# Theoretical design of high-performance thermoelectric materials and unconventional superconductors using first-principles calculations

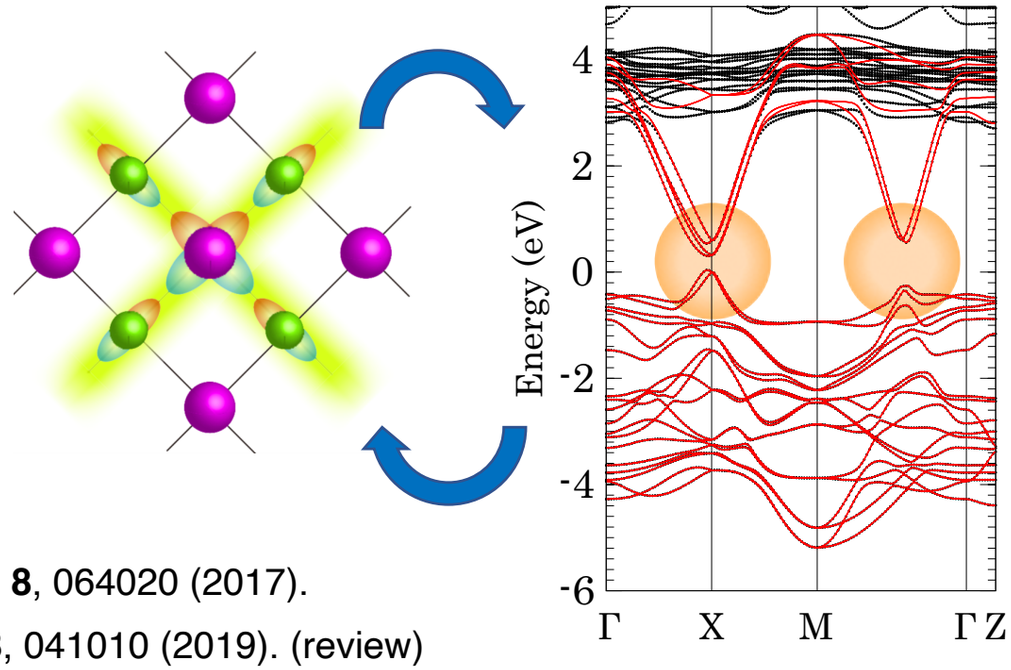
**Masayuki Ochi**

**Department of Physics, Osaka University**

# Self-introduction

| | |
|---|---|
| Name | Masayuki Ochi |
| Biography | 2009–2014 Dept. Phys, The Univ. of Tokyo<br>2014–2015 PD researcher in RIKEN CEMS<br>2015–present Research Associate in Dept. Phys, Osaka Univ. |
| Research Interest | Thermoelectrics<br>Strongly correlated materials<br>Topological phases<br>Wave function theory |

# Part 1：High thermoelectric performance by quasi-1dim gapped Dirac cone




**MO**, H. Usui, and K. Kuroki, PRAppl. **8**, 064020 (2017).

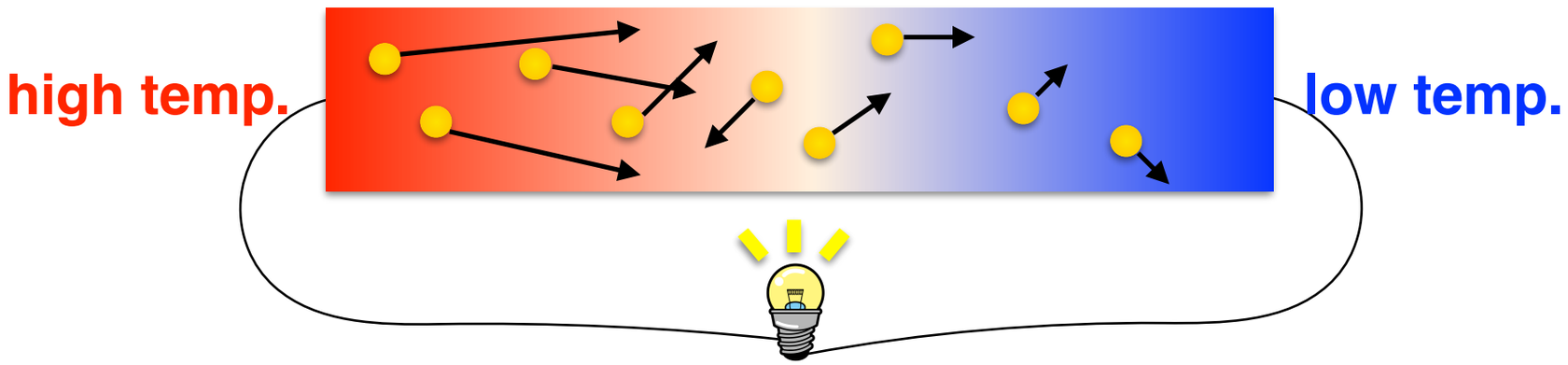
**MO**, H. Usui, and K. Kuroki, JPSJ **88**, 041010 (2019). (review)

[Collaborators] Hidetomo Usui (Shimane Univ.), Kazuhiko Kuroki (Osaka Univ.)

# Thermoelectric conversion (Thermoelectric effect)

= direct conversion of temperature difference to electric voltage and vice versa

(e.g.) Seebeck effect

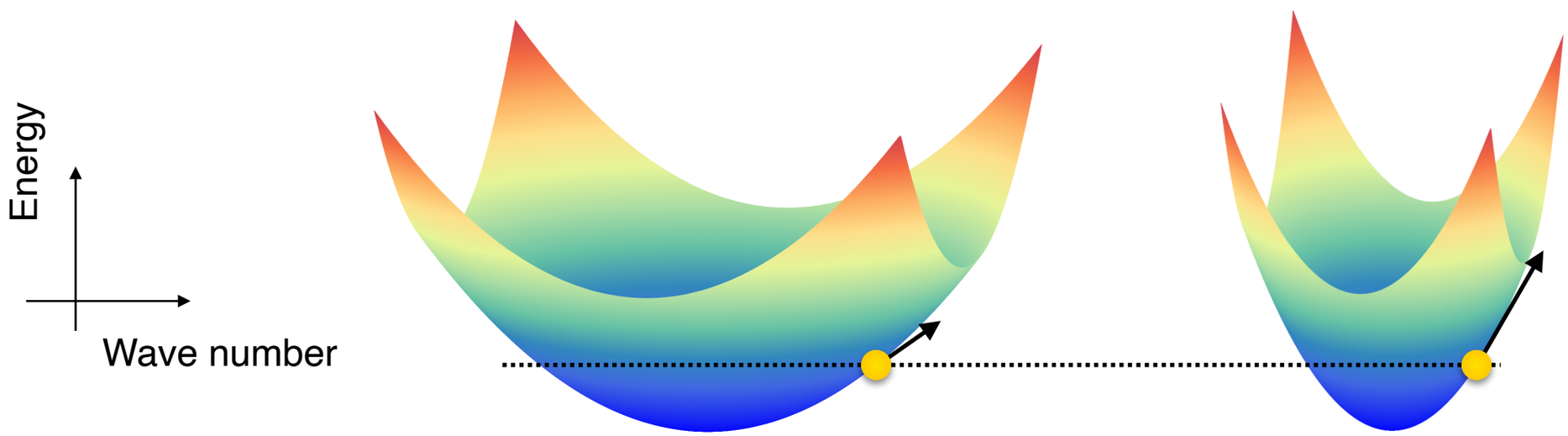



$V = -S\Delta T$ (V:voltage, S: Seebeck coeff., $\Delta T$: temperature diff.)

enables a use of waste heat as energy resource = **clean energy**

**Efficient conversion is a key for application**

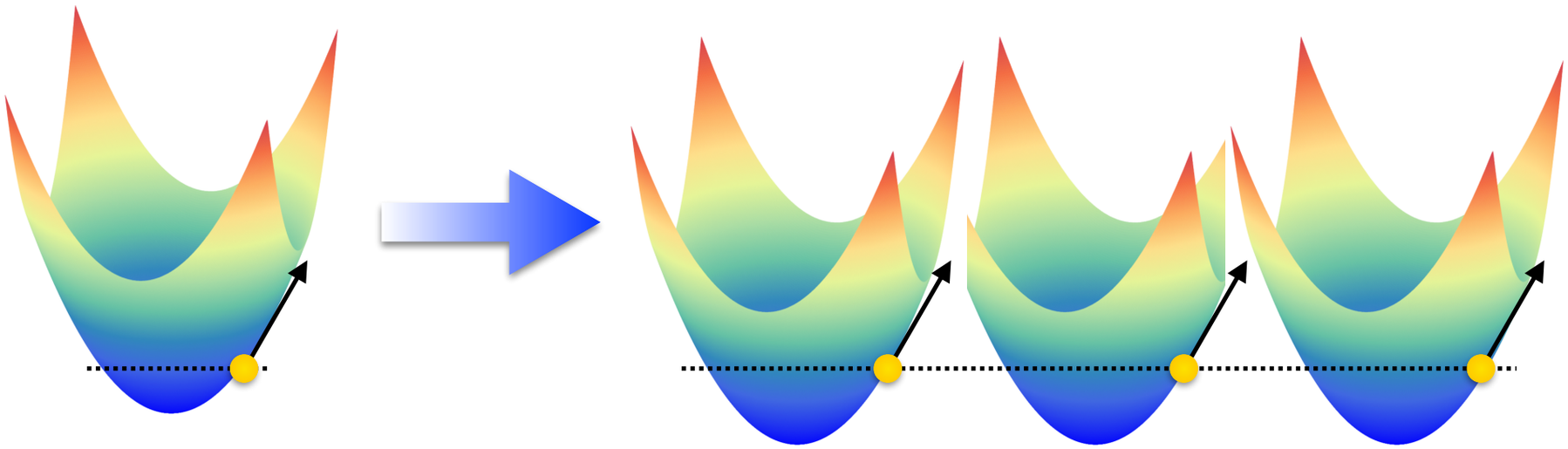
# Electronic band structure for thermoelectric effects




| | | |
|---|---|---|
| **Group velocity (slope of band dispersion)** | low | high |
| **Density of states (DOS)** | high | low |

**Trade-off relation for a simple band dispersion**

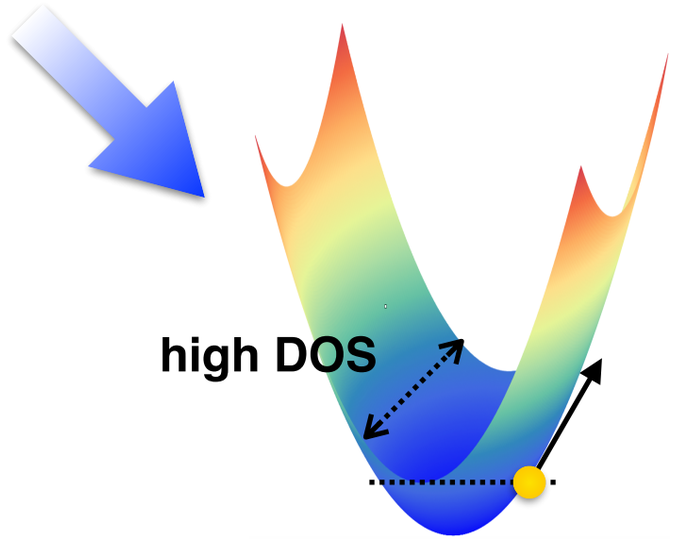
# Characteristic band shapes in good thermoelectric materials



**Multi valley**

large DOS by
valley degeneracy

Y. Pei *et al.*,
Nature **473**, 66 (2011).




**Low-dimensionality (anisotropy)**

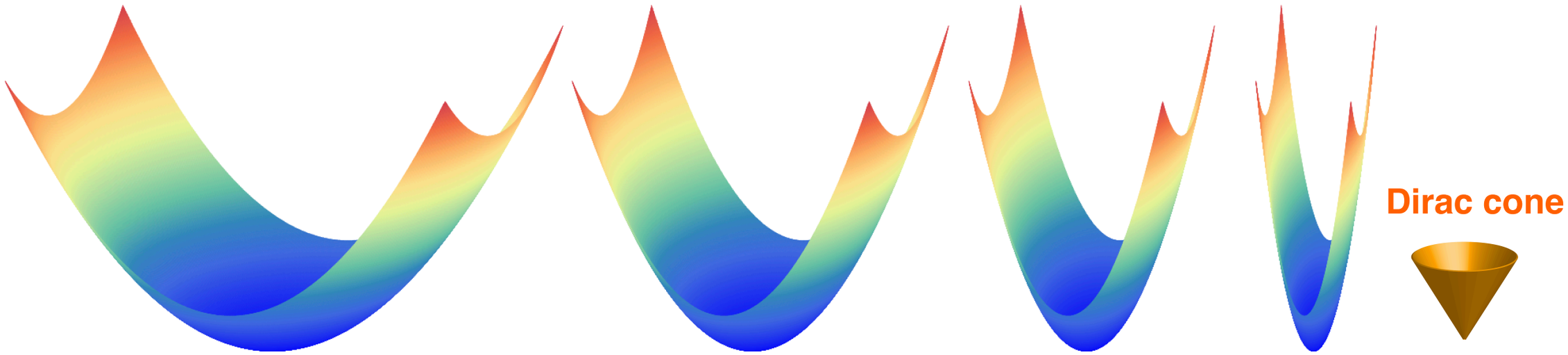
high DOS and group velocity
for one (or two) direction(s)

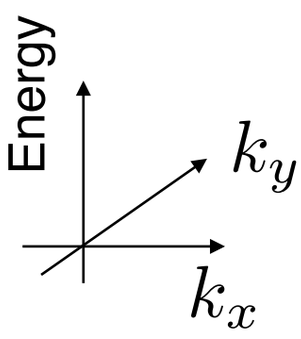
L. D. Hicks and M. S. Dresselhaus,
PRB **47**, 12727; *ibid.*, 16631 (1993).

**Characteristic band dispersion can enhance thermoelectric conversion efficiency**

# Further optimization of low-dim. band

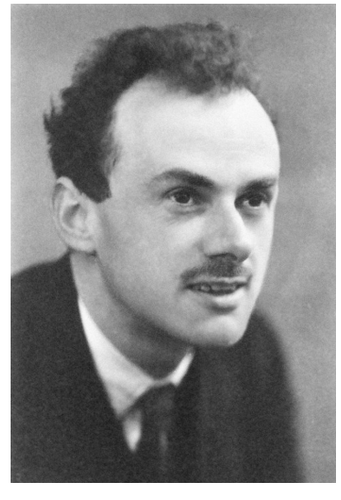
heavy mass ⟷ light mass



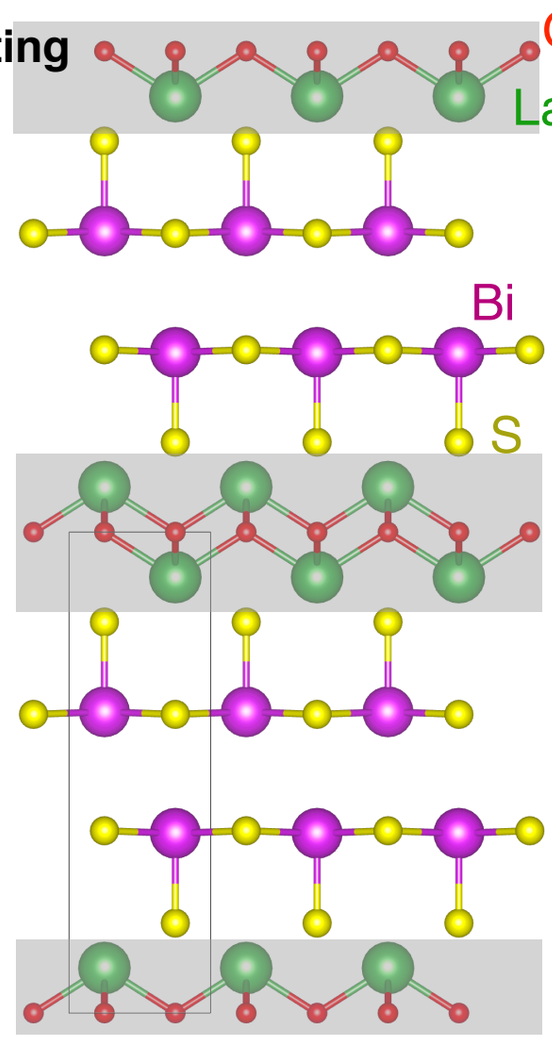

**light electron mass is better**
**for low-dim. band dispersion**

**Can we find such a band dispersion in real materials?**



Paul Dirac
© Wikipedia

# $BiS_2$ layered materials




**known as superconductors**

Y. Mizuguchi *et al.*, PRB **86**, 220510 (2012).
Y. Mizuguchi *et al.*, JPSJ **81**, 114725 (2012).

$RO_{1-x}F_xBiS_2$ ($R$ = La, Nd, etc.), $Bi_6O_4S_4(SO_4)_{1-x}$,…

High controllability (chemical pressure, carrier doping, etc)

