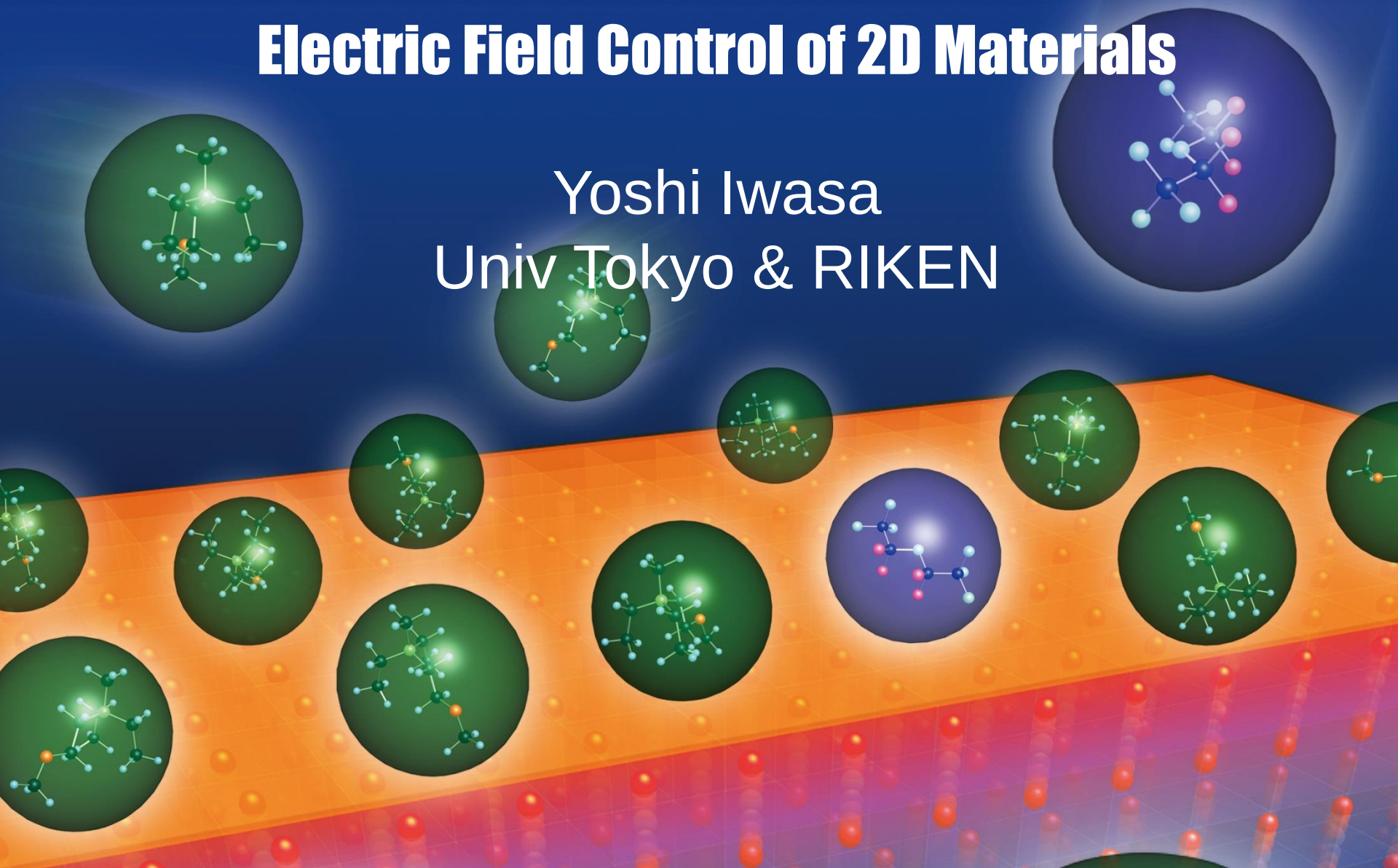
August 23-September 2, 2016
Cargèse, Corsica, France

Electric Field Control of 2D Materials

Yoshi Iwasa
Univ Tokyo & RIKEN



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Reshef Tenne

Alla Zak

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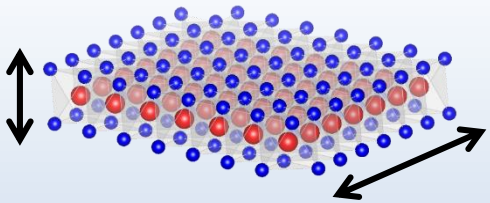
RIKEN CEMS & U Tokyo

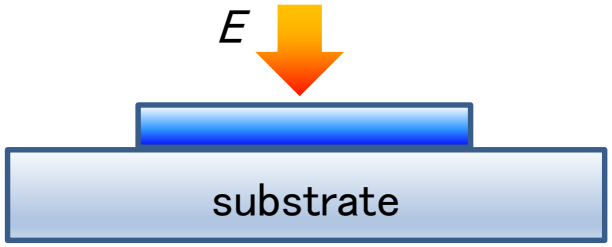
N. Nagaosa
M. Ezawa
S. Hoshino
R. Wakatsuki

Electric field effects in 2D materials

10^0 ~ 10^1 nm  10^0 ~ 10^1 μm

Small volume!

Transverse electric field



Field effect transistor

- E ~ 10^7 MV/cm

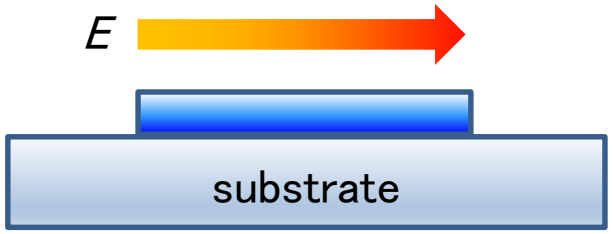
e.g.
Monolayer transistor

K. S. Novoselov *et al. Science* (2004).
B. Radisavljevic *et al. Nat. Nanotech.* (2011).

Gate-induced superconductivity

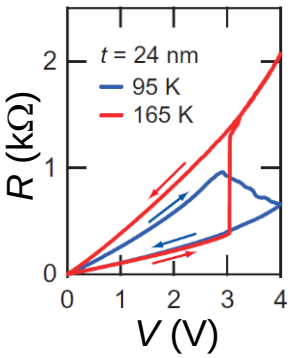
J. T. Ye *et al. Nat. Mater.* (2010).

Longitudinal electric field



Nonlinear transport

- E ~ 10^4 MV/cm
- J = 1 ~ 100 MA/cm^2.



e.g. Current switching in 1T-TaS_2.

M. Yoshida *et al. Sci. Adv.* (2015).
A. W. Tsen *et al. PNAS* (2015).
I. Vaskivskyi *et al. Nat. Commun.* (2016).

OUTLINE

(1) Transverse electric field effect

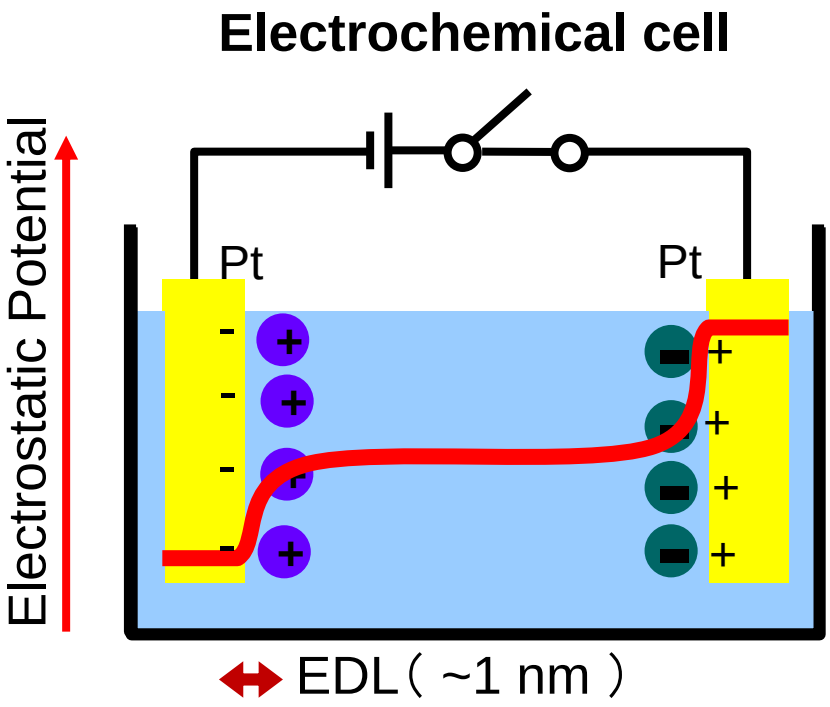
- 1-1 Electric double layer transistor (EDLT)
- 1-2 A new aspect as a 2D superconductor
- 1-3 Superconductivity in inorganic nanotubes

(2) Longitudinal electric field effect

- 2-1 Thinning effect in 1T-TaS2
- 2-2 Nonvolatile current switching

Basic Ideas

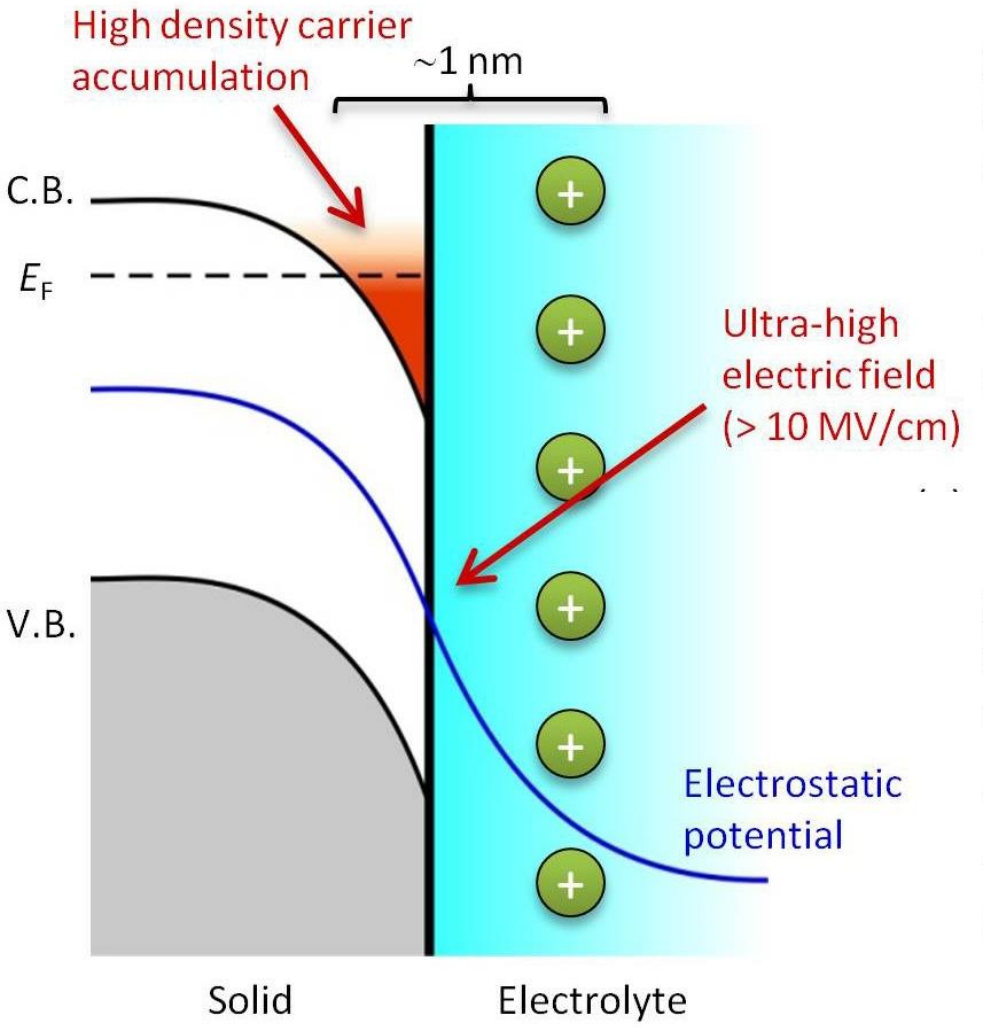
Electric Double Layer (EDL)
at interfaces between electronic and ionic conductors



Hermann von Helmholtz (1821-1894)

Helmholtz's electric double layer (1853)

Electric Double Layer



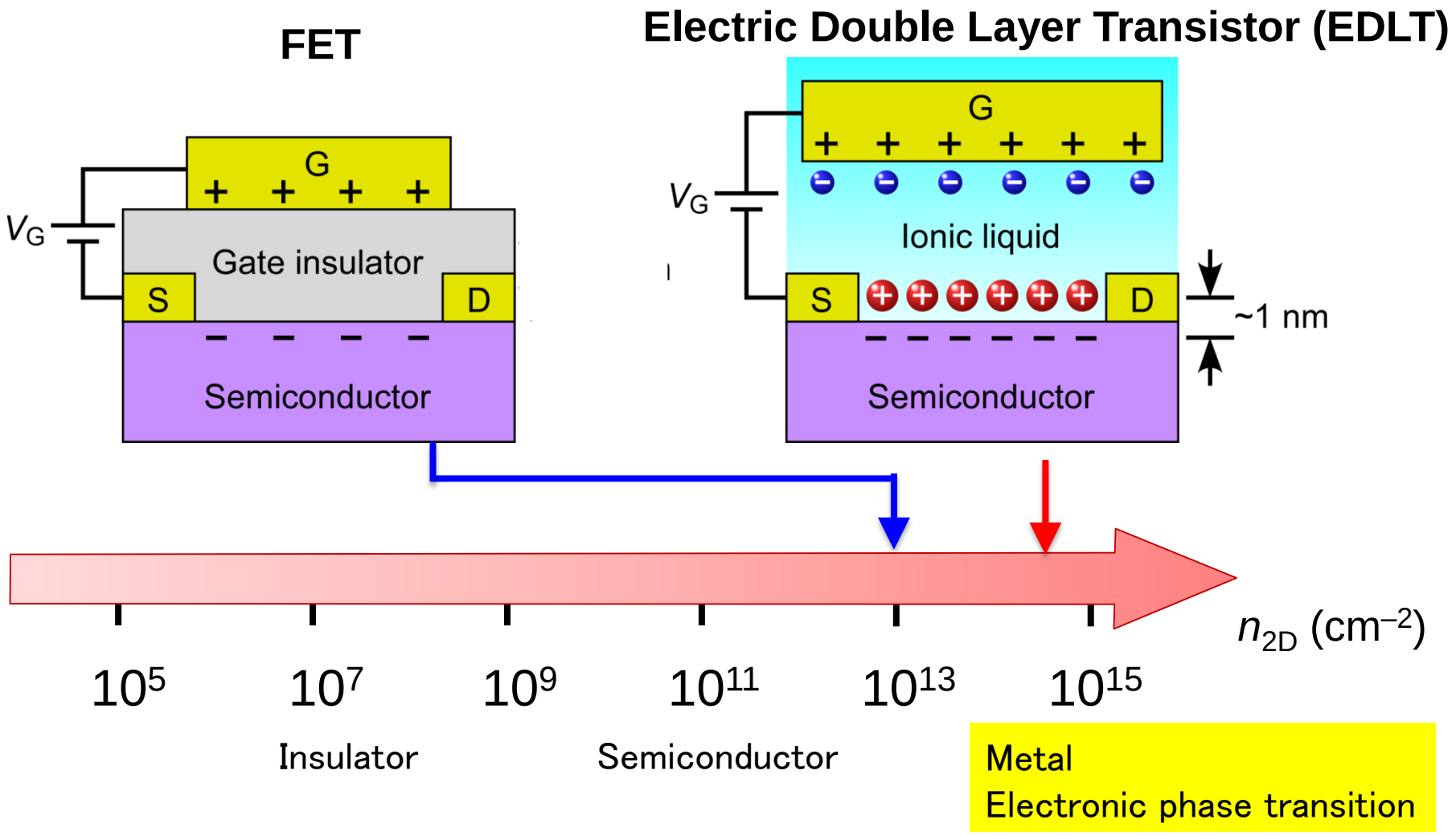
☛electrochemical interface
similar to solid heterointerface

☛High electric field x 100

☛ high density charge x 100
➡ EDLC (super capacitor)

☛Versatile

From FET to EDLT (Electric Double Layer Transistor)



History of semiconductor–electrolyte interfaces

Early works on Ge and Si

Ge J. Bardeen, Nobel Lecture (1956)

ISFET P. Bergveld: IEEE Trans. Biomed. Eng. **BM17**, 70 (1970).

Si A. Tardella, and J.-N. Chazalviel: Phys. Rev. B **32**, 2439 (1985).

Conducting polymers

H. S. White, G. P. Kittlesen , M. S. Wrighton: J. Am. Chem. Soc. **106**, 5375 (1984).

Y. Harima, T. Eguchi, K. Yamashita: Synth. Met. **95**, 69 (1998).

Carbon nanotube transistors

M. Krüger, M. R. Buitelaar, T. Nussbaumer, C. Schönenberger, and L. Forró: Appl. Phys. Lett. **78**, 1291 (2001).

S. Rosenblatt, Y. Yaish, J. Park, J. Gore, V. Sazonova, and P. L. McEuen: Nano Lett. **2**, 869(2002).

Organic transistors

M. Taniguchi and T. Kawai, Appl. Phys. Lett. **85**, 3298 (2004).

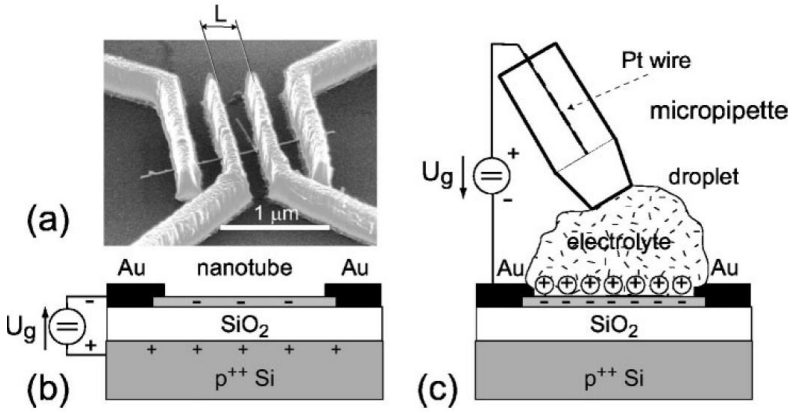
H. Shimotani, G. Diguet, Y. Iwasa: Appl. Phys. Lett. **86**, 022104 (2005).

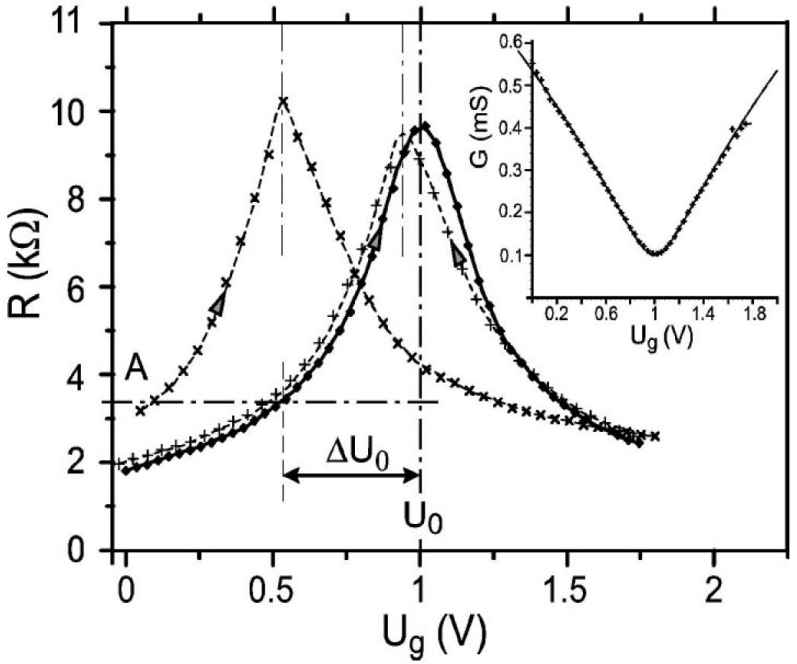
M. J. Panzer, C. R. Newman, and C. D. Frisbie: Appl. Phys. Lett. **86**, 103503 (2005).

