
PRR 2, 042046 (2020).

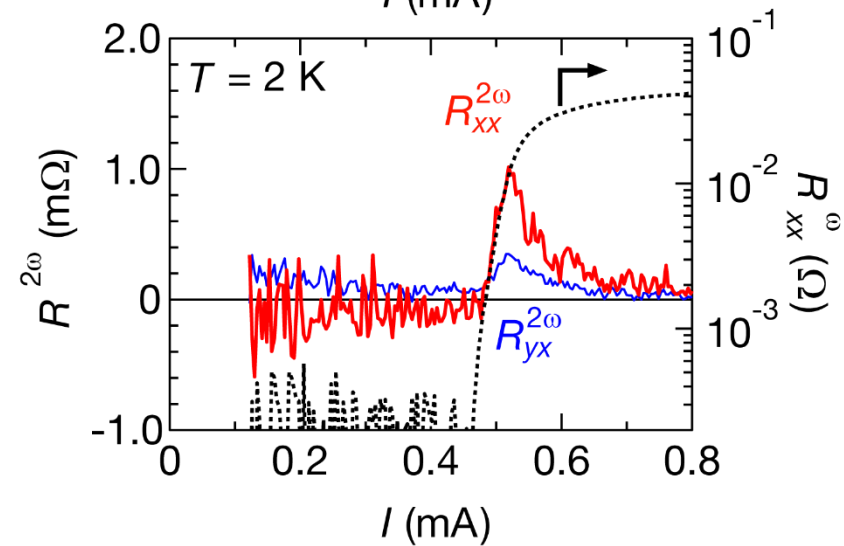
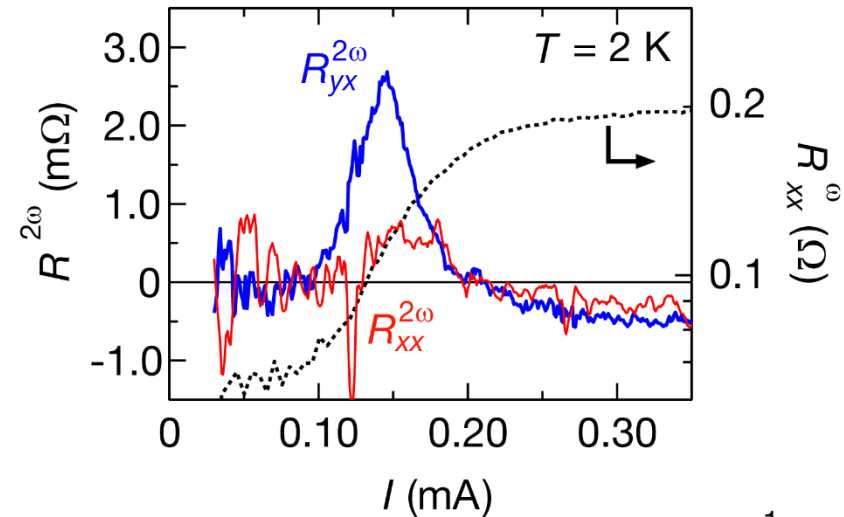
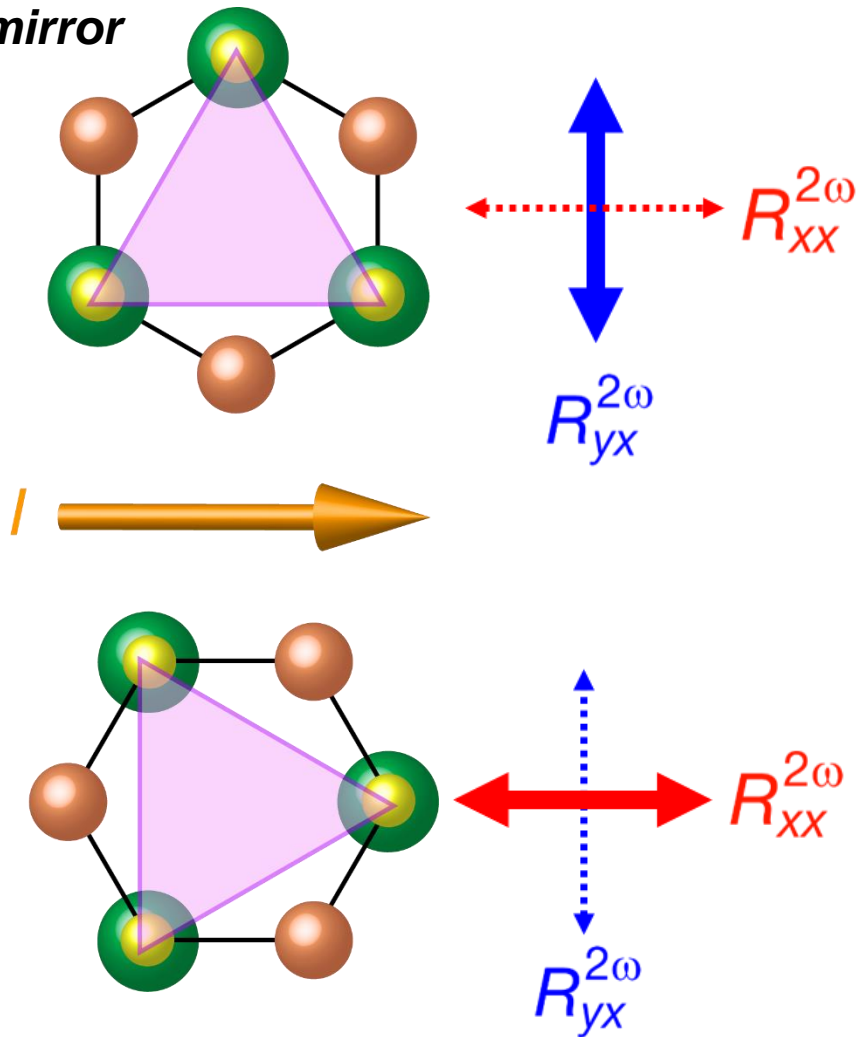
Normal state ($B=0$) : $R_{xx}^{2\omega}$ and $R_{yx}^{2\omega}$