**recently paid attention as thermoelectric materials**

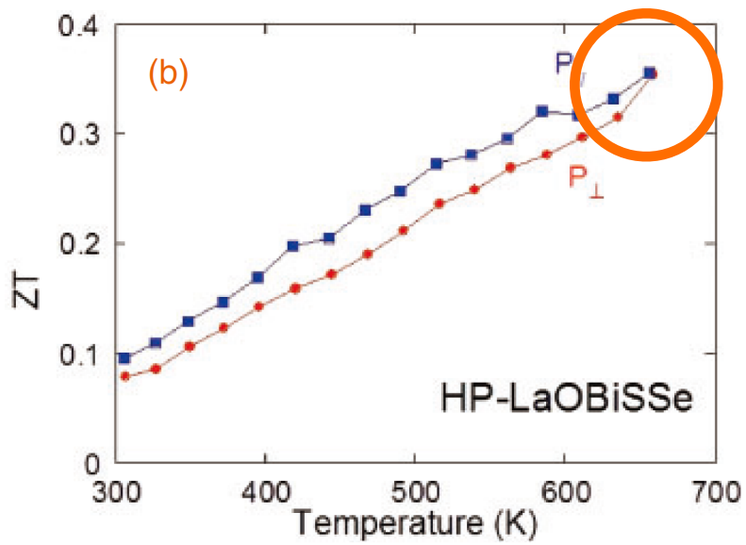
**Low thermal conductivity**

$\kappa_{lattice}$ ~ 1 W/m/K@ $T$ = 300 K

**Relatively high *ZT***

* $ZT$ = a measure of conversion efficiency

A. Nishida *et al.*, Appl. Phys. Express **8**, 111801 (2015).



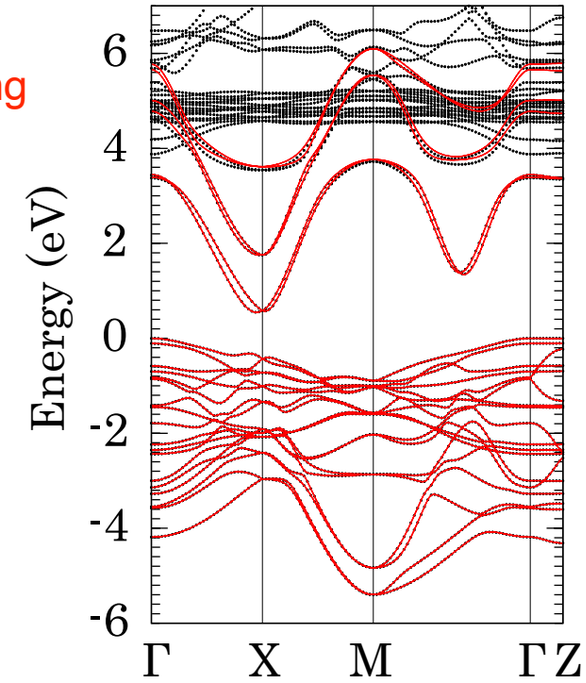

**We find that $BiS_2$ layered materials can be a platform of ideal electronic structure for thermoelectric effects: low-dim. + gapped Dirac cone + multi-valley, by appropriate atomic substitution**

# Calculation details

**DFT band calc. and Wanierization (Bi,O,S-*p* orbitals)**

Black lines: First-principles

Red lines: Wannier tight-binding




- WIEN2k for band calc.
- modified Becke-Johnson potential (known to give a relatively accurate band gap)
- wien2wannier and Wannier90 for Wannierization

$$\mathcal{H} = \sum_{ij} t_{ij} c_i^\dagger c_j$$

**Tight-binding model**: electron transfer between Wannier functions (spatially localized orbitals)

= transfer integrals are determined so as to reproduce first-principles band dispersion

Wannier is used for getting physical insight, taking a (very) fine k-mesh, etc.

$\epsilon_{n,\mathbf{k}}$

**Boltzmann transport theory**

- constant relaxation time ($\tau$) approximation
- rigid band approximation for carrier doping

$$\sigma = e^2 \mathbf{K}_0,\ \mathbf{S} = -\frac{1}{eT}\mathbf{K}_0^{-1}\mathbf{K}_1,\ \kappa_{\mathrm{el}} = \frac{1}{T}(\mathbf{K}_2 - \mathbf{K}_1\mathbf{K}_0^{-1}\mathbf{K}_1),$$

$$\mathbf{K}_\nu = \tau \sum_{\mathbf{k},n} \mathbf{v}_{\mathbf{k},n} \otimes \mathbf{v}_{\mathbf{k},n} \left[ -\frac{\partial f_0(\epsilon_{\mathbf{k},n}, T)}{\partial \epsilon} \right] (\epsilon_{\mathbf{k},n} - \mu(T))^\nu$$

σ: electrical conductivity

S: Seebeck coefficient

$\kappa_{el}$: electrical thermal conductivity

# A bit more about Boltzmann transport theory

For example, electrical conductivity along the x direction is given as follows:

$$\sigma_{xx} \propto \tau \sum_{\mathbf{k},\mathbf{n}} v^2_{x;(\mathbf{k},\mathbf{n})} \left[ -\frac{\partial f_0(\epsilon_{\mathbf{k},\mathbf{n}}, T)}{\partial \epsilon} \right]$$

see how σ depends on several quantities…

$\tau$ relaxation time (time length between electron scatterings)

: long relaxation time yields high electrical conductivity

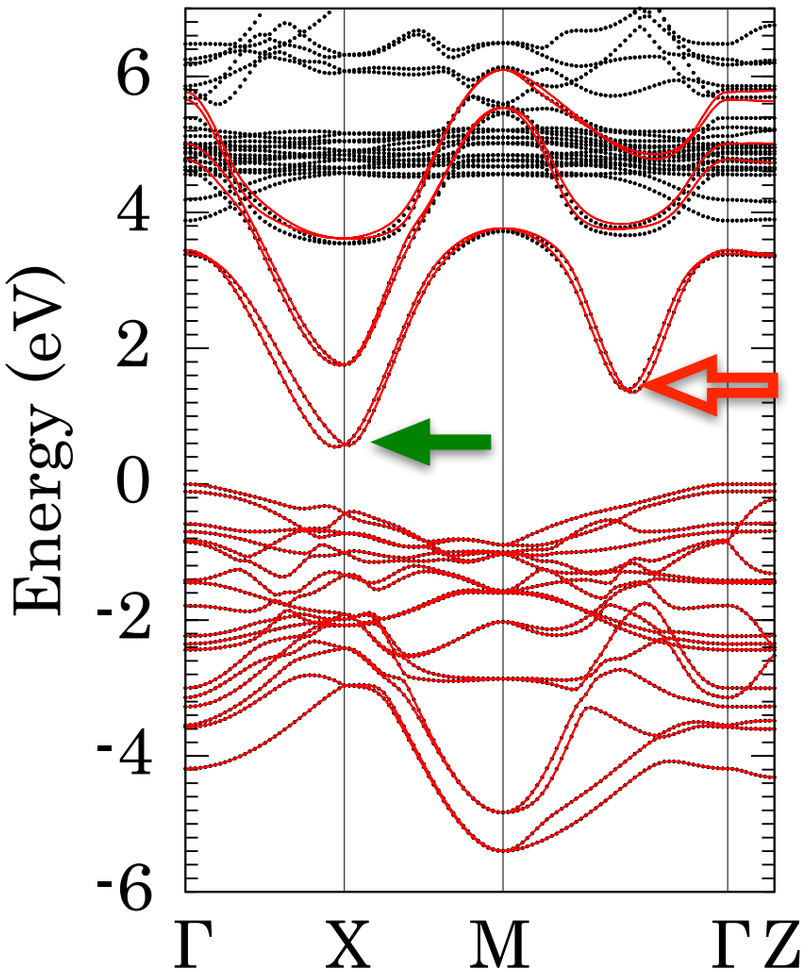
$v^2_{x;(\mathbf{k},\mathbf{n})}$ square of group velocity of the *n*-th band at a certain **k** point

: high group velocity yields high electrical conductivity

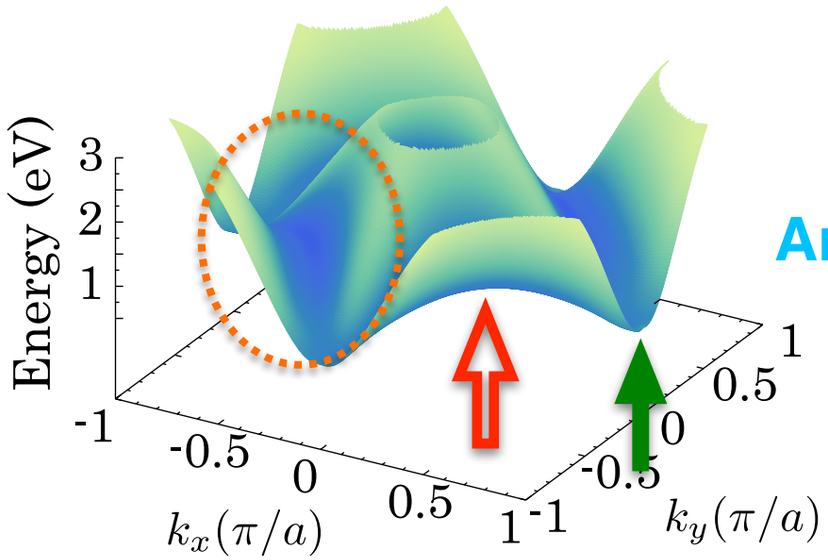
$-\frac{\partial f_0(\epsilon_{\mathbf{k},\mathbf{n}}, T)}{\partial \epsilon}$ derivative of the Fermi-Dirac distribution (having a sizable value only near μ=ε)

: only Kohn-Sham states near the Fermi level can contribute to the electrical conductivity

# $LaOBiS_2$: electronic structure

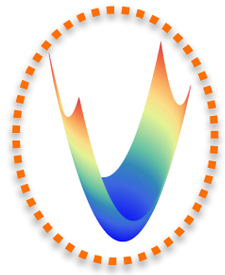



*** consider a small amount of electron carrier, i.e., near the bottom of the conduction band (shown by arrows)**

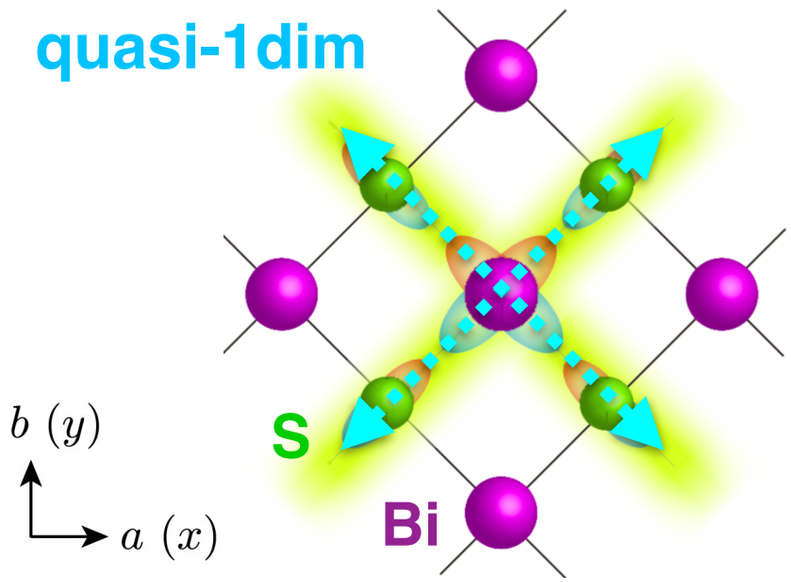



*kx*-*ky* plot for the lowest conduction band

**Anisotropy of the slope**



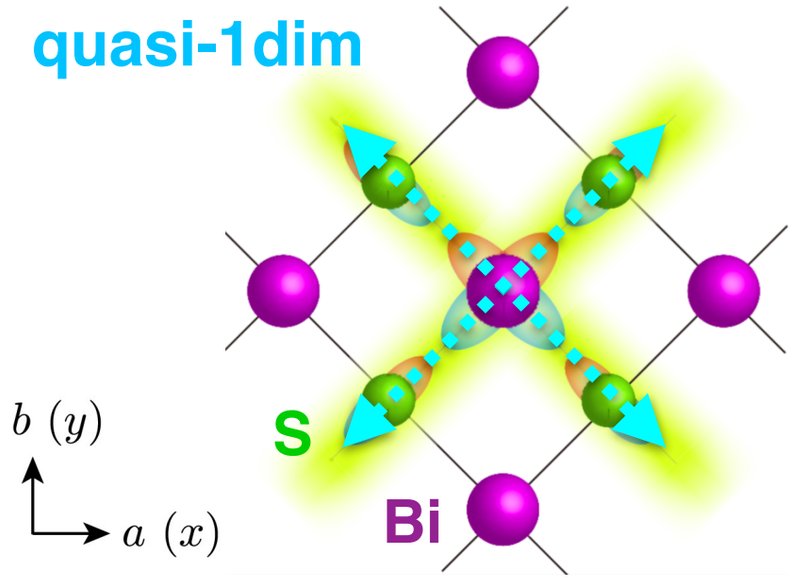
**quasi-1dim**




**Low-dimensionality by orbital anisotropy**

cf. H. Usui *et al.*, PRB **86**, 220501(R) (2012).

# What weakens anisotropy




**Several factors weaken quasi-one dimensionality**

**1. Spin-orbit coupling (relativistic effect)**

→ hybridization between $p_x$ and $p_y$

**2. Electron transfer among Bi orbitals**

∗ conduction bands mainly consist of Bi orbitals

**3. Energy difference between Bi and S orbitals**

→ large energy difference prevents electron transfer

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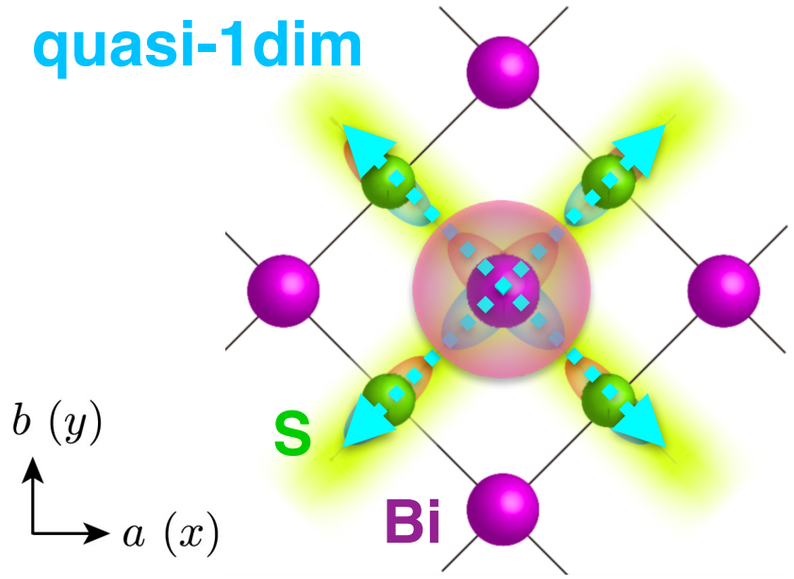