D. Nilsson and M. Berggren, Adv. Mater. 17, 353 (2005).

Carbon nanotube EDLTs

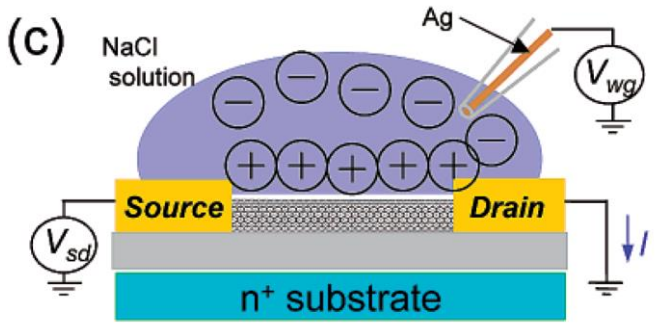
Multi-walled

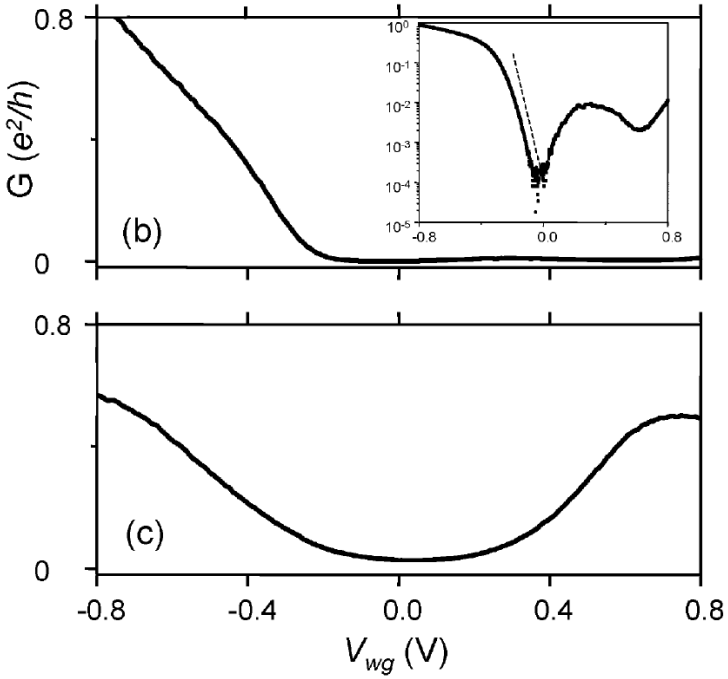




M. Krüger et al., APL (2001)

Single-walled

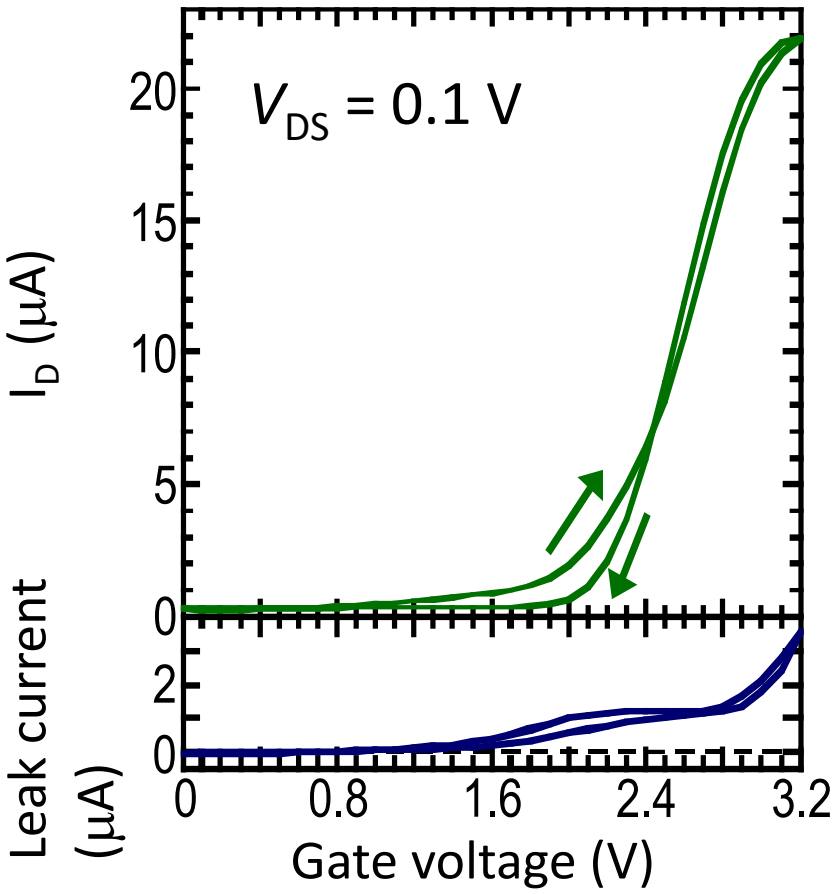




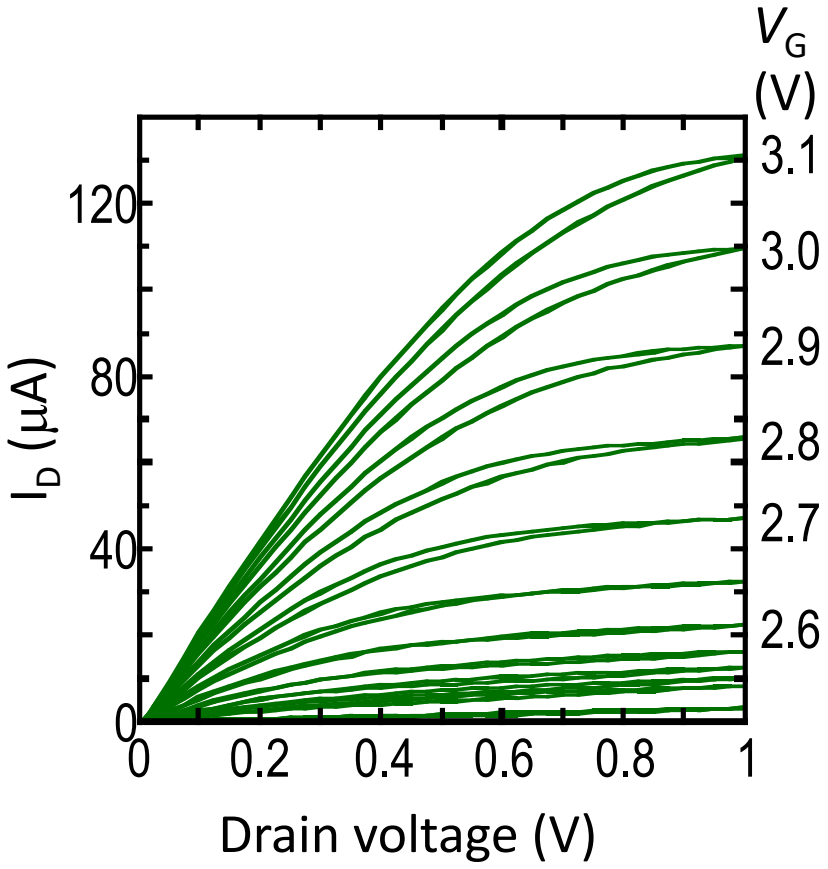
S. Rosenblatt, Nano Lett. (2002).

Characteristics of ZnO-EDLT

Transfer curve



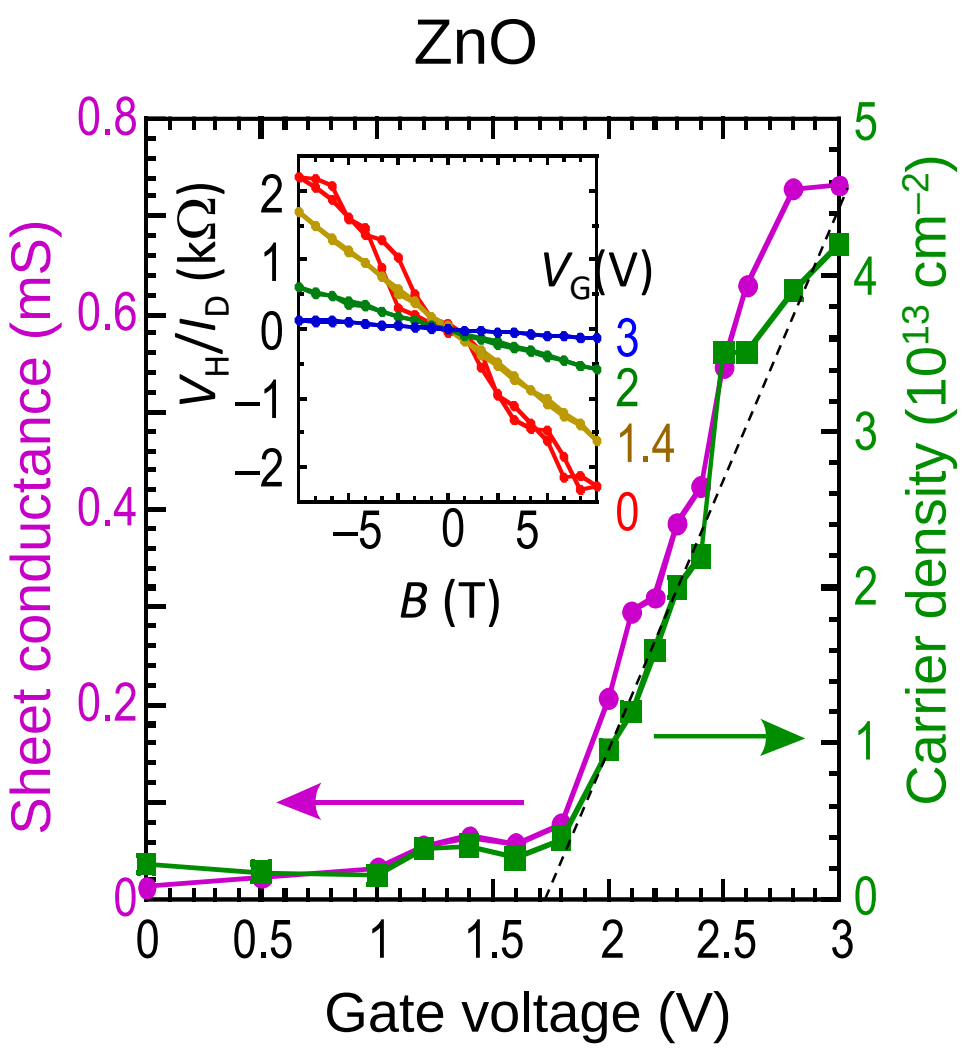
Output curve



n-type transistor operation

H. Shimotani *et al.*, *Appl. Phys. Lett.* **91**, 082106 (2007).

Hall effect measurement of EDL



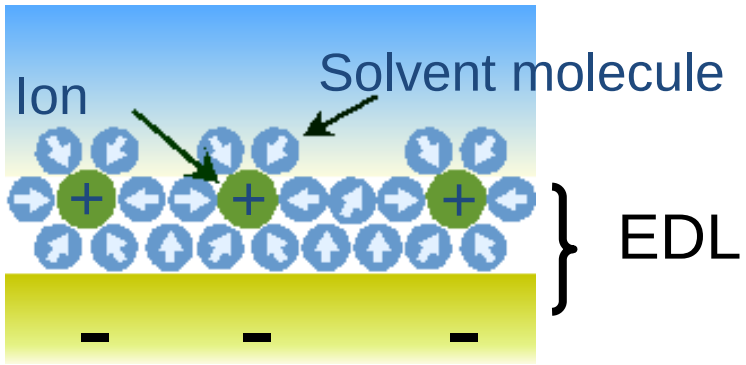
$$ne = Q = CV$$

C ~ 7.8 μF/cm^2

(cf. 15 nF/cm^2 for SiO_2)

($\varepsilon = 10\ \varepsilon_0$ for PEO solvent)

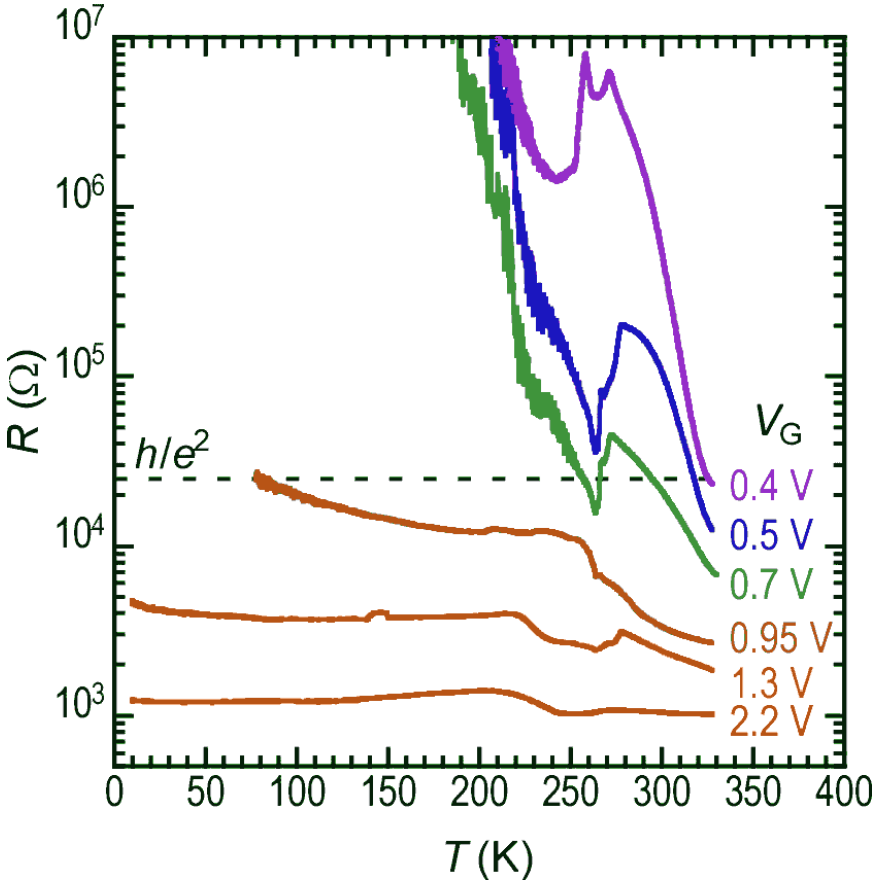
thickness of EDL ~ 1 nm



H. Shimotani *et al.*, *Appl. Phys. Lett.* **91**, 082106 (2007).

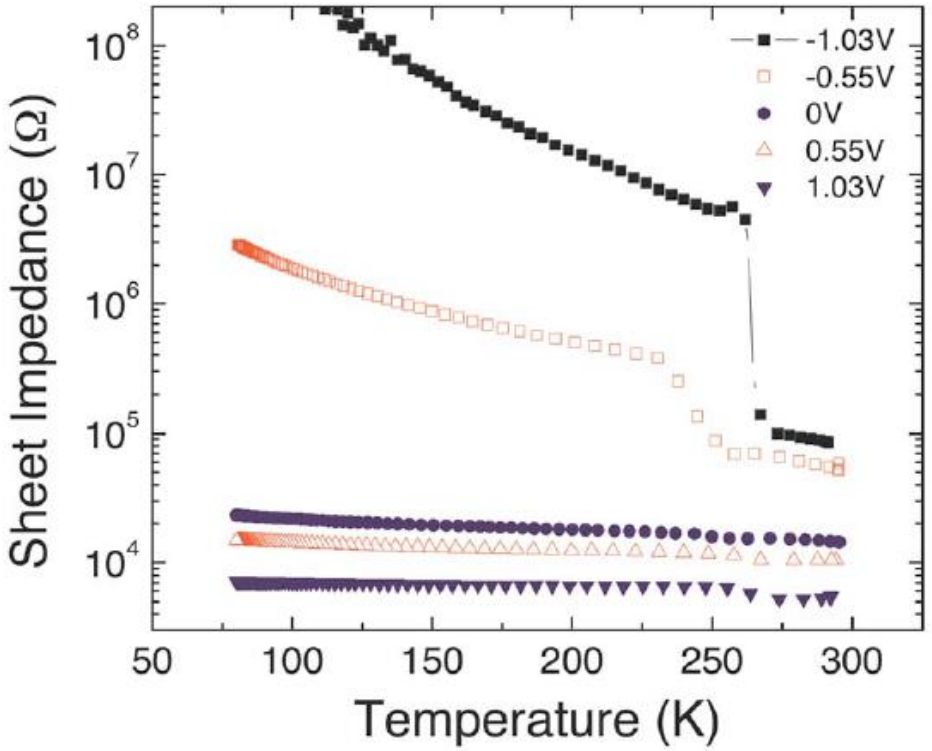
Insulator–metal transitions in oxide semiconductors

ZnO



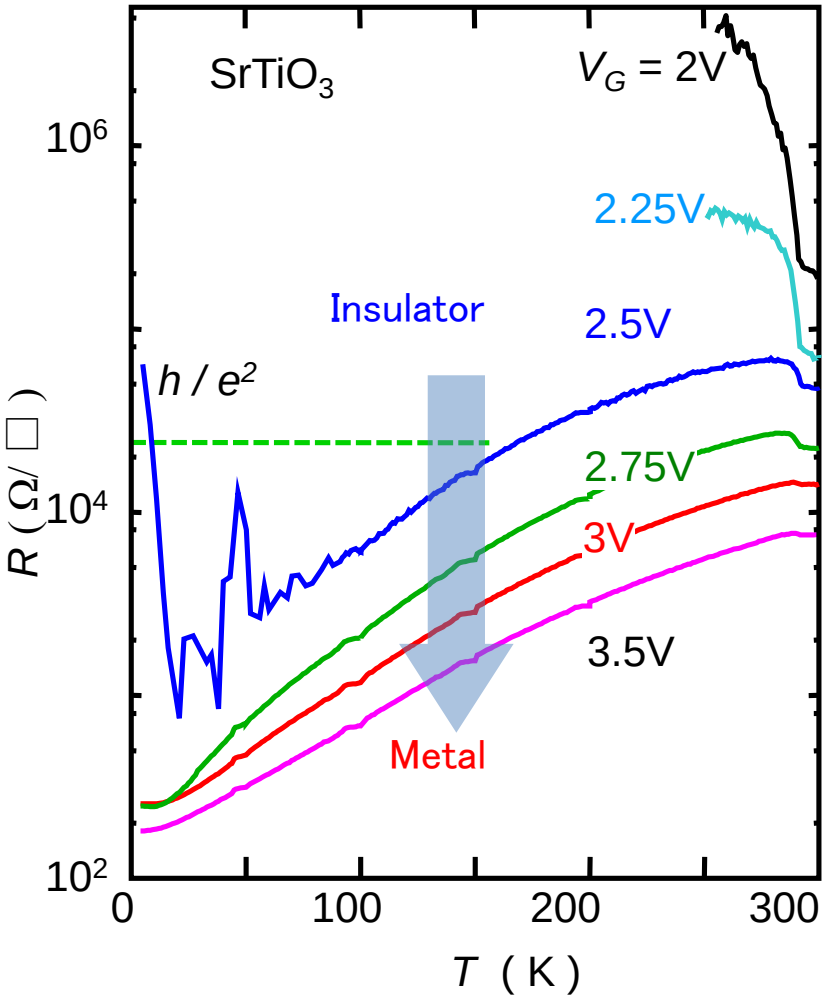
H. Shimotani *et al.*, *Appl. Phys. Lett.* (2007).

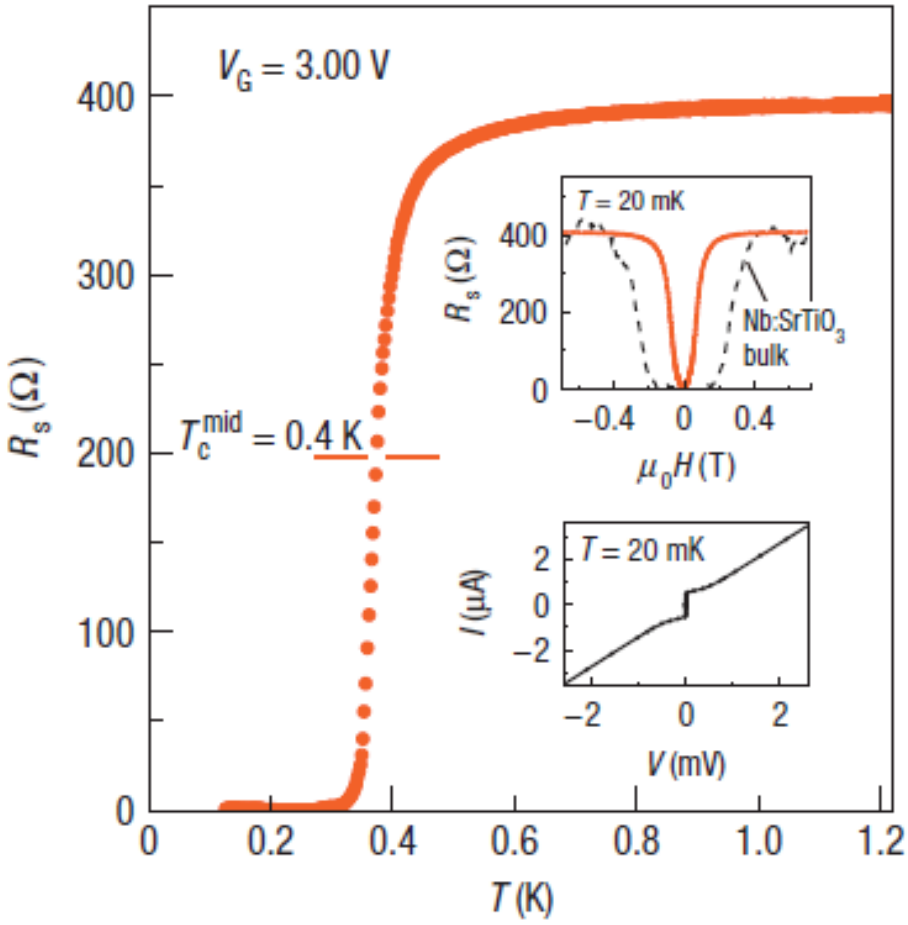
InO_x



R. Misra *et al.*, *Appl. Phys. Lett.* (2007).

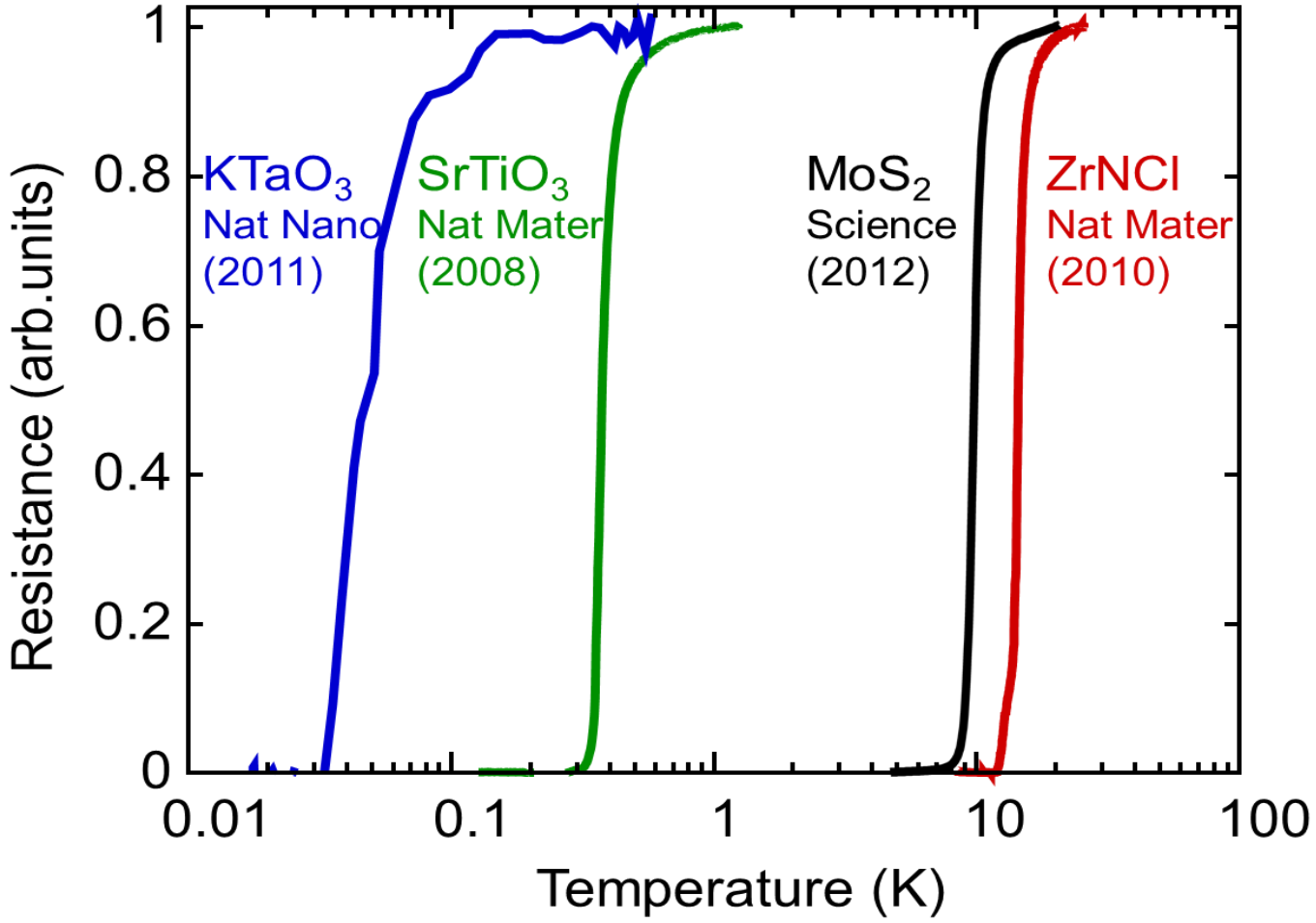
Electric field induced superconductivity in $SrTiO_3$





