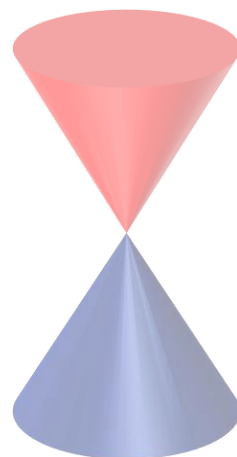
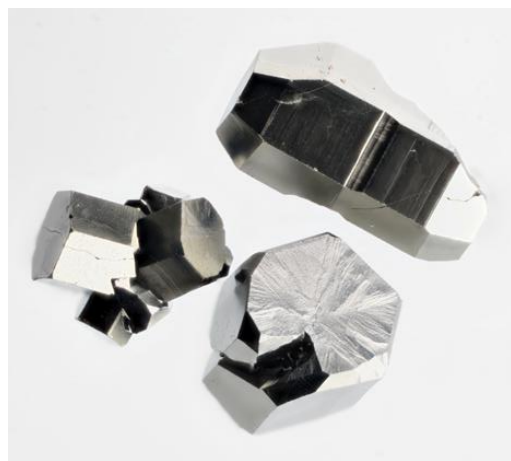


# デバイス応用に向けた酸化物の トポロジカル電子状態の解明

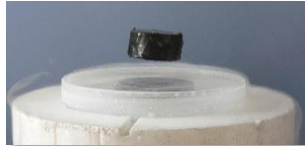
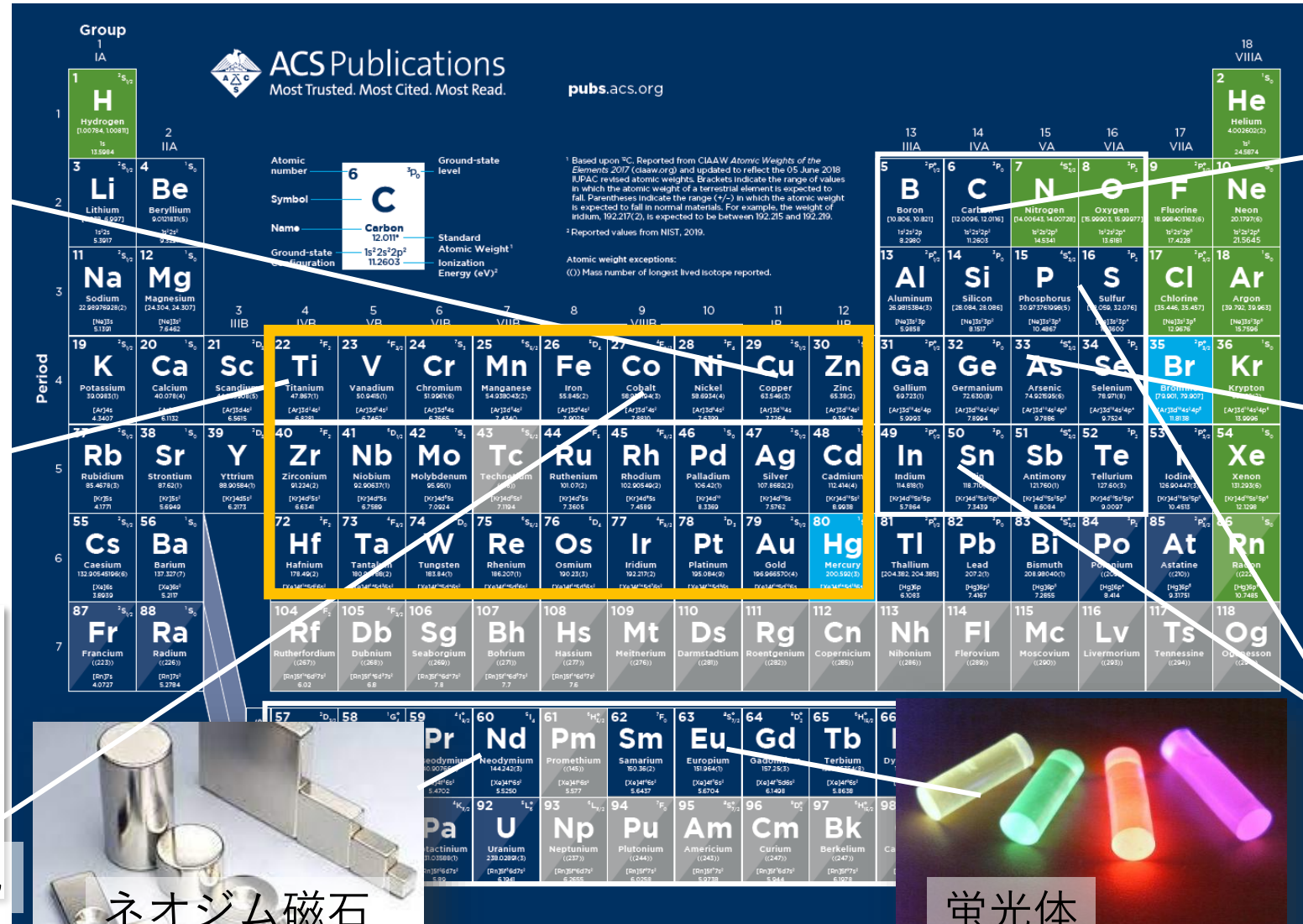


平井大悟郎

# 自己紹介

専門：固体化学・物性物理学

無機固体物質の新物質開発・結晶成長と電子物性の開拓



高温超伝導



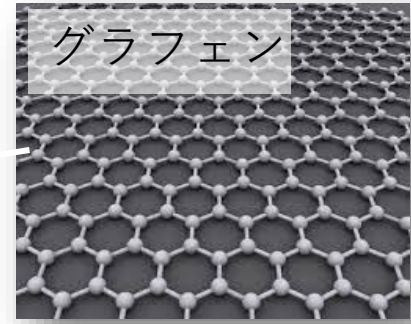
誘電体



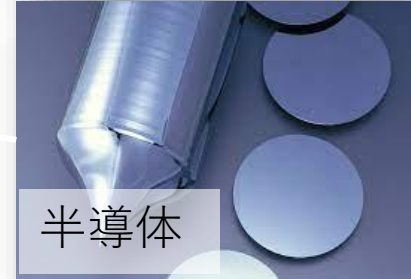
リチウムイオン電池



ネオジム磁石



グラフェン



半導体



窒化ガリウム



蛍光体

# 酸化物のイメージ

# 酸化物のイメージ

かたい

安定

電気を流さない

高温に強い

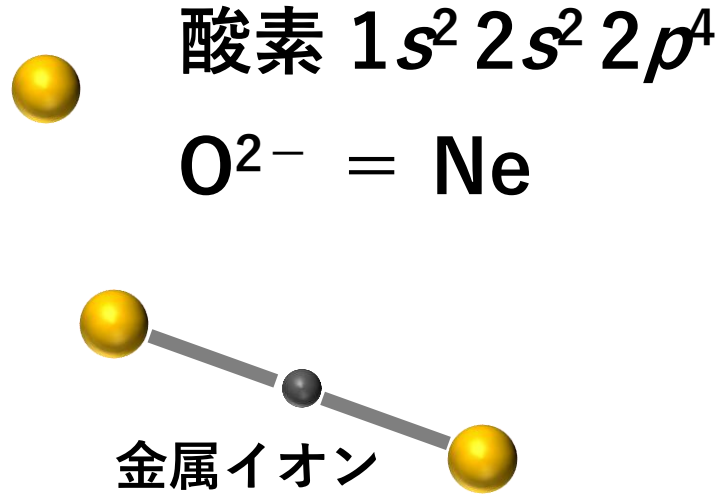


瀬戸物

灰釉大碗・小碗（11世紀中期）瀬戸蔵ミュージアム蔵

# 酸化物のイメージ

## イオン結合



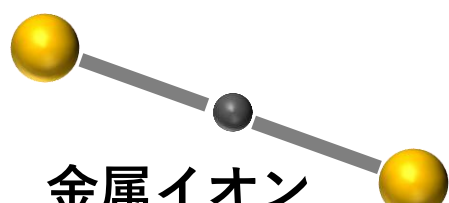
族	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

# 酸化物のイメージ

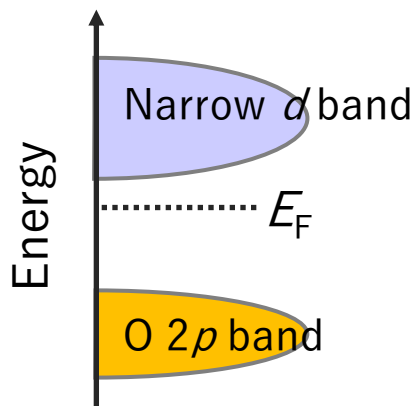
## イオン結合

酸素  $1s^2 2s^2 2p^4$

$O^{2-} = Ne$



金属イオン



酸化チタン

族	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
周期																		
1	H 2.20																	He
2	Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
3	Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
4	K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
5	Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.16	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.6
6	Cs 0.79	Ba 0.89	*	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 2.33	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
7	Fr 0.7	Ra 0.9	**	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