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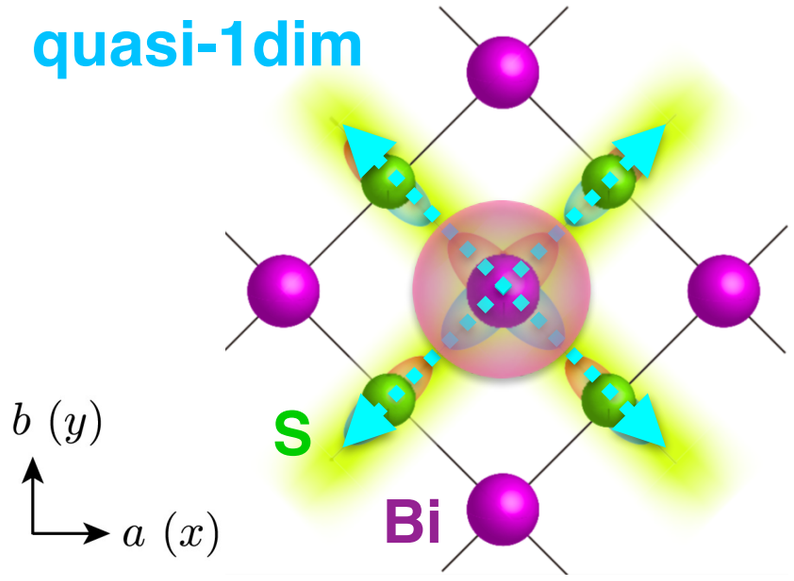
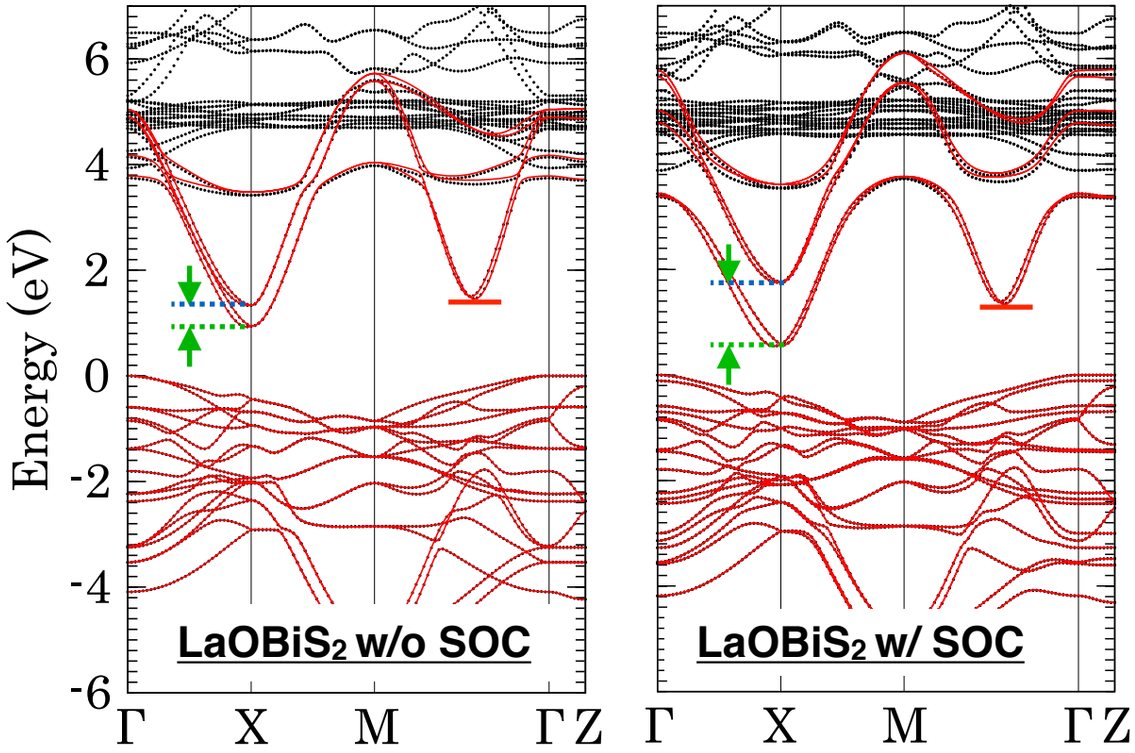
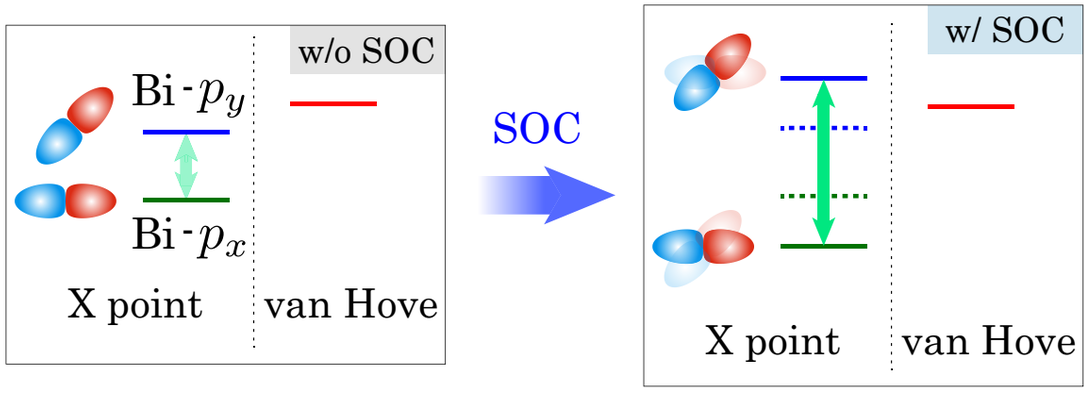
# Spin-orbit coupling (SOC)



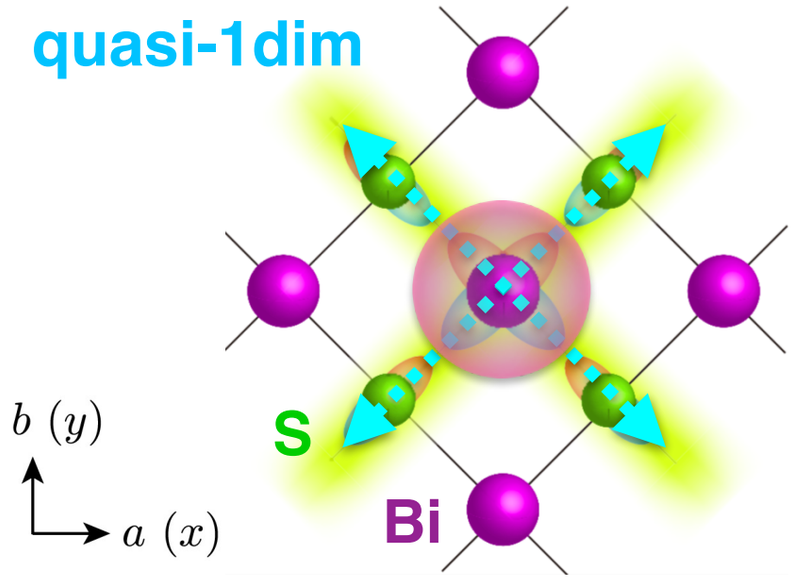




**van Hove singularity gets farther from the band edge**

**(i.e. low-dim is weakened) by SOC band splitting**

# What weakens anisotropy

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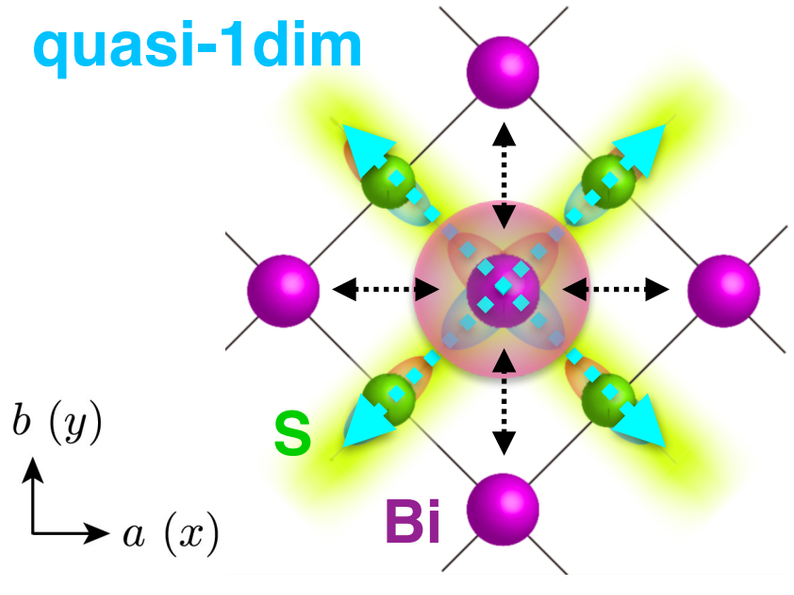


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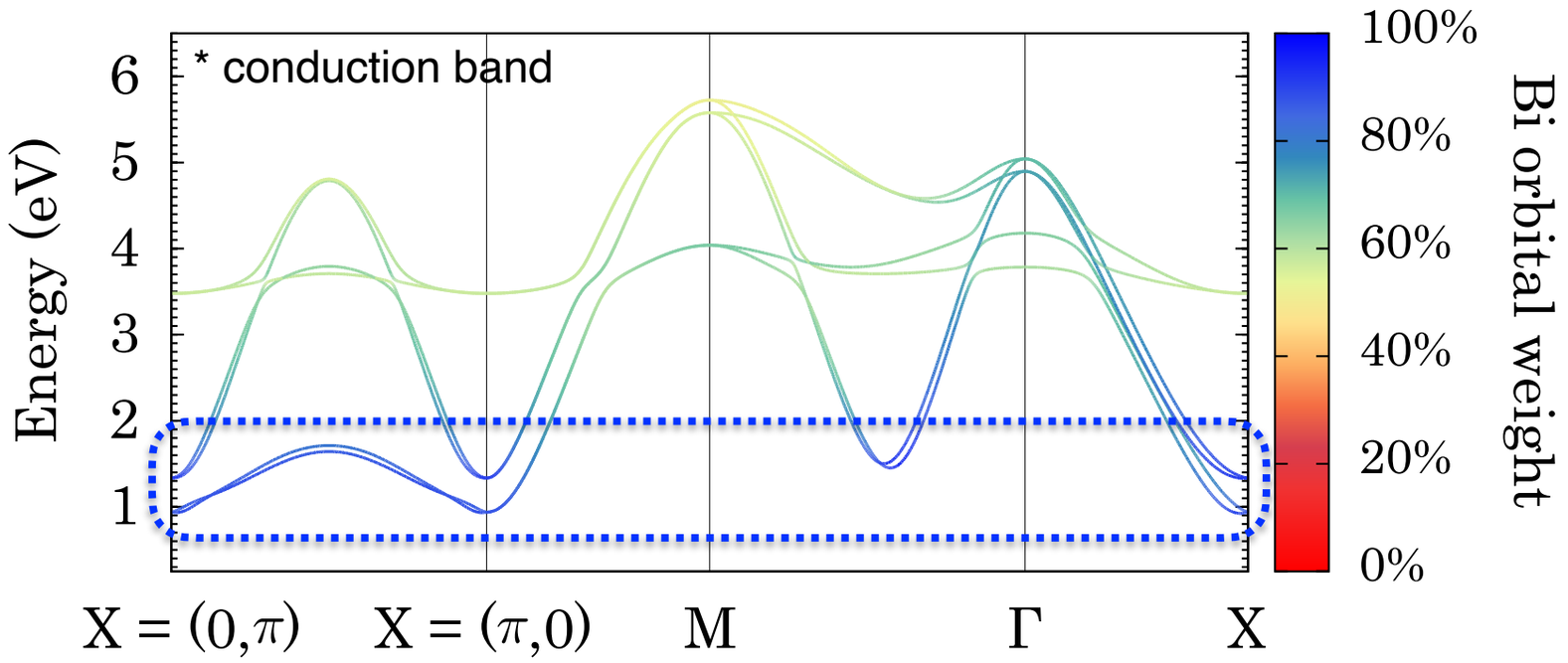
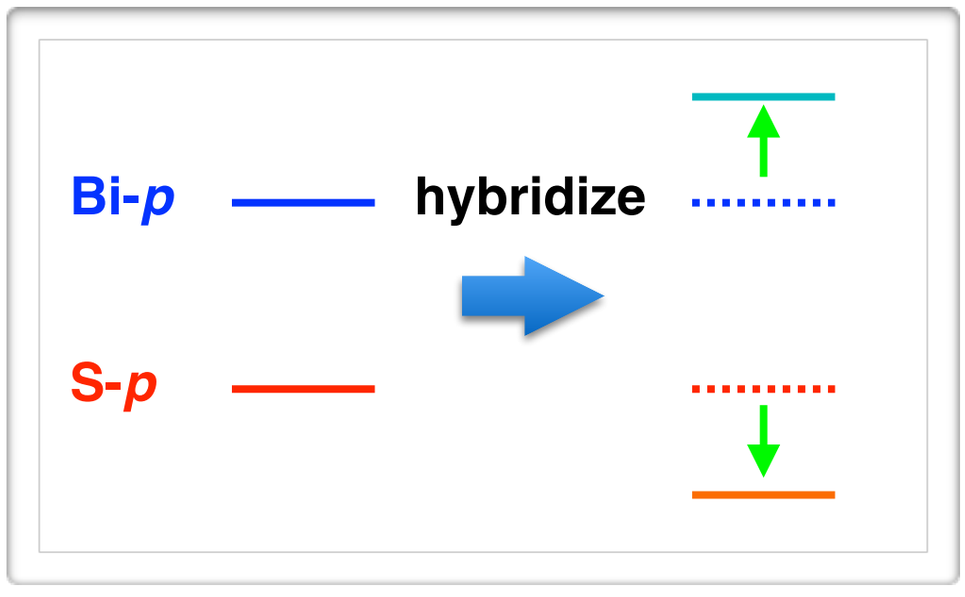
# Bi orbital weight

LaOBiS$_2$ / no SOC



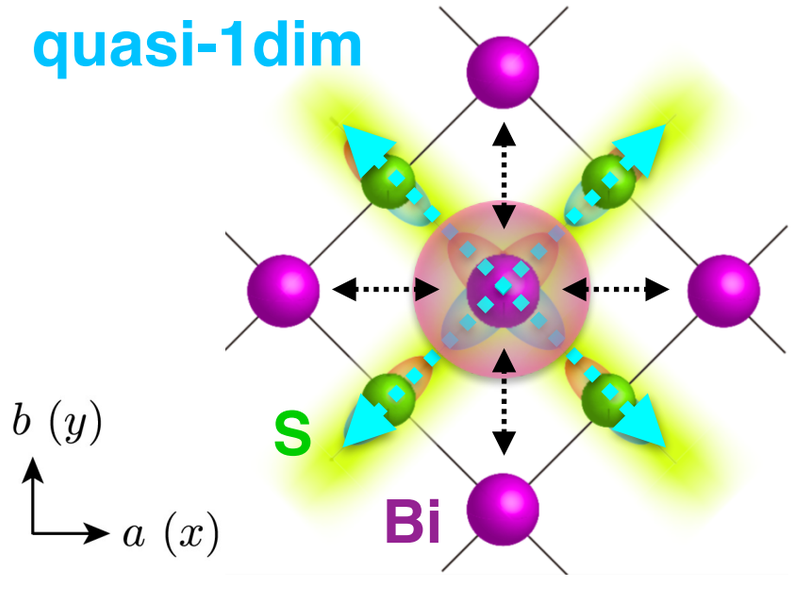

**mainly Bi orbitals**




**If hybridization is strong at a certain k-point, the anti-bonding Bi bands should have a high energy (and a sizable S orbital weight)**

**On the other hand, the anti-bonding Bi bands near the band edge should have little S weight**

# What weakens anisotropy

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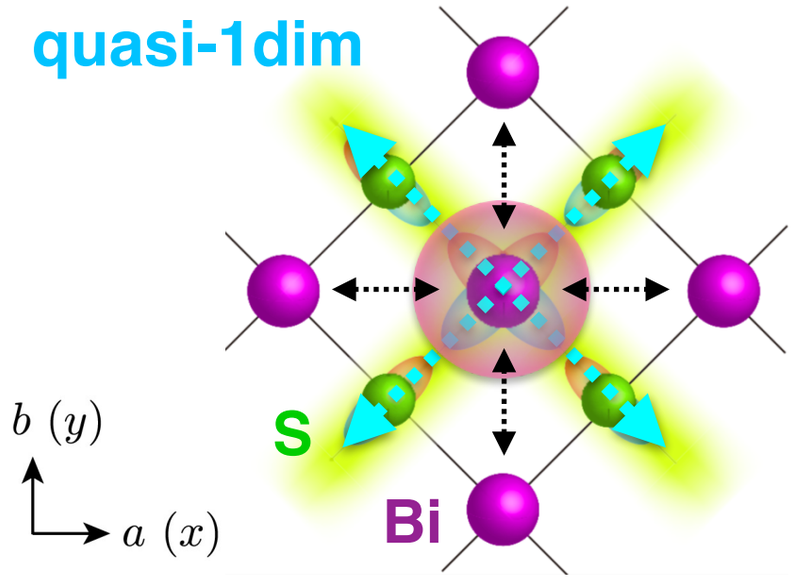


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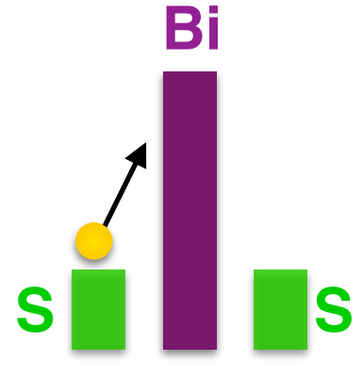

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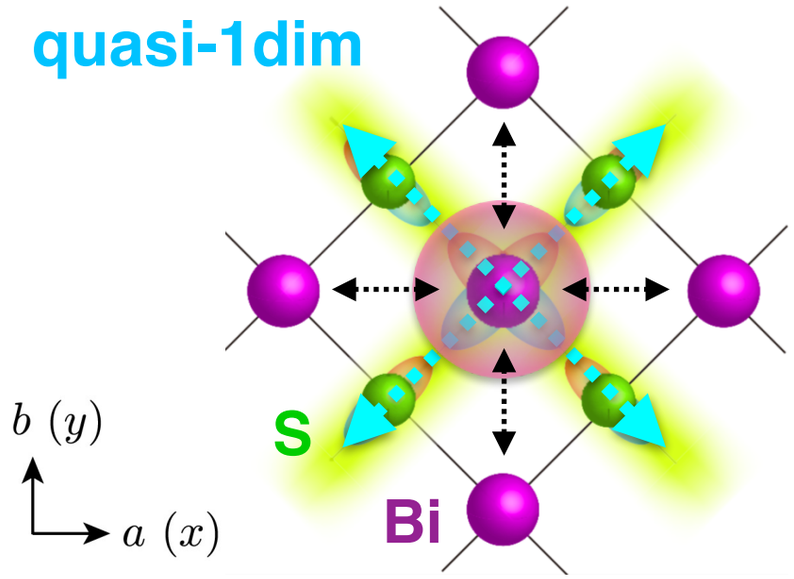