K. Ueno *et al. Nater Materials* (2008).

Superconductivity induced by EDLT



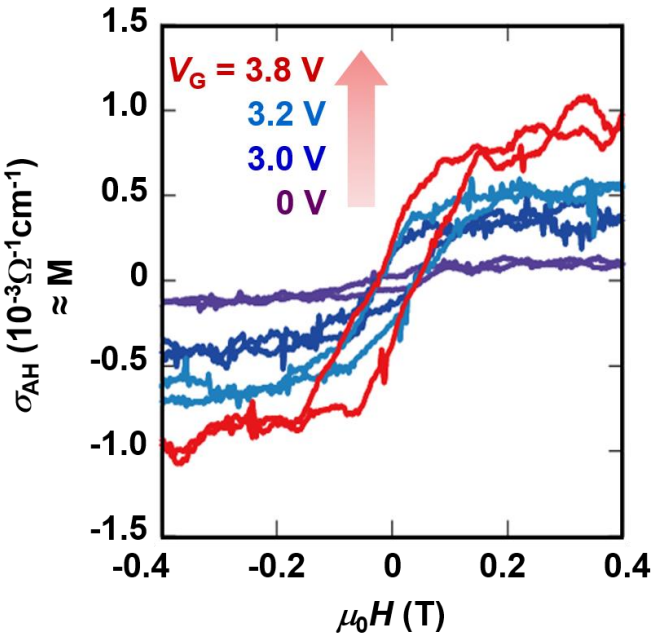
STO, YBCO: *Goldman et al., PRL (2011)*
LSCO: *Bozovic et al., Nature (2011)*
MoS_2: *Takagi et al APL (2012)*
WS_2: *Morpurgo et al., Nano Lett (2015)*
PCCO: *Ariando, PRB (2014)*

Electrochemical

TaS_2: *Y. Yu et al., Nat Nano (2015)*
$MoSe_2$, $MoTe_2$: *W. Shi et al. Sci Rep (2015)*
FeSe: J. Shiogai et al., *Nat Phys (2016)*

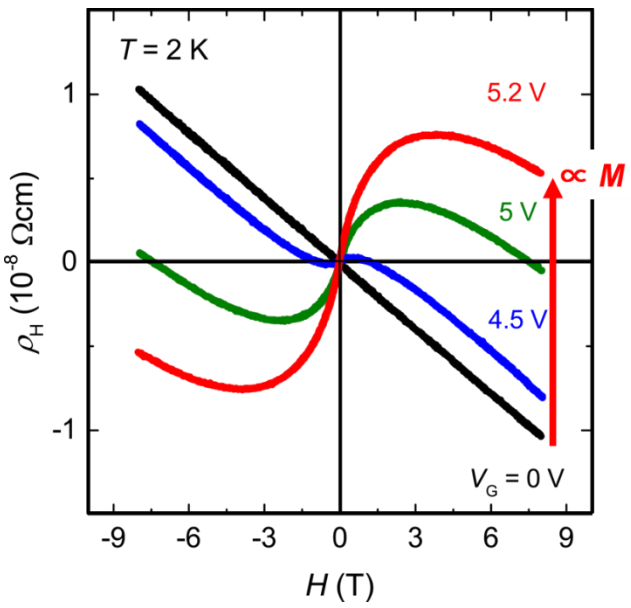
Gate induced ferromagnetism

$Co_xTi_{1-x}O_2$



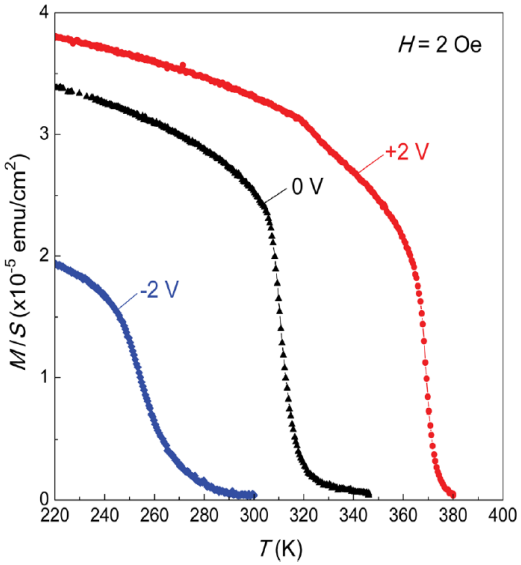
Y. Yamada *et al.*,
Science, 2011.

Pt



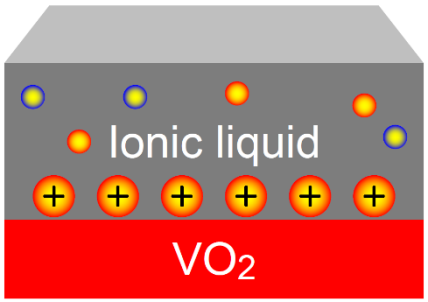
S. Shimizu *et al.*,
PRL, 2013.

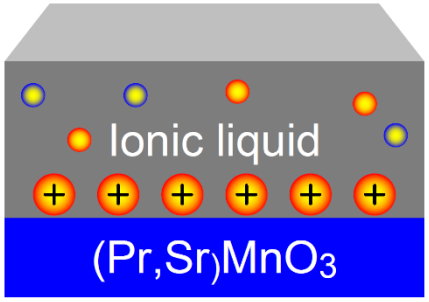
Co

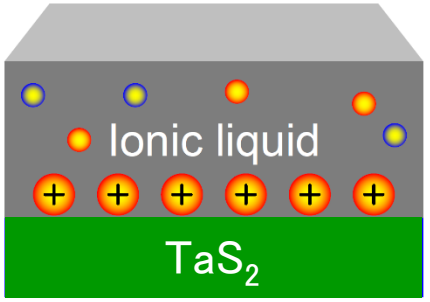


K. Shimamura *et al.*,
APL, 2012.

Electric-field induced phase transitions in correlated electron systems







M-I transitions

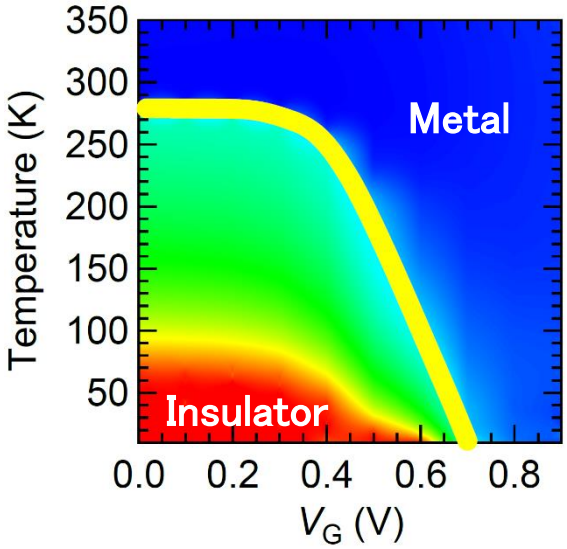
M. Nakano *et al.*,
Nature, 2012.

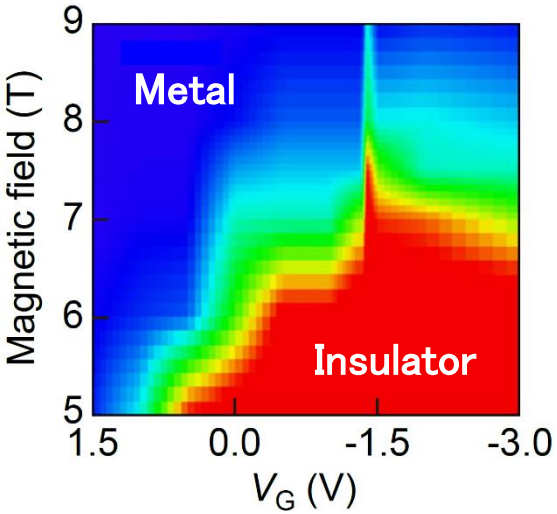
M-COO transitions

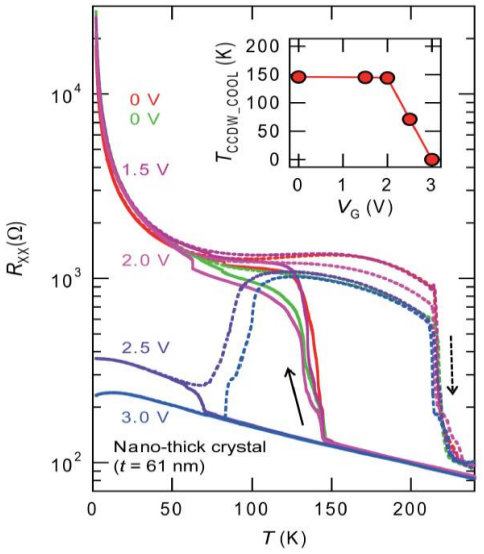
T. Hatano, *et al.*,
Sci. Rep., 2013.

CDW transitions

M. Yoshida, *et al.*,
Sci. Rep., 2014.



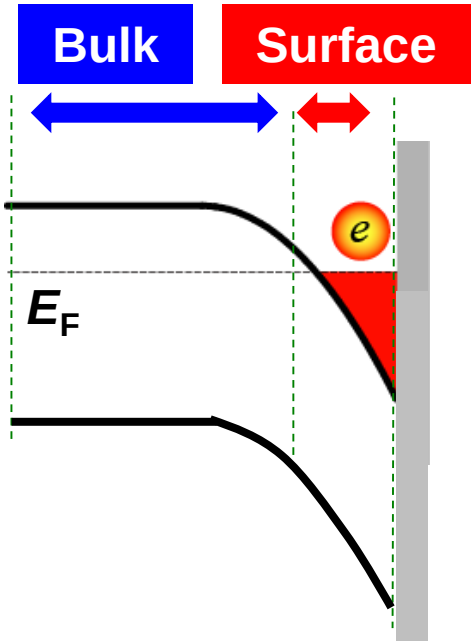




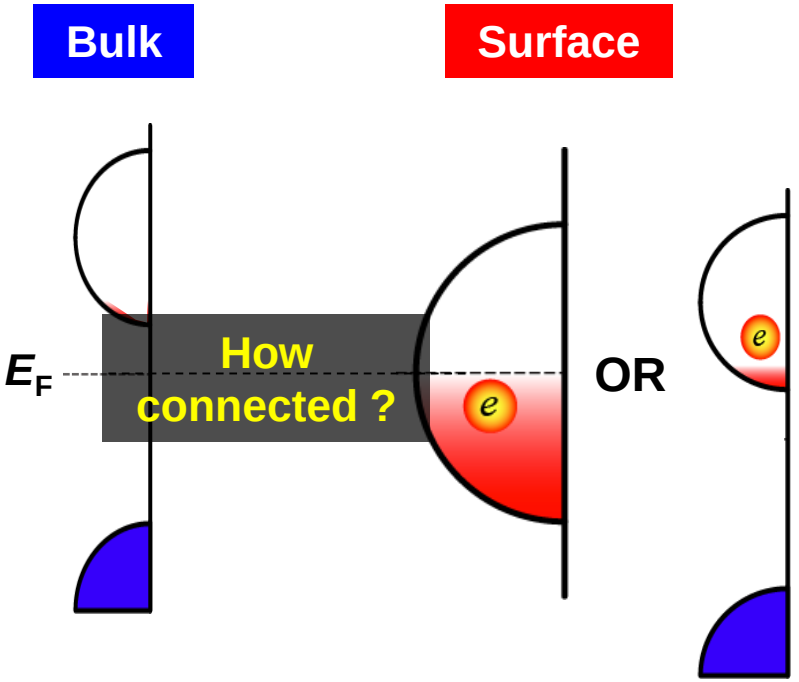
Fundamental question of correlated FETs

Conventional semiconductor ⟷ **Strongly correlated system**

Band bending

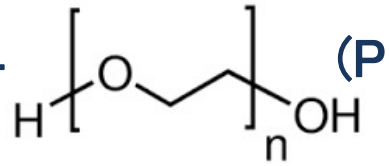


Band reconstruction



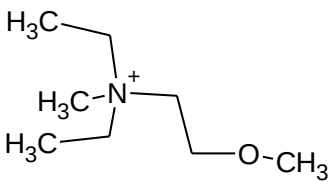
Ionic conductors as a gate dielectric

Polymer electrolytes

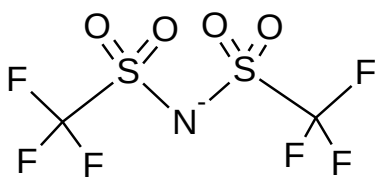
KClO4 +  (PEO or PEG)

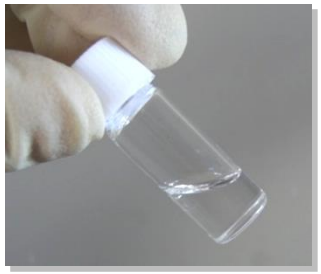
Ionic liquids

DEME



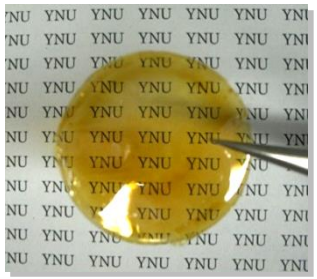
TFSI

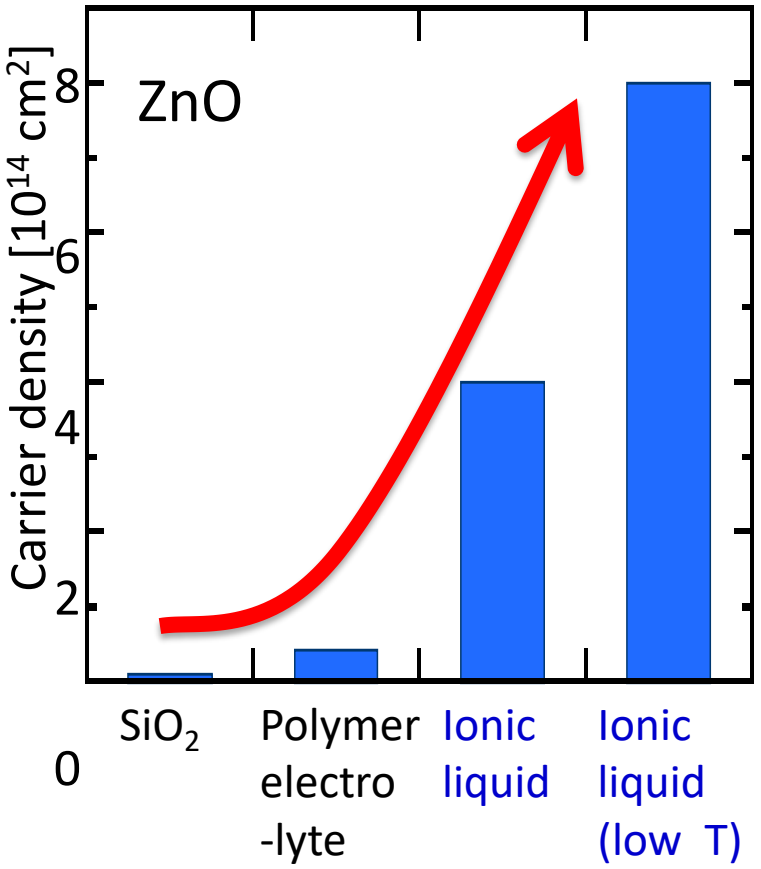




Ion gels

Ionic liquid + block copolymer

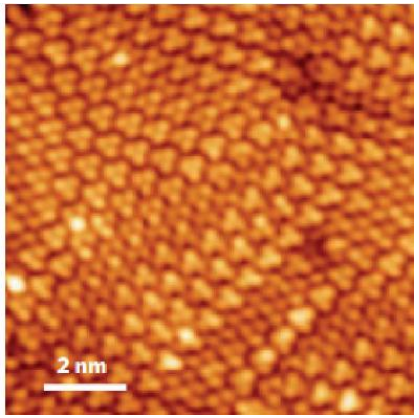




H. T. Yuan *et al.*,
Adv. Funct. Mater. 19, 1046 (2009)

Emerging 2D superconductors

MBE-grown



Pb-single layer (1L)
Science **324**, 1314 (2009).
Nature Phys. **6**, 104 (2014).

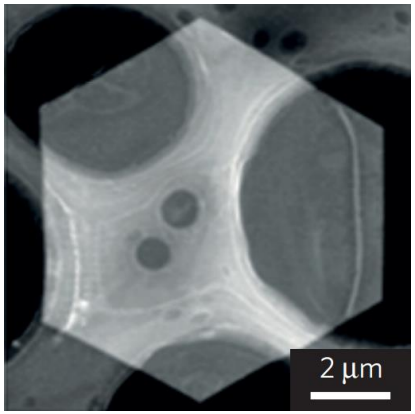
In-1L
PRL **107**, 207001 (2011).

FeSe-1L
CPL **29**, 03742 (2012).

Ga-2L
*PRL, **114**, 107003* (2015).
Science, aaa7154 (2015).

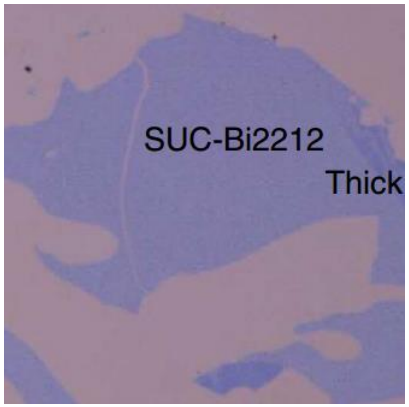
Tl-Pb-1L
PRL **115**, 147003 (2015).

CVD-grown



Mo_2C-1～2L
Nature Mat. **14**, 1135 (2015)

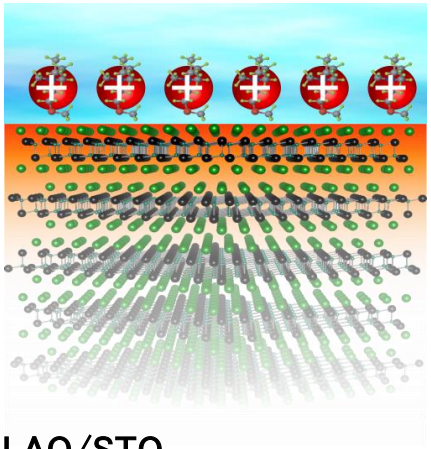
mechanically-exfoliated



BSCCO-1L
Nature Comm. **5**, 5708 (2014).

$NbSe_2$-1～2L
Nature Nano. **10**, 765 (2015).
Nature Phys: **12**, 92 (2016).
Nature Phys: **12**, 139 (2016).
Nature Phys: **12**, 208 (2016).

Interface, field effect



LAO/STO
Science **317**, 1196 (2007).
Nature **456**, 624 (2008).