Wikipedia 電気陰性度

$\text{RuO}_2$



$\text{IrO}_2$



$\text{WO}_2$



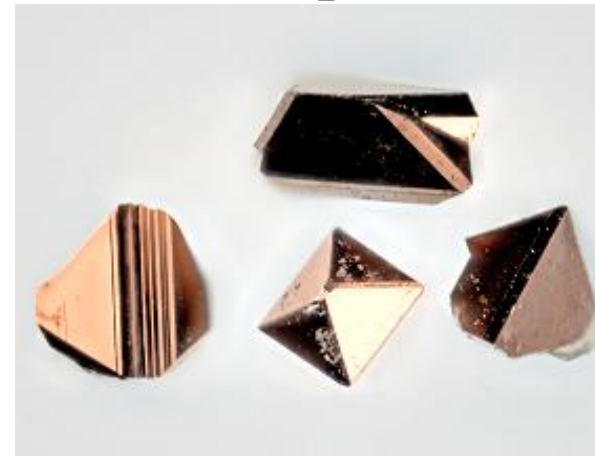
$\text{ReO}_2$



$\text{ReO}_3$

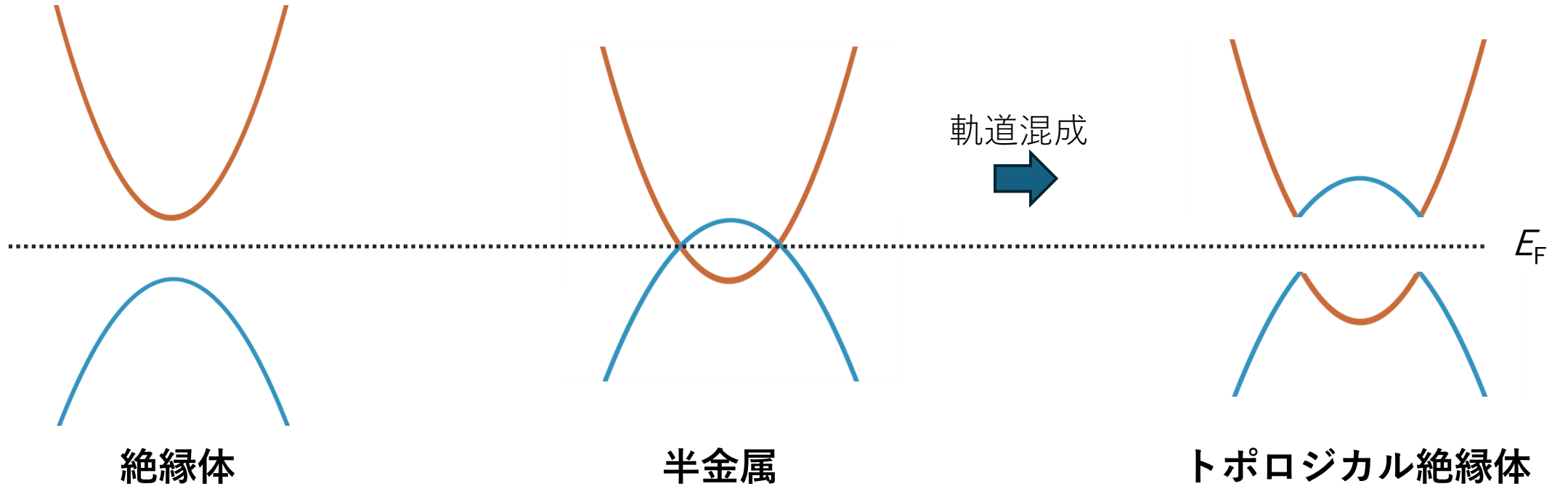


$\text{OsO}_2$

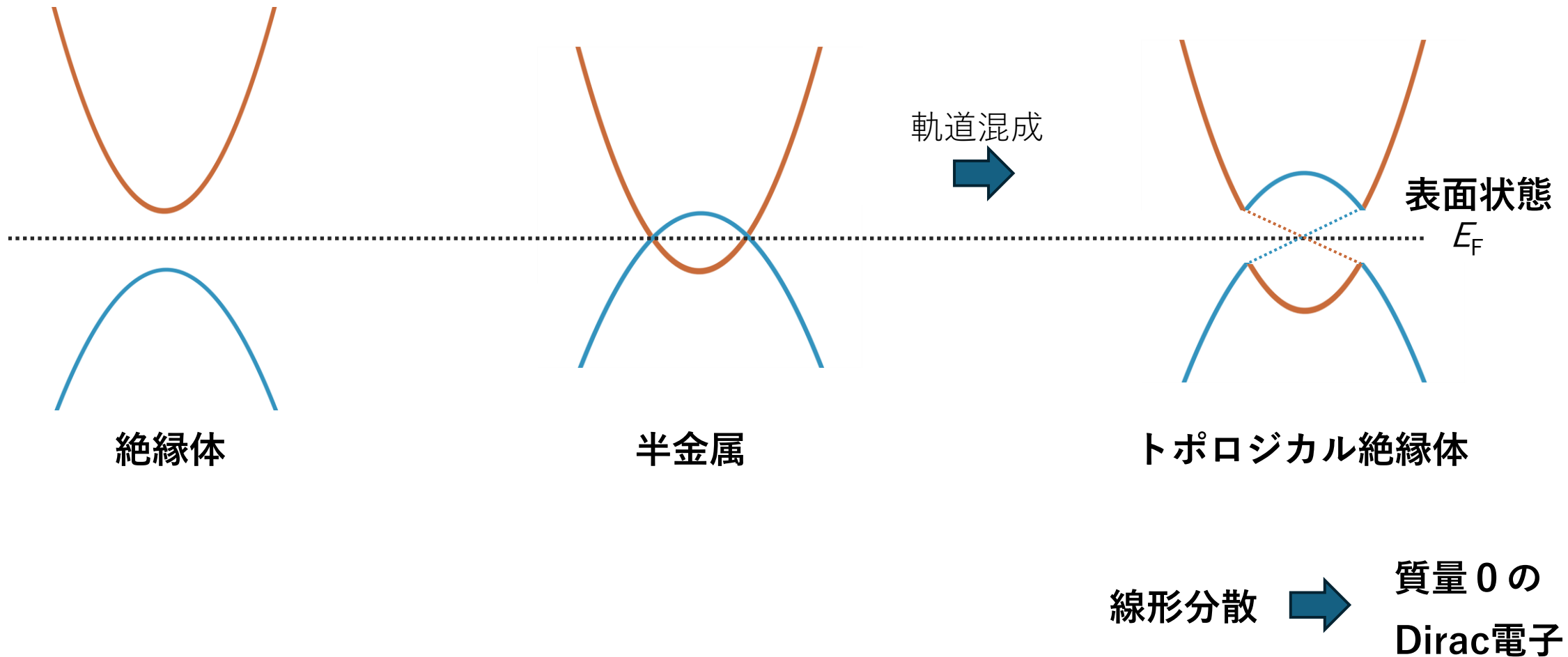


酸化物でも電子構造により極めて高い伝導性を示す

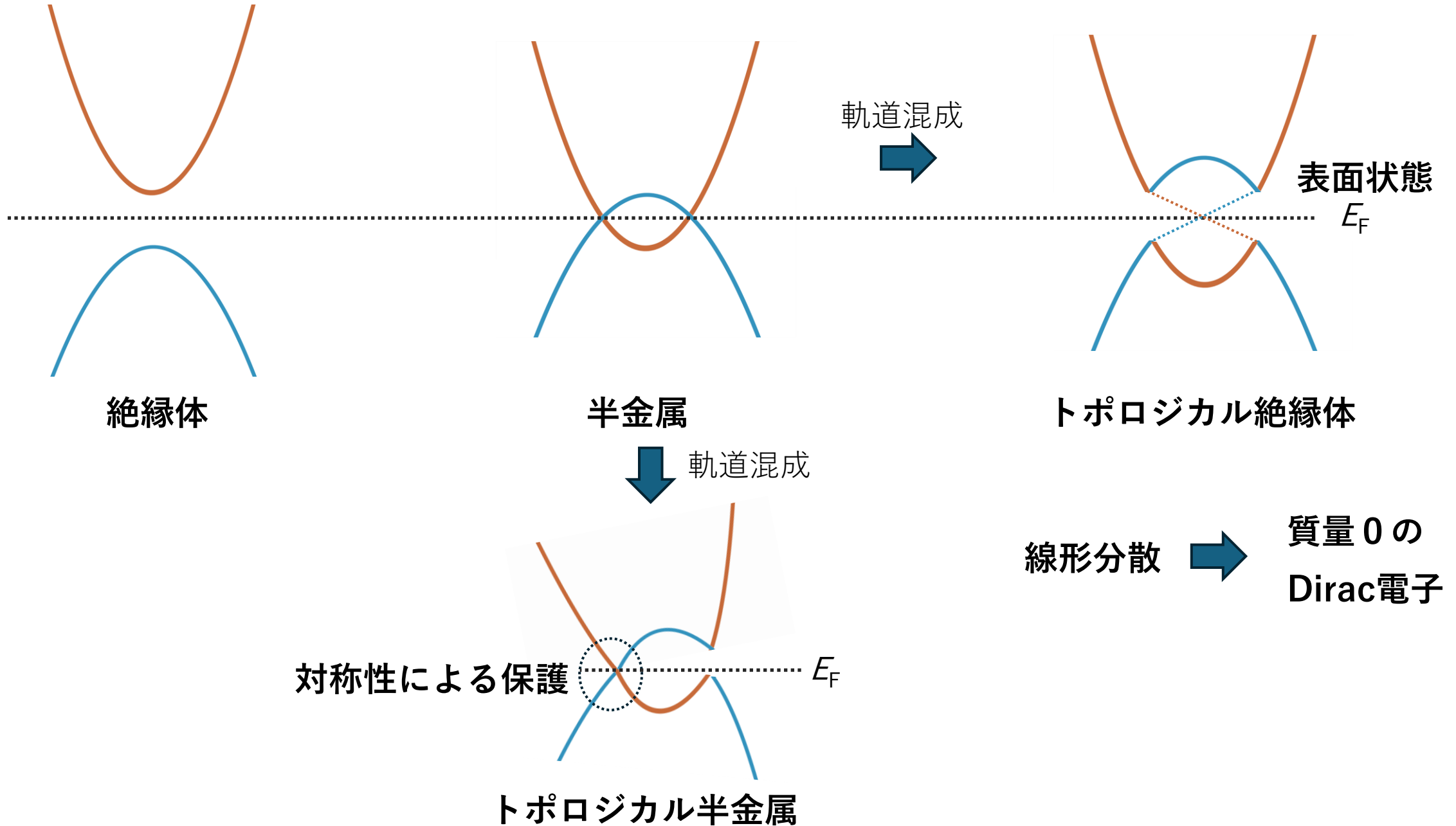
# バンドのトポロジーによる物質の分類



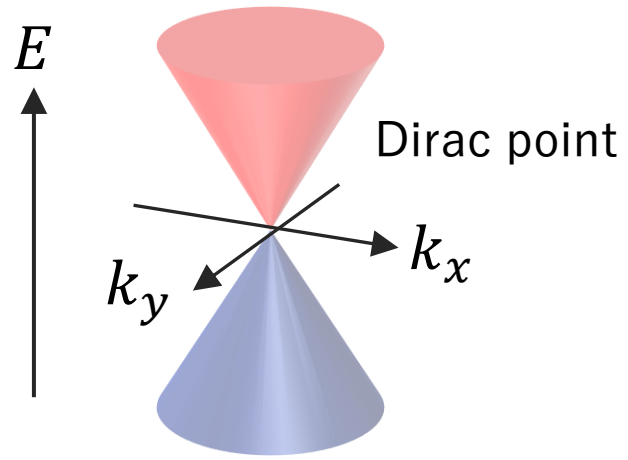
# バンドのトポロジーによる物質の分類



# バンドのトポロジーによる物質の分類

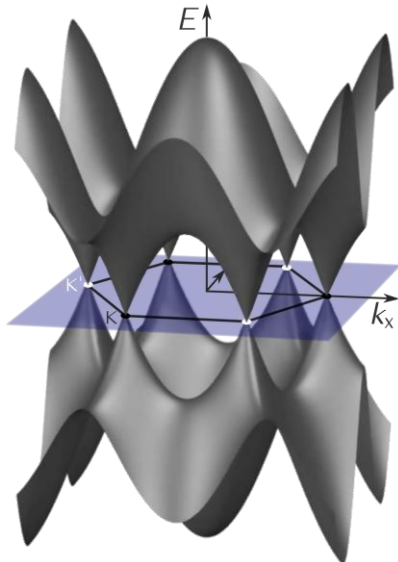


# 代表的Dirac/Weyl 半金属



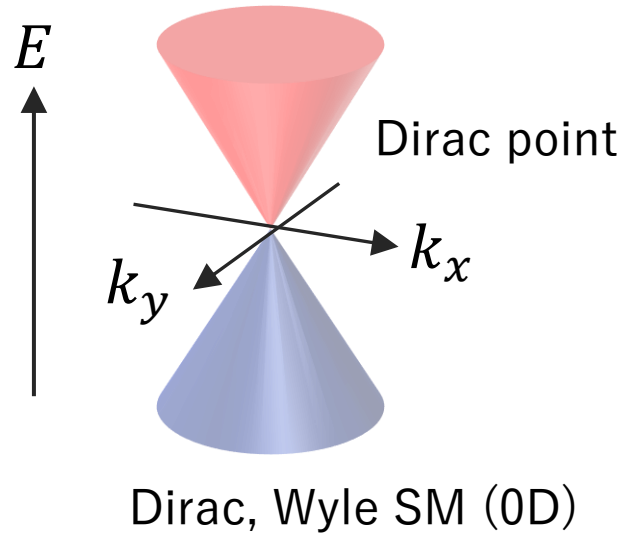
Dirac, Wyle SM (0D)

グラフェン

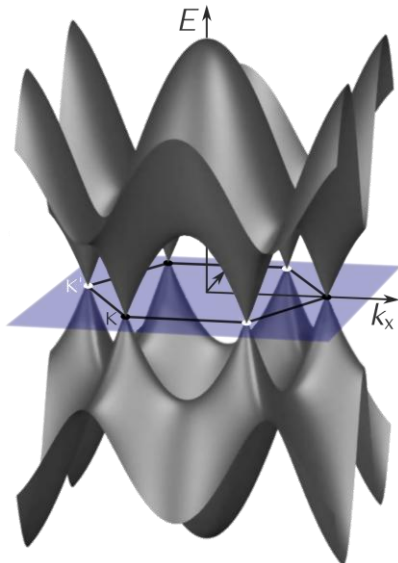


Wikipedia Graphene

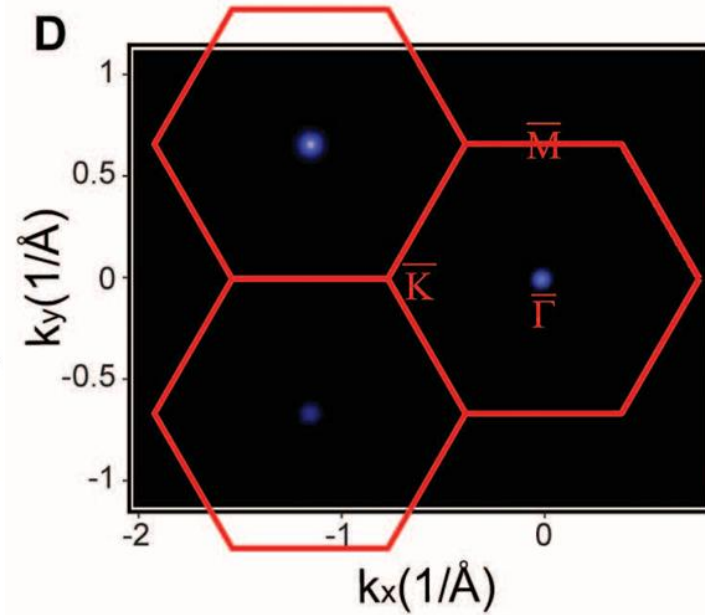
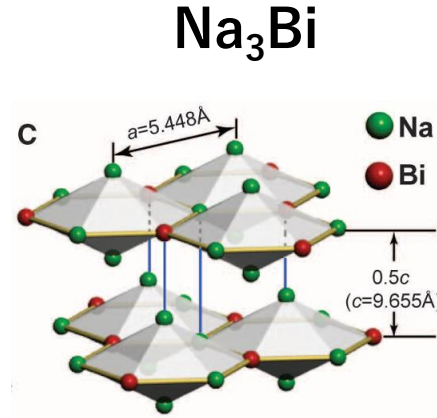
# 代表的Dirac/Weyl 半金属



グラフェン

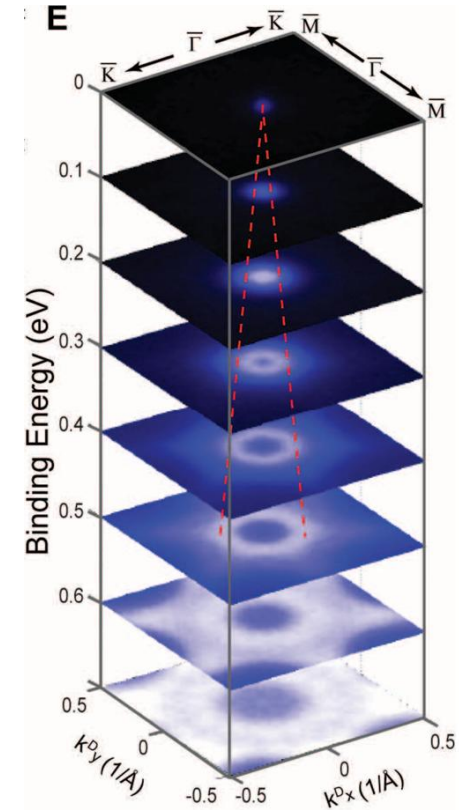


Wikipedia Graphene



Z. K. Liu *et al.*, Science **343**, 864 (2014)

ARPES

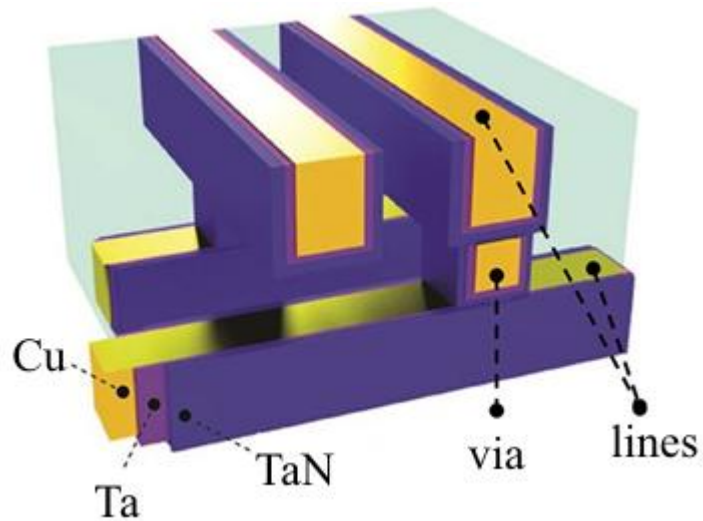


Other 3D Dirac  
Cd3As2

Weyl semimetal  
TaAs, NbAs, NbP

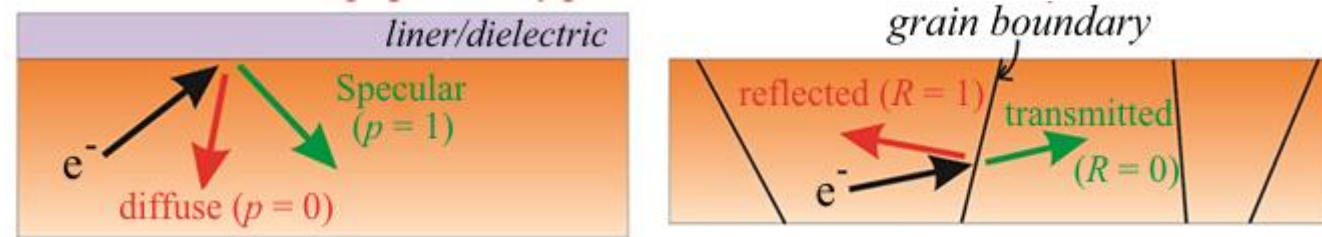
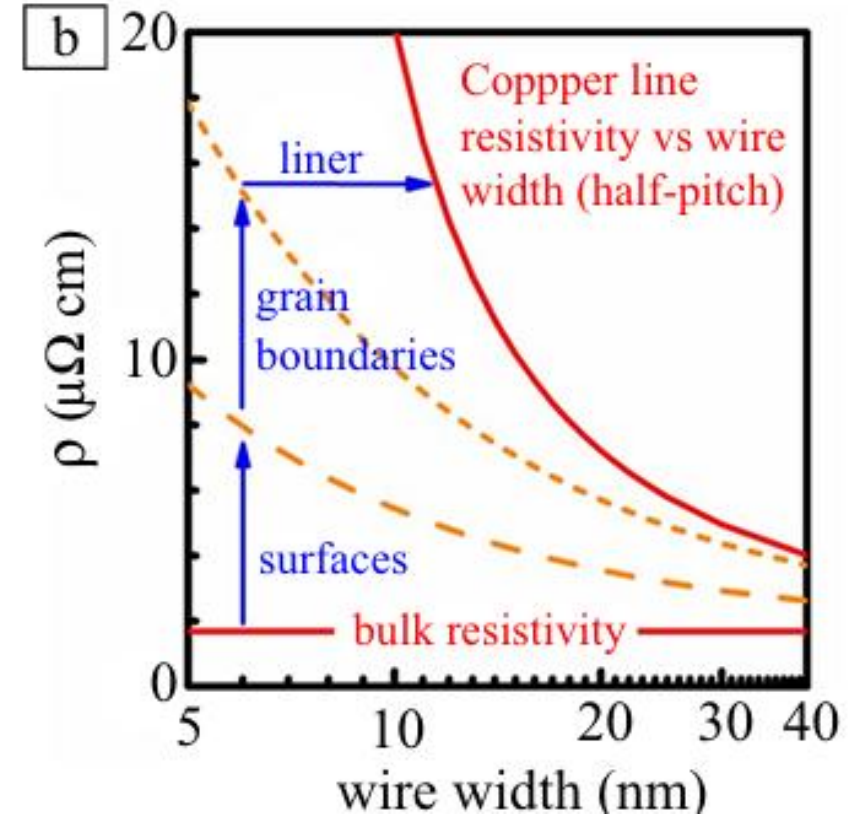
# Application: Promising material for interconnects