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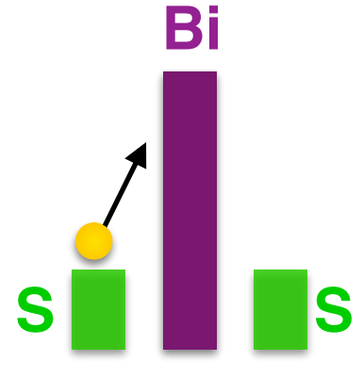
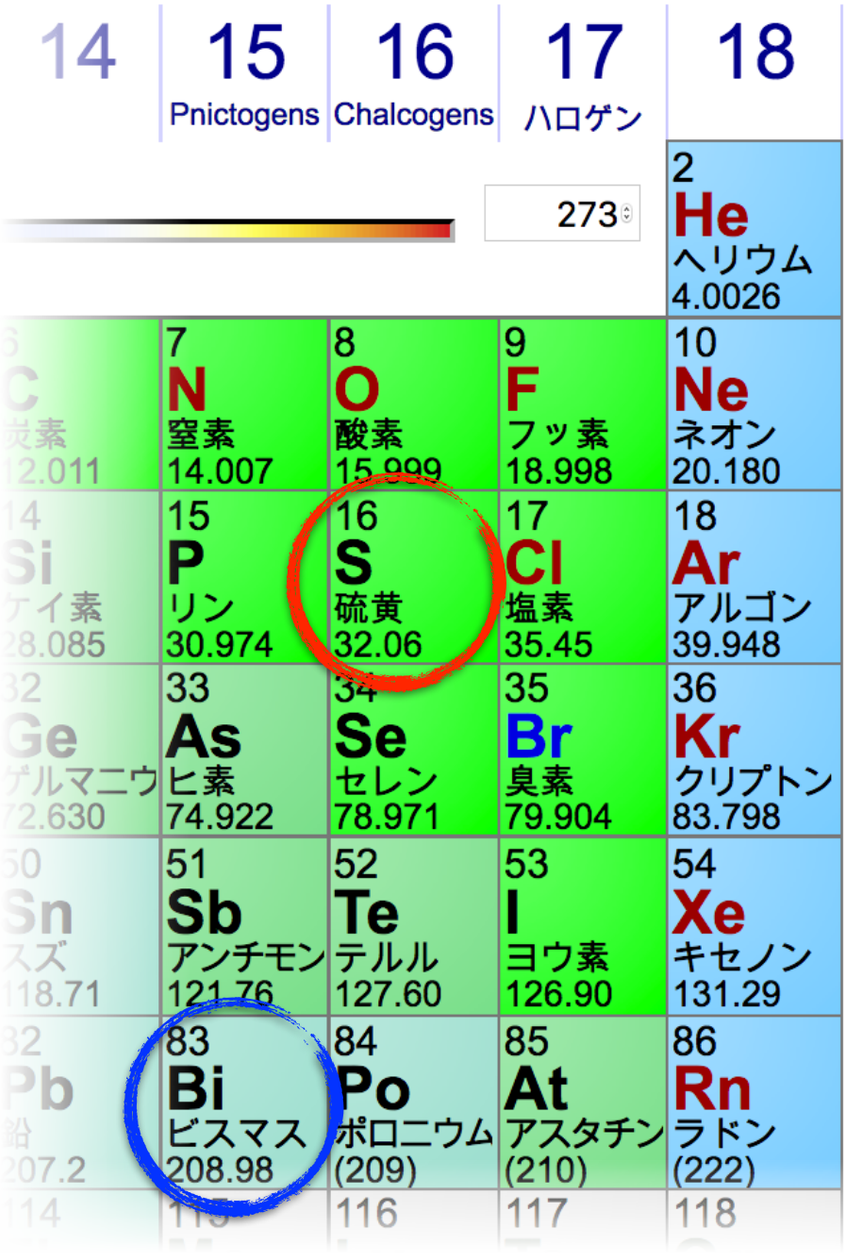
**Quasi-one dim. can be enhanced by atomic substitution**

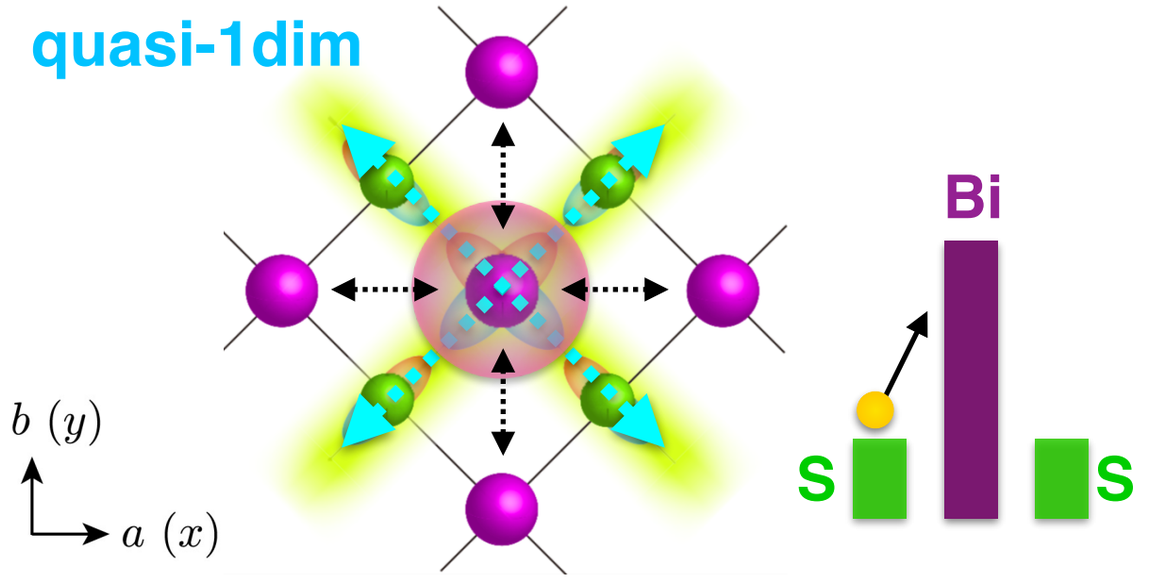



**MO** *et al.*, PRAppl. **8**, 064020 (2017).

# Band engineering




*Dynamic Periodic Table (http://www.ptable.com)*

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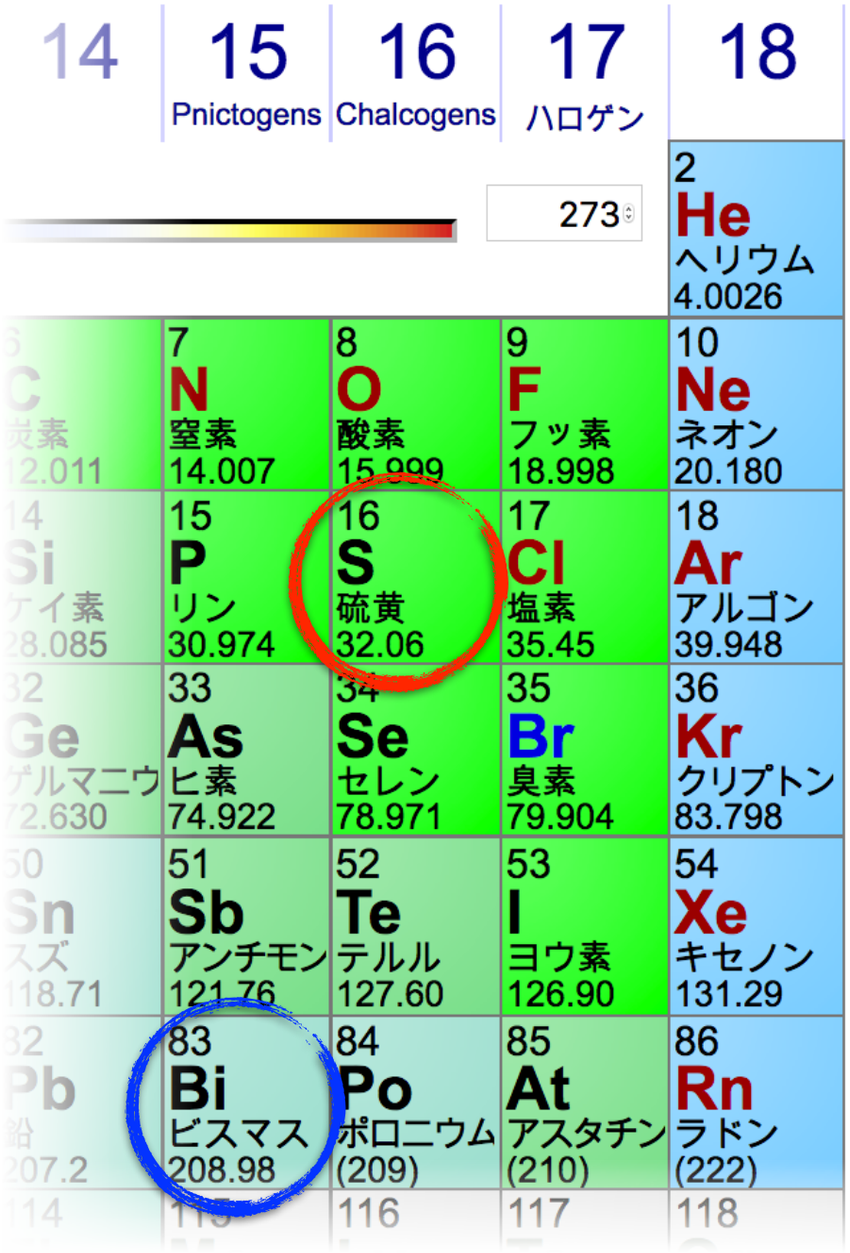


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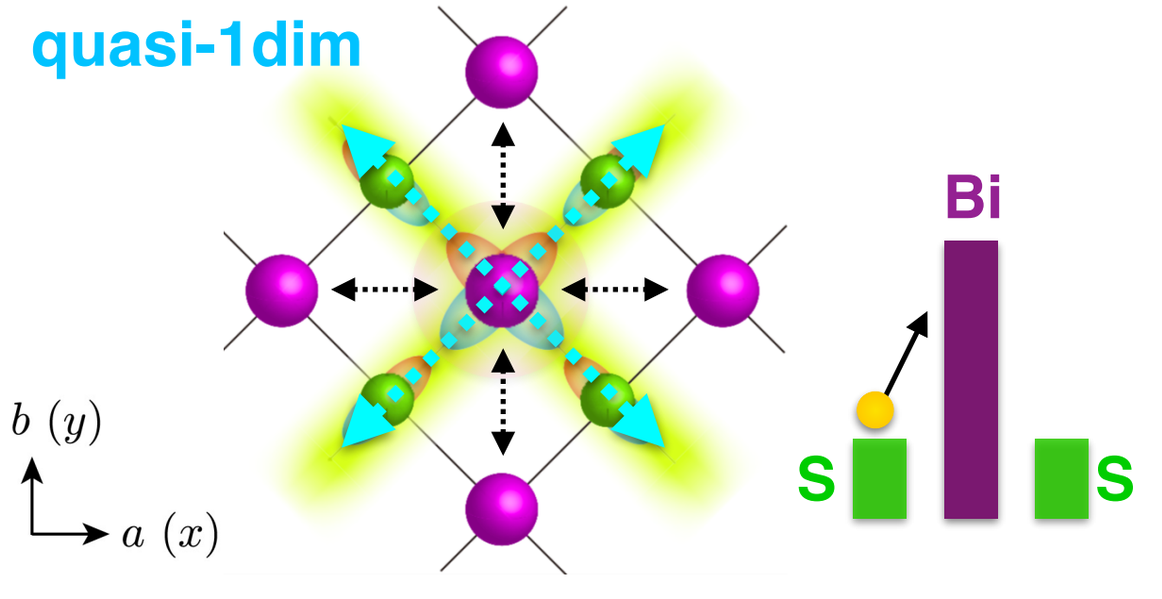


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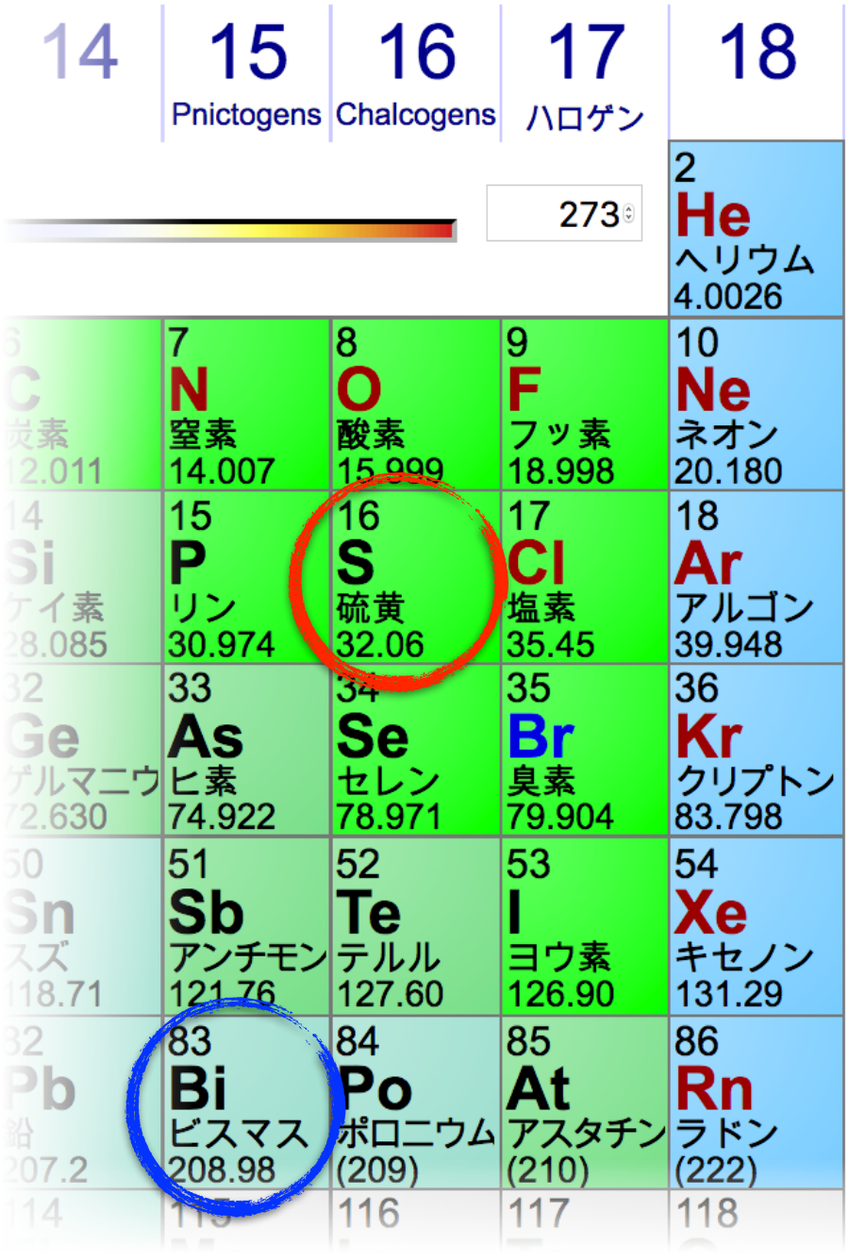


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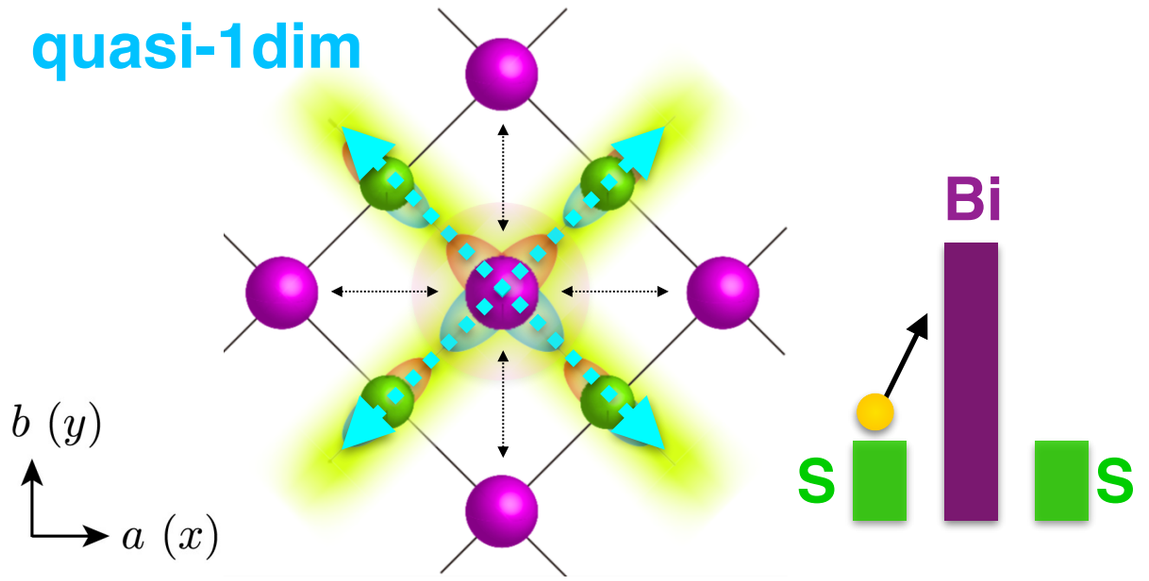