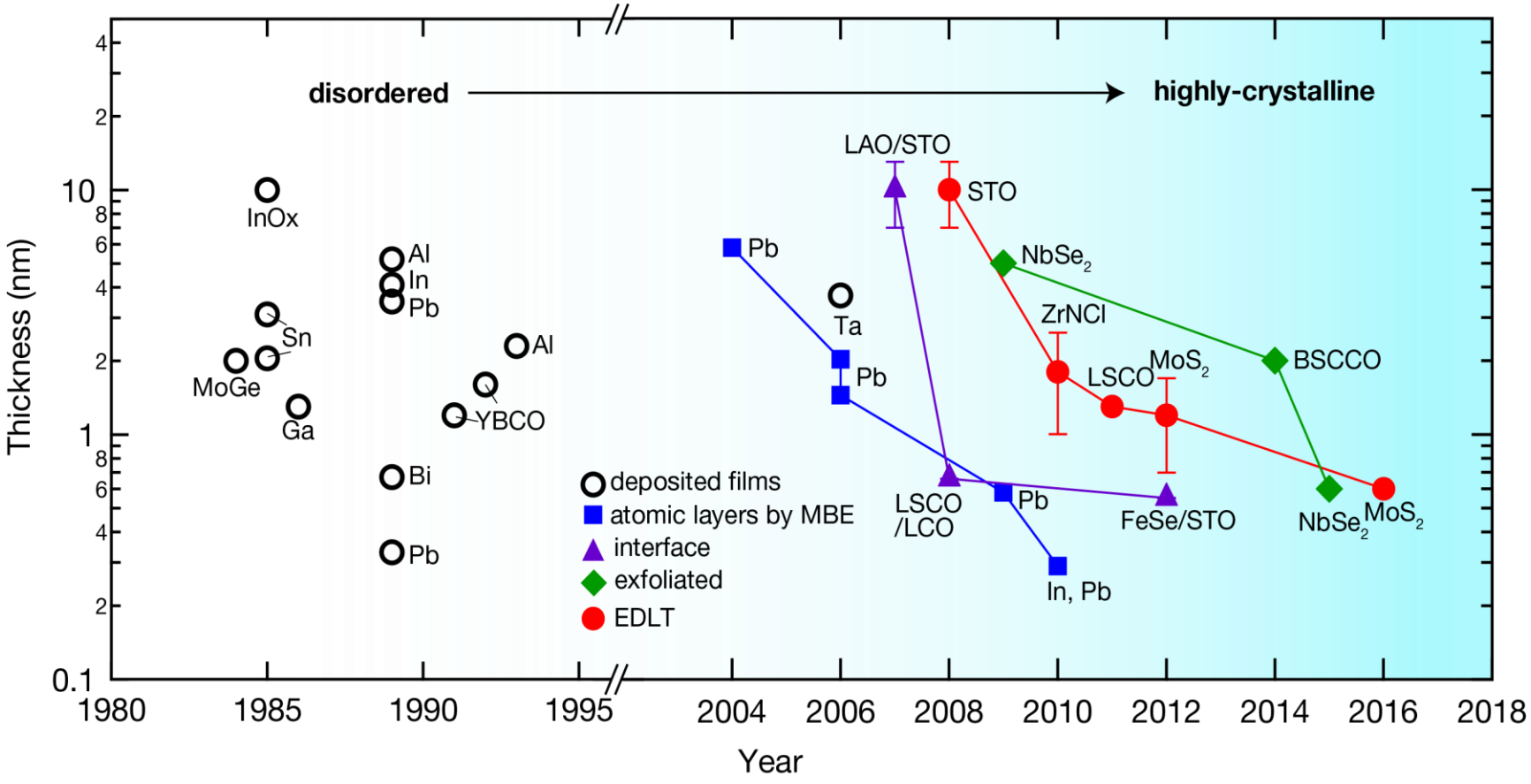
ZrNCl-quasi-1L
Nature Mat. **9**, 1314 (2010).
Science **350**, 409 (2015).

MoS_2-quasi-1L
Science **338**, 1193 (2012).
Science **350**, 1352 (2015).
Nature Phys: **12**, 144 (2016).

WS_2, $MoSe_2$ etc.
Sci. Rep. **5**, 12534 (2015)
Nano Lett. **15**, 1197 (2015).

$TiSe_2$
Nature **529**, 185 (2016)

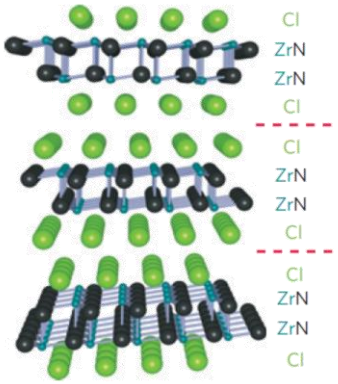
History of 2D superconductors

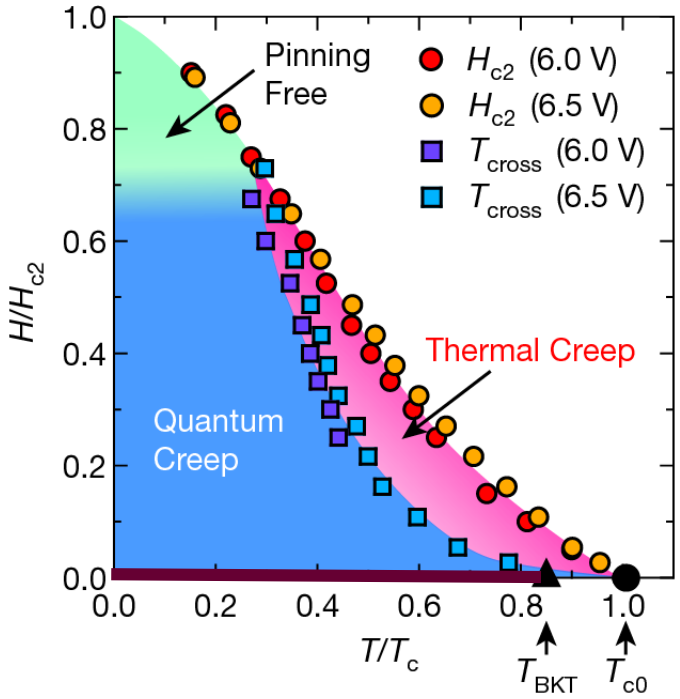


Physics of 2D superconductors

ZrNCl-EDLT

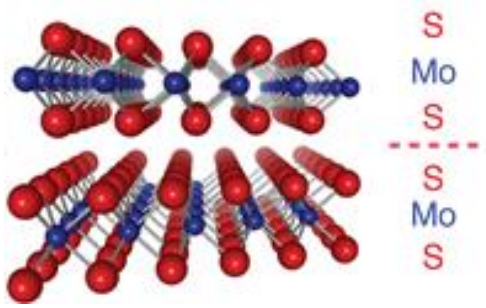
Quantum metallic states



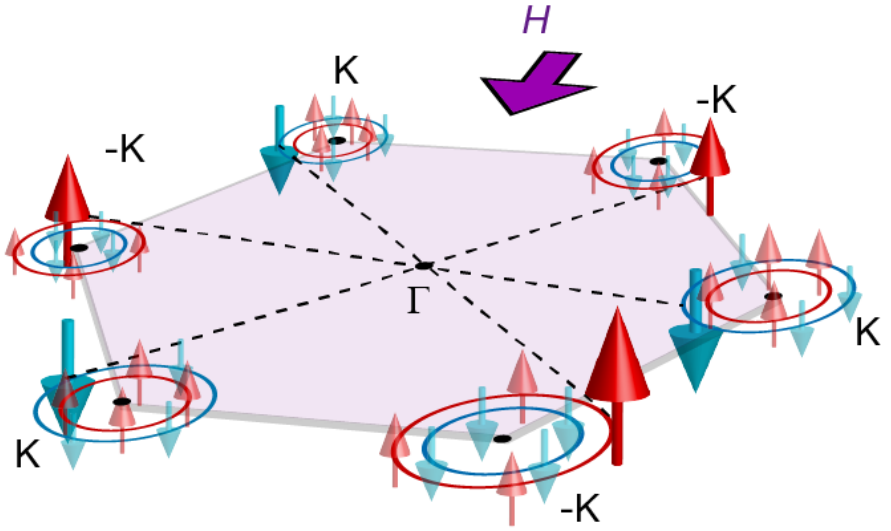


Y. Saito *et al.*
Science **350**, 409 (2015).

MoS_2-EDLT

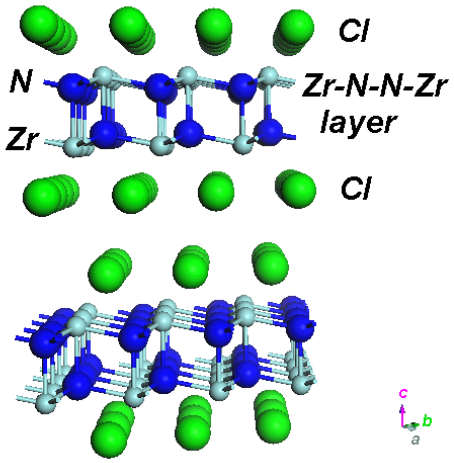


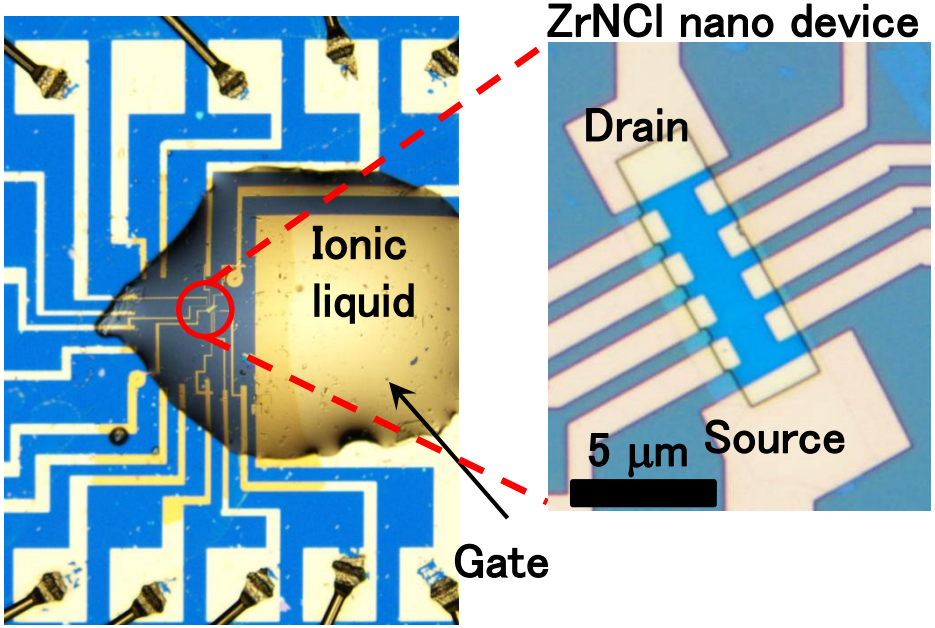
Enhanced Hc2 by spin-orbit interaction and symmetry breaking

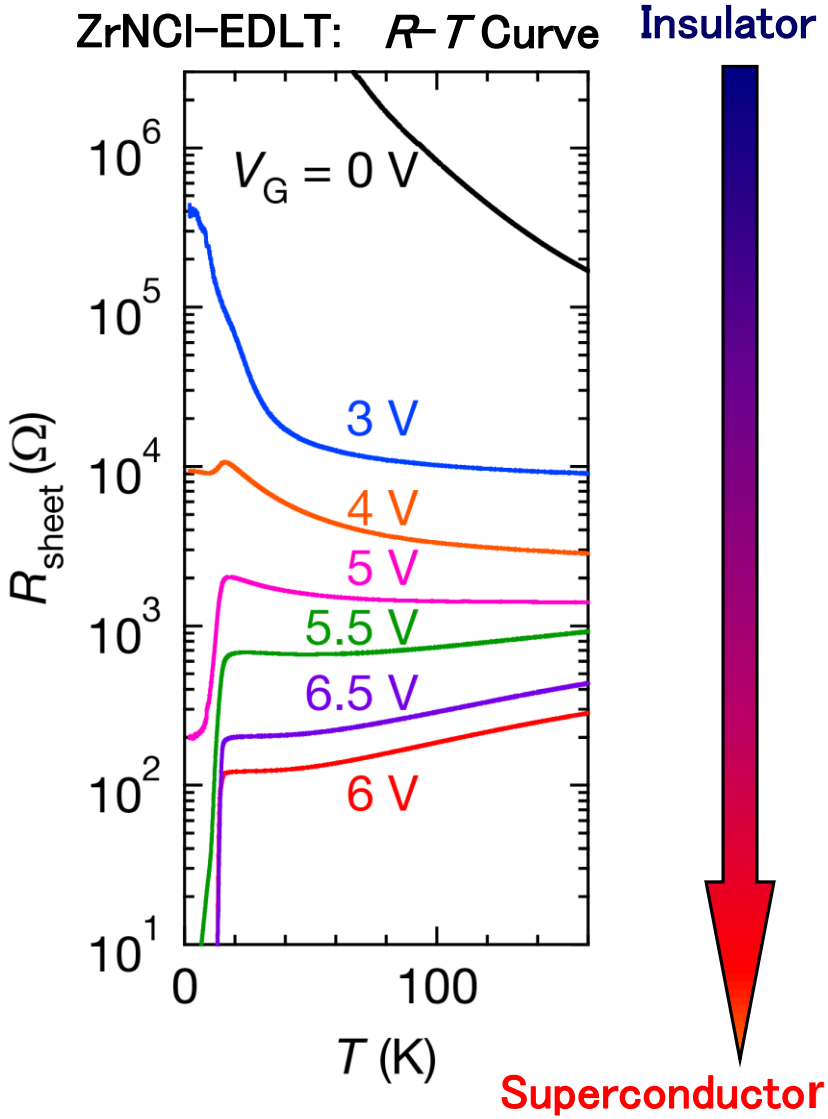


Y. Saito et al., *Nature Physics*, **12**, 144 (2016)
J. M. Lu et al., *Science* **350** 1353 (2015)

Gate Induced Superconductivity in ZrNCl

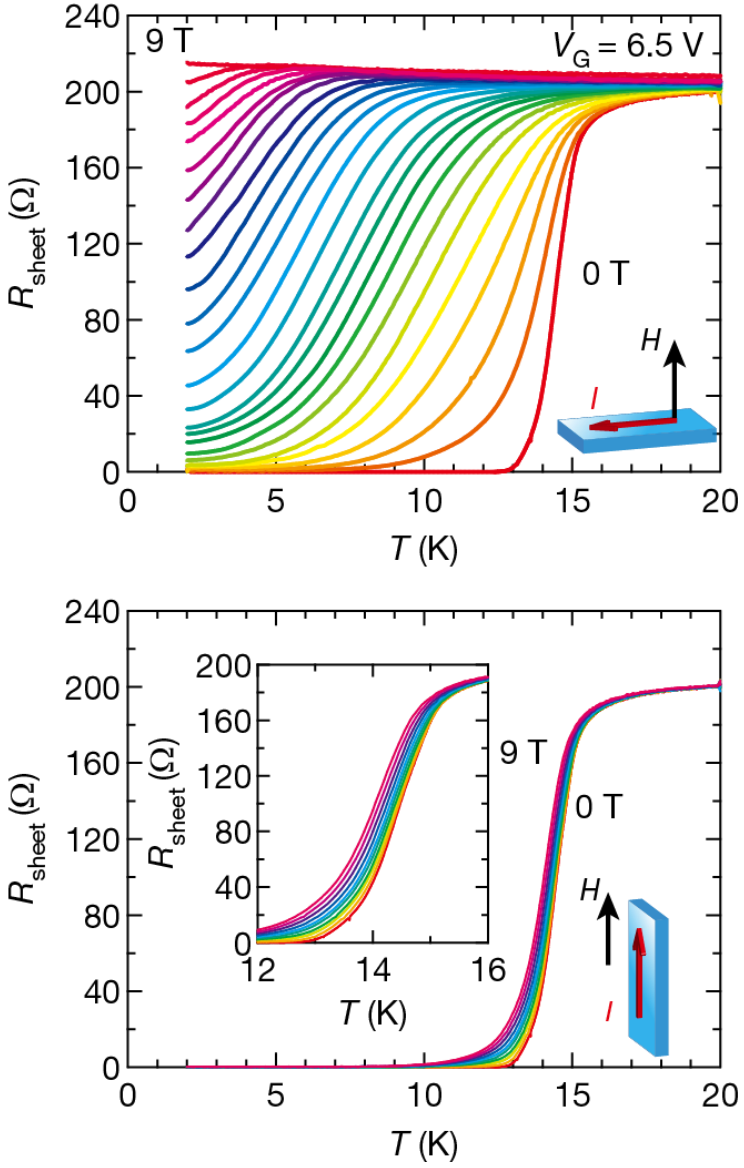


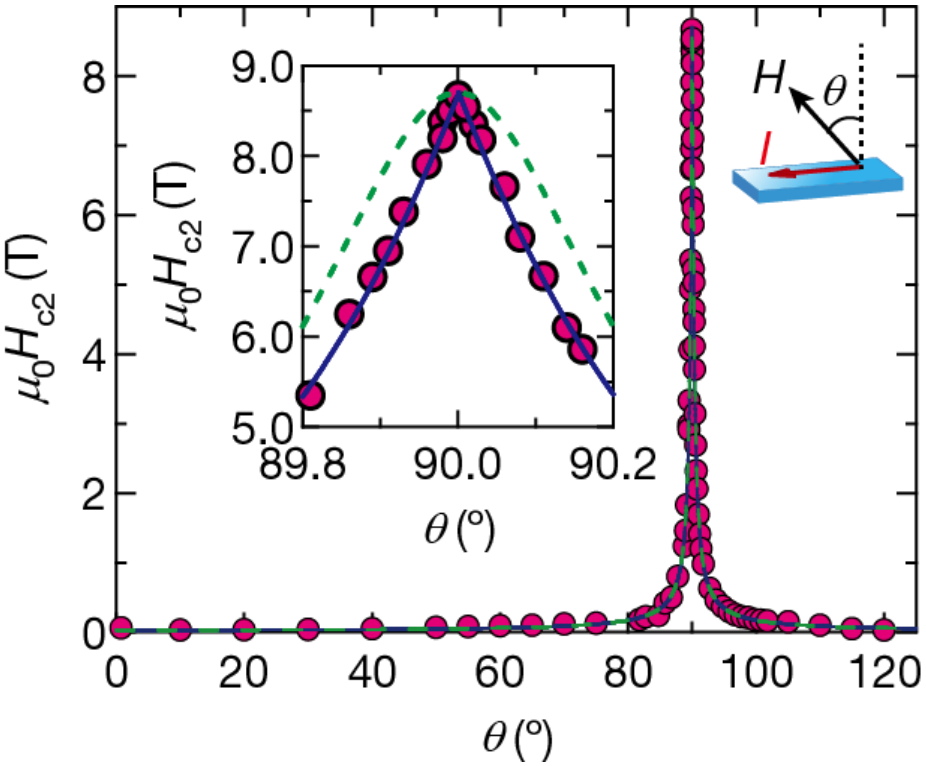




Y. Saito *et al.* *Science* **350**, 409 (2015).

R–T Curves for $H_{\perp}$ and $H_{//}$ (ZrNCl)

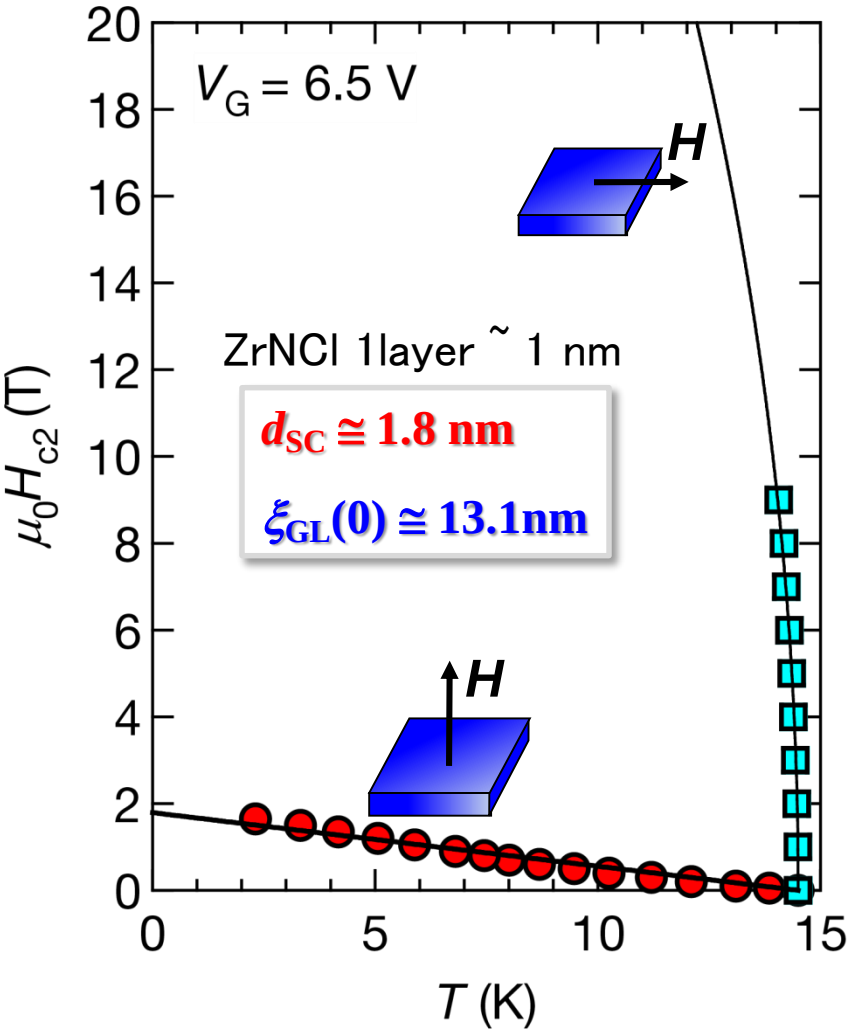




Y. Saito *et al.* *Science* **350**, 409 (2015).

Anisotropy in H_{c2} (ZrNCl)

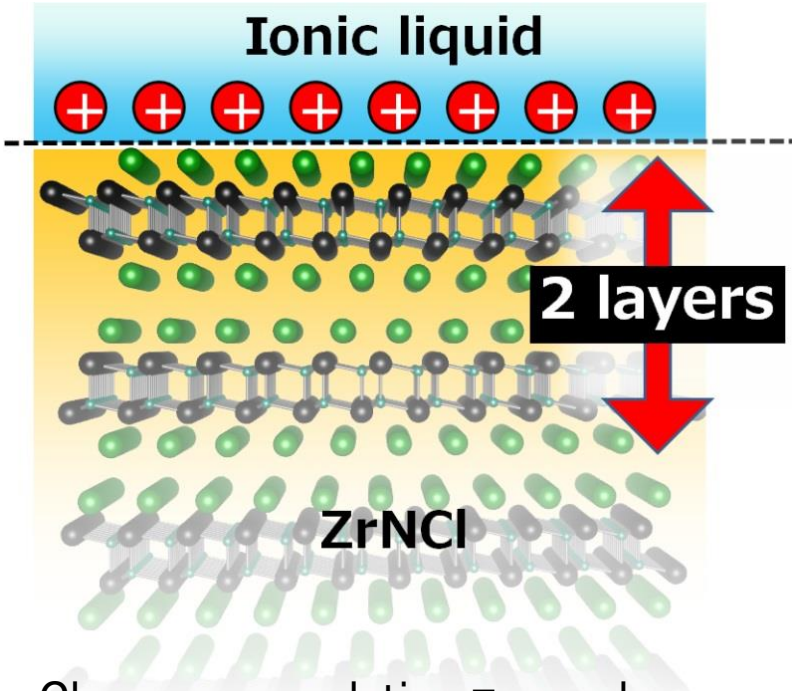
Temperature dependence of H_{c2}



2D GL model

$$\mu_0 H_{c2\perp}(T) = \frac{\Phi_0}{2\pi\xi_{GL}^2(0)}(1 - T/T_c)$$

$$\mu_0 H_{c2//}(T) = \frac{\sqrt{12}\Phi_0}{2\pi\xi_{GL}(0)d_{sc}}(1 - T/T_c)^{1/2}$$