ICチップ内の配線構造



Ta, TaN bilayer

- Cuの成長時の核生成促進
- 接着性の向上
- 誘電体へのCuの拡散を抑制



100 nm以下になると、表面での電子散乱が増加し、抵抗率が上昇する

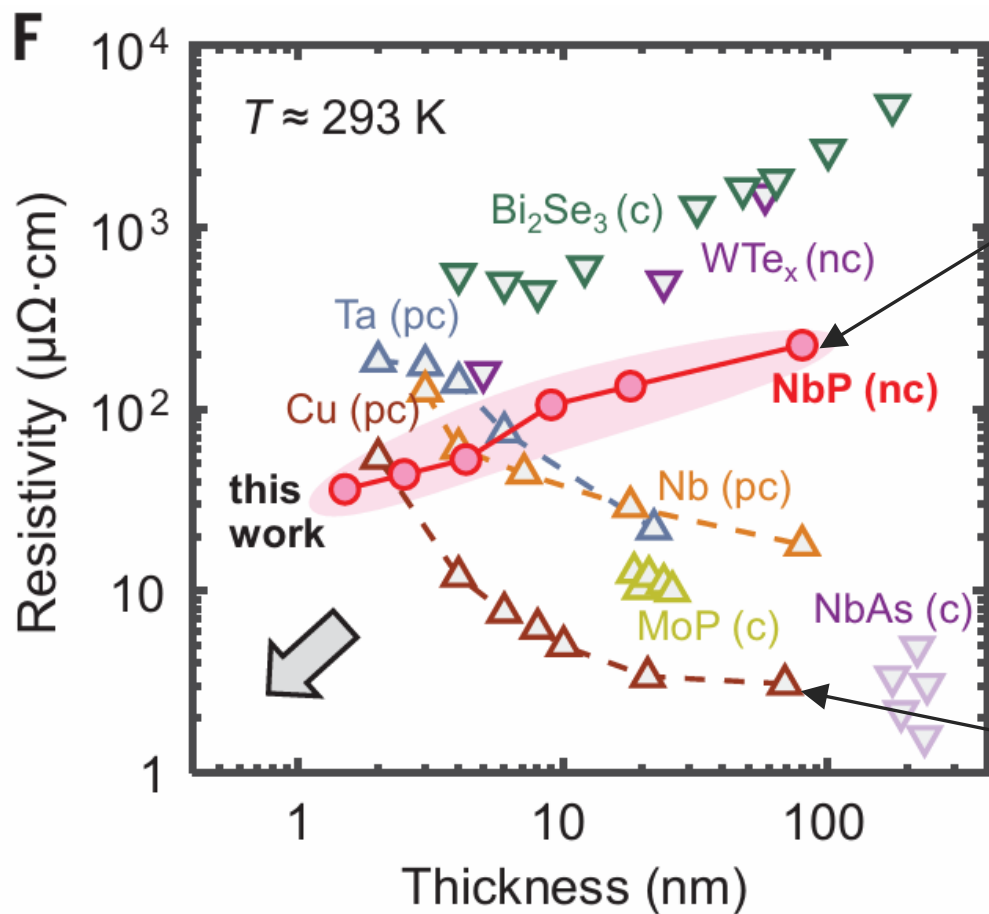
# Application: Promising material for interconnects

ELECTRONIC MATERIALS

## Shrinking interconnects beyond copper

Quantum materials can speed up the information processing in a computer chip

Mehrdad T. Kiani<sup>1</sup> and Judy J. Cha<sup>2</sup>

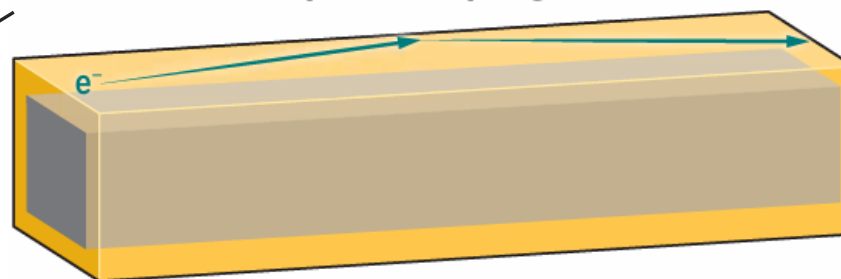


A. Khan *et al.*, *Science* **387**,62–67 (2025)

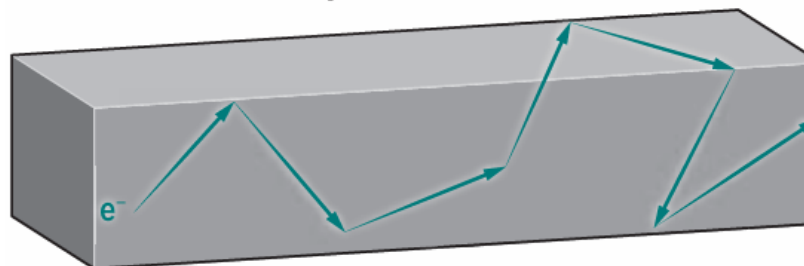
## トポロジカル物質 (NbP)

特殊な表面状態でキャリアの散乱が強く抑制され、サイズが小さくなるほど抵抗率が減少する

### Electron transport in a topological semimetal



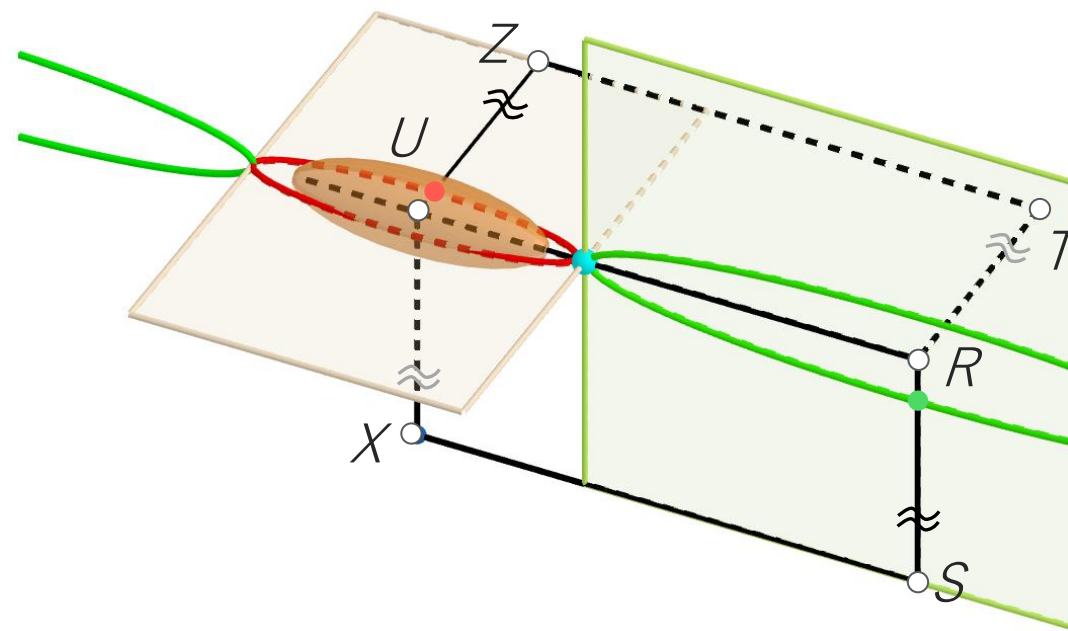
### Electron transport in an elemental metal



## 通常の金属 (銅)

100 nm以下になると、表面での電子散乱が増加し、抵抗率が上昇する

# レニウム (Re) 酸化物における新規トポロジカル電子状態

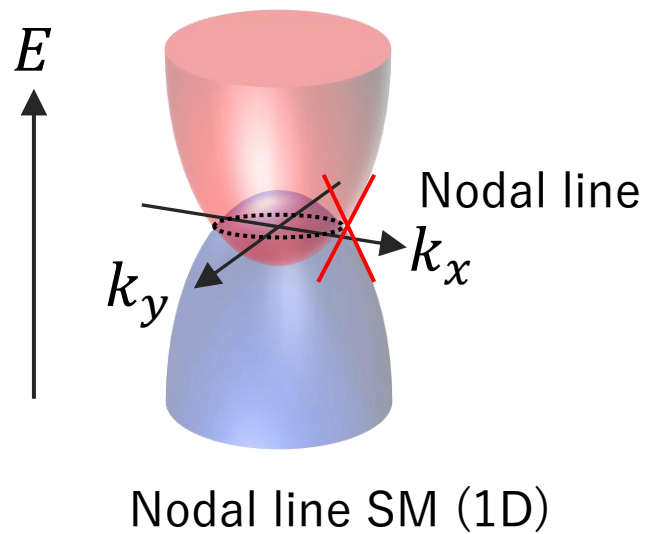
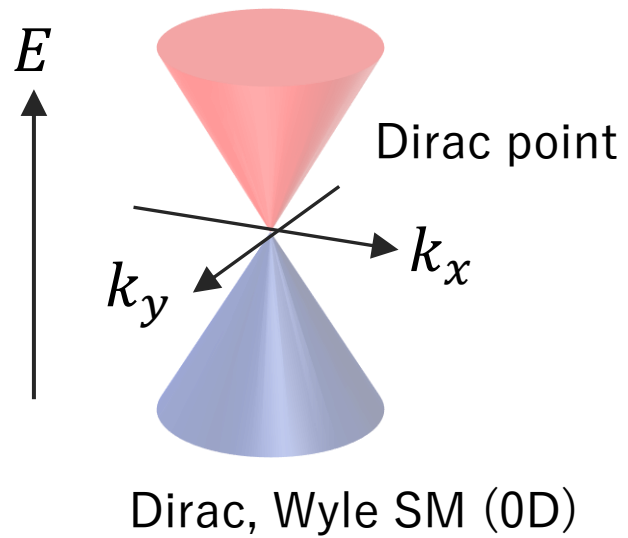


D. Hirai, et al., JPSJ 90, 094708 (2021) **Editor's choice**

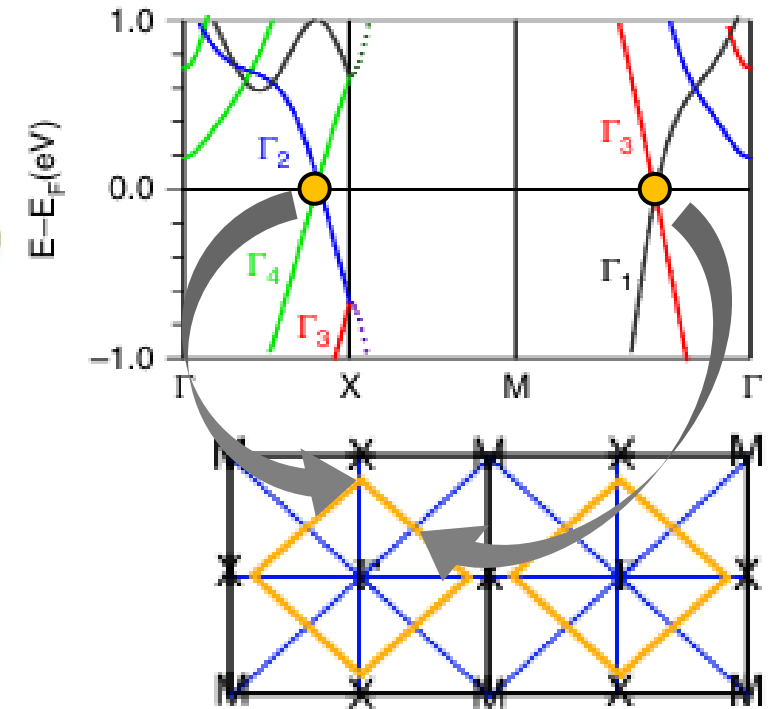
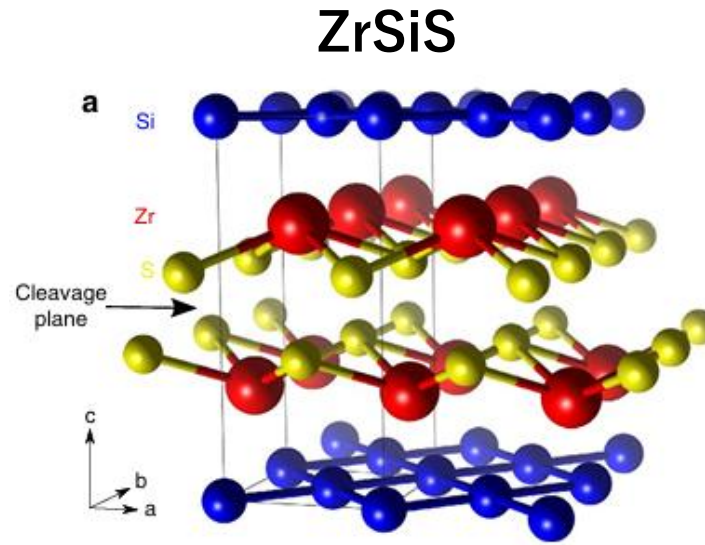
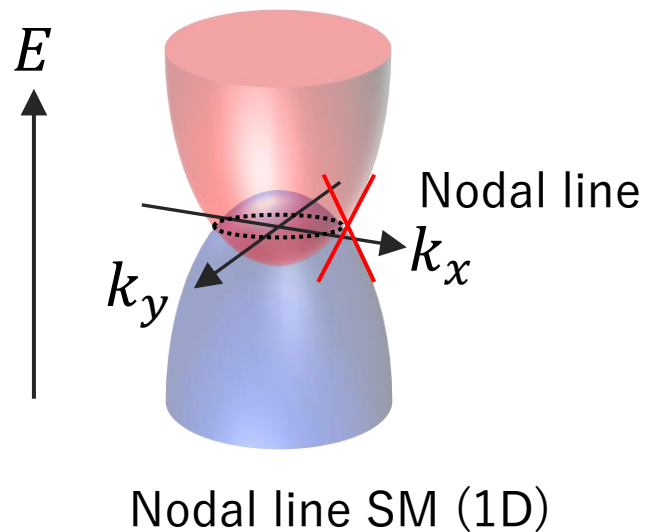
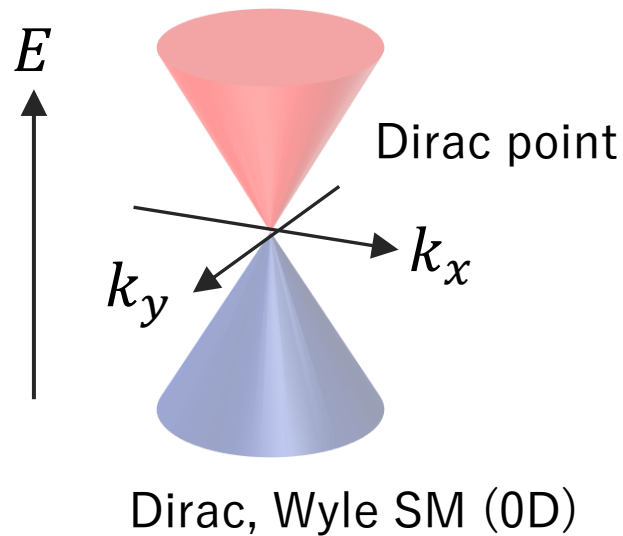
D. Hirai *et al.*, J. Phys.: Condens. Matter, **35**, 405503 (2023)