- Nonlinear response reflecting **trigonal symmetry**

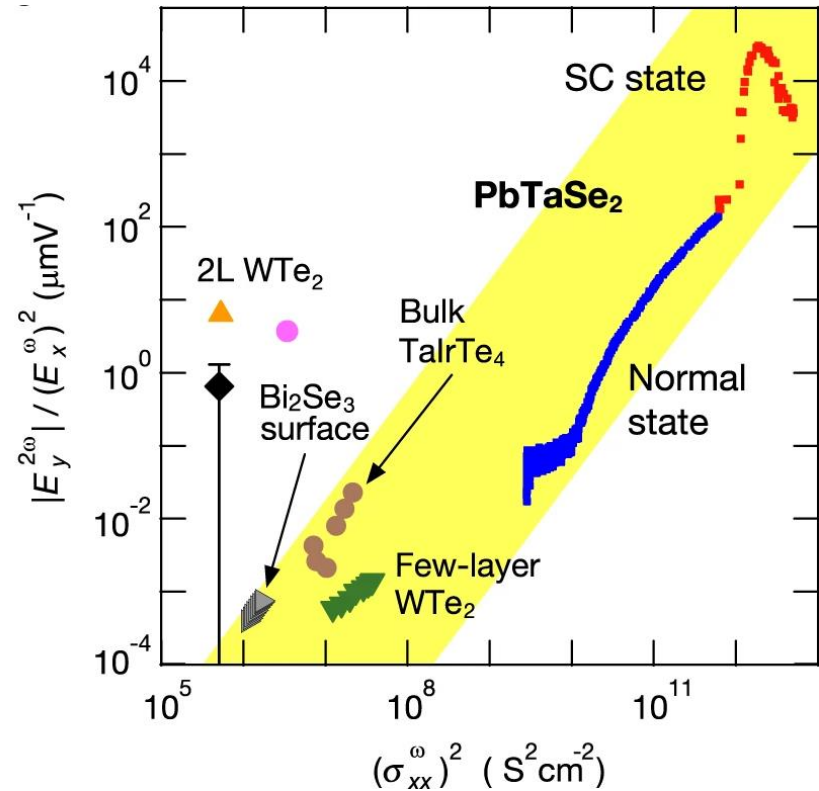
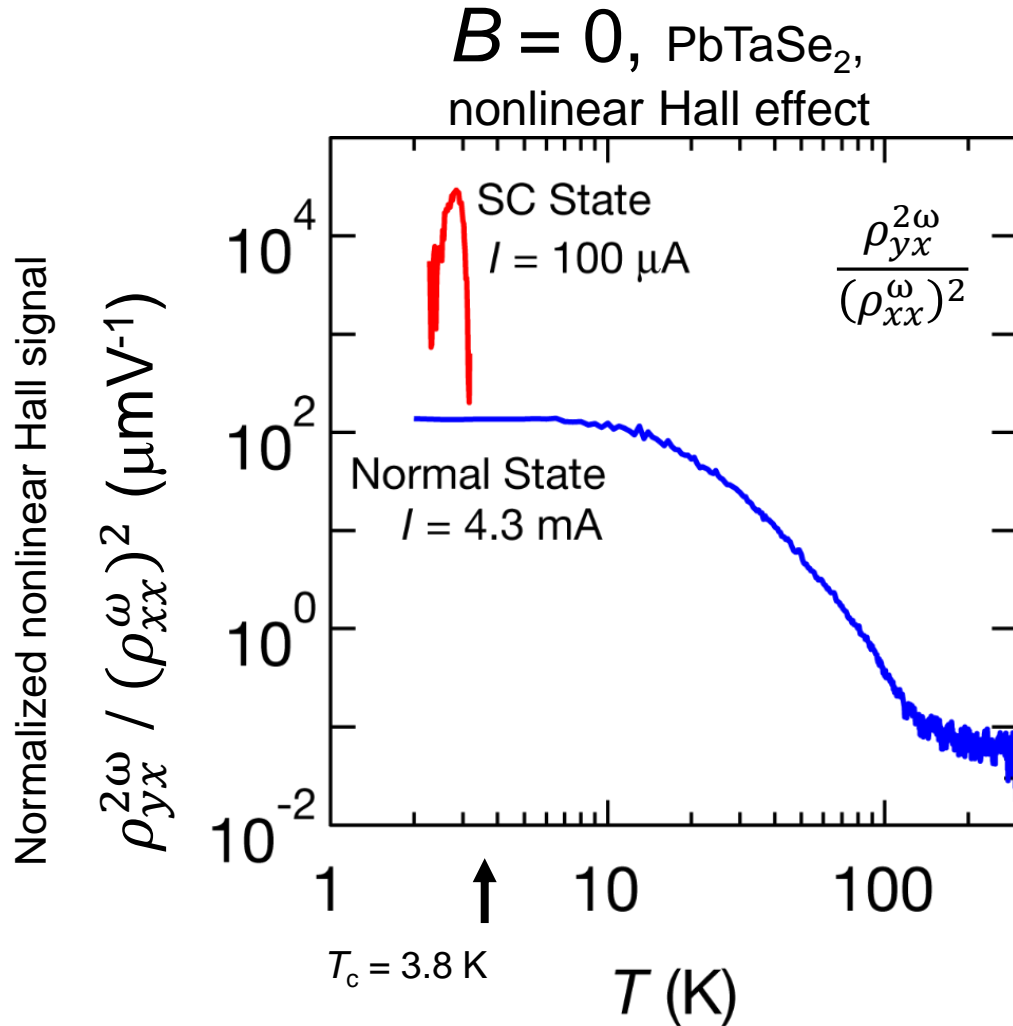
Superconducting state ($B=0$) : $R_{xx}^{2\omega}$ and $R_{yx}^{2\omega}$