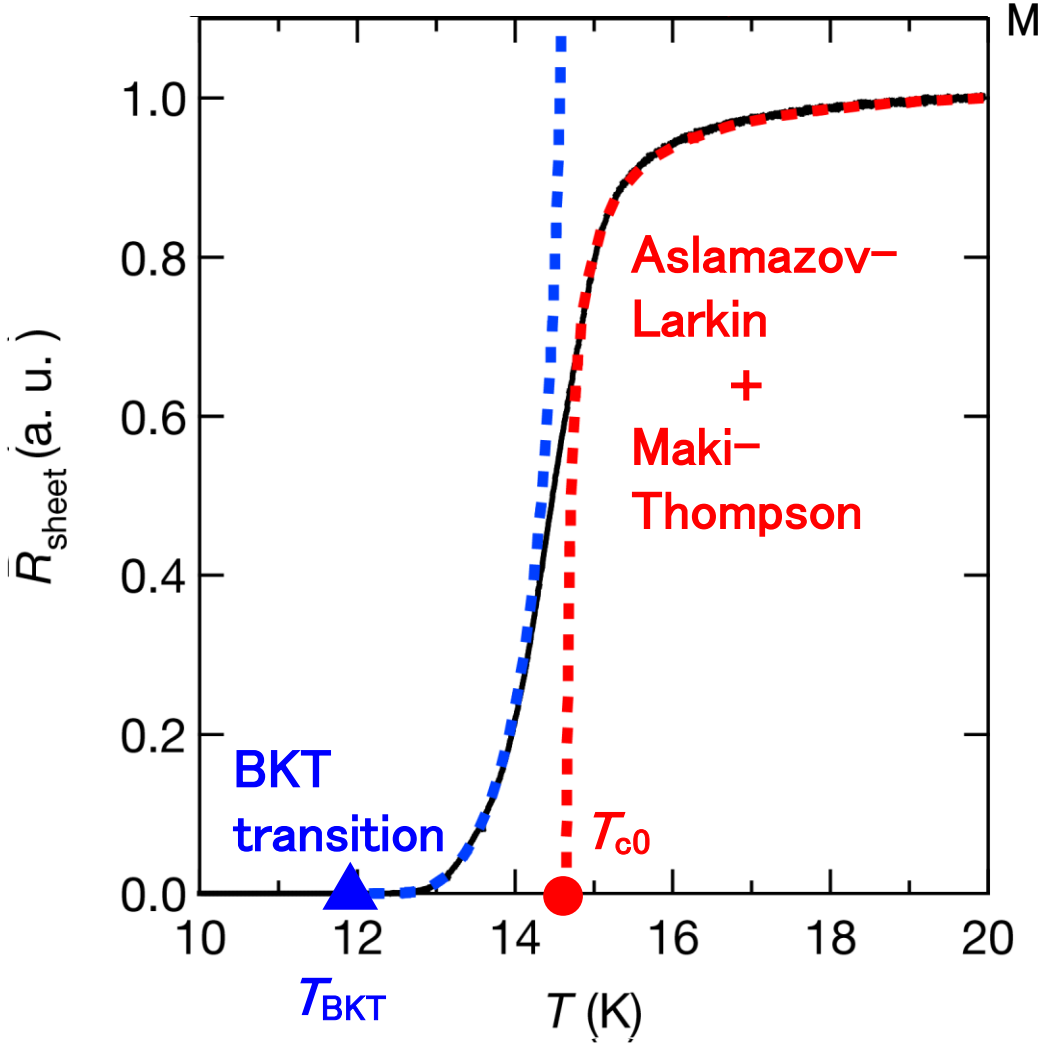


Charge accumulation = monolayer

1st principle calculation

T. Brumme et al. PRB (2014)

Superconducting fluctuation near T_c in ZrNCl

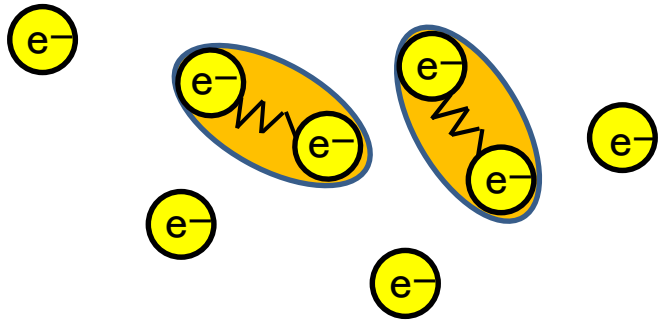


Macroscopic wave function

$$\Phi = \Phi_0 \exp(i\phi)$$

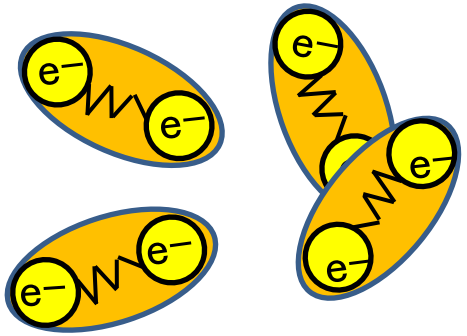
Amplitude Fluctuation

AZ+MT analysis

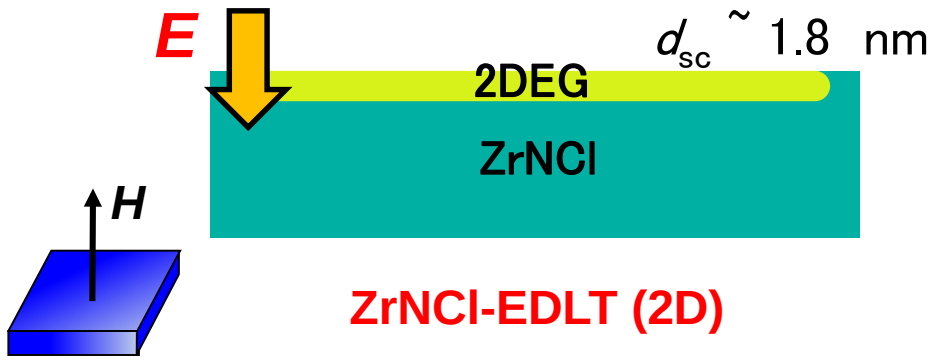


Phase Fluctuation

BKT transition

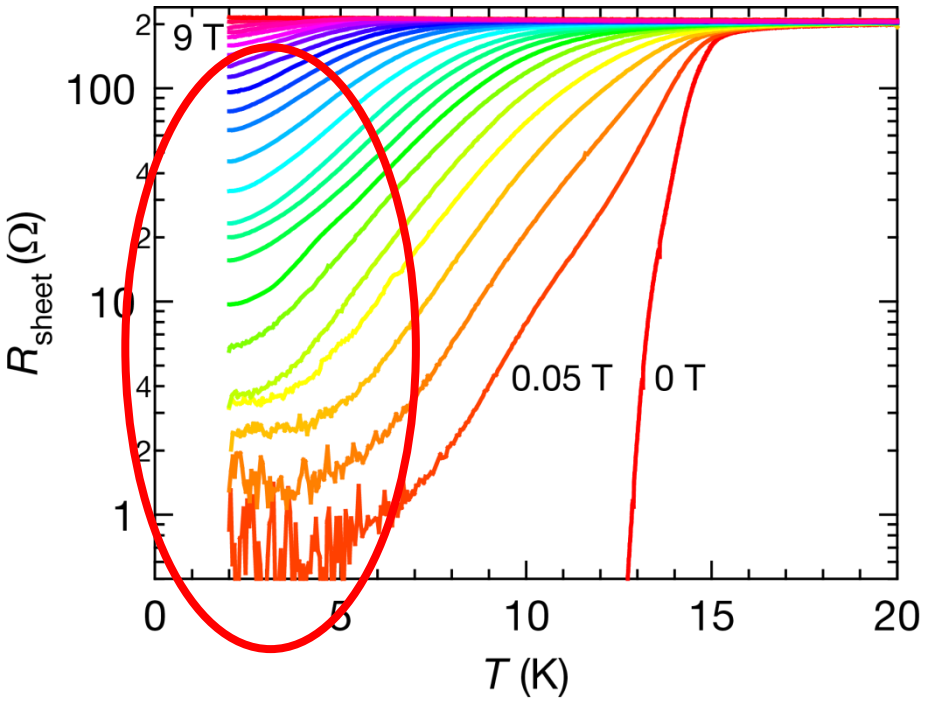


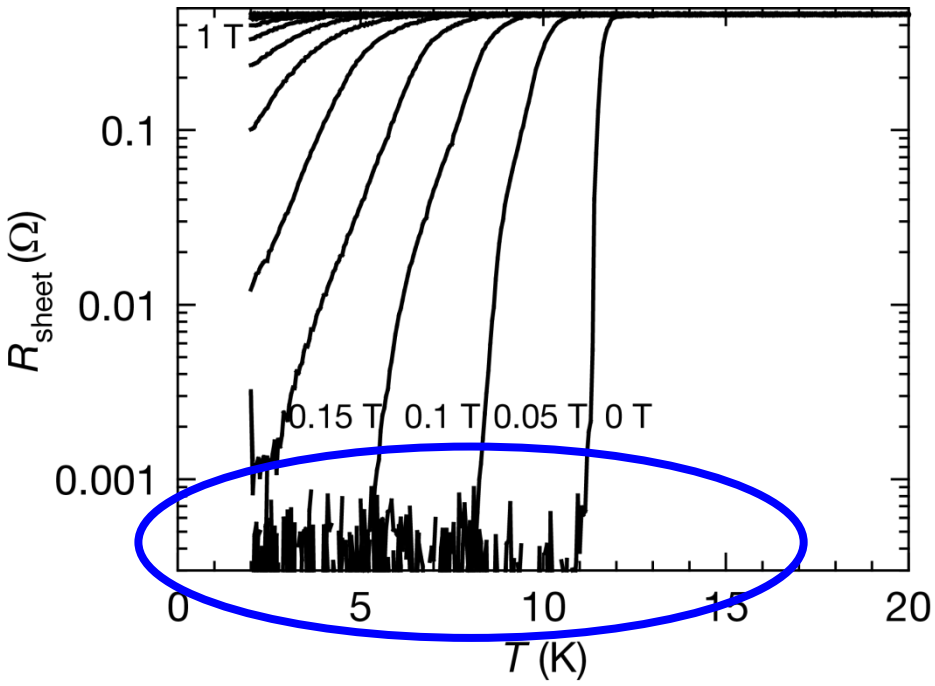
Interface (2D) vs bulk (3D) : *R(H)* – *T* curve



ZrNCl-EDLT (2D)

Li_xZrNCl (3D Anisotropic)

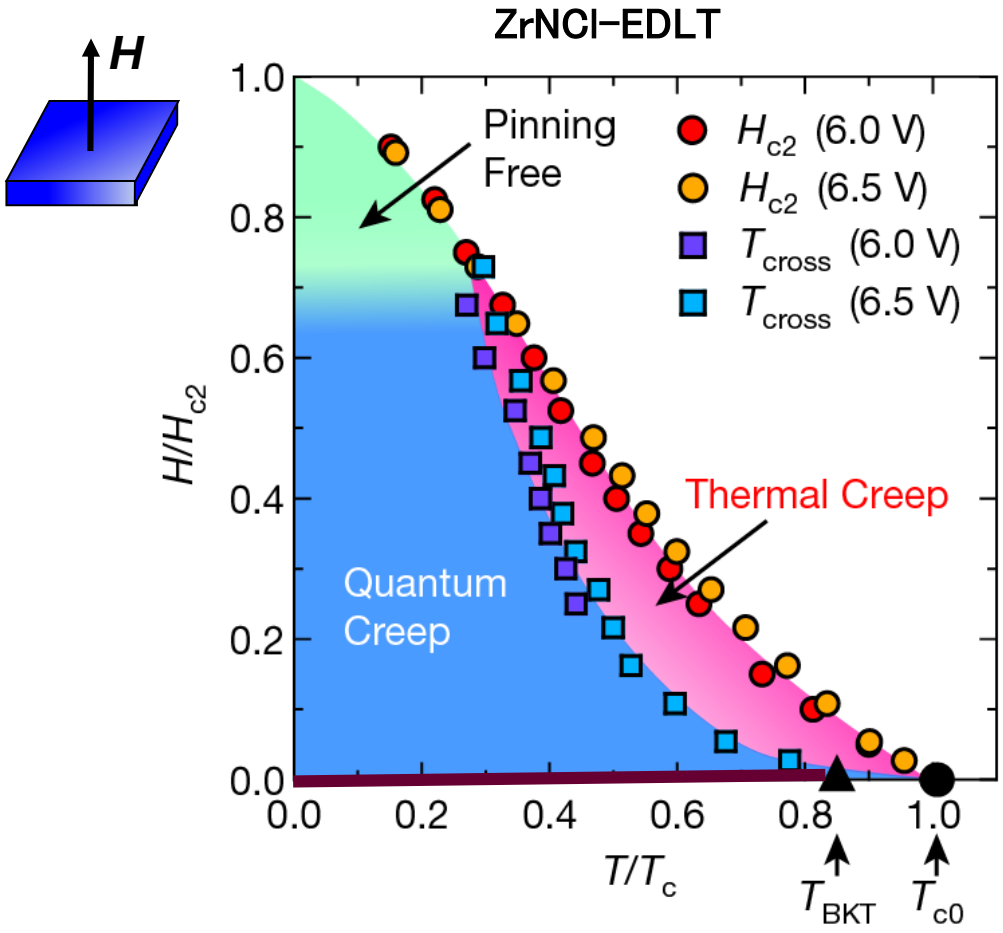




Flattening resistance at low temperature

Quantum metals in highly-crystalline 2D SCs

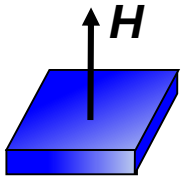
Quantum metal induced by vortex fluctuation due to weak pinning

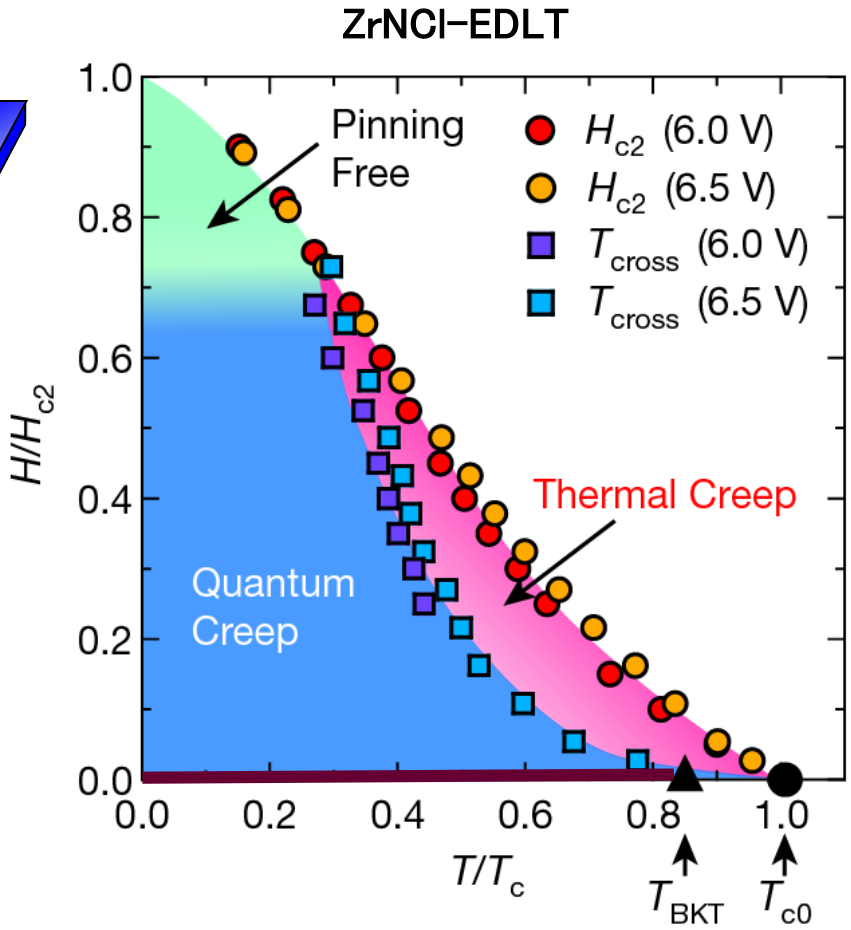


Y. Saito *et al. Science* **350**, 409 (2015).

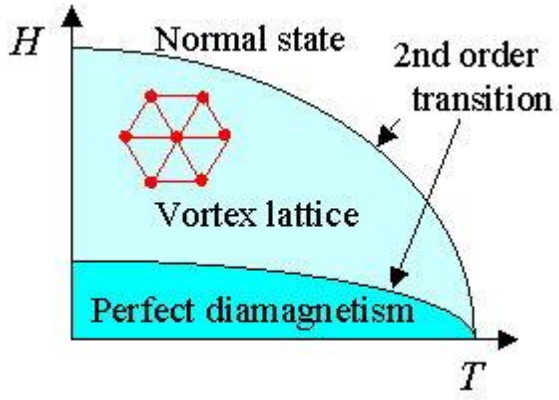
Quantum metals in highly-crystalline 2D SCs

Quantum metal induced by vortex fluctuation due to weak pinning

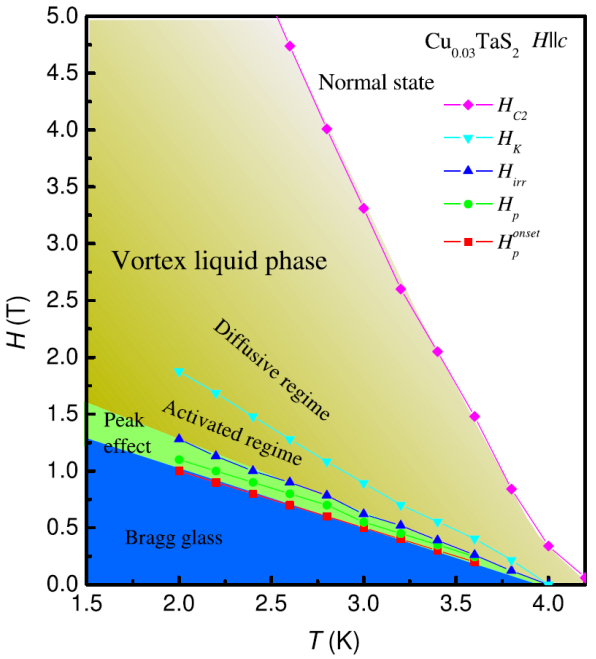




Y. Saito *et al. Science* **350**, 409 (2015).

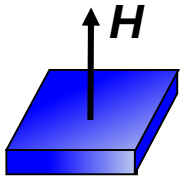


$Cu_{0.03}TaS_2$ (Zhu et al., J. Phys. Cond. Mater 22, 505704 (2010)