解説記事：固体物理 2023年3月号 「単純な5d酸化物 $\beta$ -ReO<sub>2</sub>におけるディラック点が描く鎖」

# Nodal line 半金属



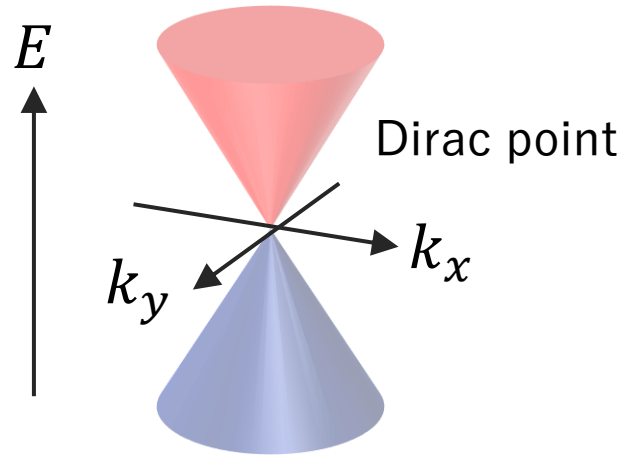
# Nodal line 半金属



## Other Nodal line SMs

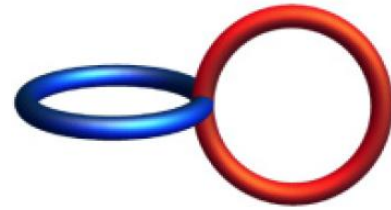
**PdTaSe<sub>2</sub>, Ca<sub>3</sub>P<sub>2</sub>, Cu<sub>3</sub>PdN, CaAgP**

# 様々なトポロジカル電子状態



Dirac, Wyle SM (0D)

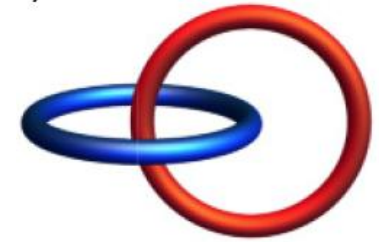
Topological configurations formed by nodal lines



Nodal chain

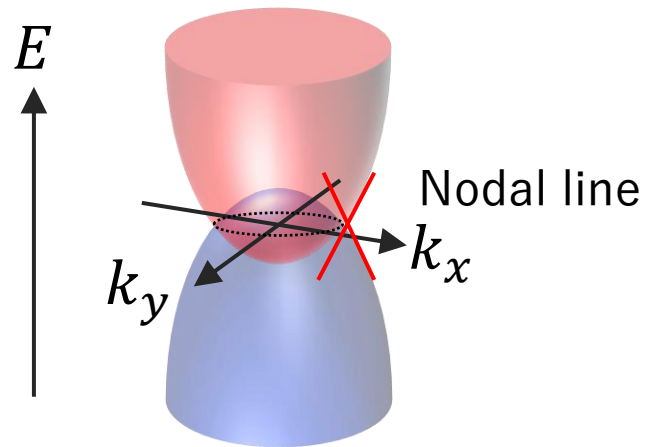


Nodal knot



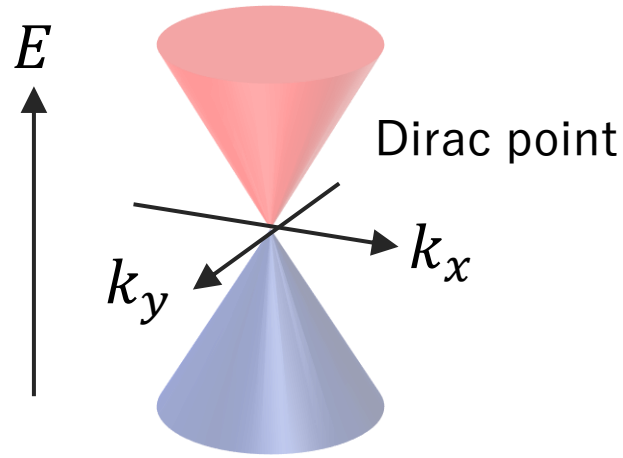
Nodal link

C.-J. Yi *et al.*, Phys. Rev. B. **97**, 201107(R) (2018)

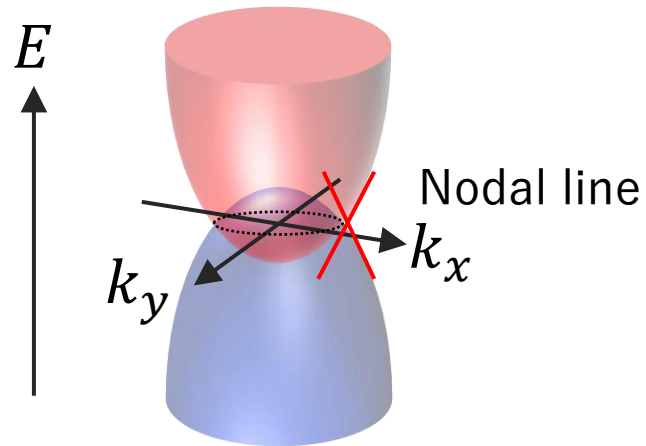


Nodal line SM (1D)

# ノード鎖半金属

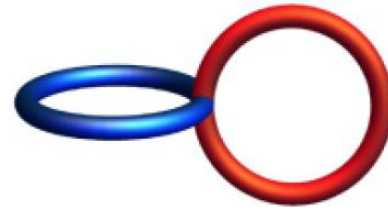


Dirac, Wyle SM (0D)



Nodal line SM (1D)

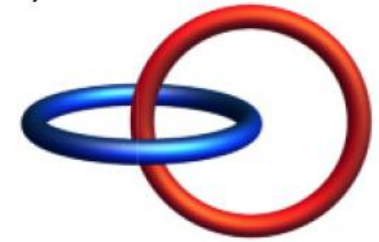
Topological configurations formed by nodal lines



Nodal chain



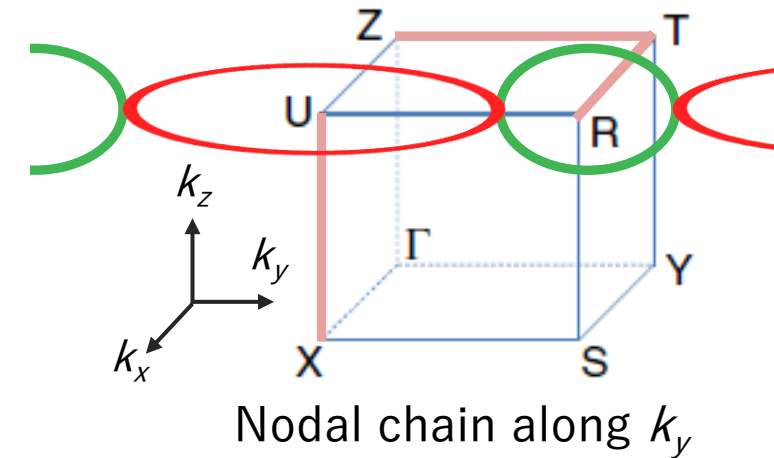
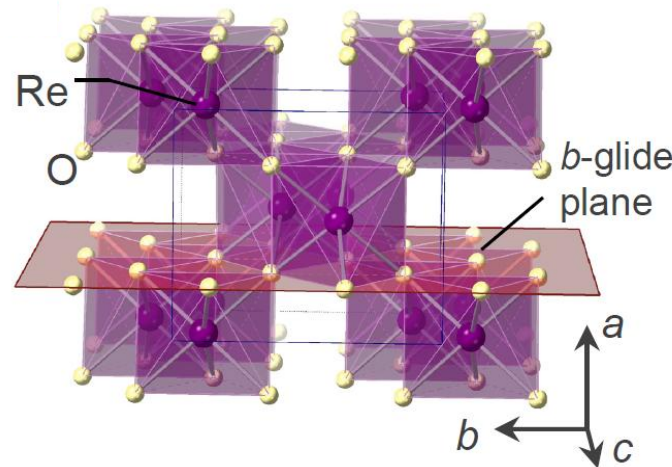
Nodal knot



Nodal link

C.-J. Yi *et al.*, Phys. Rev. B. **97**, 201107(R) (2018)

$\beta$ -ReO<sub>2</sub> (space group *Pbcn*)



Nodal chain along  $k_y$

# レニウム酸化物の純良単結晶育成

Hf	Ta	W	Re	Os	Ir	Pt	Au
72	73	74	75	76	77	78	79

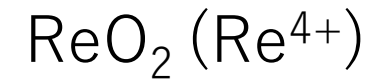
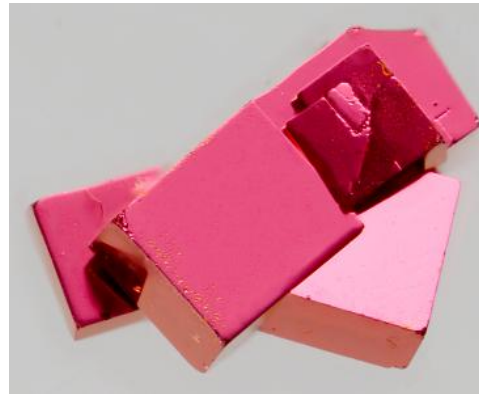
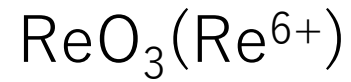
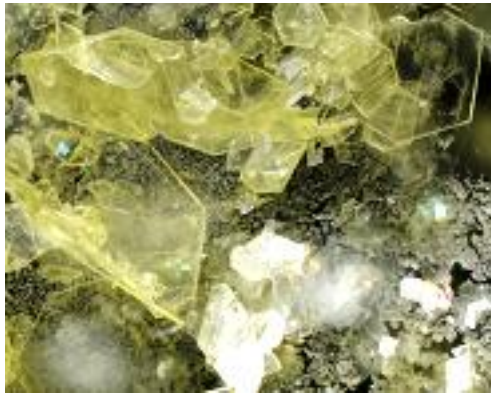
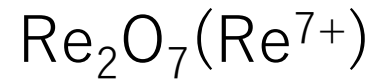
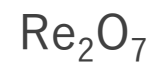


Photo by Dr. Hamane

Home made pure raw material for pure samples



sublimation  
purification

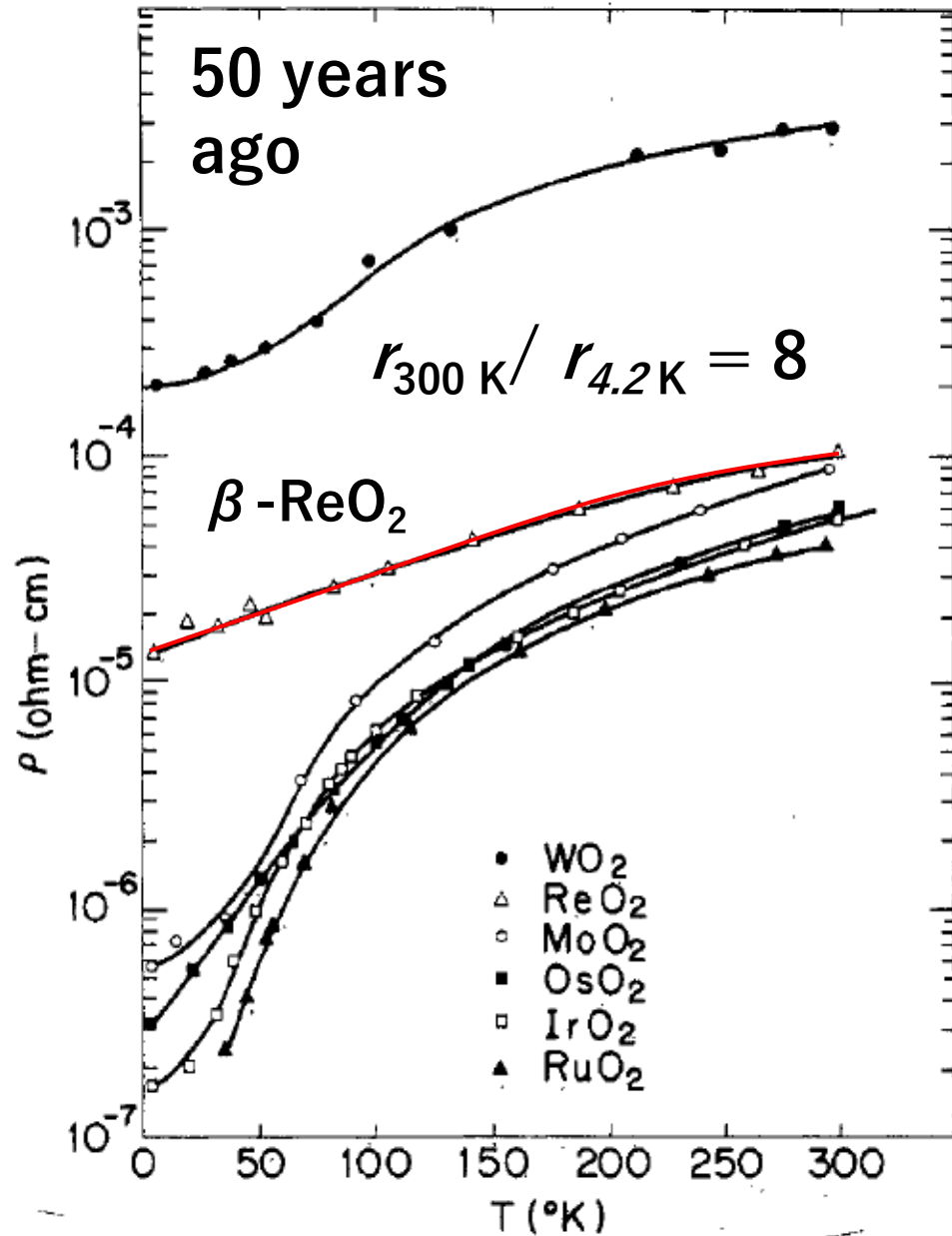


300° C

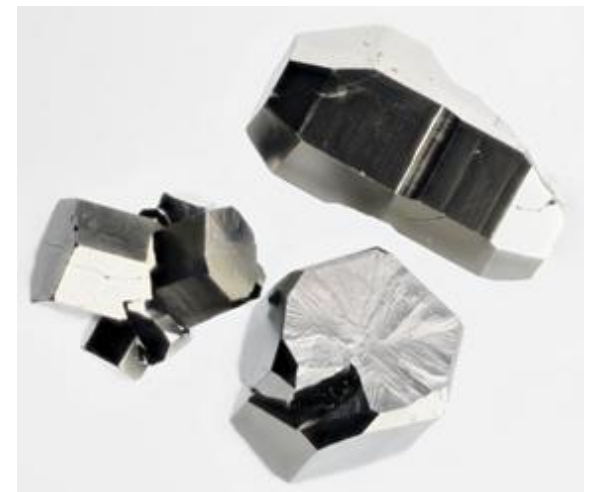
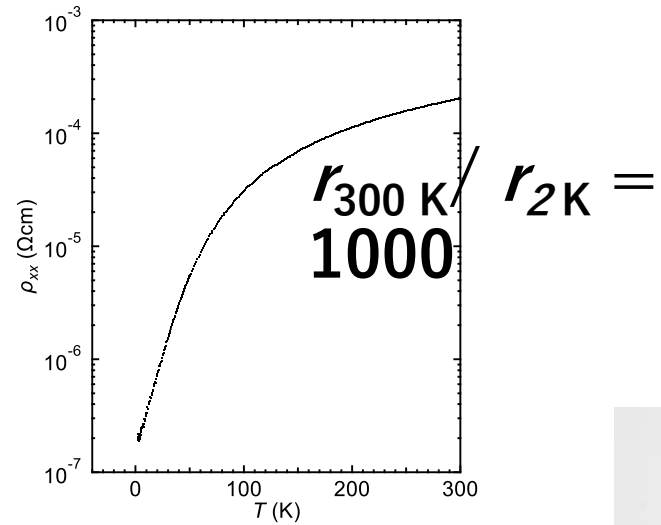