$V^{2\omega}$ // *mirror*



- **Peak structure** consistent with trigonal symmetry

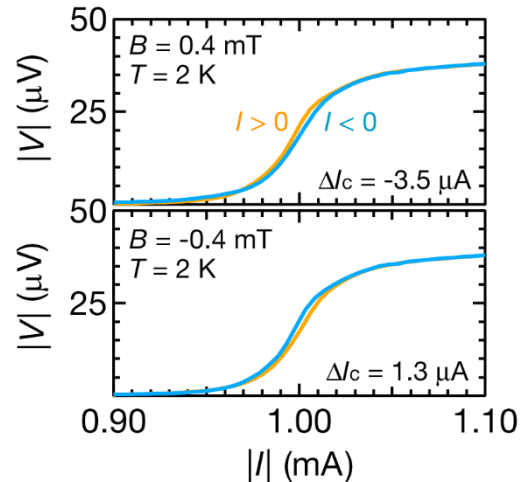
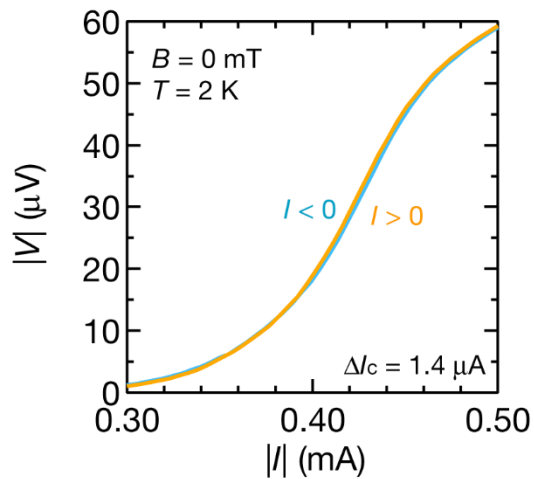
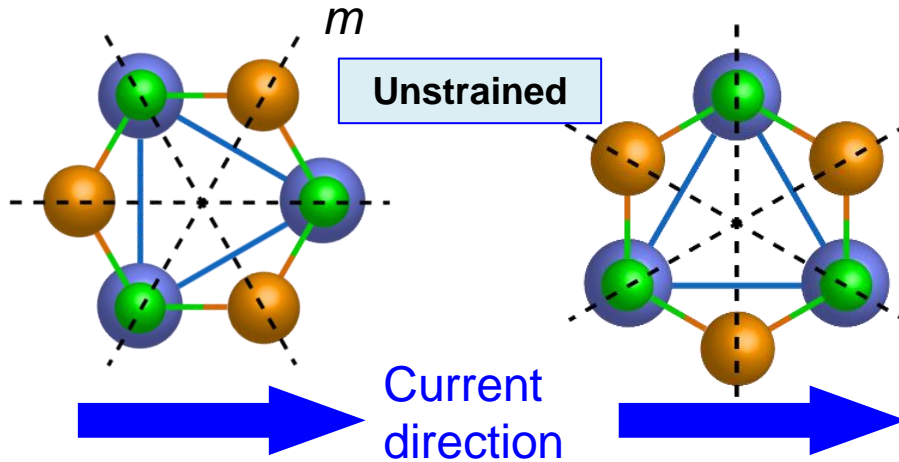
Enhancement of nonlinear Hall effect in SC state