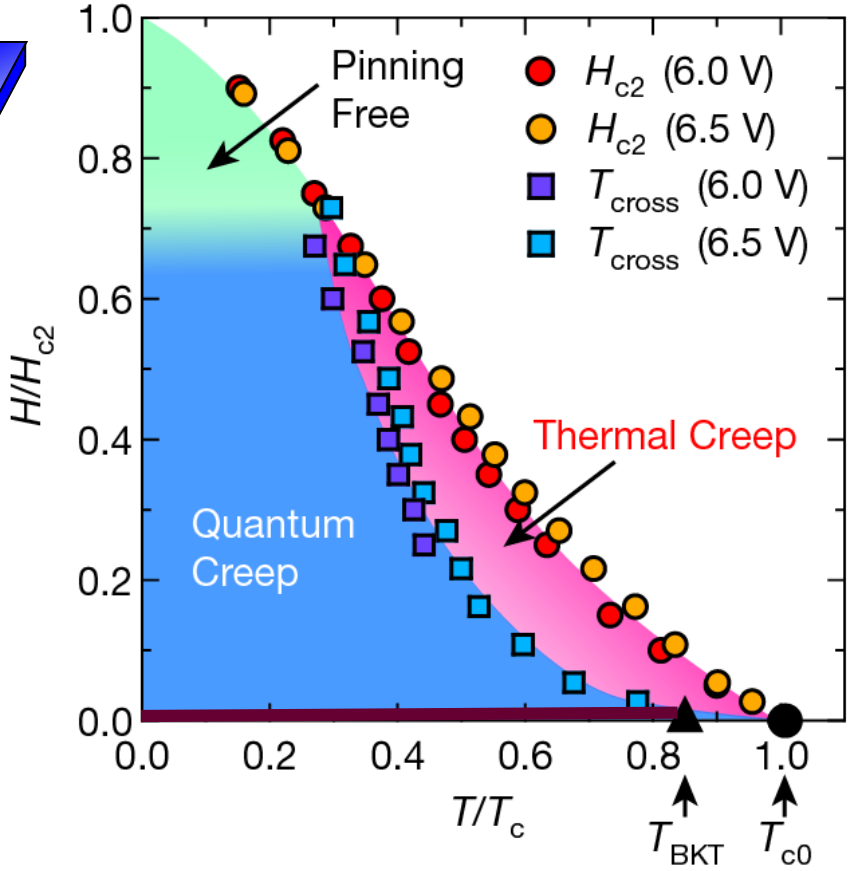


Quantum metals in highly-crystalline 2D SCs

Quantum metal induced by vortex fluctuation due to weak pinning

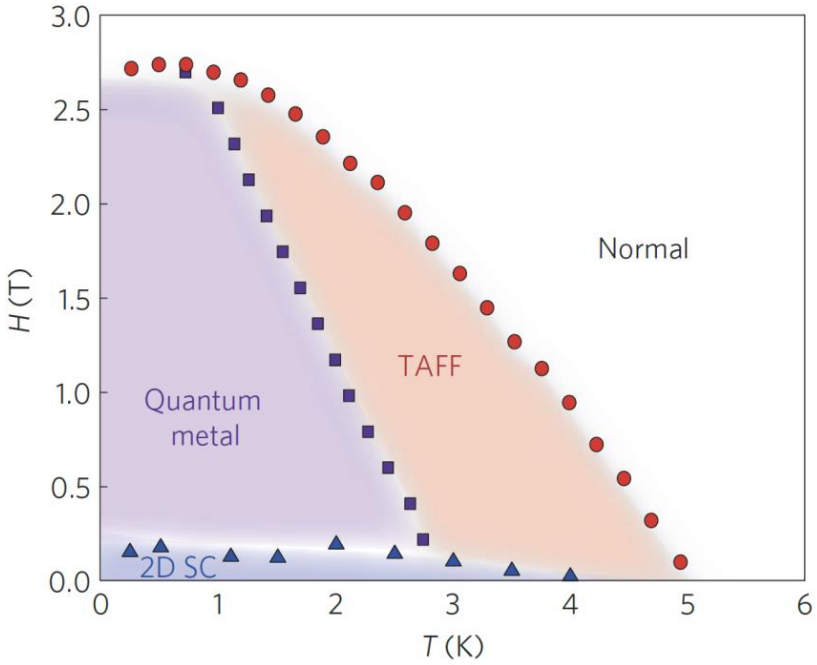


ZrNCl-EDLT



Y. Saito *et al. Science* **350**, 409 (2015).

h-BN capped bilayer NbSe2

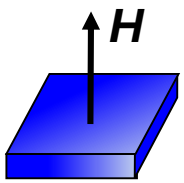


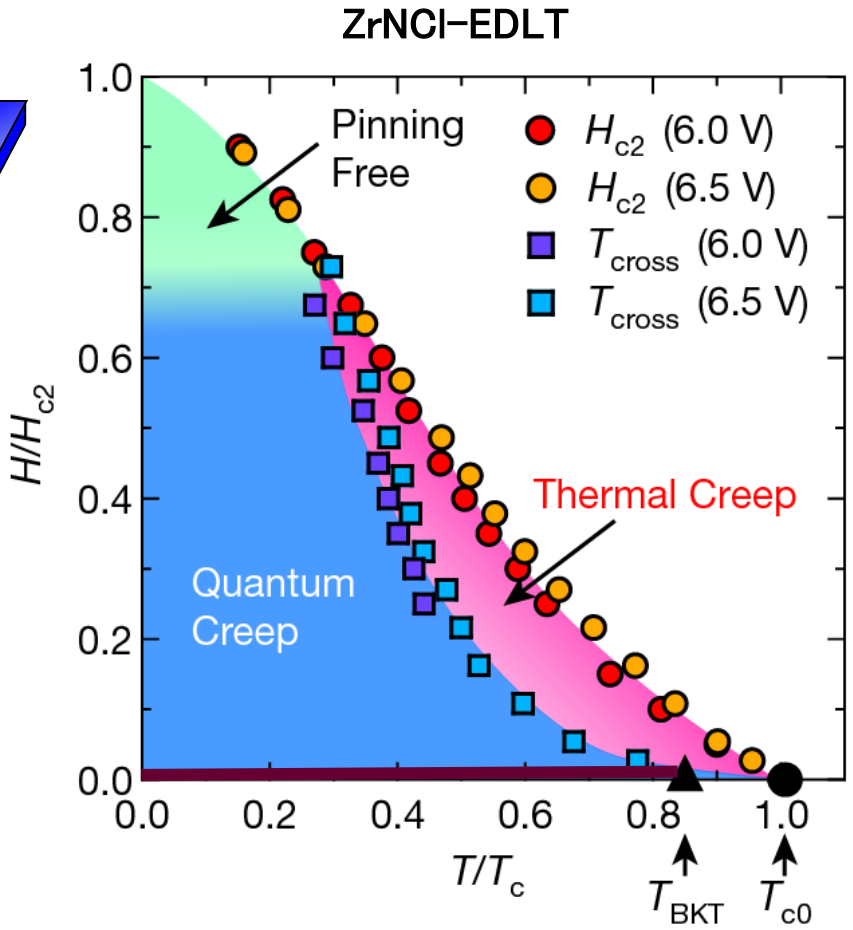
Bose metal

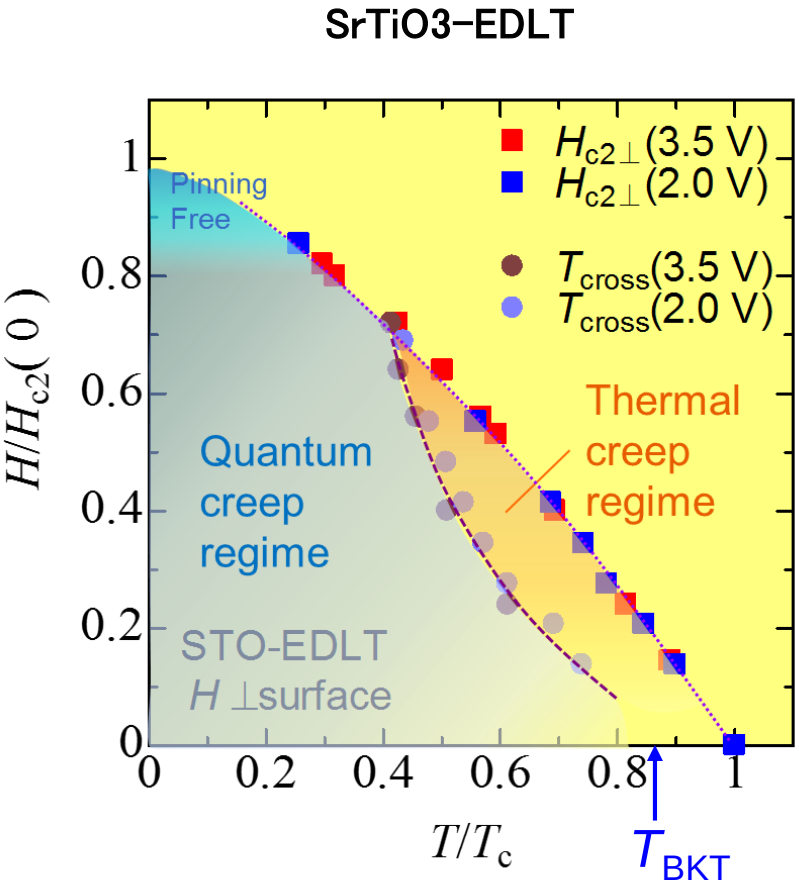
A. W. Tsen *et al. Nature Phys.* **12**, 208 (2016).

Quantum metals in highly-crystalline 2D SCs

Quantum metal induced by vortex fluctuation due to weak pinning

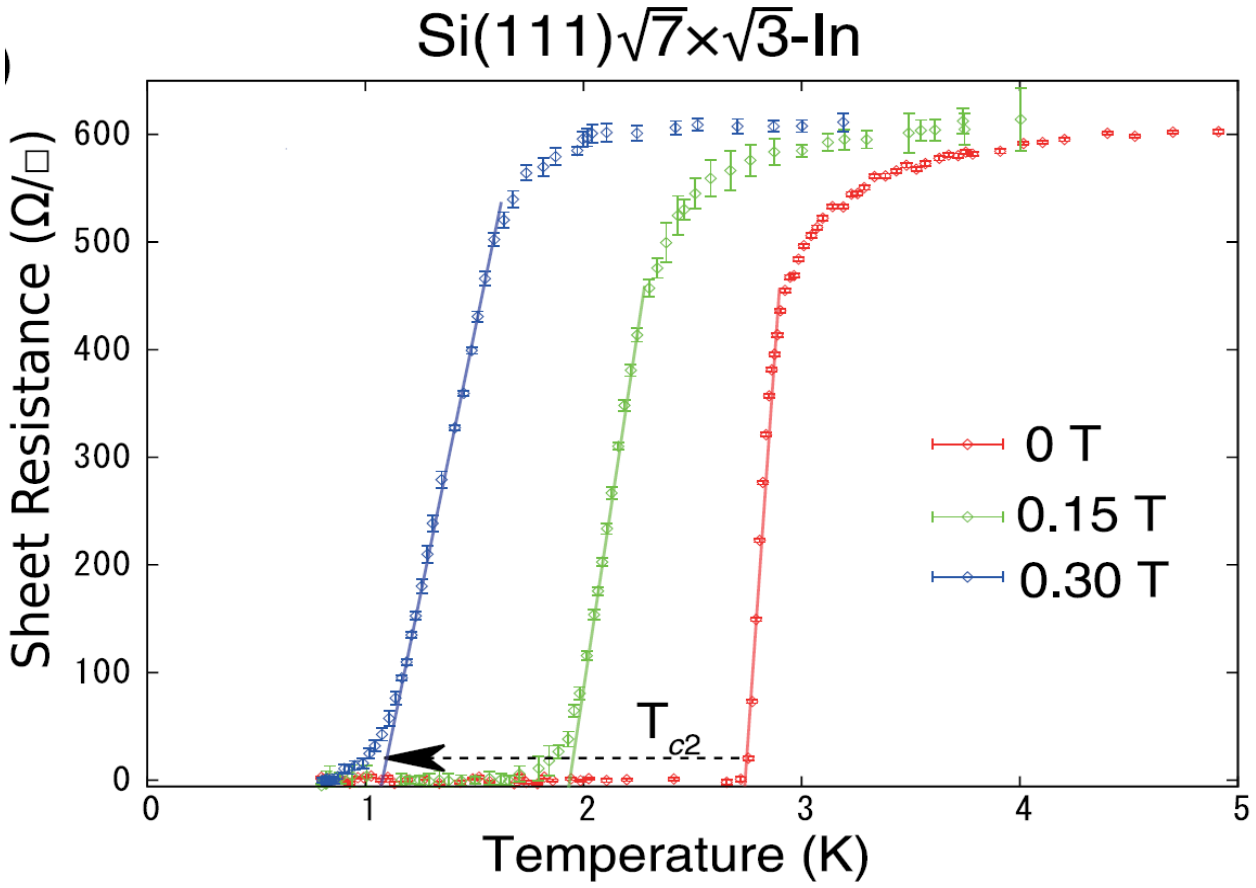






Y. Saito *et al. Science* **350**, 409 (2015).

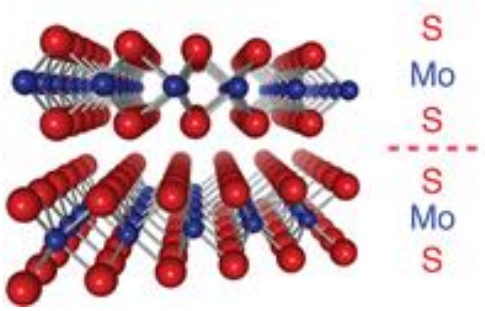
Robust zero-resistance in In monolayer

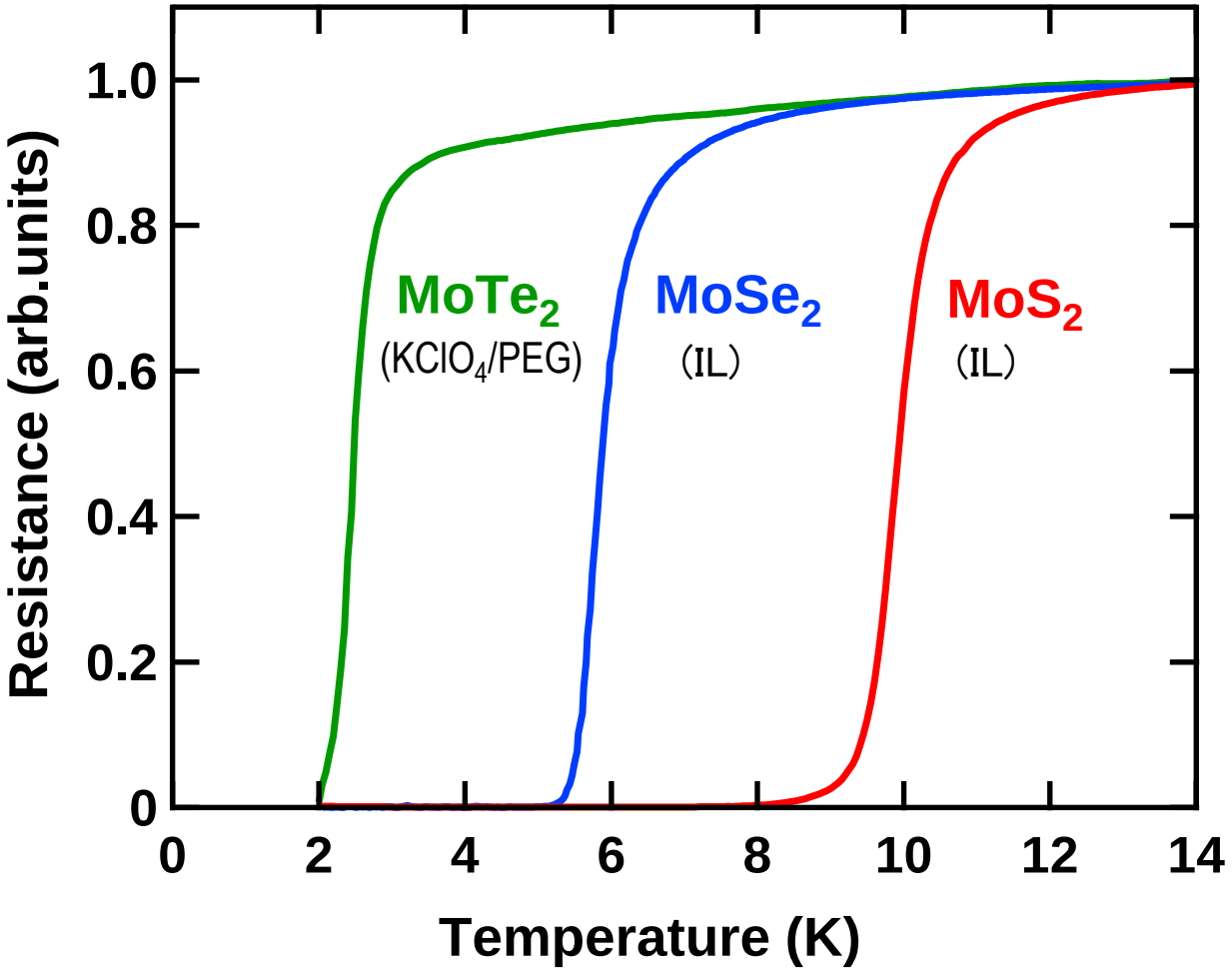


No significant broadening in the MBE grown In monolayer maybe due to the grain boundaries

M. Yamada, T. Hirahara and S. Hasegawa, *Phys. Rev. Lett.* **110** 237001 (2013).

Gate-induced superconductivity in MoX_2

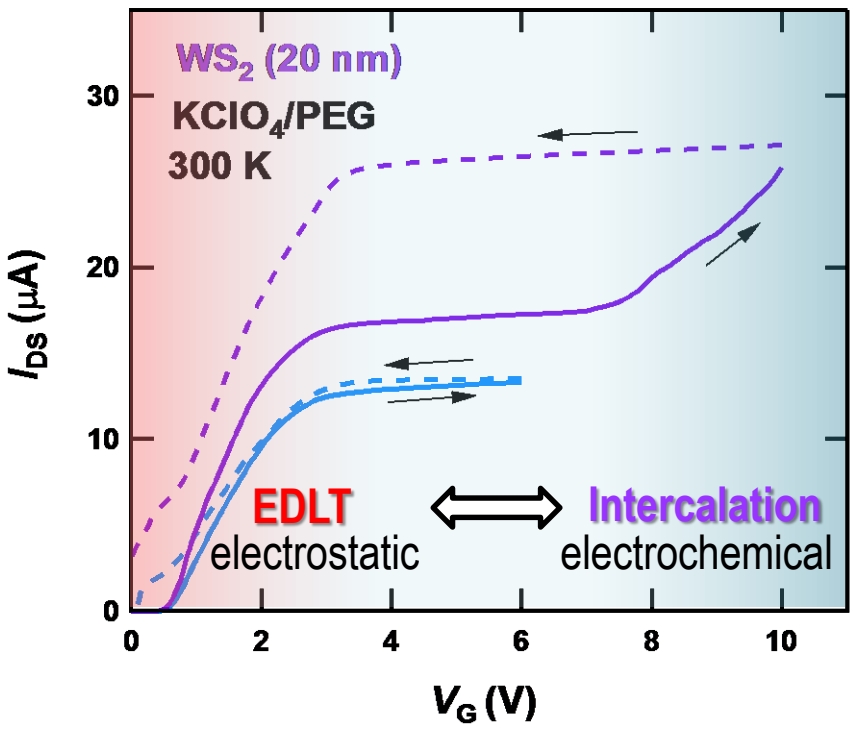




W. Shi et al. Sci Rep 5, 12534 (2015)

Superconductivity in WS_2

❑ $I_{DS} - V_G$ Curves

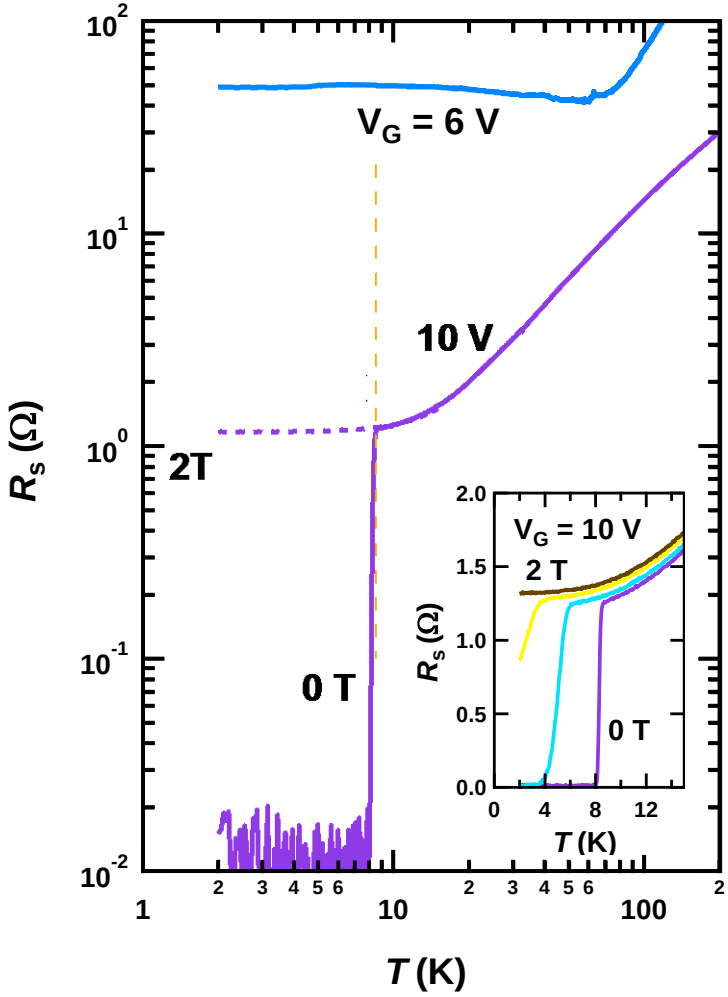


○ **Reversible gate control of intercalation**

❖ *Superconductivity in WS_2*

T_c = 8.6 K (potassium -doped)

❑ $R - T$ Curves (log plot)

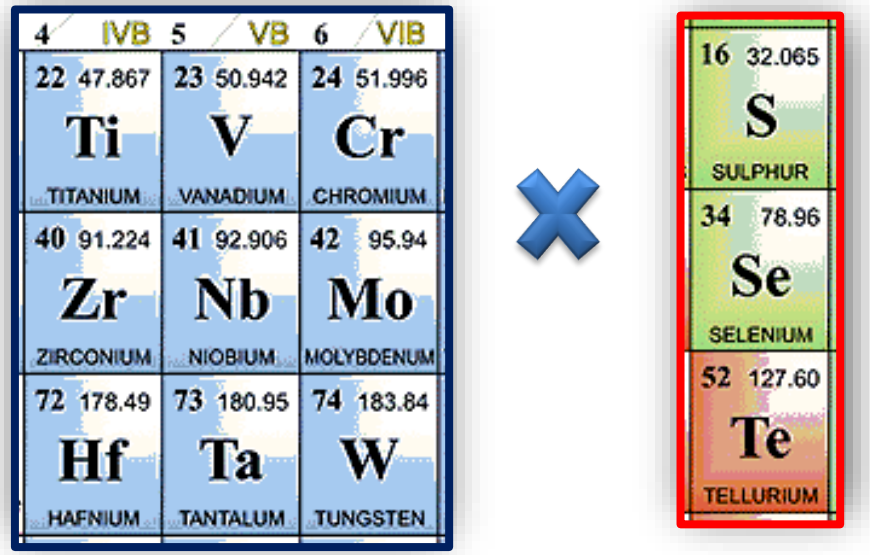


W. Shi et al. Sci Rep 5, 12534 (2015)

Cf) S. Jo et al., Nano Lett. 15 1197 (2015)