Highly hygroscopic

# 超純良 $\beta$ - $\text{ReO}_2$ 単結晶の物性



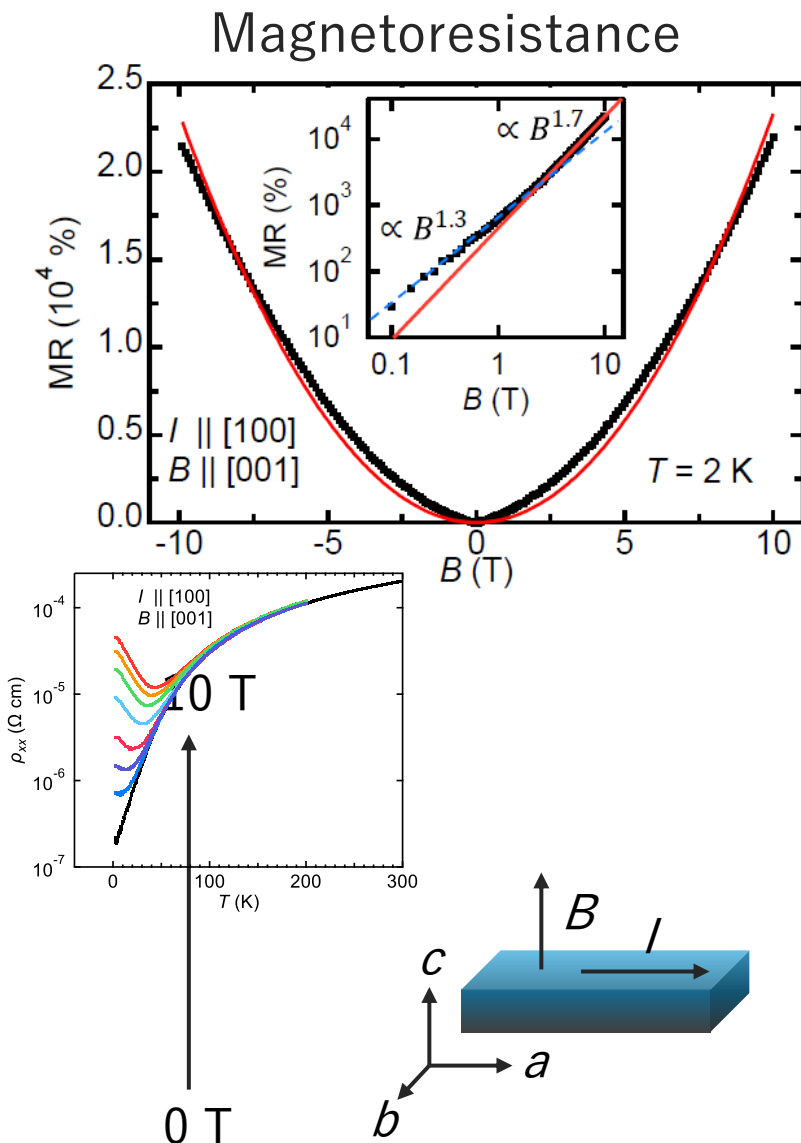
D. B. Rogers *et al.*, Inorg. Chem. **8**, 841 (1969)



D. Hirai *et al.*, JPSJ **90**, 094708 (2021)

# Extremely large magnetoresistance

D. Hirai *et al.*, JPSJ **90**, 094708 (2021)

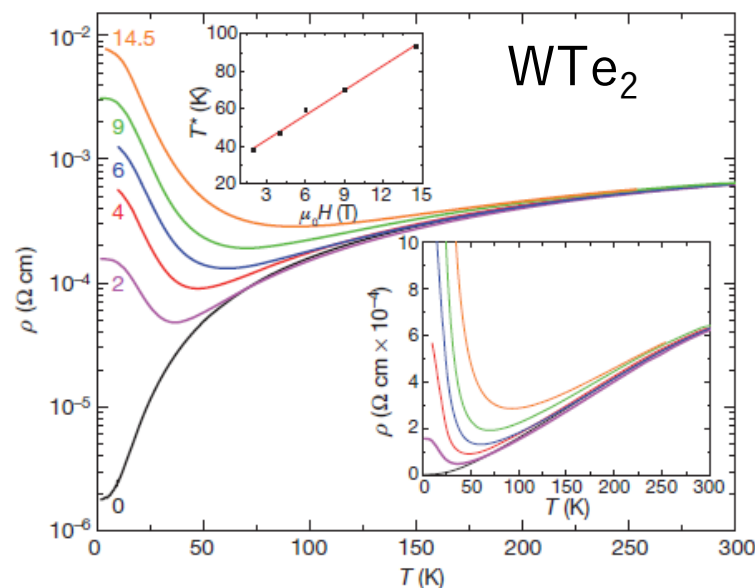


- ✓ Extremely large magnetoresistance (XMR) of 22,000% @ 2 K 10 T (a few % for ordinary metal)



presence of Dirac electron

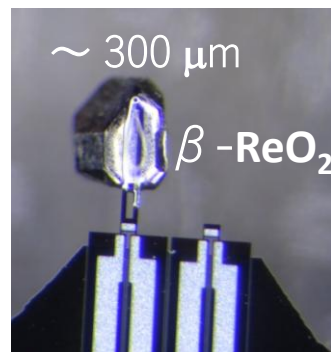
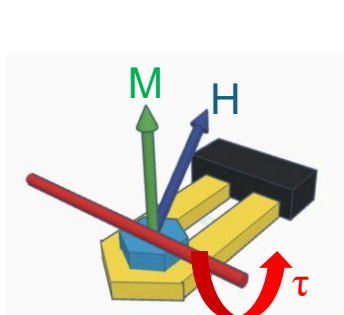
Weyl semimetal



M. N. Ali *et al.*, Nature **514**, 205 (2014)

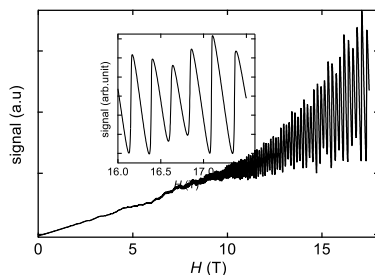
# Experimental determination of Fermi surface

dHvA oscillations in magnetic torque

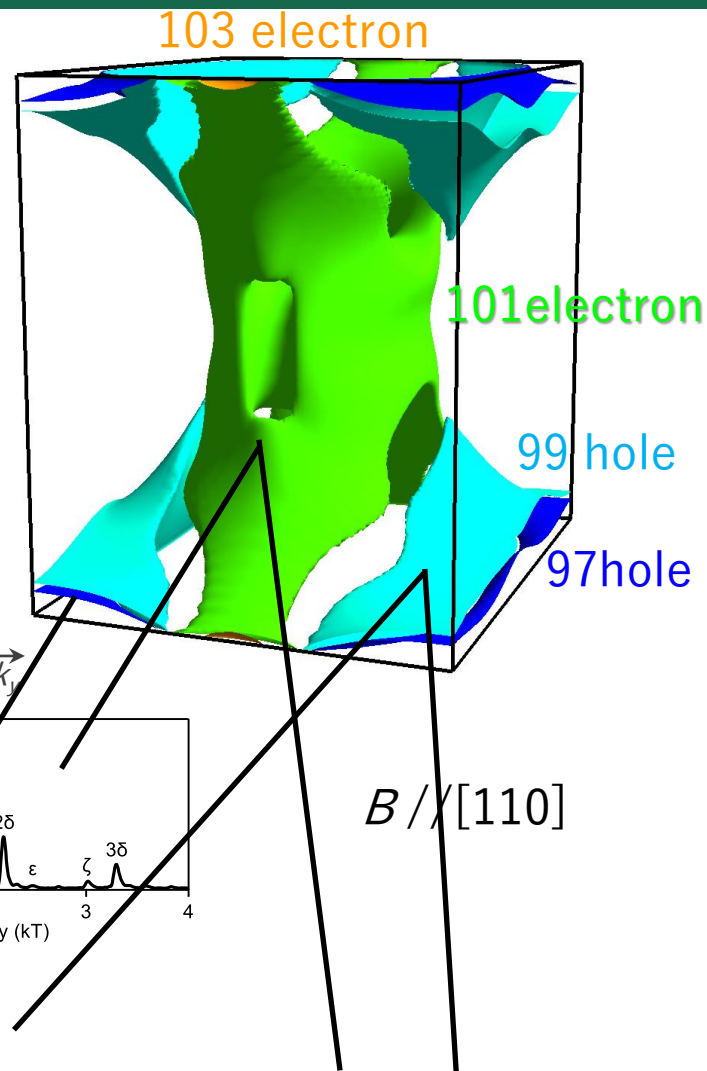
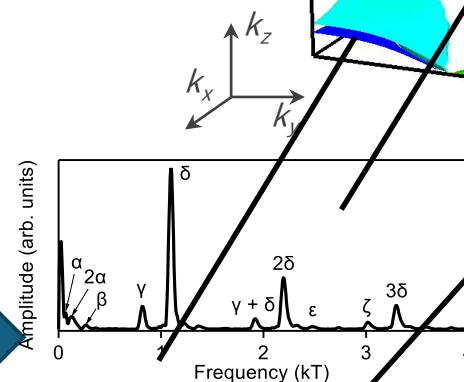


温度 : 30 mK  
磁場 : 17.5 T

@NIMS Quantum Material Properties Group



FFT

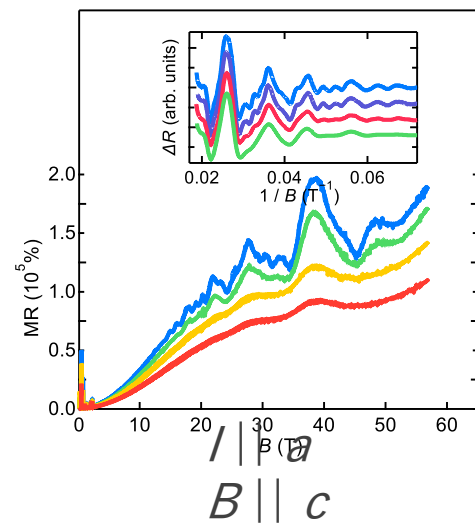
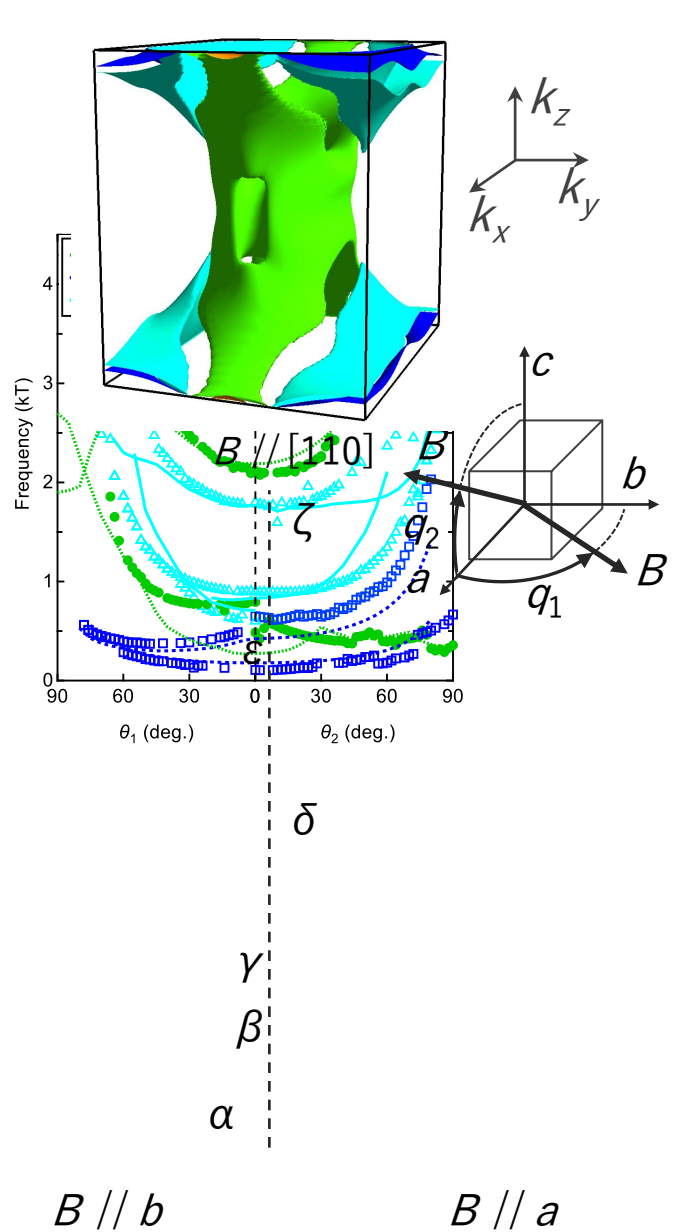


$T = 30\text{mK}$

$$F_Q = \frac{\hbar}{2\pi e} A_F$$

dHvA frequencies are related to the extreme value cross section of the Fermi surface ( $A_F$ ) perpendicular to the magnetic field