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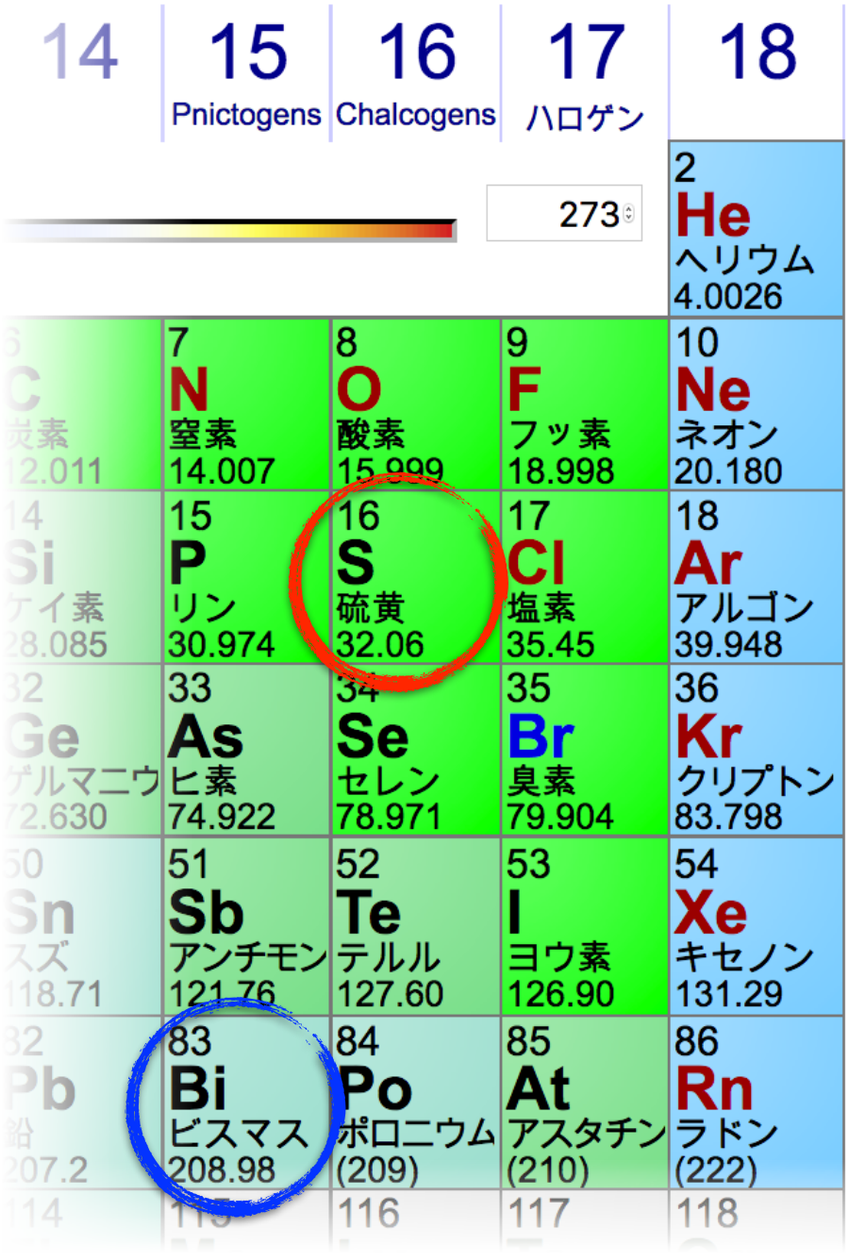


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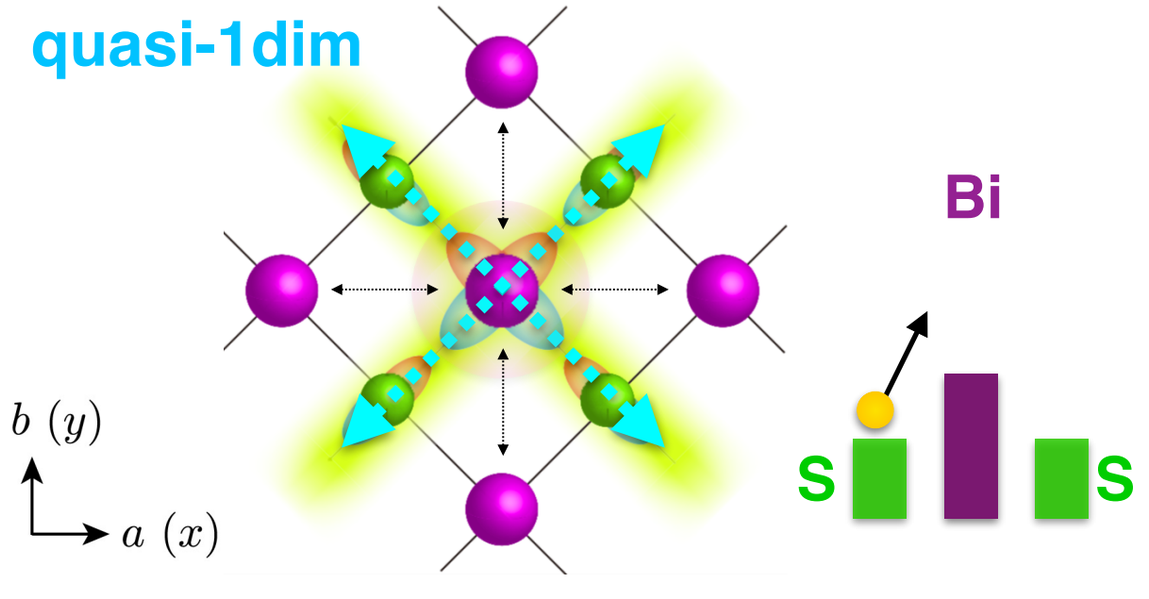


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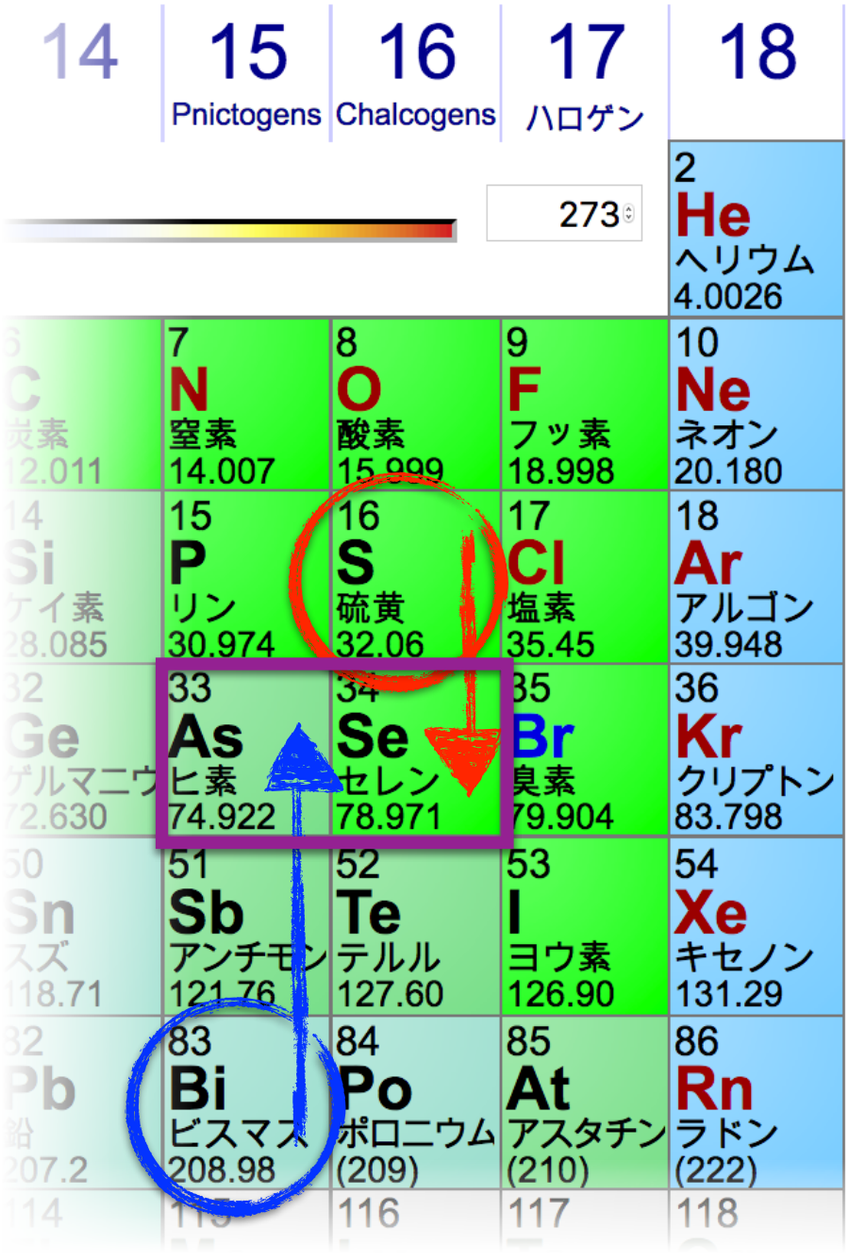


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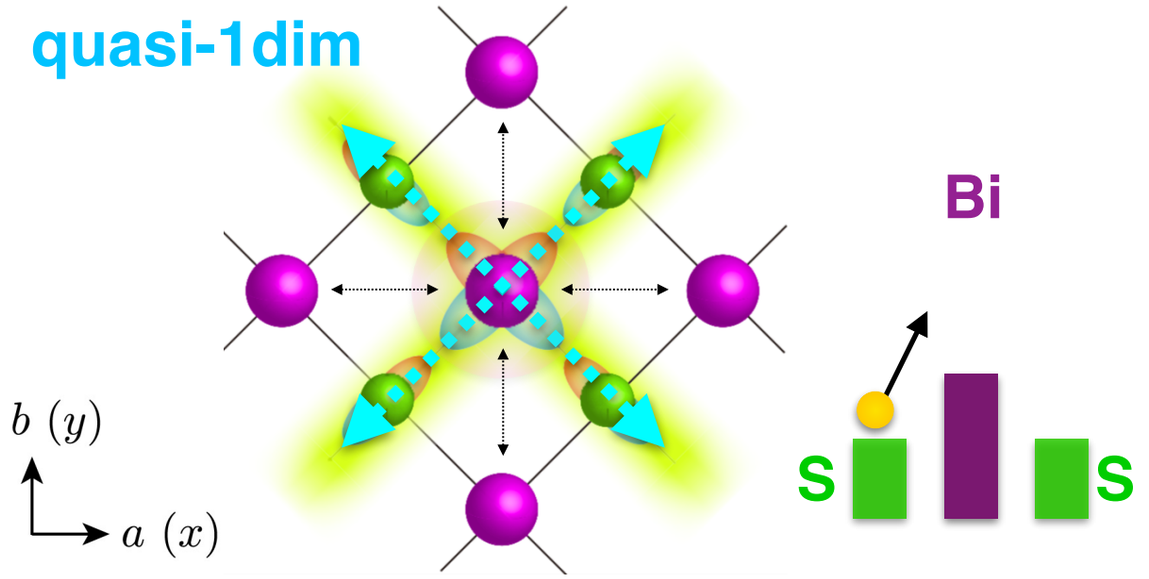



**1. Spin-orbit coupling (Relativistic effect)**

→ **use a light Pnictogen (than Bi)**

**2. Electron transfer among Bi orbitals**

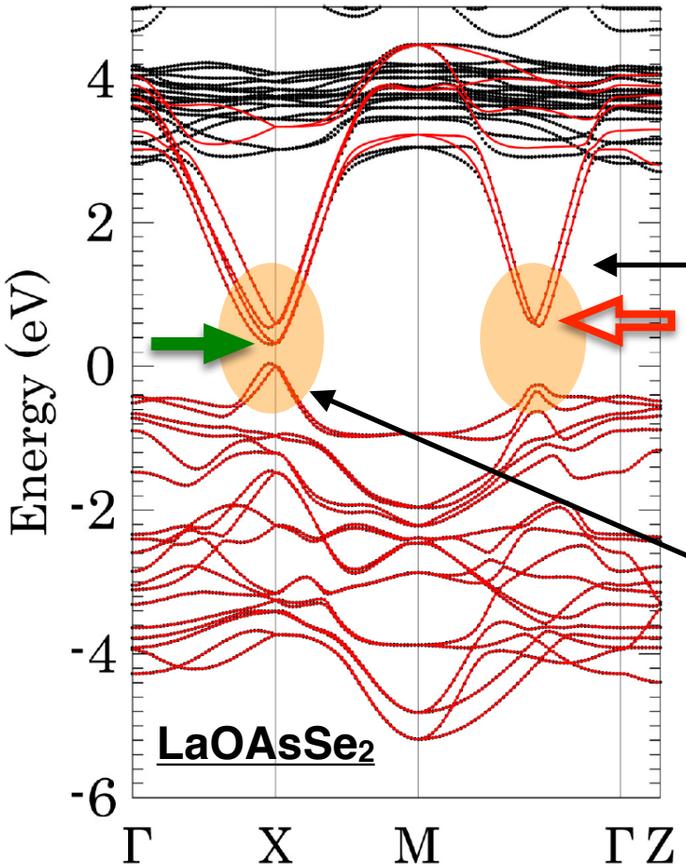
→ **use a light Pnictogen and heavy chalcogen**

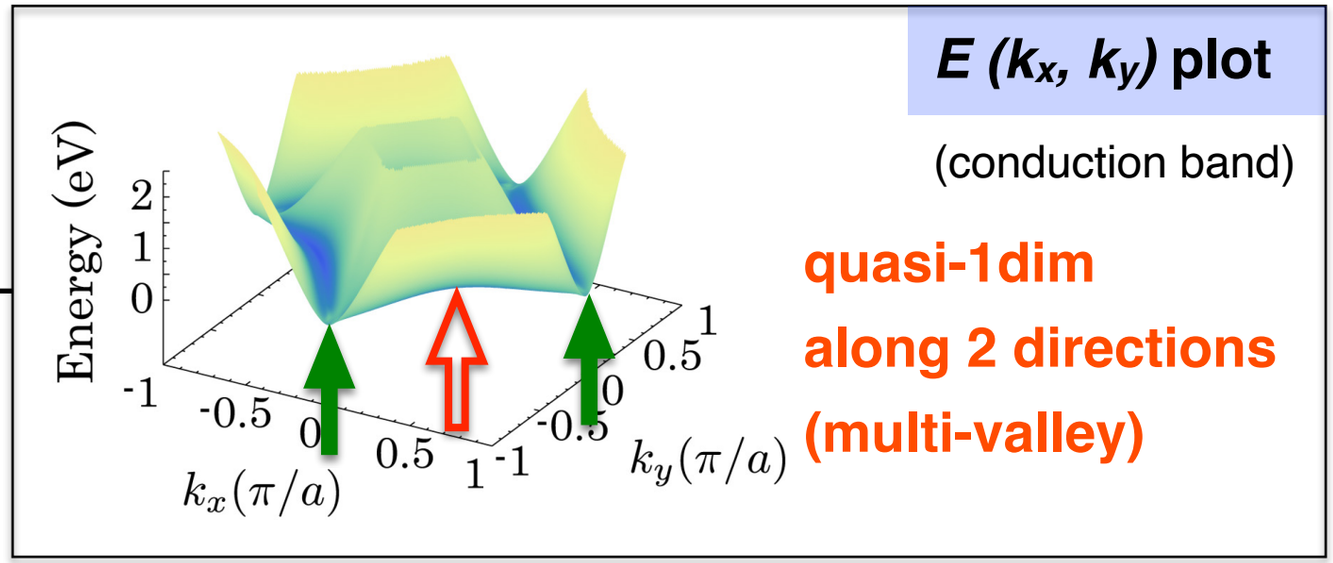
**3. Energy difference between Bi and S orbitals**

→ **use a light Pnictogen and heavy chalcogen**

**MO** *et al.*, PRAppl. **8**, 064020 (2017).

# Ideal electronic structure: quasi-1dim gapped Dirac cone




**$E\ (k_x,\ k_y)$ plot**

(conduction band)