2. Longitudinal electric field effect

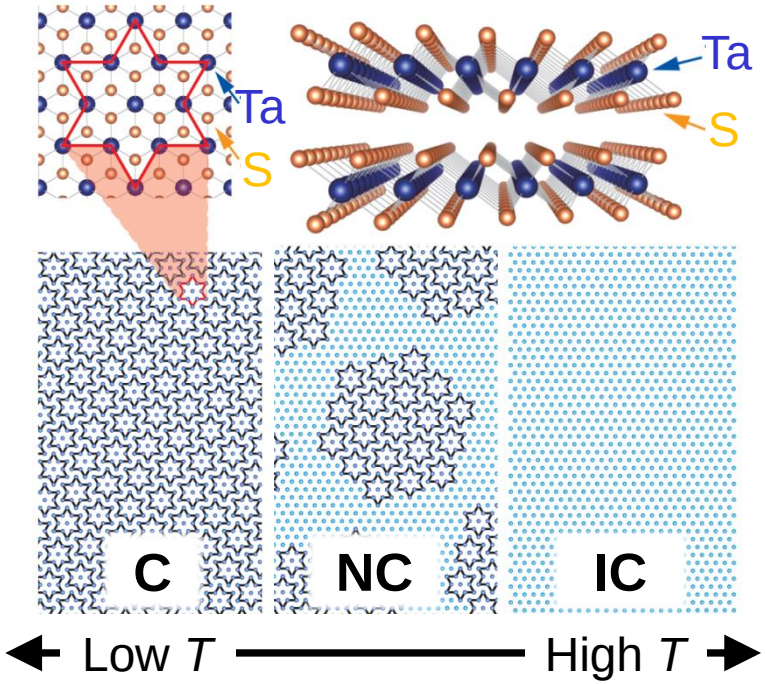
Nonvolatile and Memristive switching in TaS_2

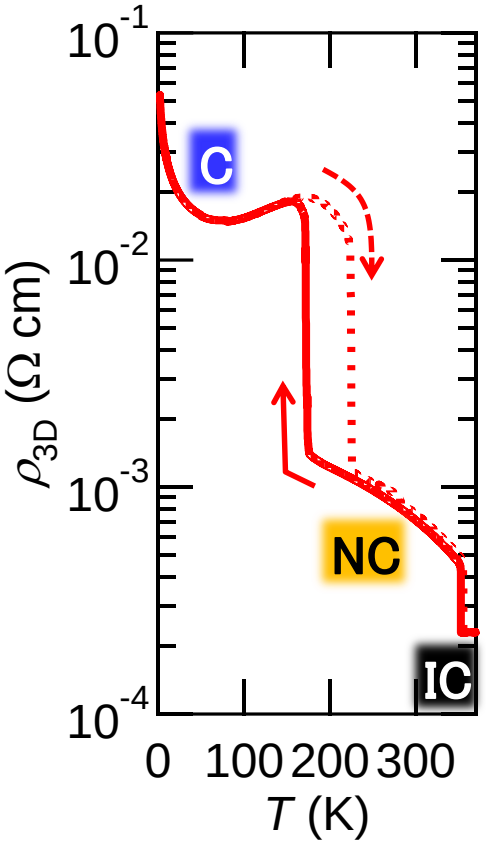


M. Yoshida
PII-12
Next week

1T-TaS_2: Electronic phase transition system

1T-TaS_2 : Charge density wave (CDW) system

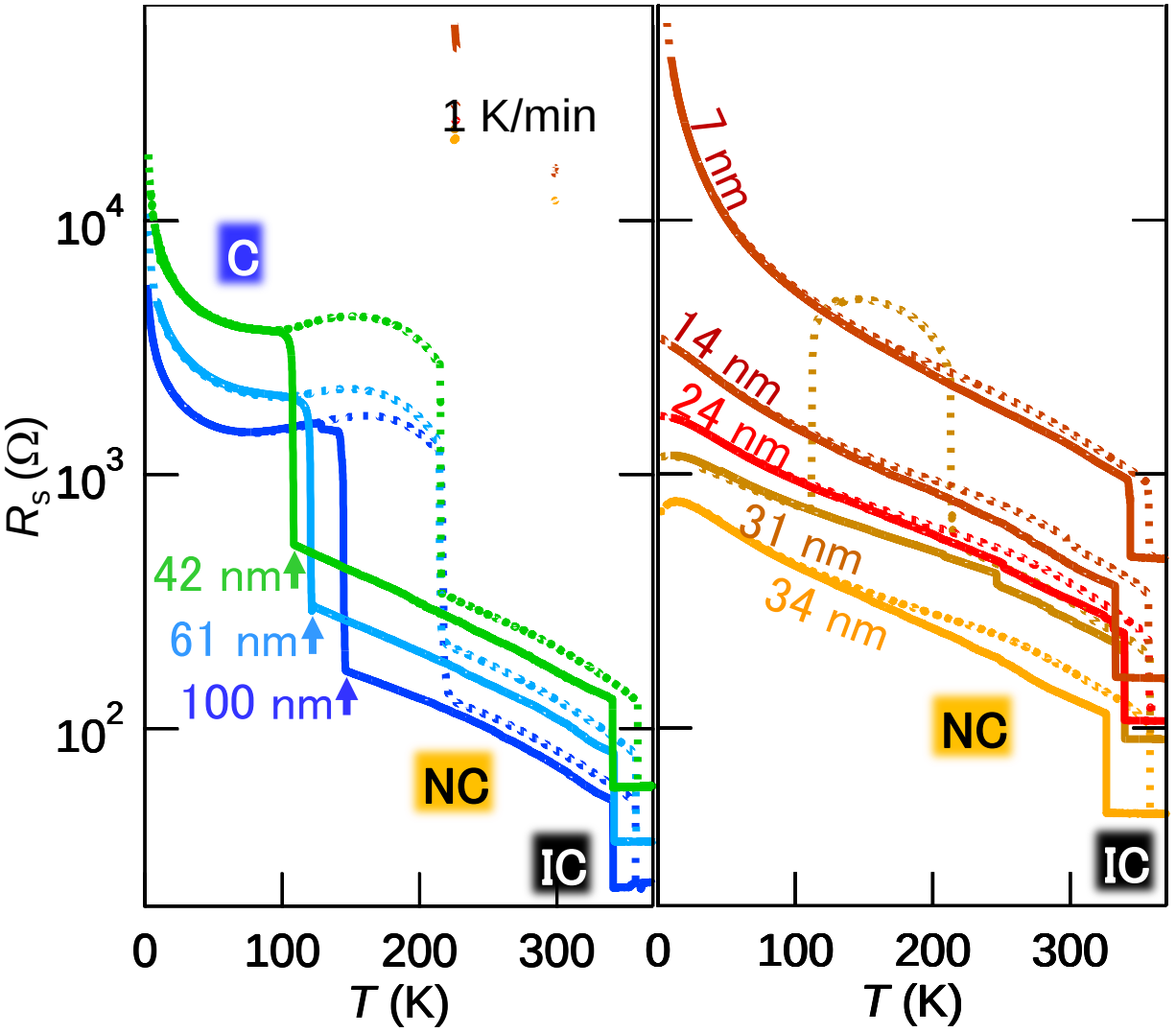


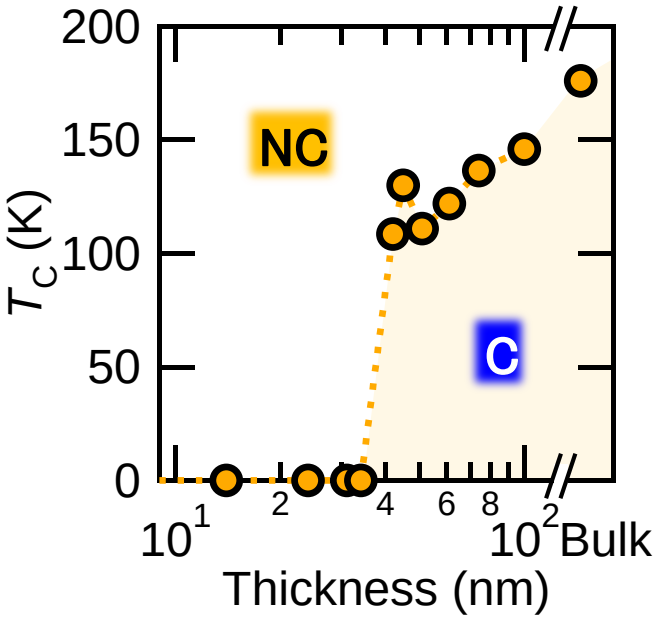


- Commensurate
- Nearly-commensurate
- In-commensurate

Thickness dependent phase transitions

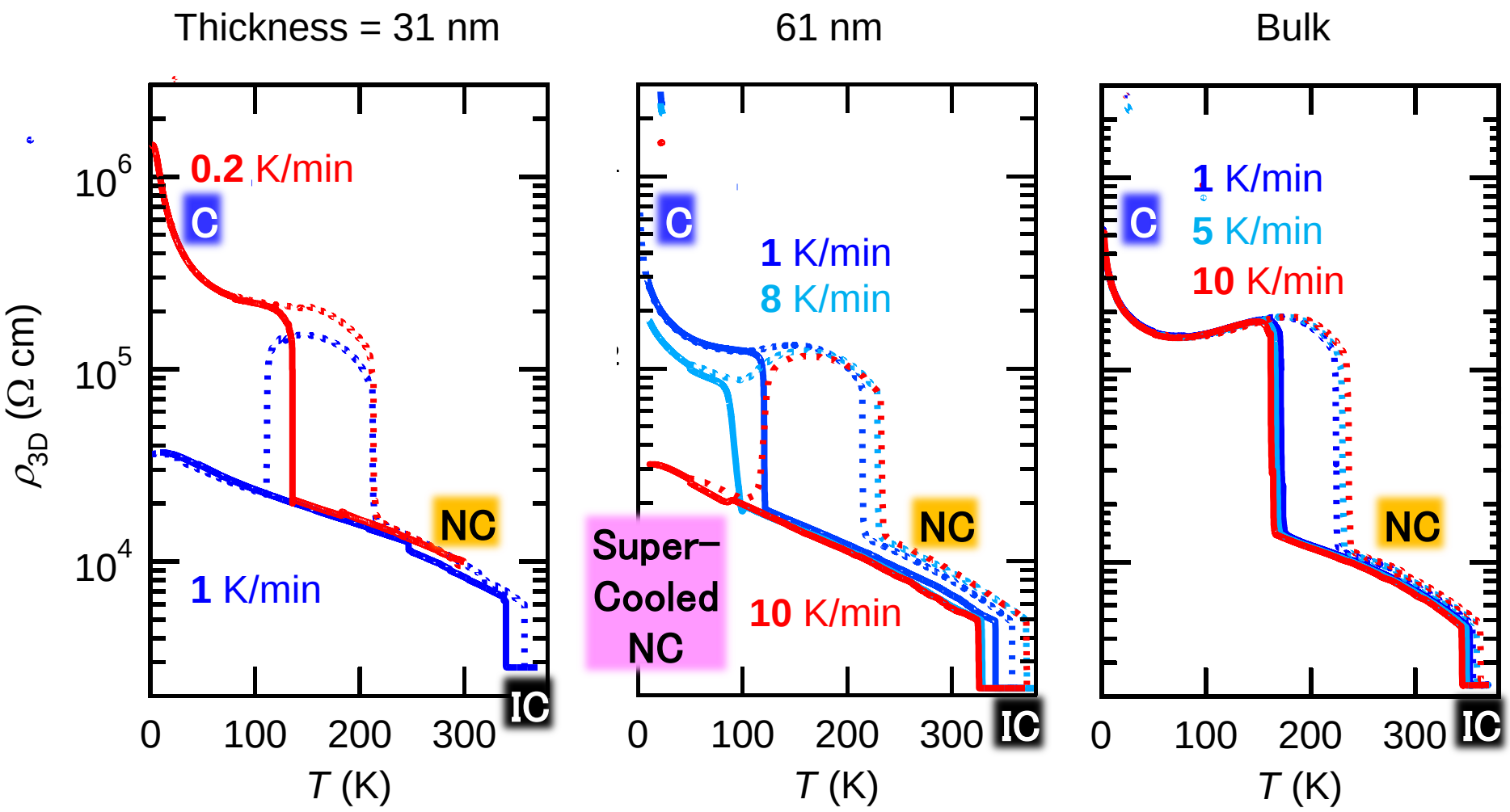
M. Yoshida *et al.*,
Sci. Rep. **4,** 7302 (2014).



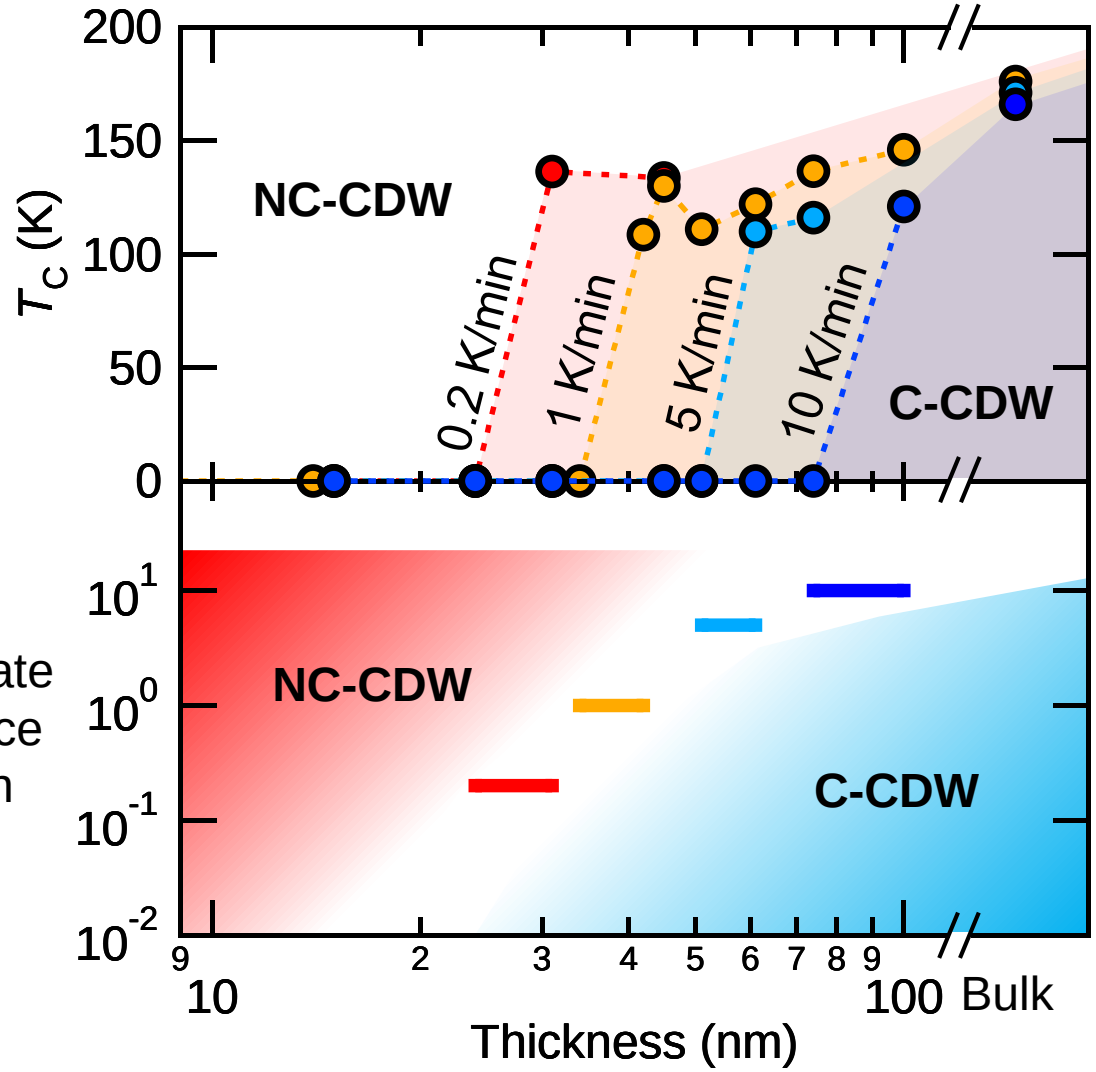


Abrupt suppression of NC-C transition on cooling. → Consider **kinetics**.

Cooling-rate-dependent phase transition



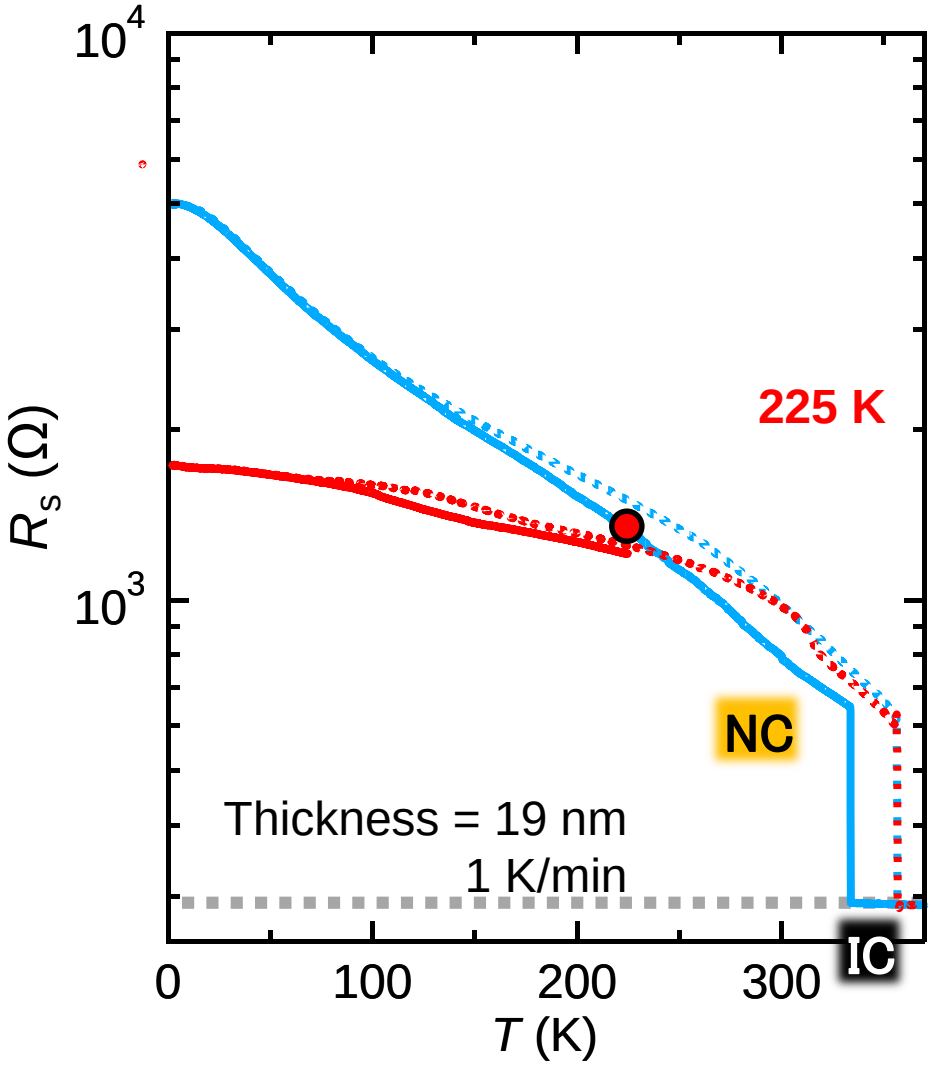
Phase diagram considering kinetics

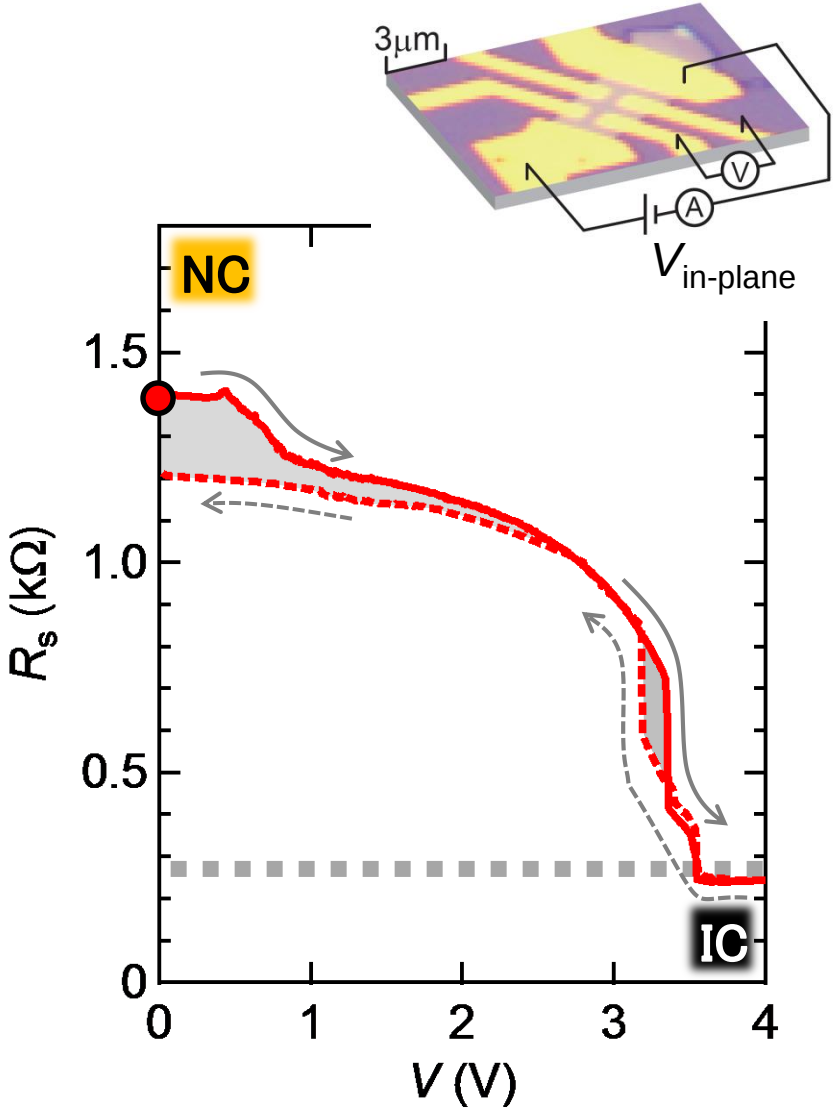


The ordering **kinetics** of the transition becomes **slow** by thinning.