# Experimental determination of Fermi surface

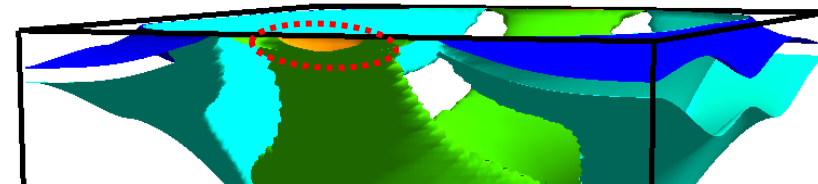


$T/K =$   
 1.5  
 2.0  
 3.0  
 4.2

$T/K =$   
 1.5  
 4.2  
 5.7  
 9.0

Frequency: 100 T

103 electron

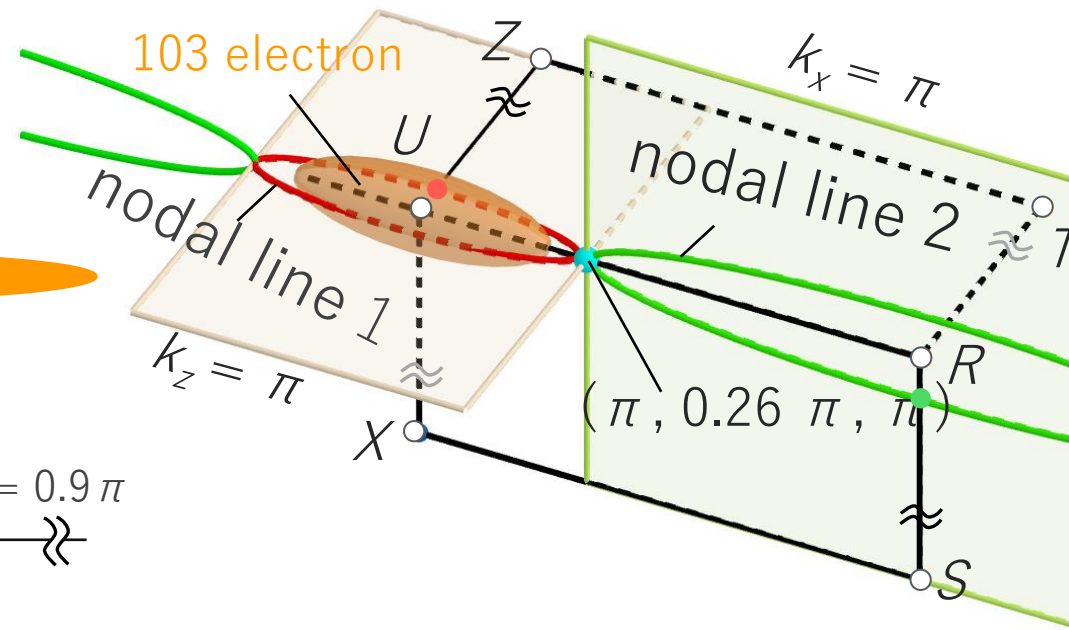
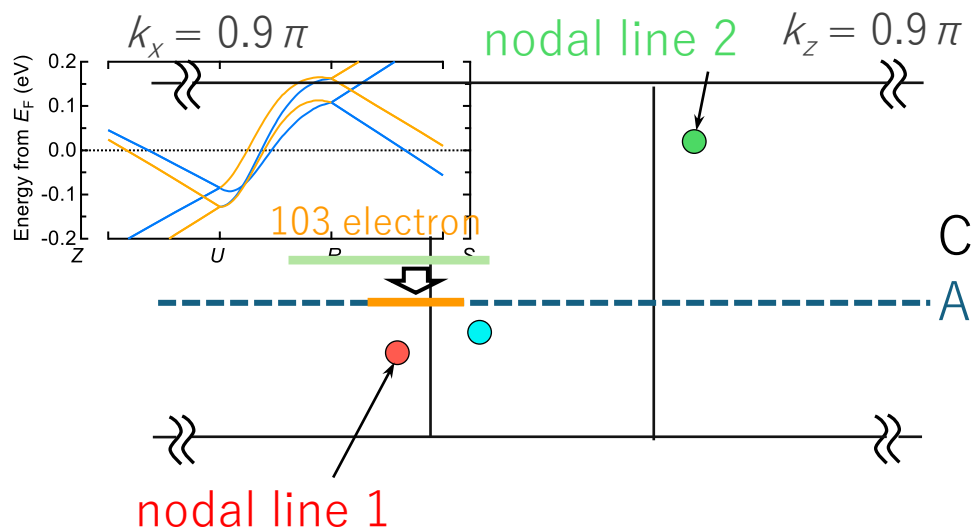


# Small electron pocket & Nodal chain

Shape of 103 electron pocket estimated from QOs



Elongated along the  $k_y$



Calculated  $E_F$   
Actual  $E_F$

The area of 103 electron is nearly half of calculated value

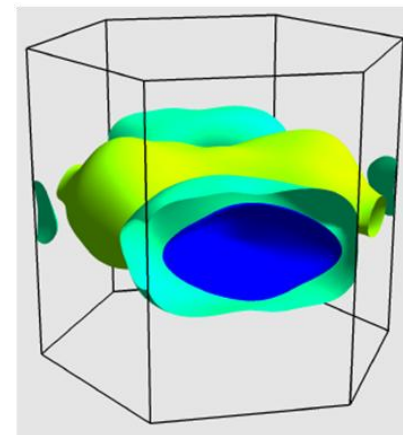
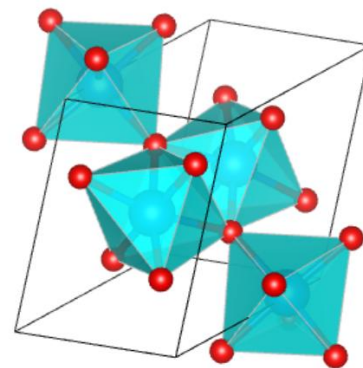
$E_F$  is lower than expected

**Nodal chain is confirmed at very close to  $E_F$**

D. Hirai, et al., JPSJ 90, 094708 (2021) Editor's choice      D. Hirai et al., J. Phys.: Condens. Matter, 35, 405503 (2023)

解説記事：固体物理 2023年3月号 「単純な5d酸化物  $\beta$ - $\text{ReO}_2$  におけるディラック点が描く鎖」

# 遷移金属二酸化物におけるトポロジカル電子状態



Y. Muramatsu, D. Hirai *et al.*, APL Materials, **13**, 011119 (2025)

M. Hiraishi, D. Hirai, *et al.*, Phys. Rev. Lett., **132**, 166702 (2024) **Editor's suggestion**

S. Gyo, D. Hirai, *et al.*, PNAS, **123**, e2526641123 (2026)

# Other transition-metal dioxides

$\text{WO}_2$



$\text{RuO}_2$



$\text{IrO}_2$



$\text{OsO}_2$



# Other transition-metal dioxides

WO<sub>2</sub>



RuO<sub>2</sub>



IrO<sub>2</sub>



OsO<sub>2</sub>



Crystal structure of TMO<sub>2</sub>

Cr	Mn	Fe	Co
Mo	Tc	Ru	Rh
W	Re	Os	Ir

$\alpha$ -PbO<sub>2</sub>

rutile

Distorted rutile

# Other transition-metal dioxides

WO<sub>2</sub>



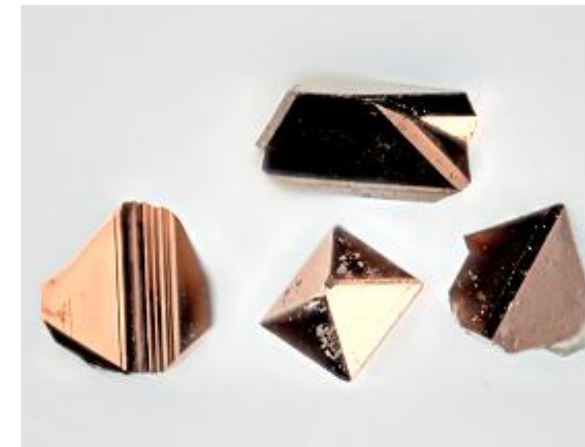
RuO<sub>2</sub>



IrO<sub>2</sub>



OsO<sub>2</sub>



Crystal structure of TMO<sub>2</sub>

Cr	Mn	Fe	Co
Mo	Tc	Ru	Rh
W	Re	Os	Ir

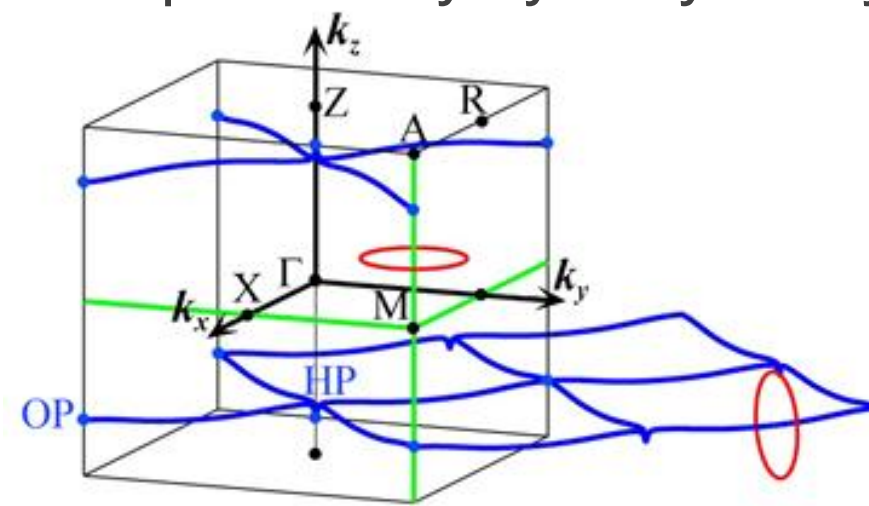
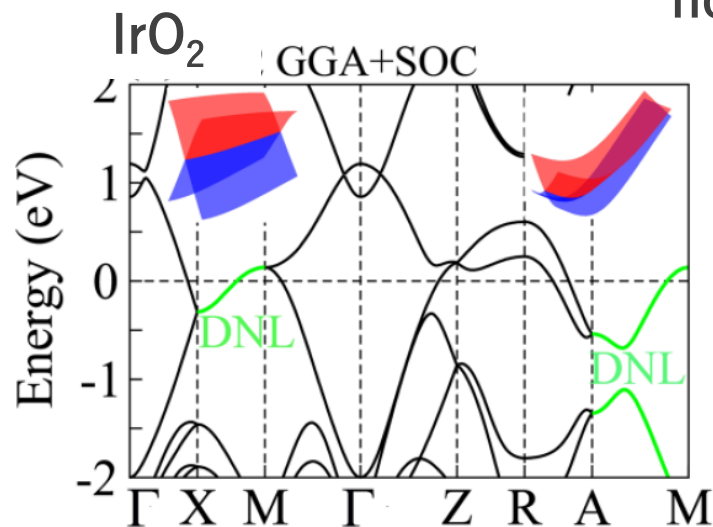
$\alpha$ -PbO<sub>2</sub>

rutile

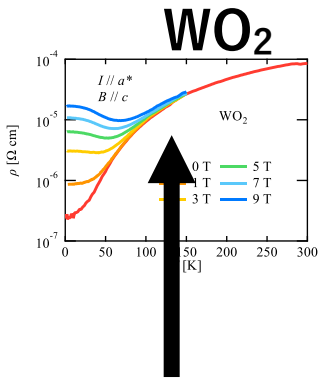
Distorted rutile

rutile-type TMO<sub>2</sub> are predicted to be nodal line semimetals

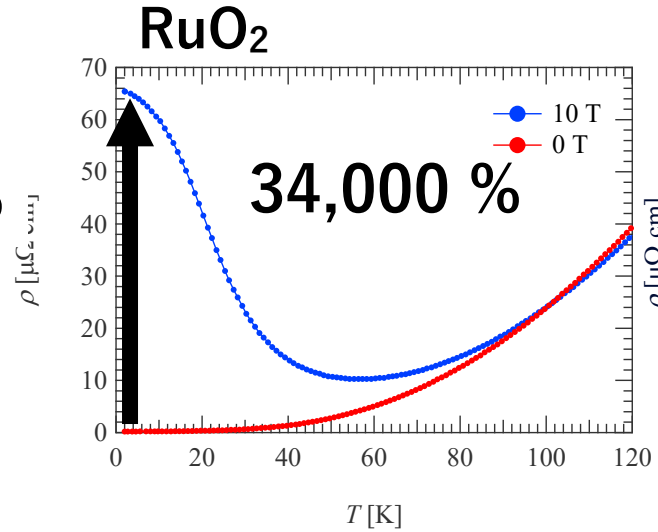
nodal line protected by crystal symmetry



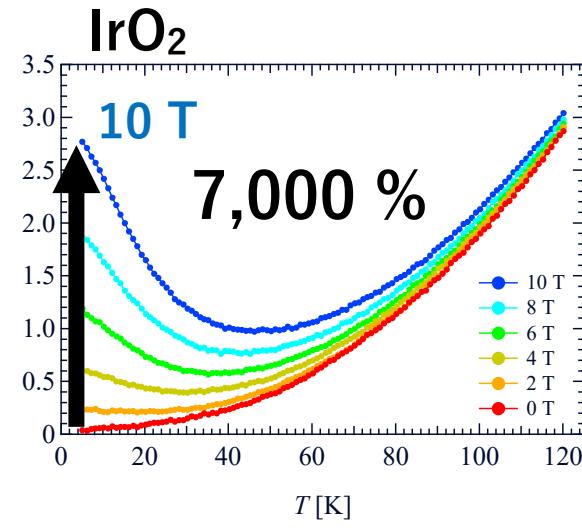
# Extremely large magnetoresistance



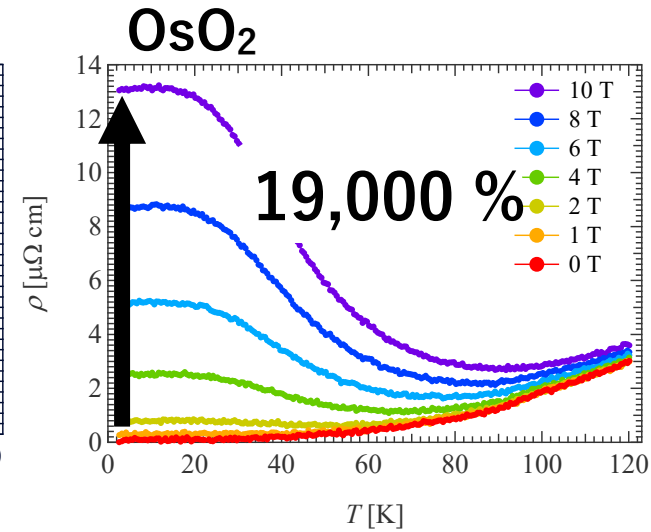
13,200 %



34,000 %



7,000 %



19,000 %

XMR for all the compounds

Dirac electrons everywhere?