SDE under TRS was not observed in trigonal lattice

Zero magnetic field
(B -even) diode effect

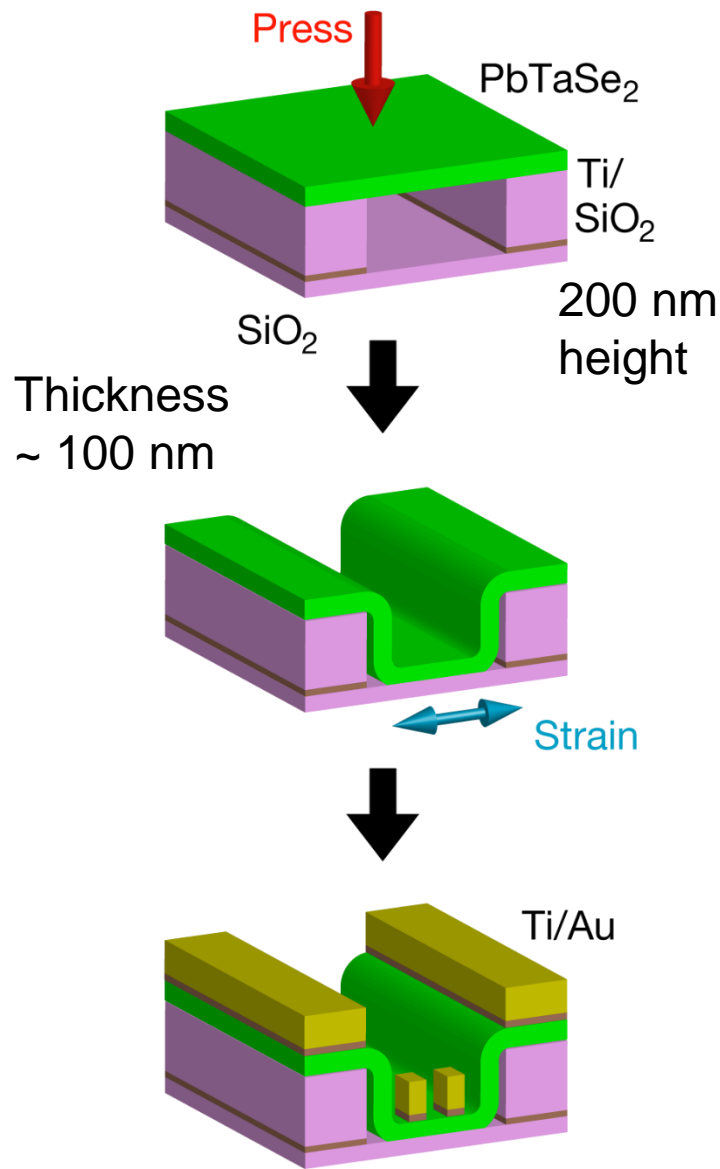
B -odd diode effect



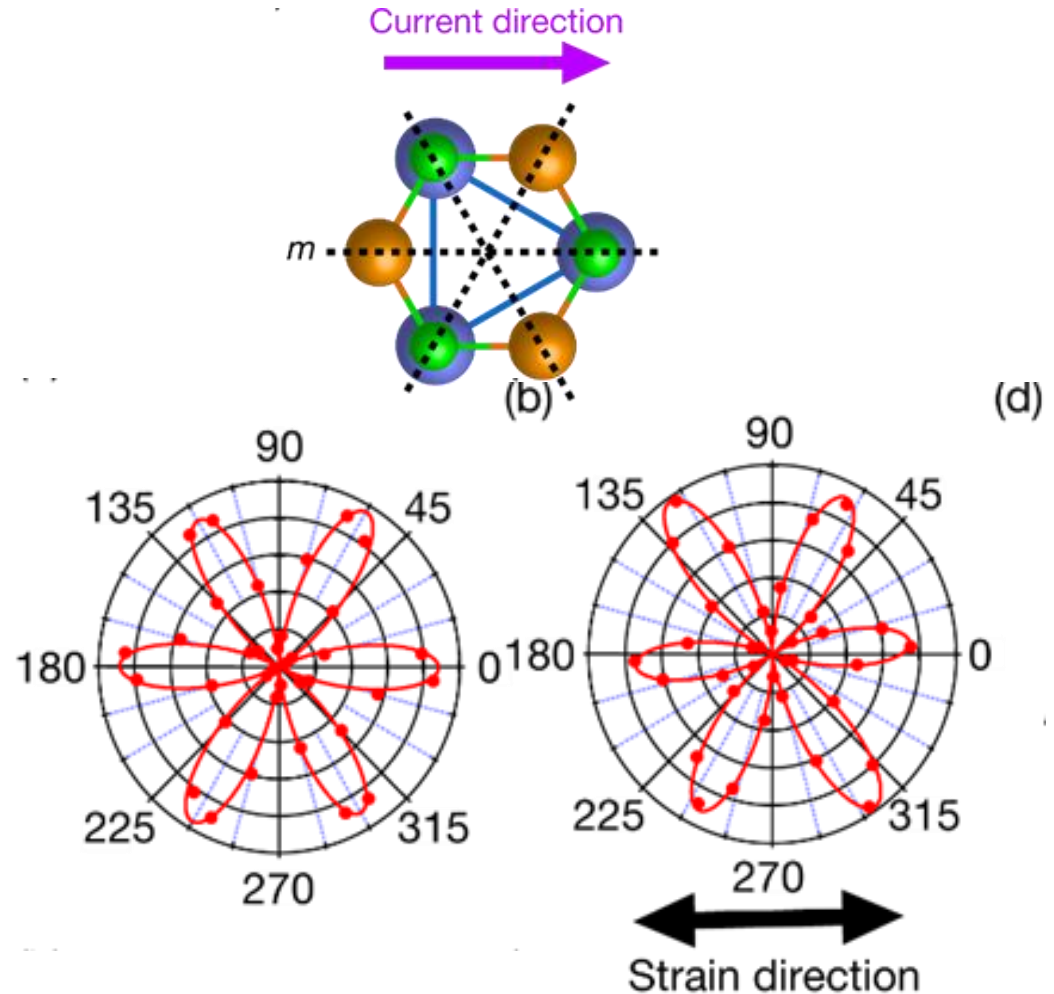
No appreciable diode effect???