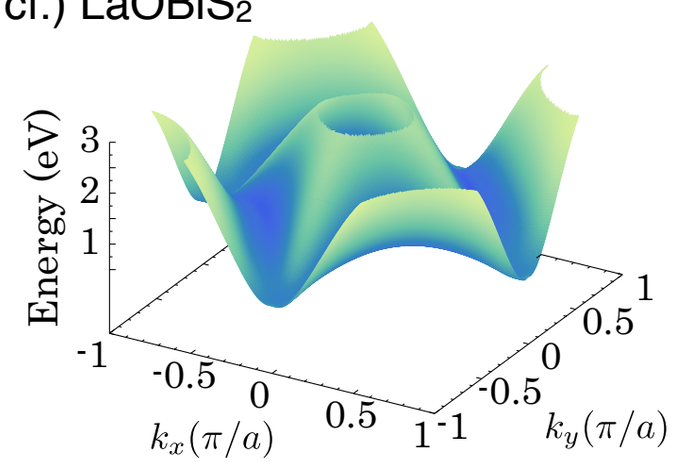
**quasi-1dim**
**along 2 directions**
**(multi-valley)**

**gapped Dirac cone**

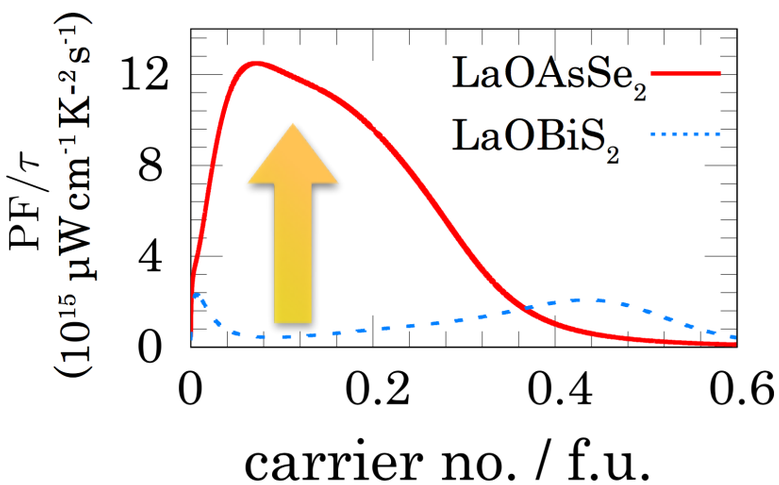
**One of the ideal band dispersion**

* gap = prevents electron & hole cancelation

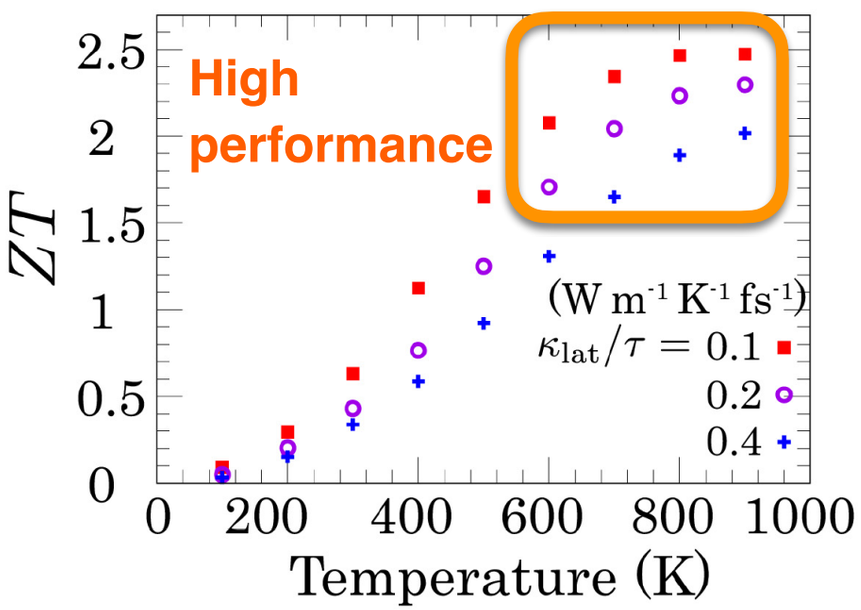
cf.) $LaOBiS_2$




$PF = \sigma S^2$

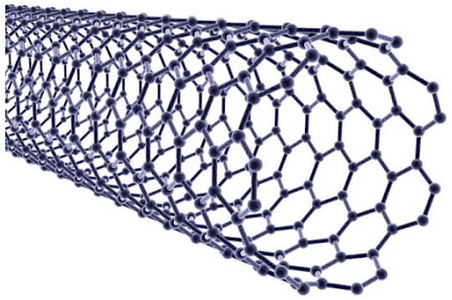



$ZT = \sigma S^2 T/\kappa$



# Relation to other thermoelectric materials

## Carbon nanotube



**1dim (gapped) Dirac cone**

high mobility but high thermal conductivity

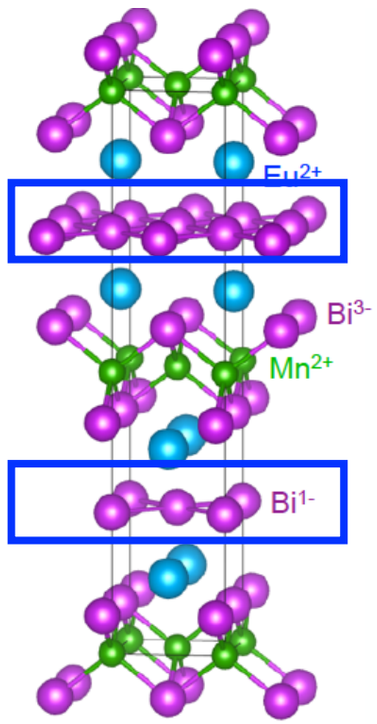
R. S. Prasher *et al.*, PRL **102**, 105901 (2009). Y. Nakai *et al.*, Appl. Phys. Express **7**, 025103 (2014). T. Yamamoto and H. Fukuyama, JPSJ **87**, 024707 (2018); *ibid.* 114710 (2018).

## $A$MnBi$_2$ ($A$ = Ca, Sr, Eu)

also have a $p_{x,y}$ **network on the Bi square lattice**

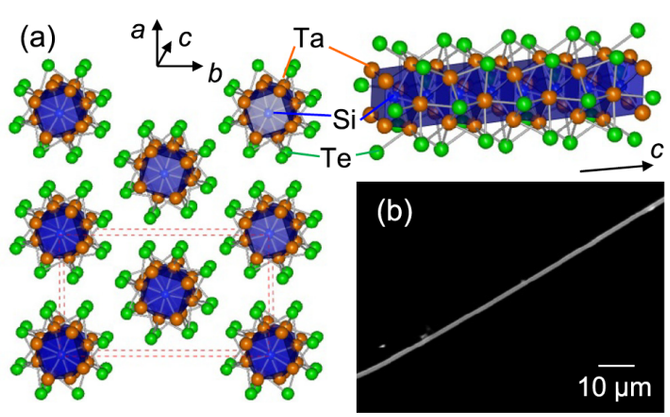
→ **quasi-1dim gapped Dirac cone**

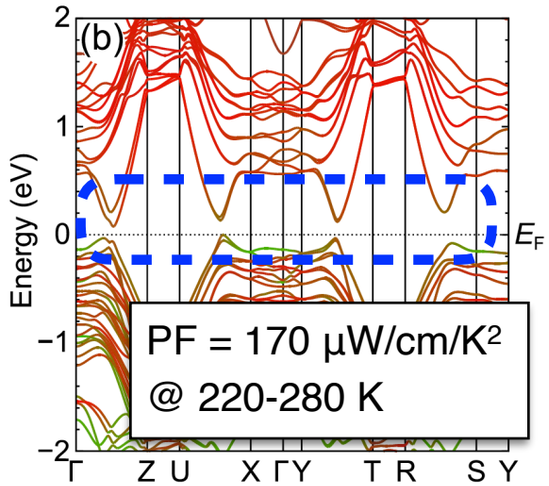
* gap is induced by SOC



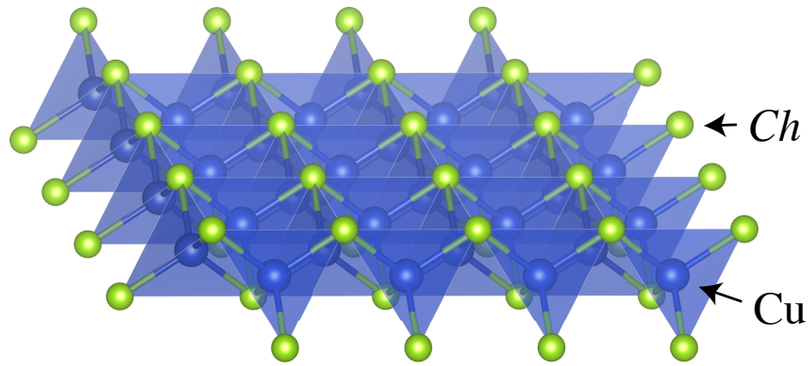

## $Ta_4SiTe_4$

T. Inohara *et al.*, APL **110**, 183901 (2017).




## Low-dim. in the Cu$Ch$ ($Ch$ = S, Se) layer



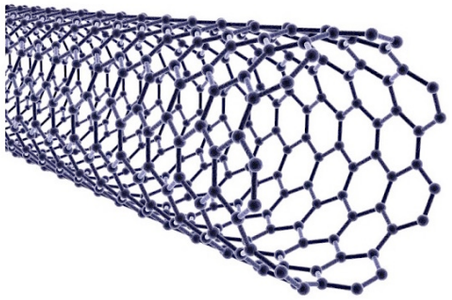

hidden 1-dim network on the square lattice

→ similarity to $BiS_2$ systems

**MO** *et al.*, PRMater. **2**, 085401 (2018).

# Relation to other thermoelectric materials

## Carbon nanotube



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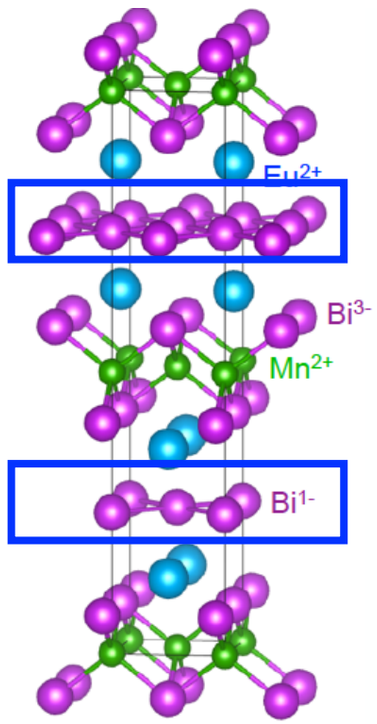


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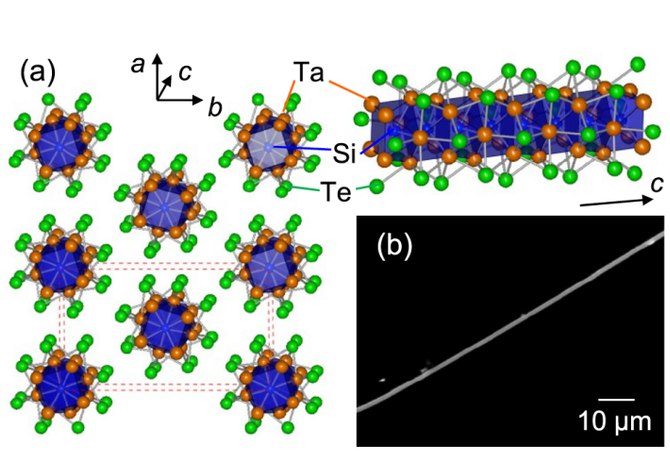
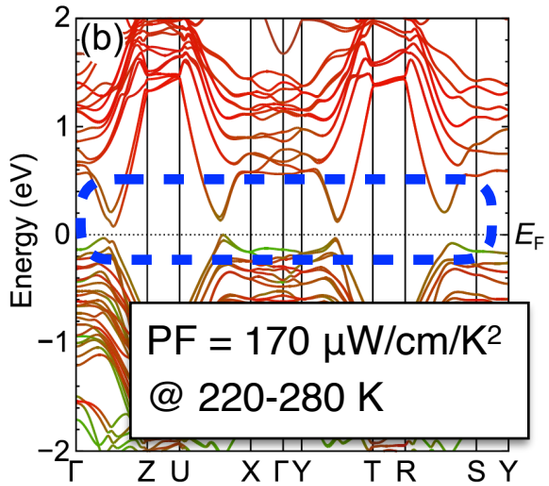
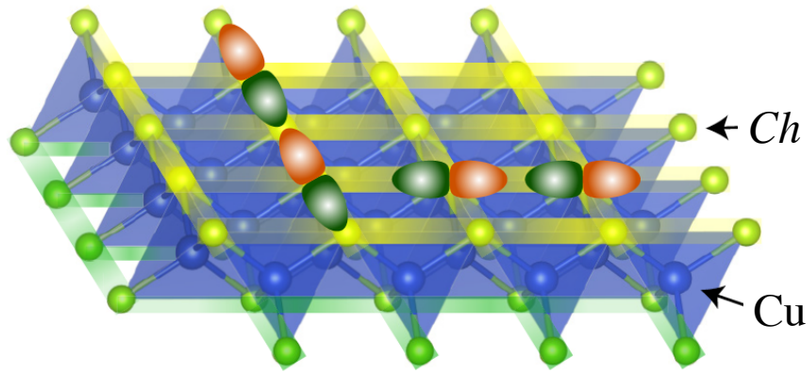