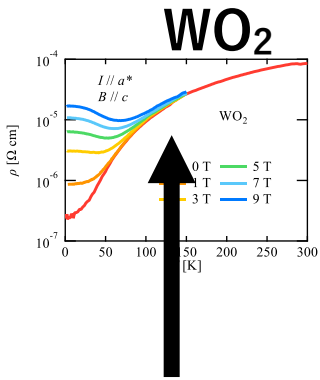


村松君

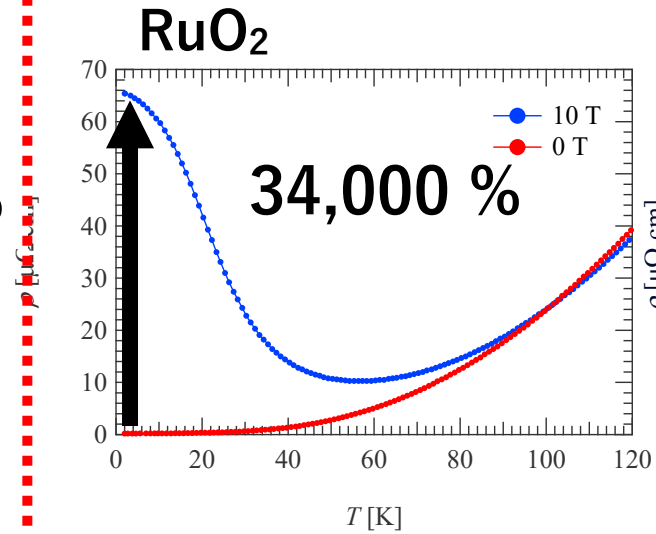


宮田君

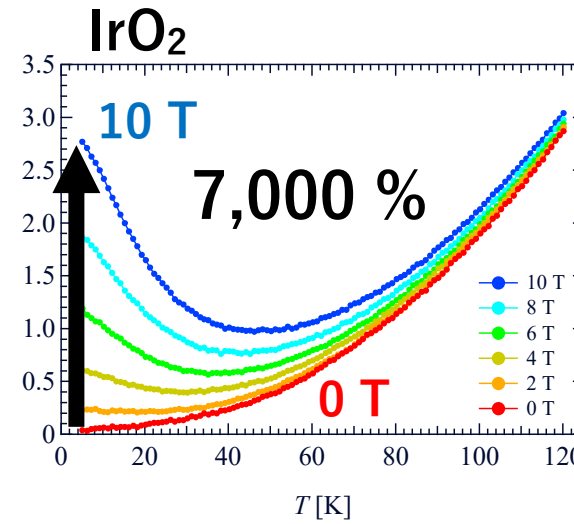
# Extremely large magnetoresistance



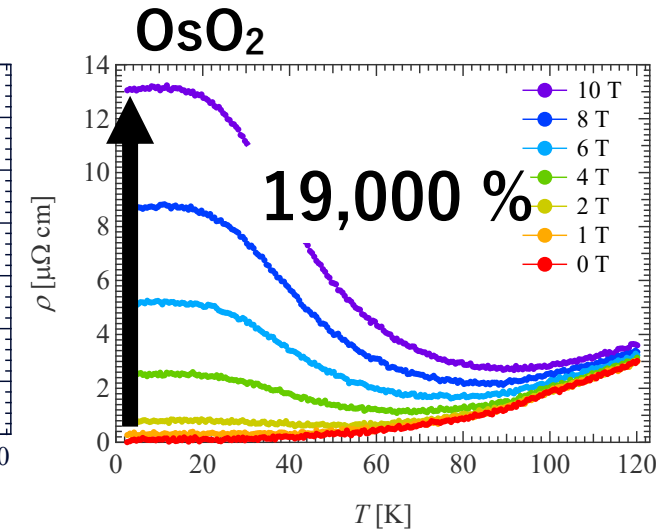
13,200 %



34,000 %



7,000 %

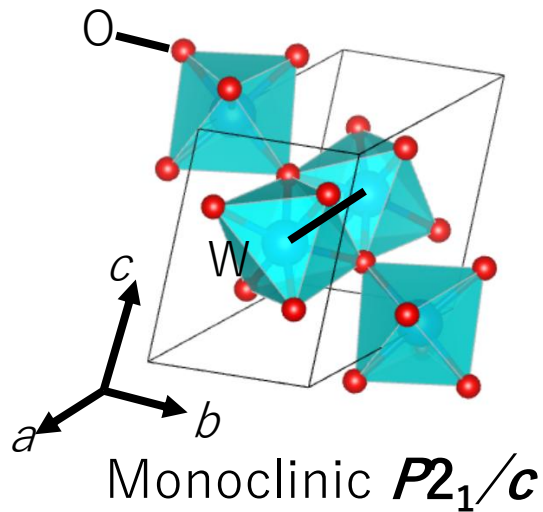


19,000 %

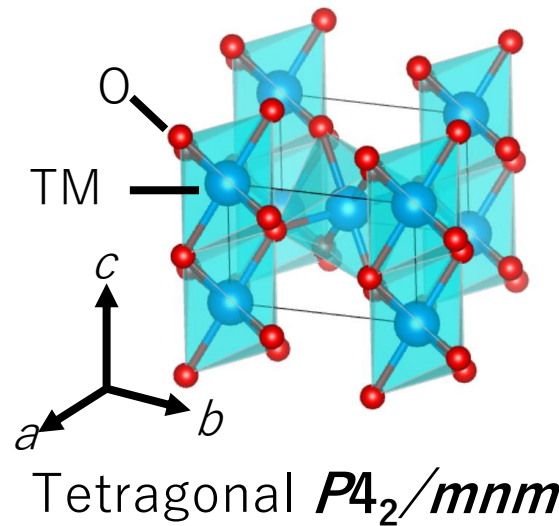
XMR for all the compounds

Dirac electrons everywhere?

Distorted rutile



rutile



Dimerization of TM

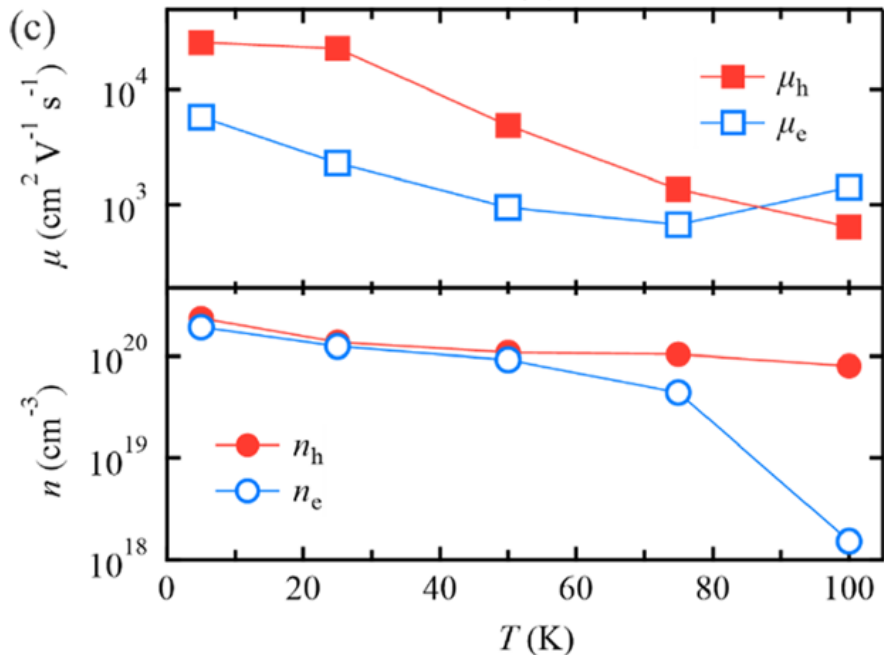
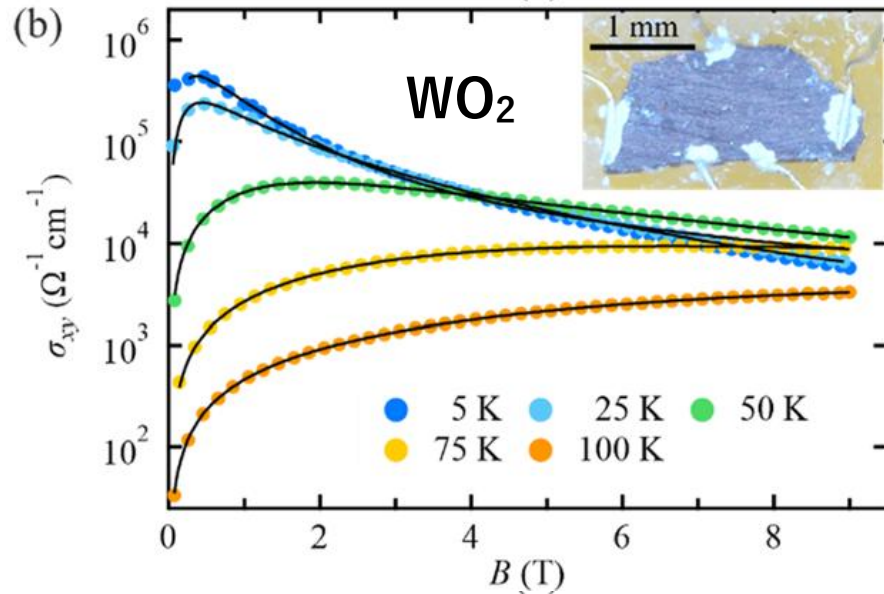


村松君

宮田君

# Dirac electrons in WO<sub>2</sub>

## Conductivity



## 2キャリアモデル

ホール伝導度  $\sigma_{xy}$  (縦磁気抵抗とホール抵抗率から) に対するフィッティング

$$\sigma_{xy} = n_h \mu_h^2 / (1 + \mu_h^2 B^2) - n_e \mu_e^2 / (1 + \mu_e^2 B^2)$$

➤ 低温で  $n_h \doteq n_e$  ( $n_h/n_e \doteq 0.8$ ) **キャリアの補償**

➤ 低温に向けホール移動度が増大

➤ 26,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>@5 K Weyl半金属MoTe<sub>2</sub>やWTe<sub>2</sub>と同等の値

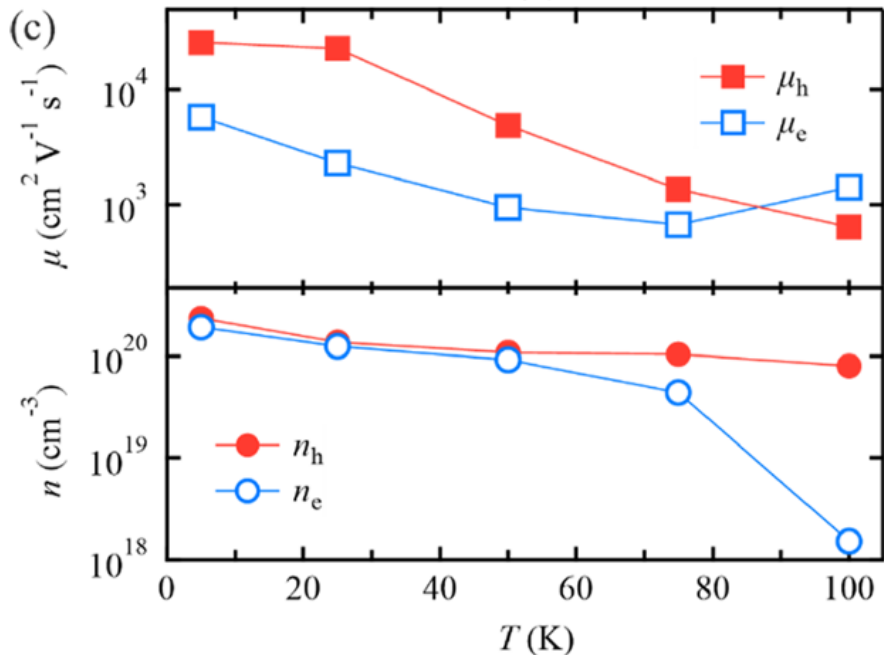
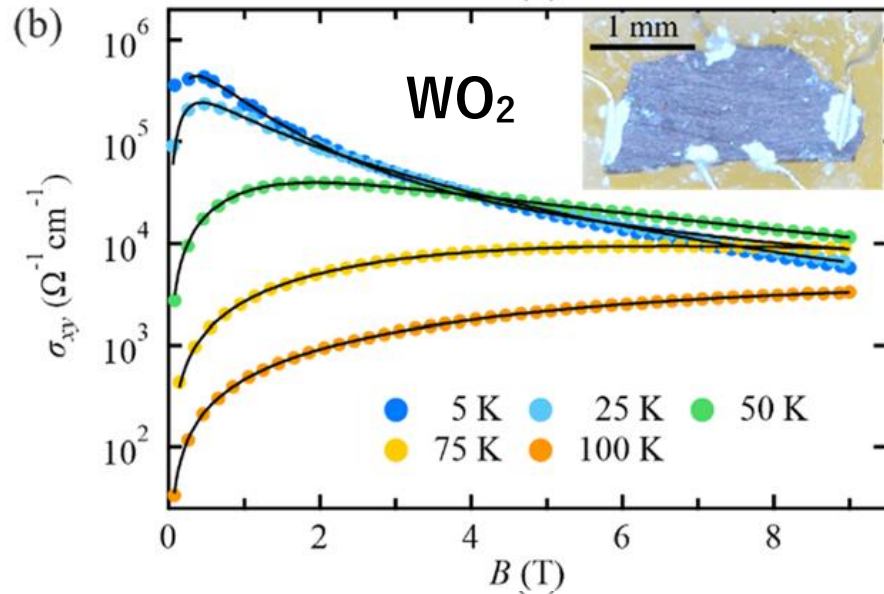
**超高移動度キャリアの存在**



村松君

# Dirac electrons in WO<sub>2</sub>

## Conductivity



## 2キャリアモデル

ホール伝導度  $\sigma_{xy}$  (縦磁気抵抗とホール抵抗率から) に対するフィッティング

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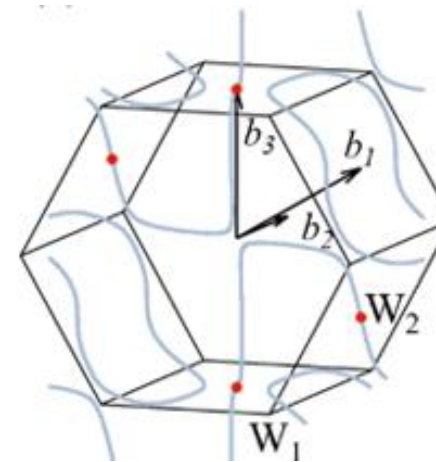
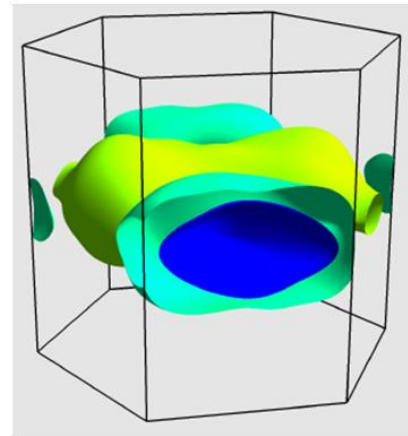
➤ 26,000 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>@5 K Weyl半金属MoTe<sub>2</sub>やWTe<sub>2</sub>と同等の値