→ Reduce symmetry by application of strain

Application of strain and its detection by SHG



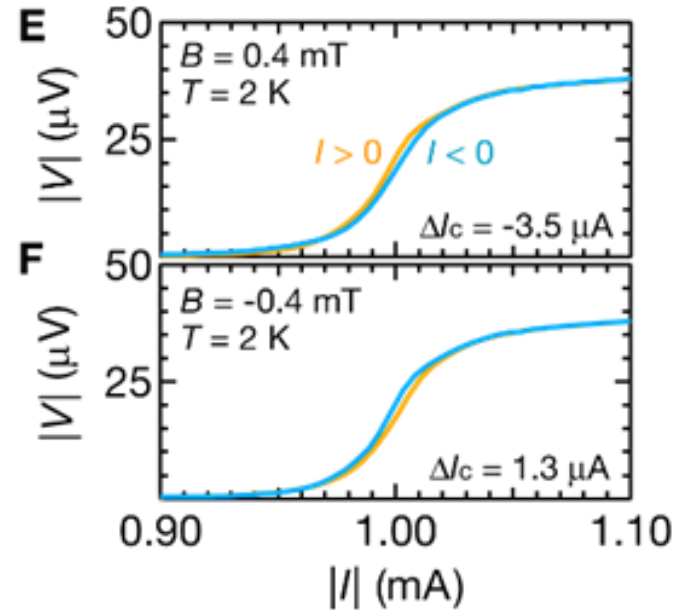
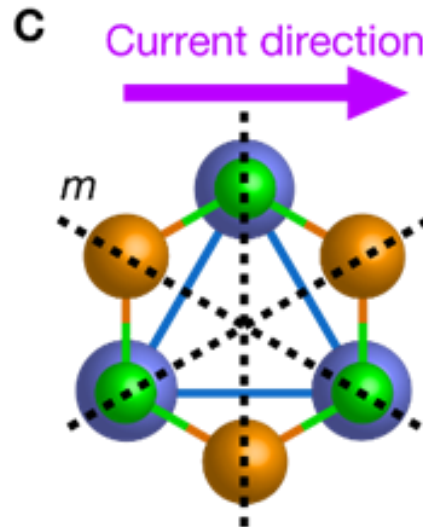
Armchair



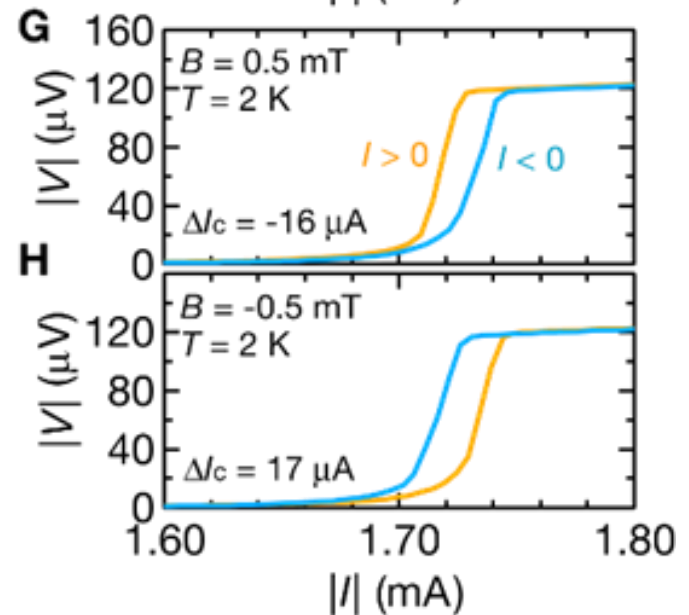
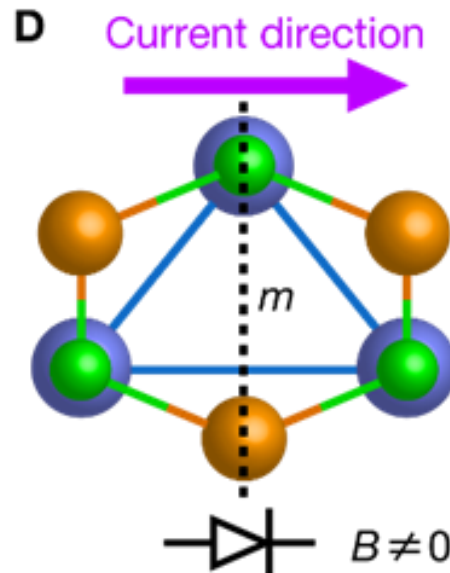
Strain magnitude
 $\sim 0.2\%$

Current & strain along zigzag direction

Unstrained

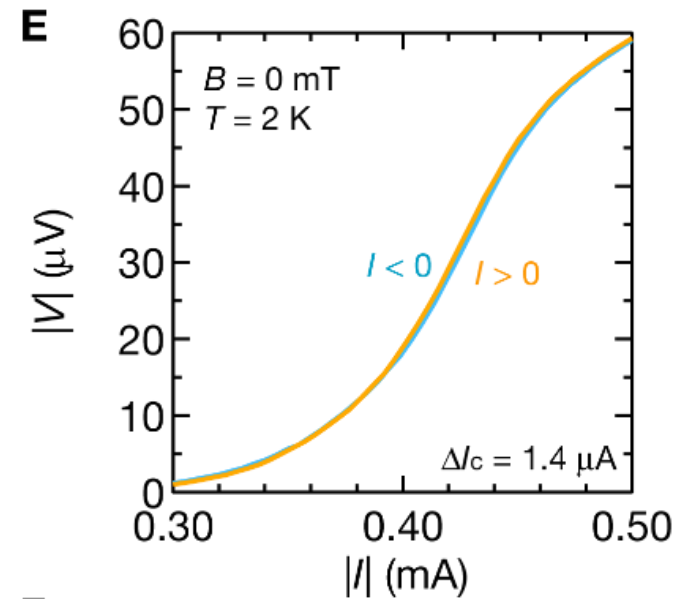
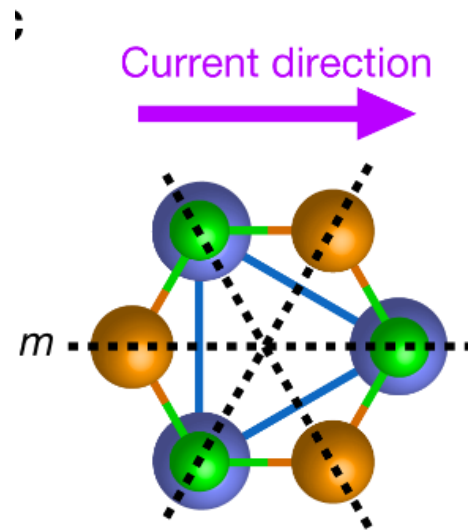