## Low-dim. in the Cu*Ch* (*Ch* = S, Se) layer

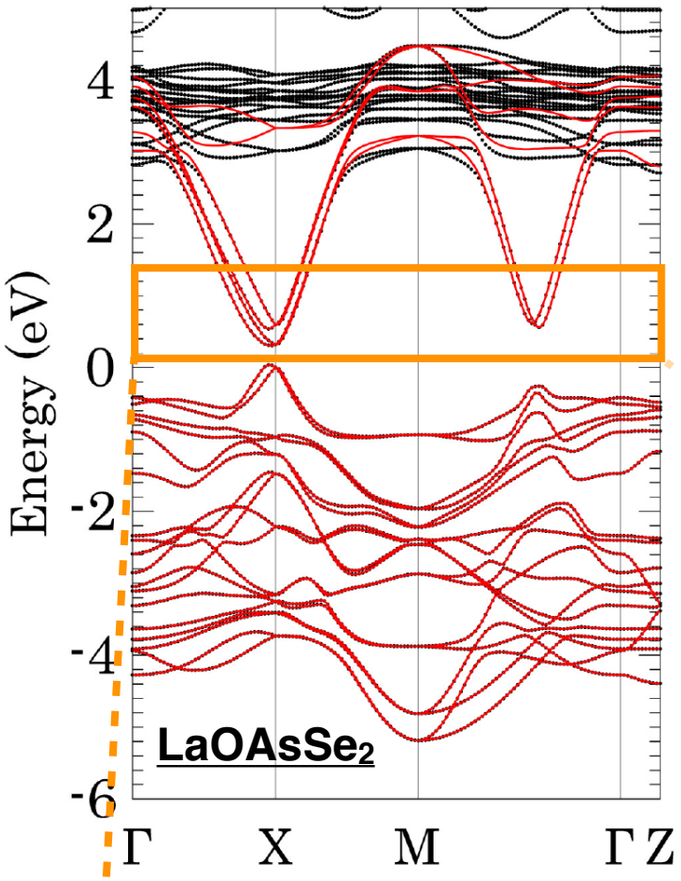



hidden 1-dim network on the square lattice

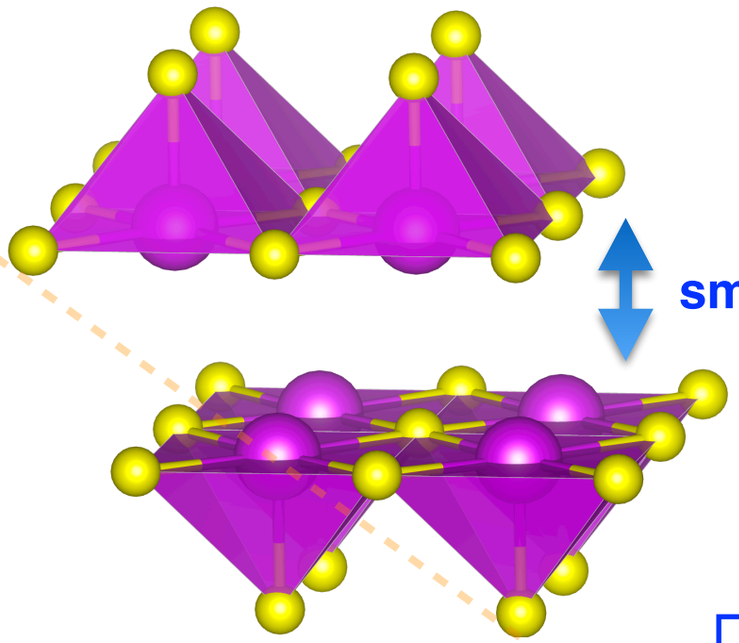
→ similarity to $BiS_2$ systems

**MO** *et al.*, PRMater. **2**, 085401 (2018).

# Another important factor: quantum interference




**quantum intereference is another key for multi-valley**

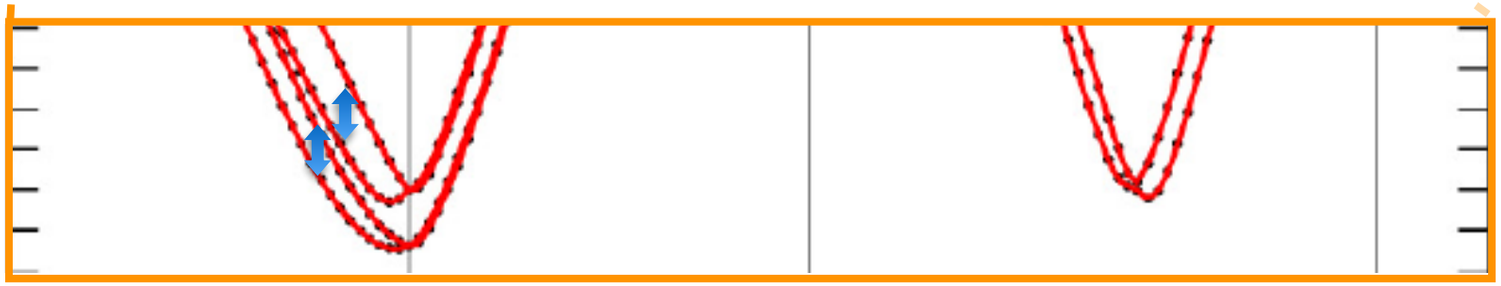


**small bilayer splitting**

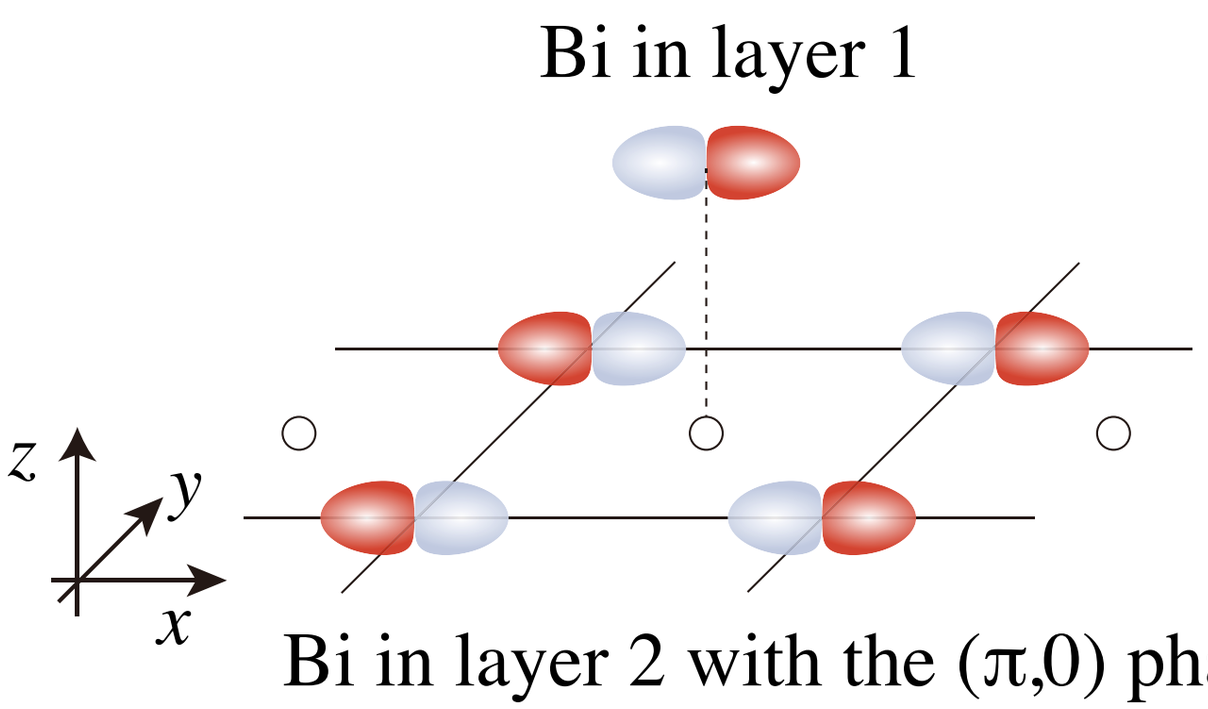
*** no split at the X point**

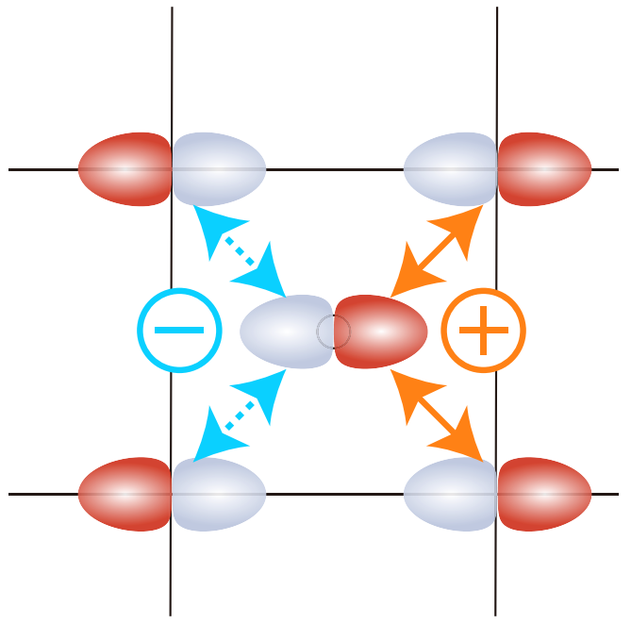
**Why suppressed (prohibited)?**

**= quantum interference**



# Orbital symmetry and quantum interference

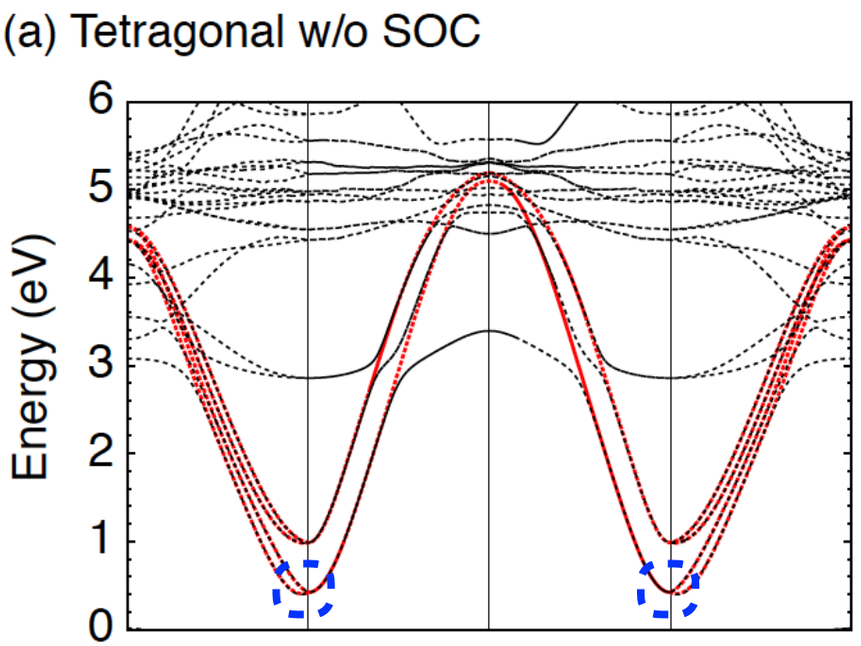


**Inter-layer coupling is prohibited at the X = (π,0) point by symmetry**

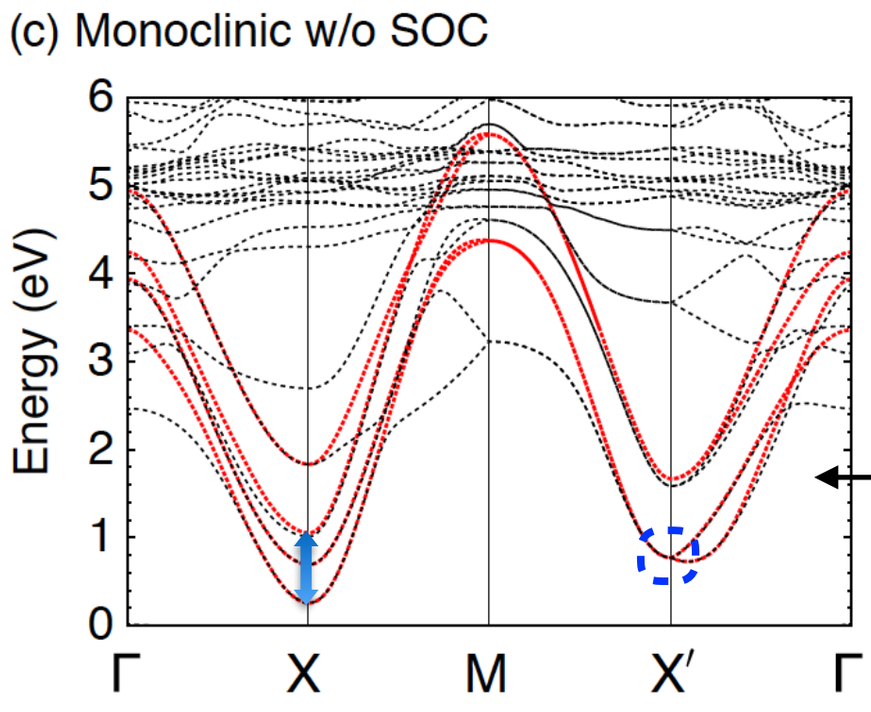
**MO** *et al.*, JPSJ **85**, 094705 (2016).

# Band-edge degeneracy by quantum interference




**Symmetry forbids the band splitting at X**

**→ band-edge degeneracy (multi-valley)**



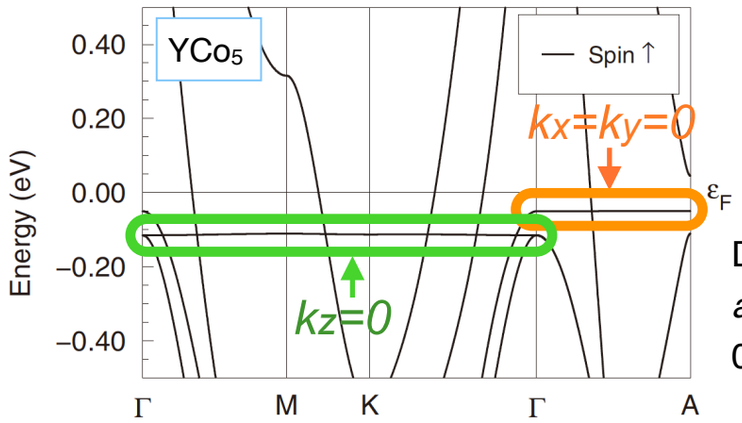

at 3.8 GPa, with monoclinic distortion

: symmetry lowering allows band splitting

**MO** *et al.*, JPSJ **85**, 094705 (2016).

# Quantum interference and materials functionalities

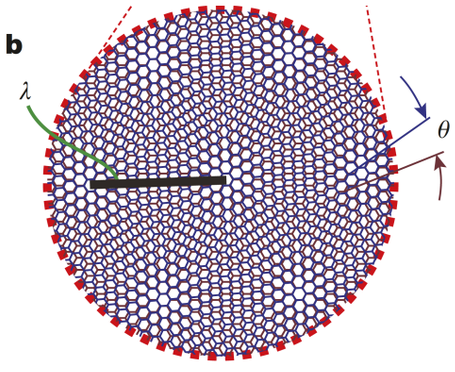
## flat band and ferromagnetism

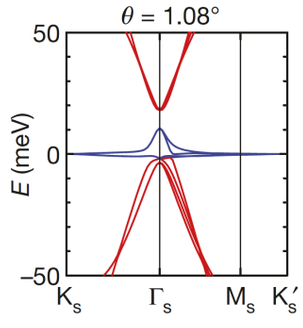



D. Koudela *et al.*, PRB **77**, 024411 (2008).

**MO** *et al.*, PRB **91**, 165137 (2015).

## Twisted bilayer graphene



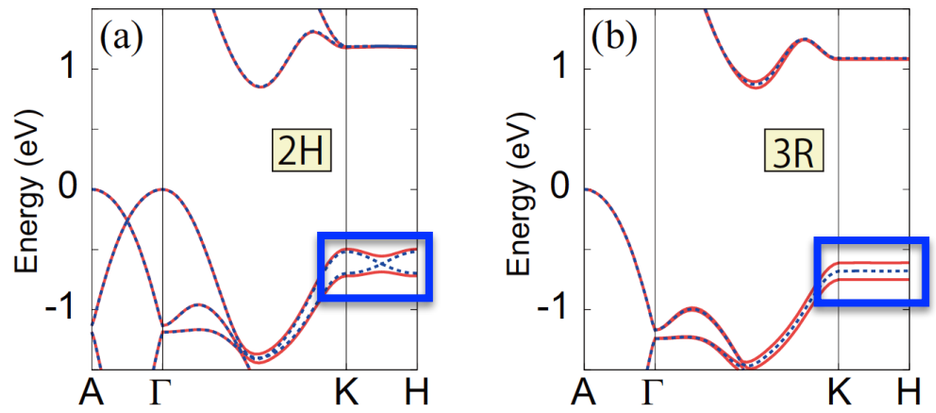



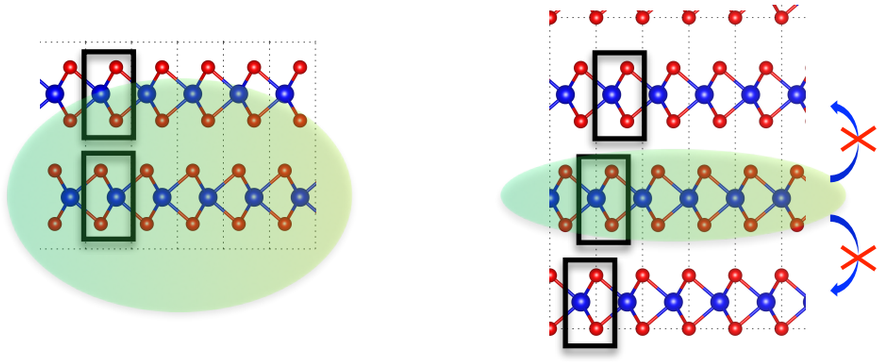

**narrow bandwidth → strong correlation**

Y. Cao *et al.*, Nature **556**, 43-50; ibid., 80-84 (2018).

**MO** *et al.*, PRB **98**, 081102(R) (2018).

## exciton confinement for $MoS_2$



R. Akashi, **MO**, *et al.*, PRAppl. **4**, 014002 (2015).

# Toward experimental realization of high-thermoelectric performance

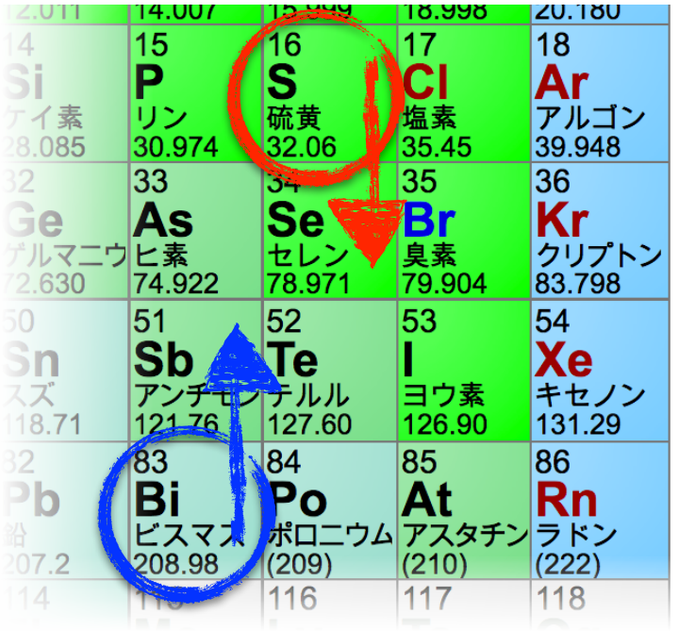
***Ln*(O,F)$SbSe_2$ (*Ln* = La, Ce)**

Y. Goto *et al.*, JPSJ **87**, 074703 (2018).

Low $\kappa$ = 0.8 W/m/K for Ce

but carrier doping is very difficult

→ high $\rho > 10^0$ Ωm@room temperature




**Future issues:**

(1) **Carrier control**

(2) **monoclinic instability**

Bi→Sb induces monoclinic instability and then the thermoelectric performance can be degraded

Also F substitution (for carrier doping) becomes difficult by monoclinic distortion

calc：N. Hirayama, **MO**, *et al.*, PRB **100**, 125201 (2019).