**超高移動度キャリアの存在**

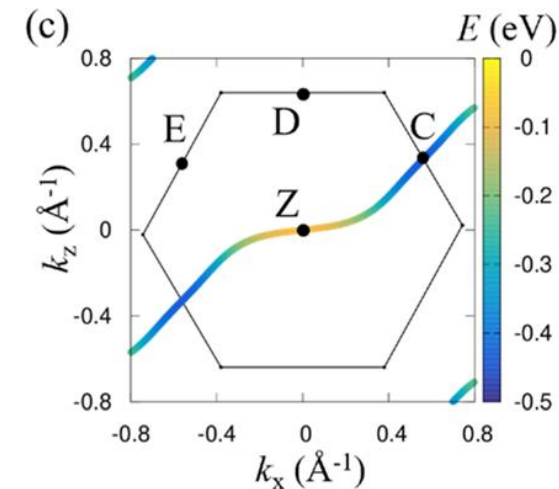


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## Theory

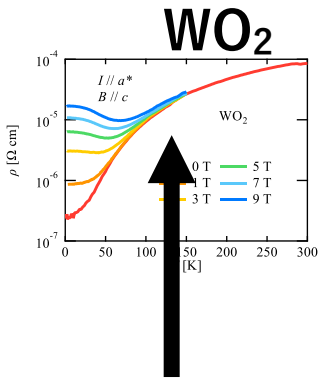


Dirac points

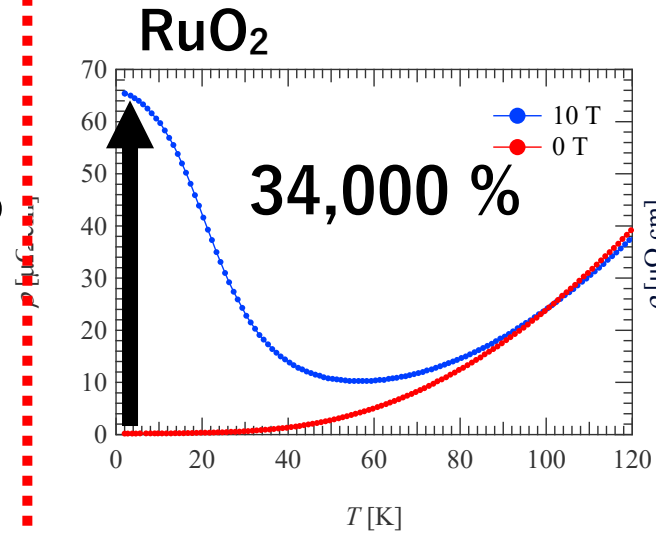


Dirac Nodal line

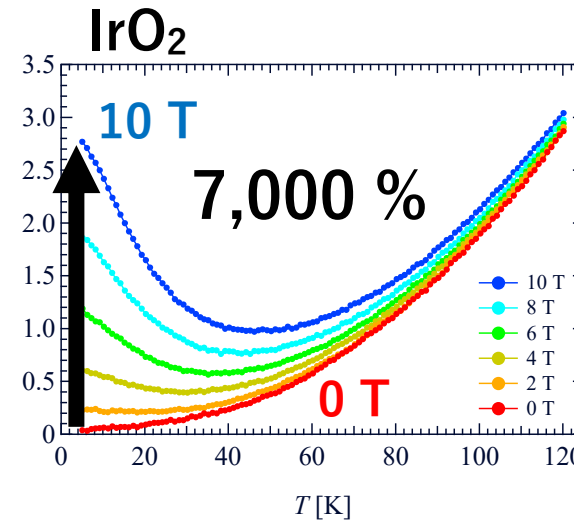
# Extremely large magnetoresistance



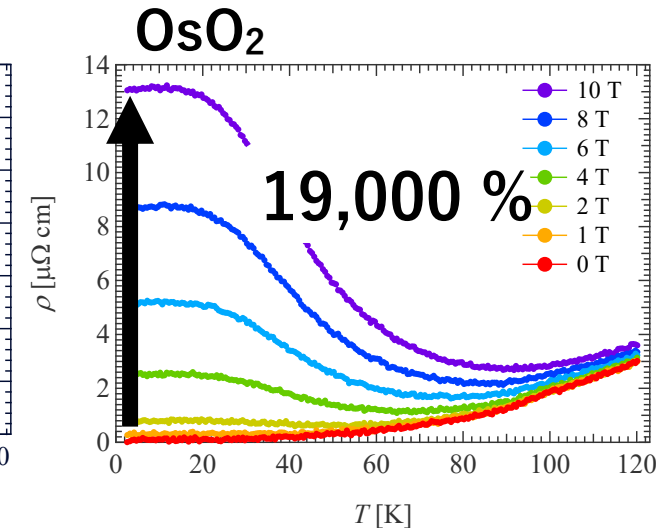
13,200 %



34,000 %



7,000 %

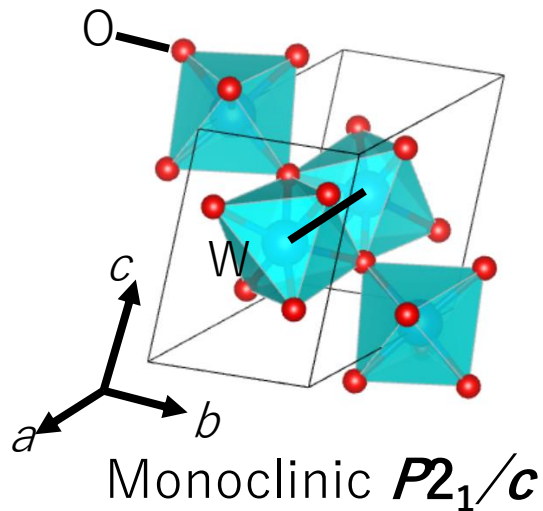


19,000 %

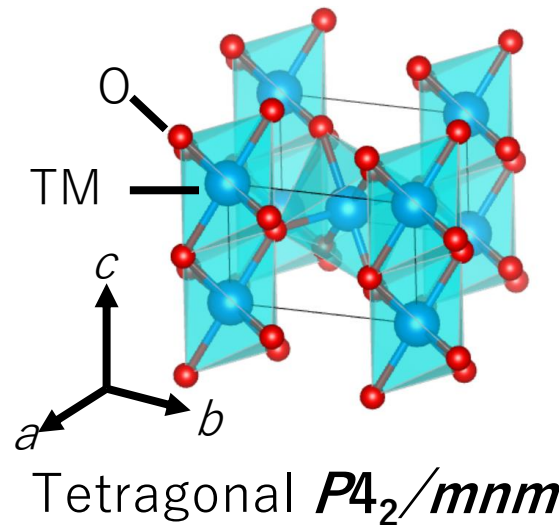
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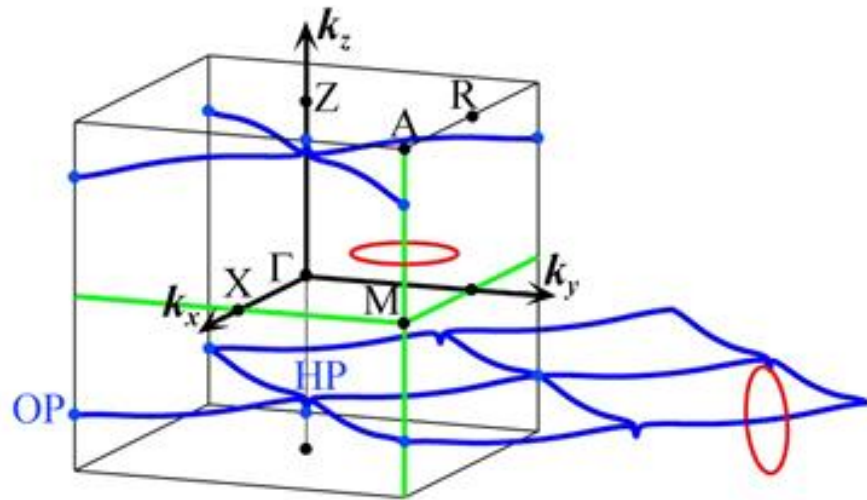


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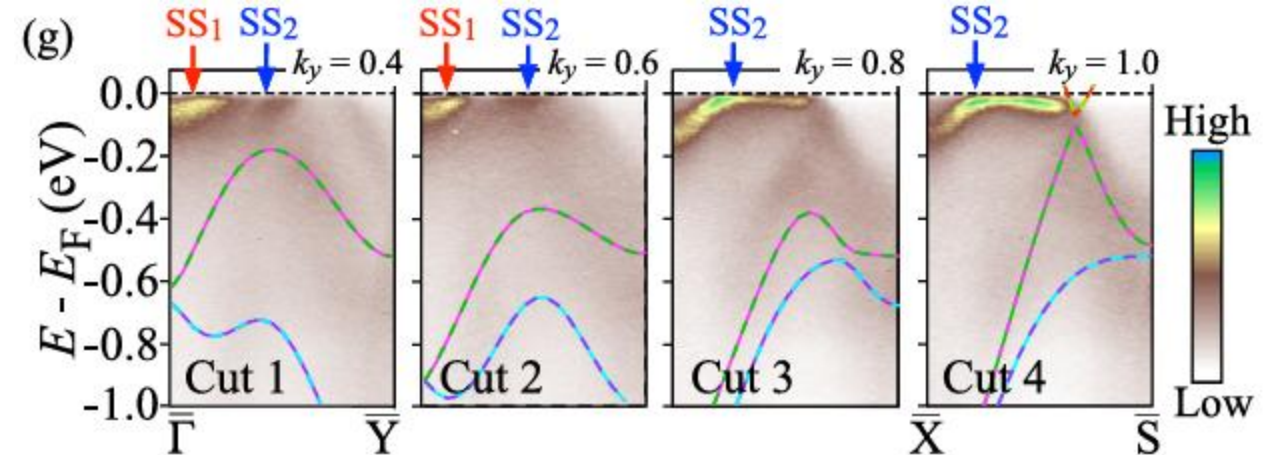
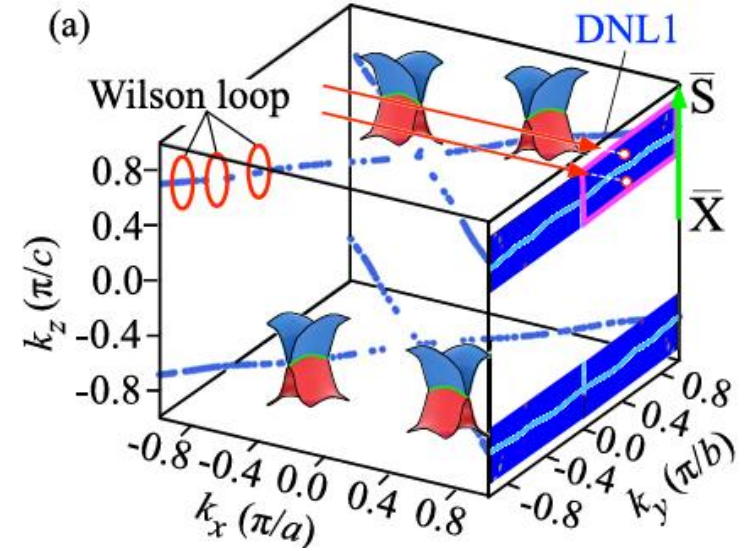
宮田君

# RuO<sub>2</sub> Surface state

RuO<sub>2</sub>



Y. Sun *et al.*, Phys. Rev. B **95**, 235104 (2017).



T. Osumi *et al.*, Phys. Rev. B, **113**, 085116 (2026)

Topological surface states originating from Dirac nodal line were observed in RuO<sub>2</sub>

# Summary

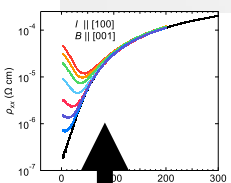
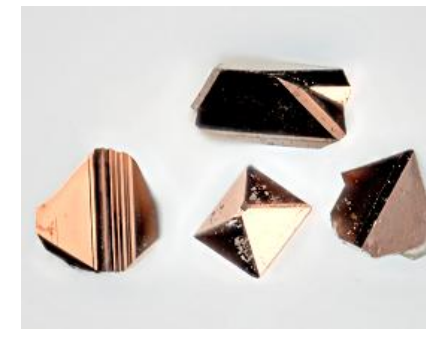
ReO<sub>2</sub>

WO<sub>2</sub>

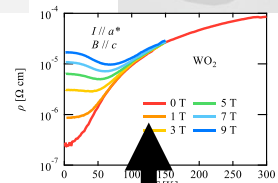
RuO<sub>2</sub>

IrO<sub>2</sub>

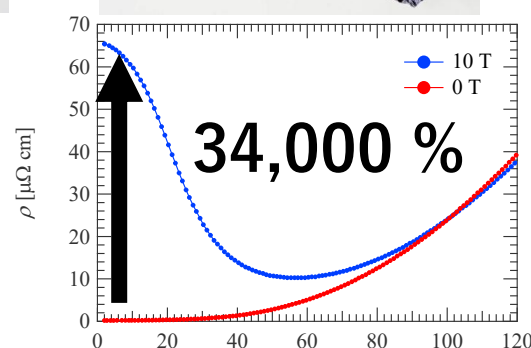
OsO<sub>2</sub>



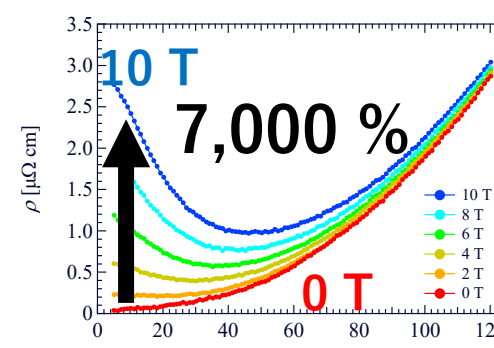
22,000 %



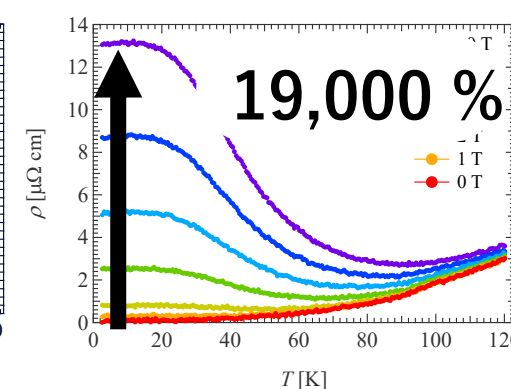
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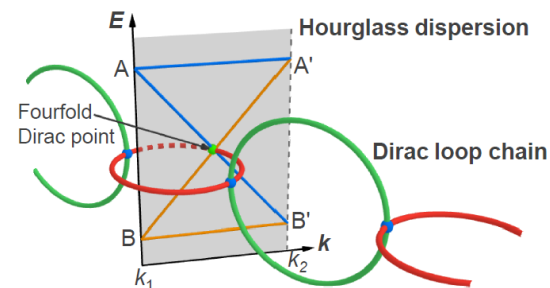
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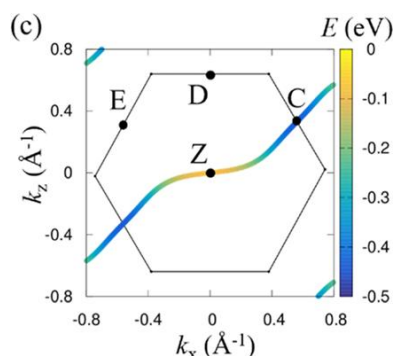
7,000 %



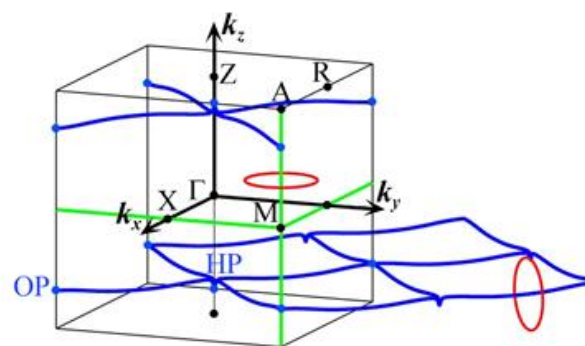
19,000 %



D nodal chain SM



D nodal line SM



D nodal line SM?

Crystal structure of TMO<sub>2</sub>

Cr	Mn	Fe	Co
Mo	Tc	Ru	Rh
W	Re	Os	Ir

rutile

Distorted rutile α-PbO<sub>2</sub>

D. Hirai, et al., JPSJ 90, 094708 (2021) Editor's choice

解説記事：固体物理 2023年3月号

D. Hirai et al., J. Phys.: Condens. Matter, 35, 405503 (2023)

Y. Muramatsu, D. Hirai et al., APL Materials, 13, 011119 (2025)

# Acknowledgement



名大 竹中研



丸山君



村松君



宮田君



林君



竹中康司



NIMS 量子物質特性グループ



宇治 進也



鴻池 貴子



服部 裕也



寺嶋 太一



横国大



河村 光晶



大阪大



小口 多美夫



京都大



見波 将