Strained

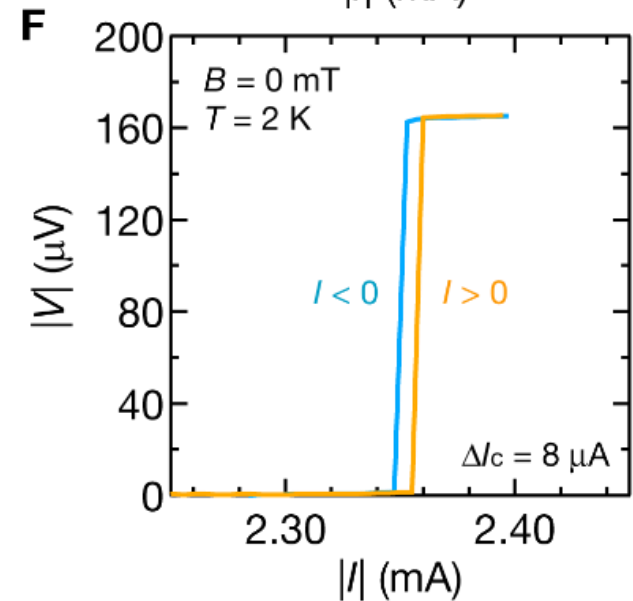
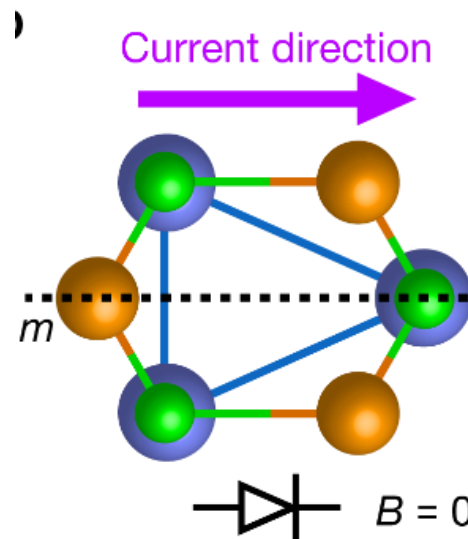


Current & strain along armchair direction

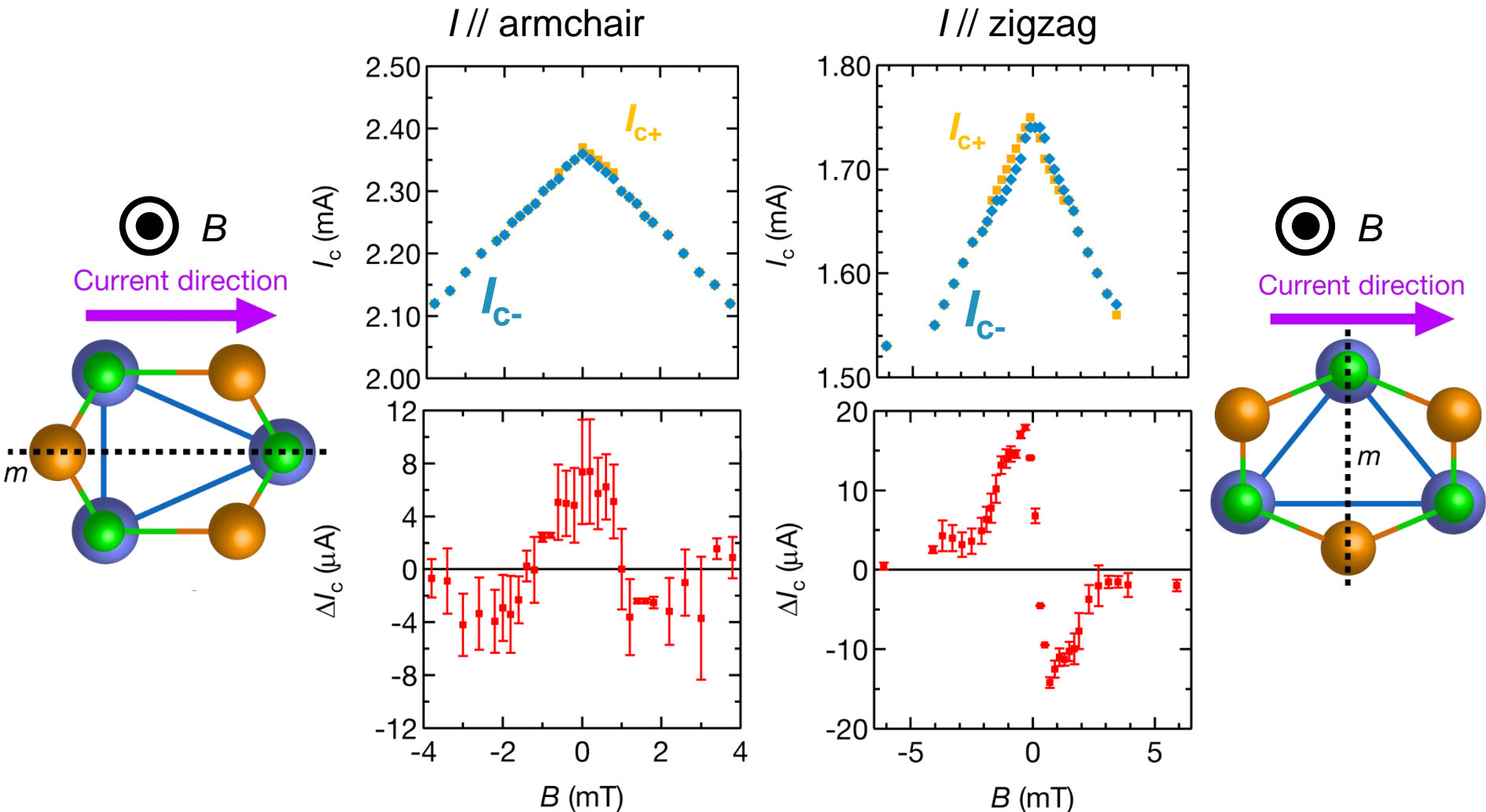
Unstrained



Strained



Magnetic Field Dependence in Strained Devices



B -even in armchair and B -odd in zigzag configuration
→ Diode effect originating from **crystal symmetry**