M. Yoshida *et al., Sci. Adv.* **1,** e1500606 (2015).

Nonvolatile switching from the NC state by $V_{\text{in-plane}}$

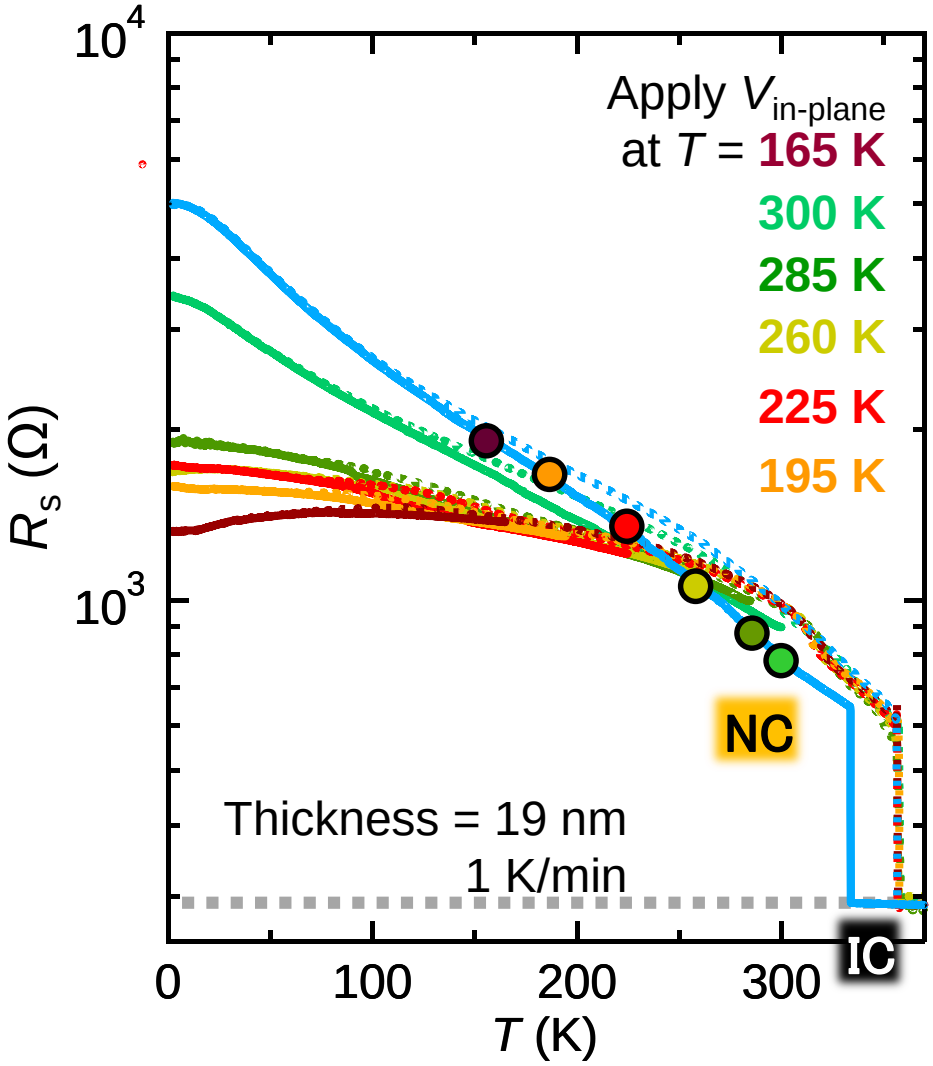


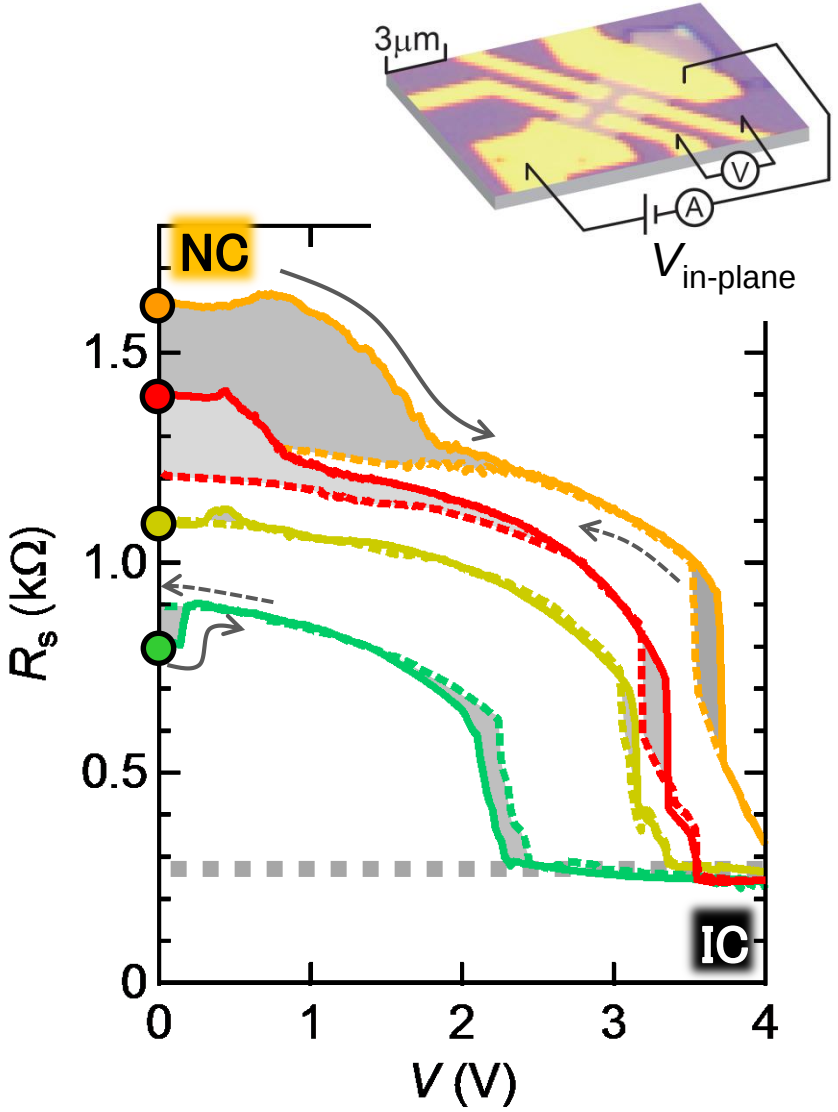


M. Yoshida *et al., Sci. Adv.* **1,** e1500606 (2015).

A. W. Tsen *et al. PNAS* (2015).
I. Vaskivskyi *et al. Nat. Commun.* (2016).

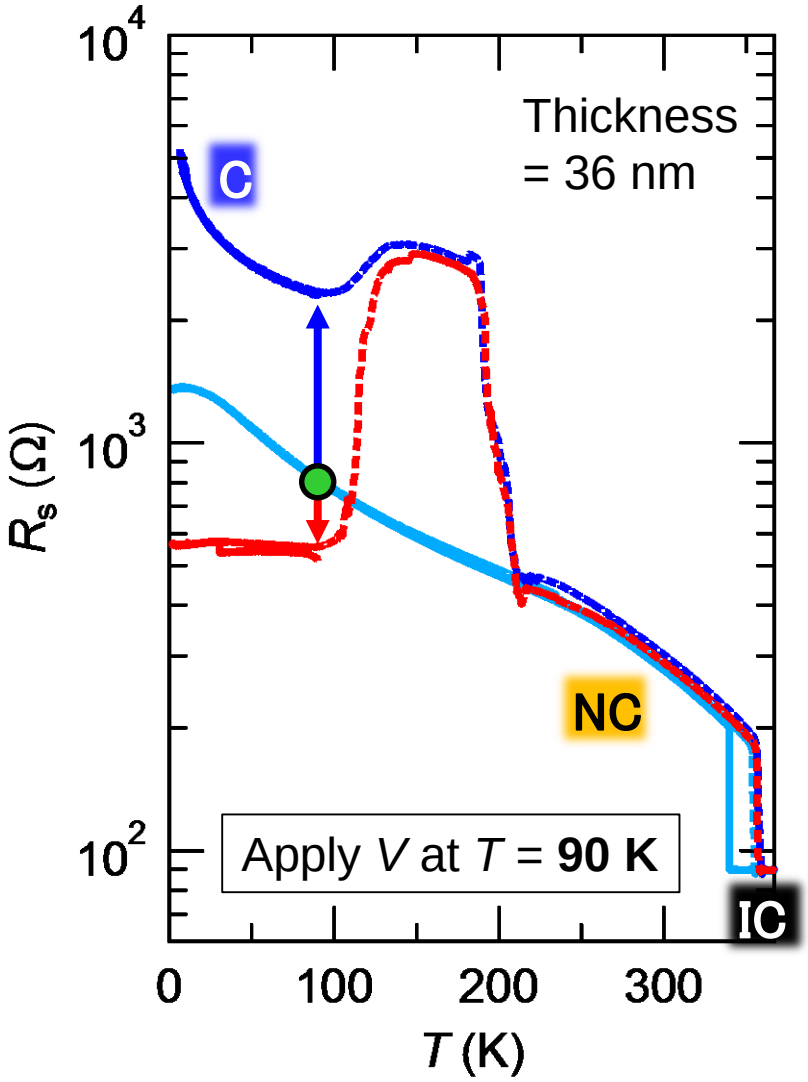
Multiple metastable state by $V_{\text{in-plane}}$

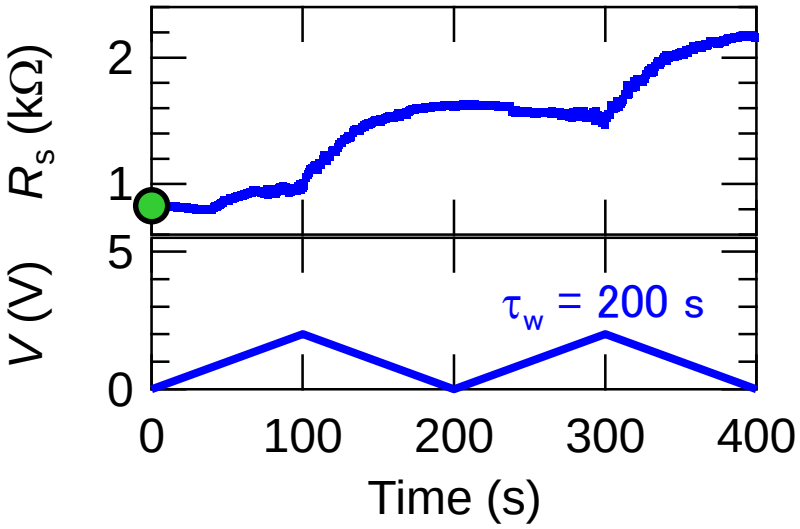


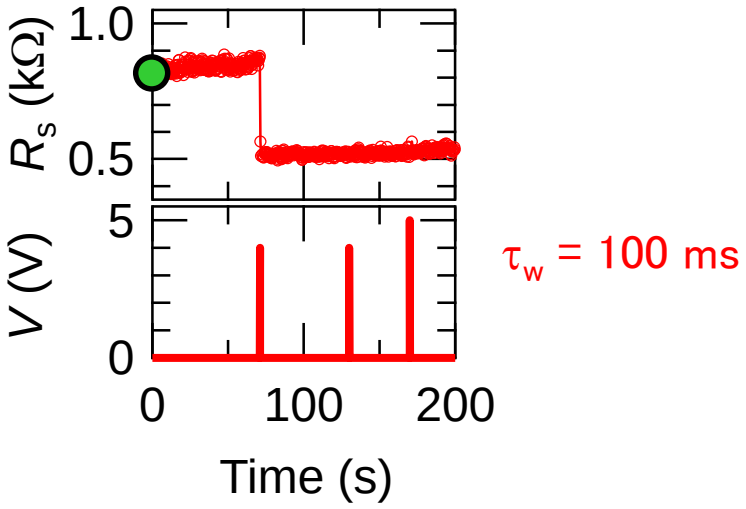


M. Yoshida *et al., Sci. Adv.* **1,** e1500606 (2015).

Switching to various electronic states

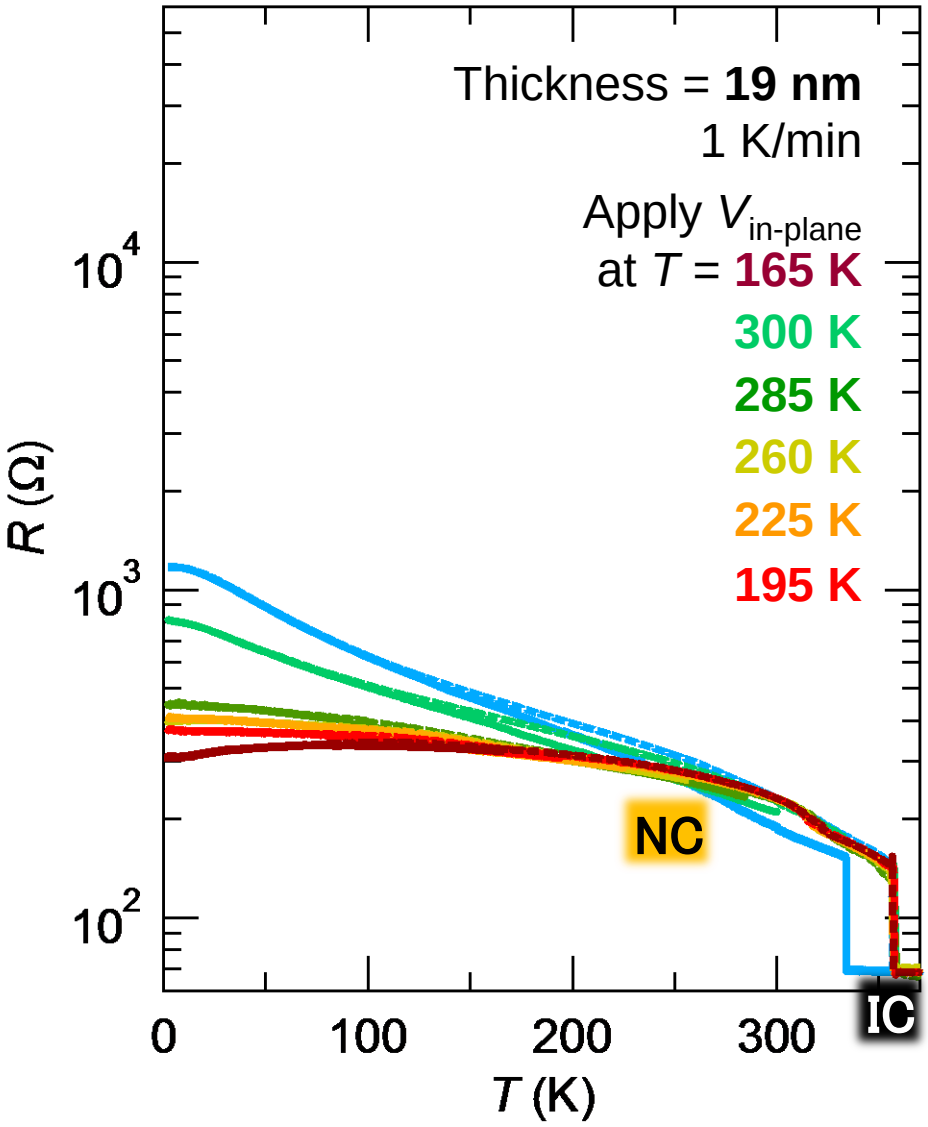


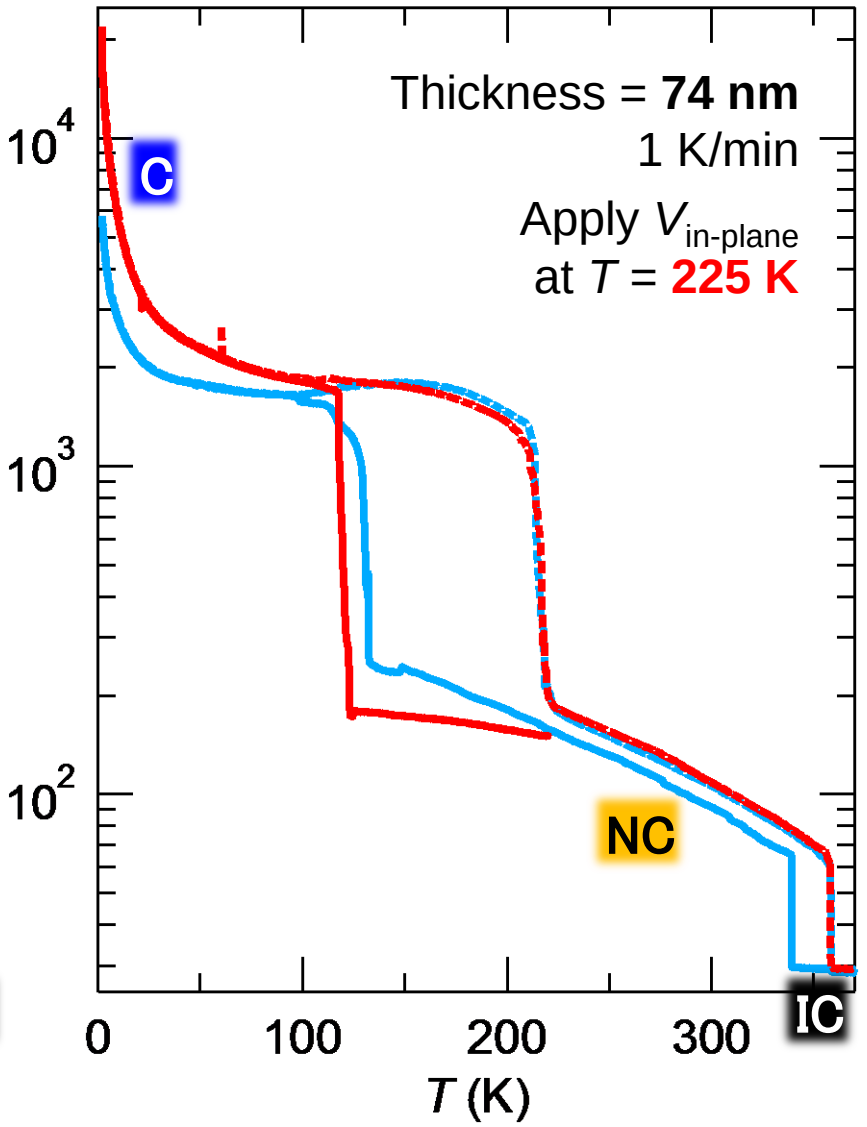




Memristive switing

The stability of the voltage-induced metastable states

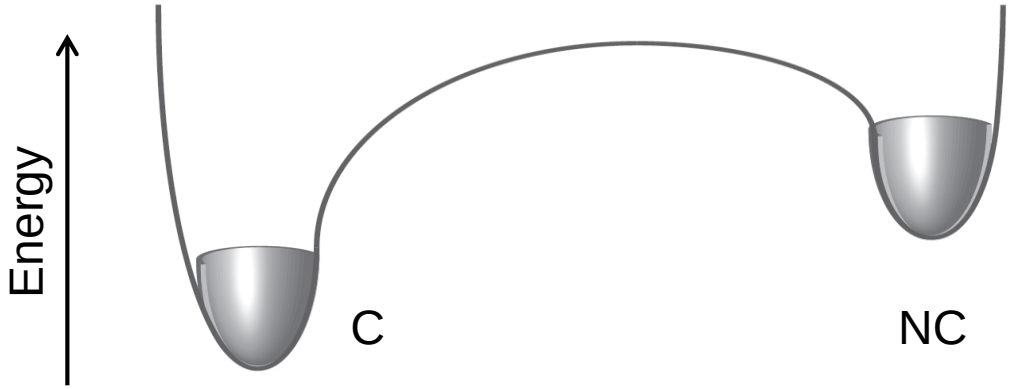




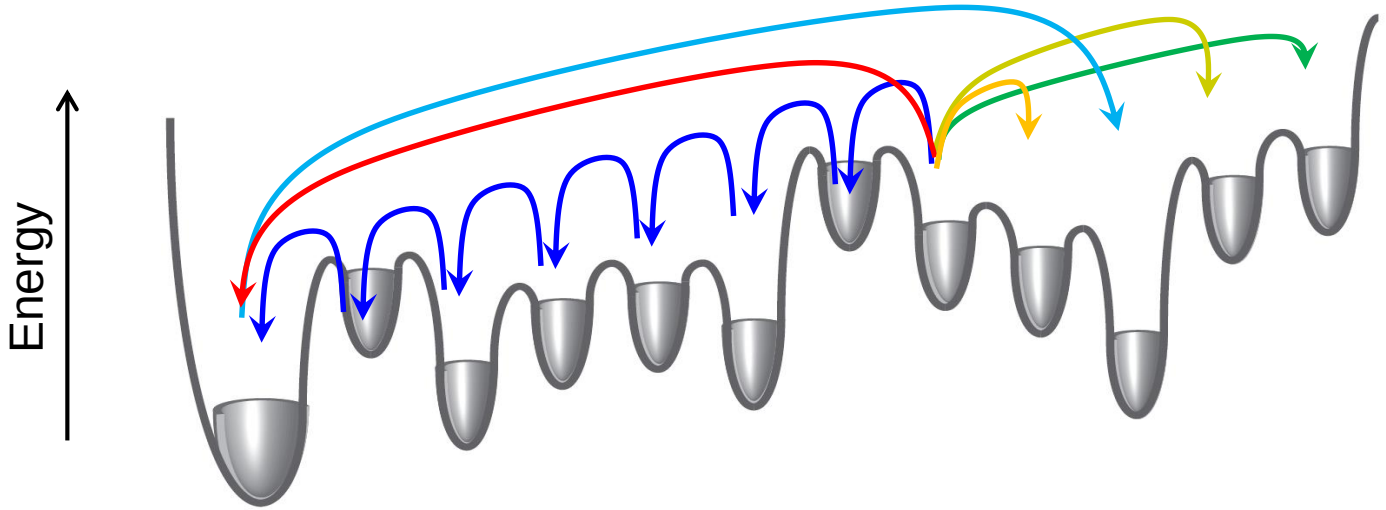
The metastable states can also exist in thick crystals, but are fragile.

Energy landscapes

Bulk



Thin flake



Summary

New states of matter in 2D materials created by electric fields

Transverse electric field: $E \sim 10^7$ V/cm

(1) 2D superconductivity by EDLT

(2) Quantum metallic states under magnetic fields in ZrNCl

(3) Superconductivity in WS2 nanotube/
transport reflecting tublar and chiral structure

Longitudinal electric field: $E \sim 10^4$ V/cm

(1) Many metastable states, possibly semimetallic in TaS2

(2) Non-volatile memristive switching