Discussion on longitudinal nonreciprocity

Nonlinear response of longitudinal transport σ_{xx} under TRS

Materials	Phenomena	Band theory	Experiment
PN junction	Nonreciprocal transport	allowed	
Conductor (BiTeBr)	Nonreciprocal transport	forbidden	Observed with B
Semiconductor (TMD nanotube, vdW hetero, Strain)	Bulk photovoltaic effect (shift current)	allowed	Observed w/o B
Superconductor (PbTaTe ₂)	Nonreciprocal transport Superconducting diode effect	forbidden	Observed w/o B (e-e interaction)

Single band model in polar conductor

Noncentrosymmetric crystals

- × Spatial inversion symmetry
- ✓ Translational symmetry

$$\rightarrow \varepsilon(k, \sigma) = \varepsilon(-k, -\sigma) \text{ under TRS}$$

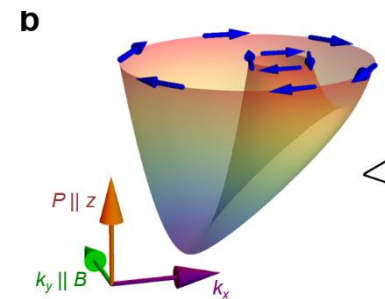
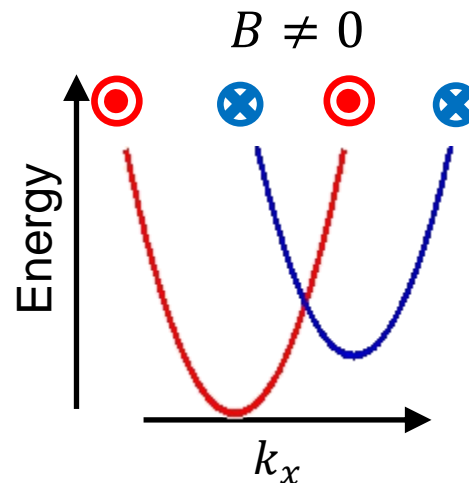
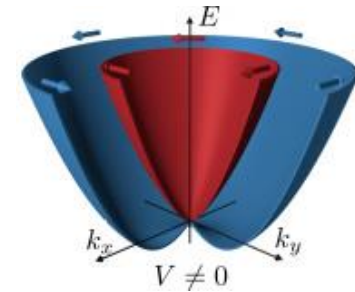
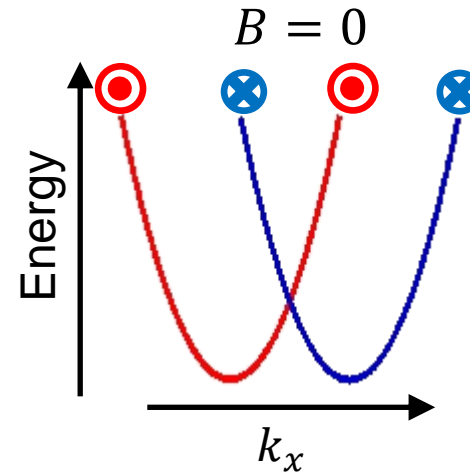
Thus nonreciprocity is not allowed.



Break TRS by magnetic field, and

$$\rightarrow \varepsilon(k, \sigma) \neq \varepsilon(-k, -\sigma)$$

Then reciprocity is allowed within band scheme



Discussion

- In PN junction, nonreciprocity is allowed because of the lack of translational symmetry.
- BPVE from shift current model is a 2 band phenomenon, and the band picture allows nonreciprocity within the 2 band model.
- $R_{xx}^{2\omega}$ is allowed by breaking TRS (finite B).
- Nonlinear Hall effect is allowed within a single band model even under TRS.
- Nonreciprocity under TRS is allowed when one takes electron correlation or scattering into account.

Discussion on SDE under TRS

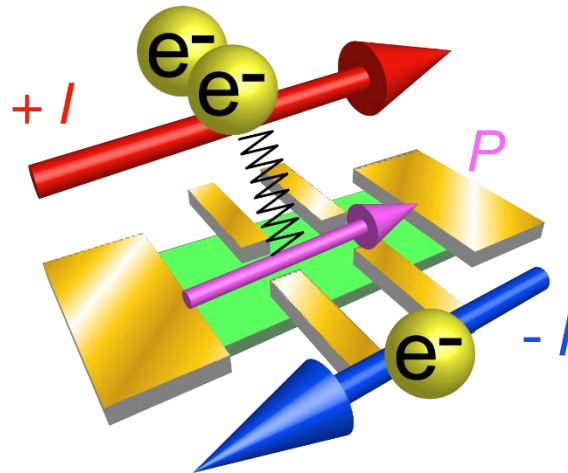
Under TRS, I_{c+} and I_{c-} are equivalent \rightarrow **Diode effect under TRS is not allowed**

Nonreciprocal transport under **TRS** becomes allowed by **electron correlation**

T. Morimoto & N. Nagaosa, *Sci. Rep.* **8**, 2973 (2018).



Interaction between **electric polarization** and **current**



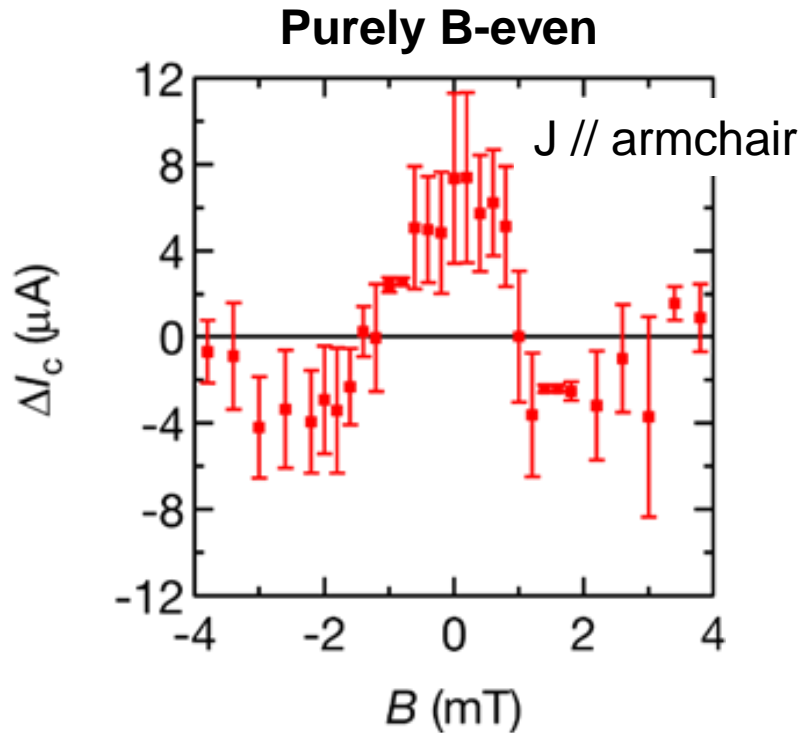
Discussion

Nonlinear response of longitudinal transport σ_{xx}

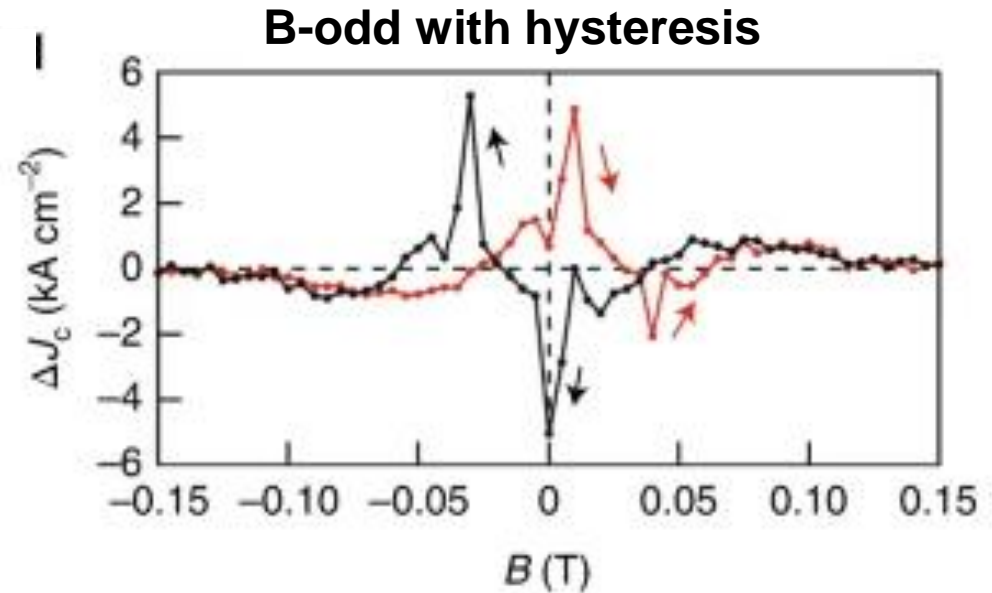
Materials	Phenomena	Band theory	Experiment
PN junction	Nonreciprocal transport	allowed	
Conductor (BiTeI)	Nonreciprocal transport	forbidden (scattering, e-e interactions)	Observed with B
Semiconductor (TMD nanotube, vdW hetero, Strain)	Bulk photovoltaic effect (shift current)	allowed (Interband)	Observed w/o B
Superconductor (PbTaTe ₂)	Nonreciprocal transport Superconducting diode effect	forbidden (e-e interactions)	Observed w/o B (e-e interaction)

Comparison between w/o and w TRS

Strained PbTaSe2 (TRS)



SC/FM Multilayers by Ono group
(Broken TRS)



Liu, Itahashi *et al.*, *Scie. Adv.*, accepted

Narita, Ono *et al.*, *Nat. Nano.* **17**, 823 (2022).

Twisted trilayer Graphene: *Nat. Phys.* **18**, 1221 (2022)

Twisted BISCCO; *Science* **382**, 1422 (2023)

Kagome CsV3Sb5, *Nature* **630**, 64 (2024)

Chiral molecule/TaS2, *Nature* **632**, 69 (2024)

➔ Probe for broken TRS in superconductors

Summary

- Polar semiconductors
 - Bulk photovoltaic effect
- Polar semiconductors/metals
 - Nonreciprocal transport (2nd harmonic resistance)
 - Nonlinear Hall effect
- Noncentrosymmetric superconductors
 - Nonreciprocal transport/Nonlinear Hall effect
 - Superconducting diode effect



“It is only slightly overstating the case to say that
physics is the study of symmetry”

P. W. Anderson, “More is different” Science 177, 393 (1972)