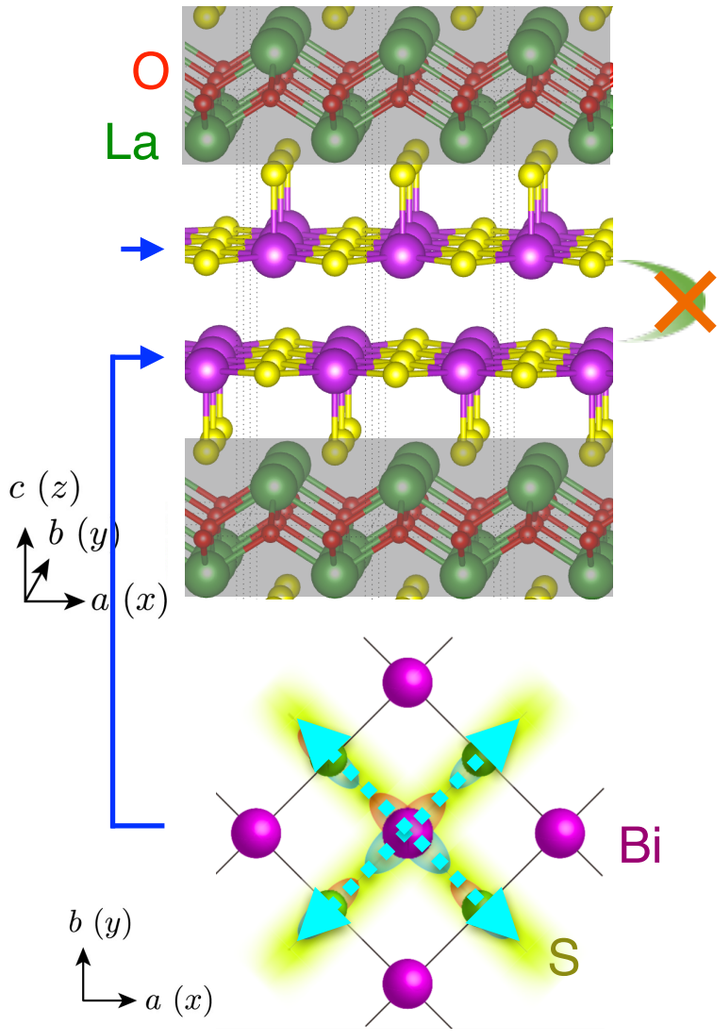
Control the blocking layer?

4-layer systems? → tetragonal becomes stable

cf.) material design of 4-layer systems:

K.Kurematsu, **MO**, *et al.*, JPSJ **89**, 024702 (2020).

# Summary of Part 1




1 ) Insulating layer：suppress coupling along z-direction

2 ) quant. interference：suppress bilayer coupling

3 ) Orbital anisotropy on the square lattice：quasi-1D

（controllable dimensionality by atomic substitution)

**q1D gapped Dirac cone = ideal band structure**

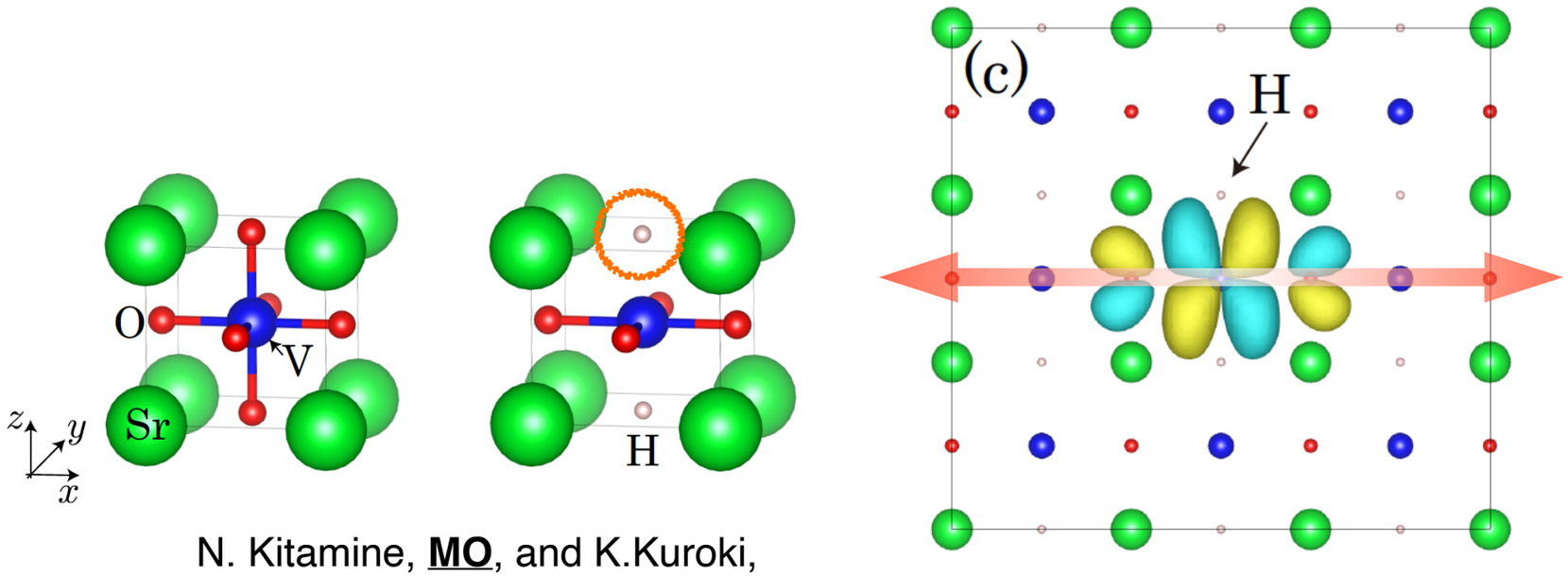
**(low-dim + high group velocity + multi-valley)**


**[Refs]** **MO**, R. Akashi, and K. Kuroki, JPSJ **85**, 094705 (2016).

**MO**, H. Usui, and K. Kuroki, Phys. Rev. Appl. **8**, 064020 (2017).

**MO**, H. Usui, and K. Kuroki, J. Phys. Soc. Jpn. **88**, 041010 (2019). (review)

# Part 2：Possible superconductivity in transition-metal oxyhydrides



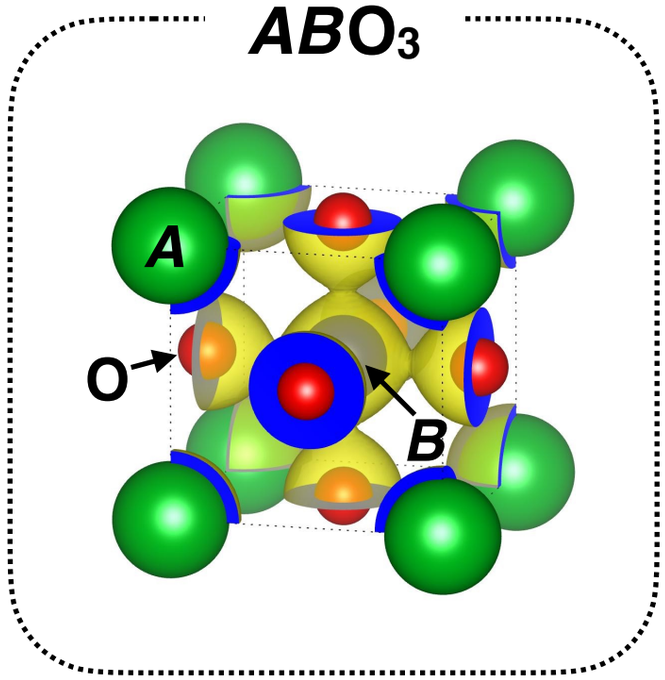

N. Kitamine, **MO**, and K.Kuroki,
arXiv:2007.01553 (2020).

[Collaborators] Naoya Kitamine, Kazuhiko Kuroki (Osaka Univ.)

# Transition-metal oxides

**Playground of many kinds of intriguing physics**

**(superconductivity, magnetism, ferroelectricity,…)**




***A* = Ca, Sr, Ba, Y, La, etc.**

carrier doping, chemical pressure

***B* = Transition metal (V, Cr, Mn, Fe, Ru,…)**

governs materials properties

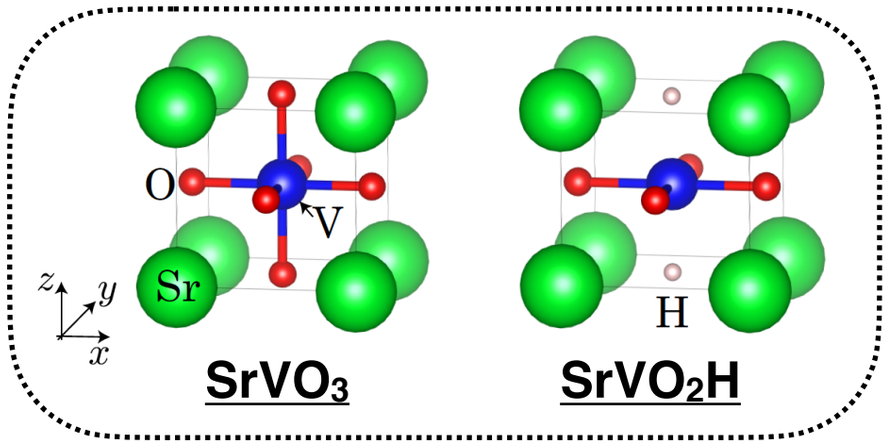
**O → H, F, N, Cl,…**

**New degrees of freedom**

**for material design**

# Transition-metal oxy**hydrides**

## Crystal field (environement for cation)



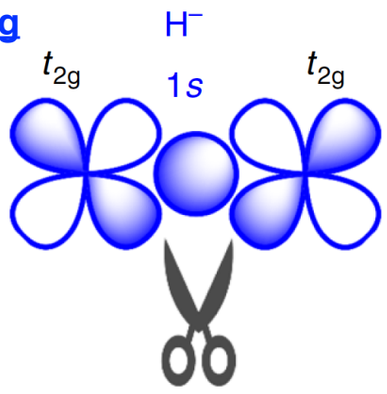

**$SrVO_3$** **$SrVO_2H$**

*x, y, z directions are equivalent*

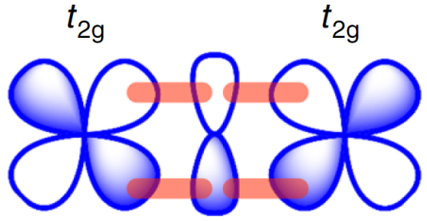
*z is inequivalent*

## Bond breaking between $t_{2g}$

H-*s* has a different parity to that for M-$t_{2g}$ (*d* orbital), then breaks a chemical bond between *d* orbitals

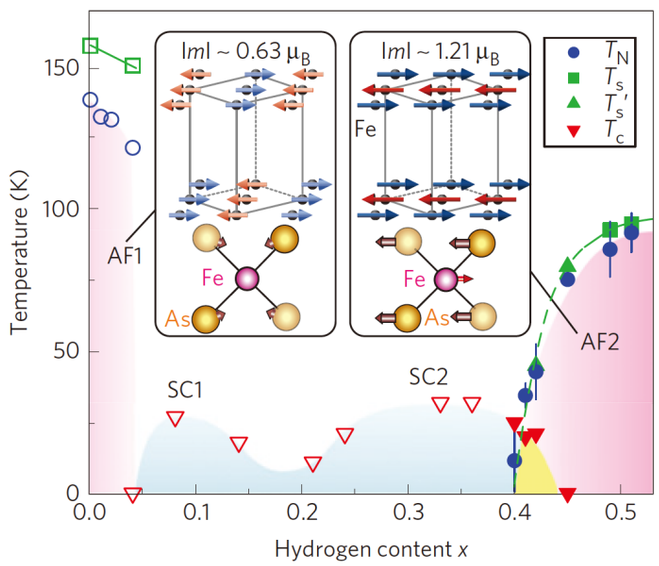



cf.) H. Kageyama *et al.*, *Nature Commun.* **9**, 772 (2018).

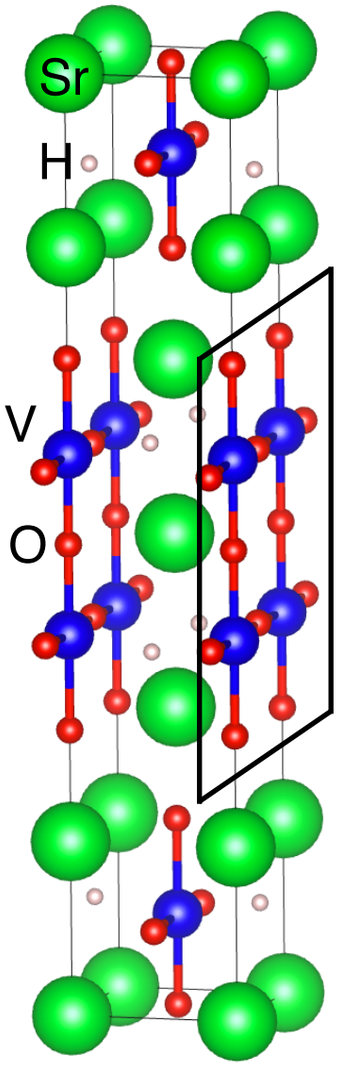



## Carrier doping by substitute $H^-$ for $O^{2-}$

e.g.) $LaFeAsO_{1-x}H_x$: S. Iimura *et al.*, *Nature Commun.* **3**, 943 (2012); M. Hiraishi *et al.*, *Nature Phys.* **10**, 300 (2014). (Fig.)



# Theoretical proposal for unconventional superconductivity



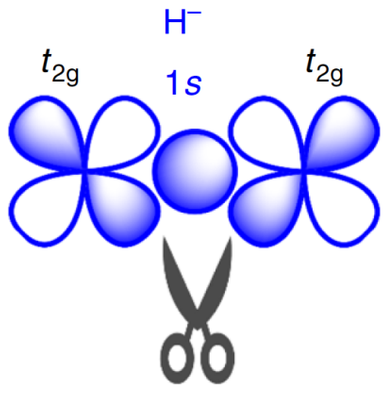

$Sr_3V_2O_5H_2$

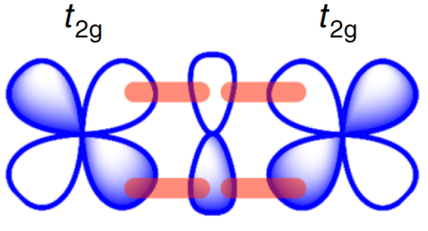
**Ladder structure**

→ **unconventional superconductivity?**


- E. Dagotto *et al.*, *Phys. Rev. B* **45**, 5744 (1992).
- T. M. Rice *et al.*, *EPL* **23**, 445 (1993).
- E. Dagotto and T. M. Rice, *Science* **271**, 618 (1996).
- K. Kuroki *et al.*, *Phys. Rev. B* **72**, 212509 (2005).
- D. Ogura *et al.*, *Phys. Rev. B* **96**, 184513 (2017).


Naoya Kitamine

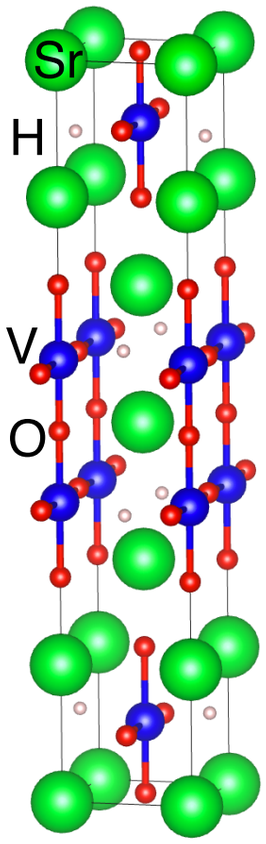



**We investigate whether this material can host superconductivity by theoretical calculation**

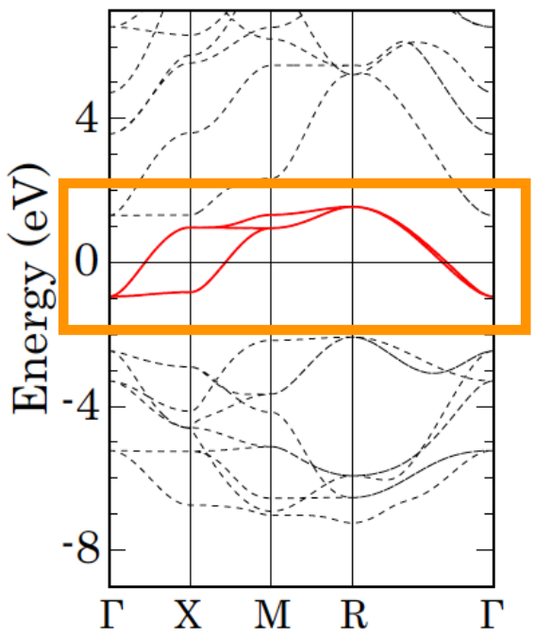
# Method: First-principles calculation and an effective model

**Crystal structure**




**First-principles band structure**

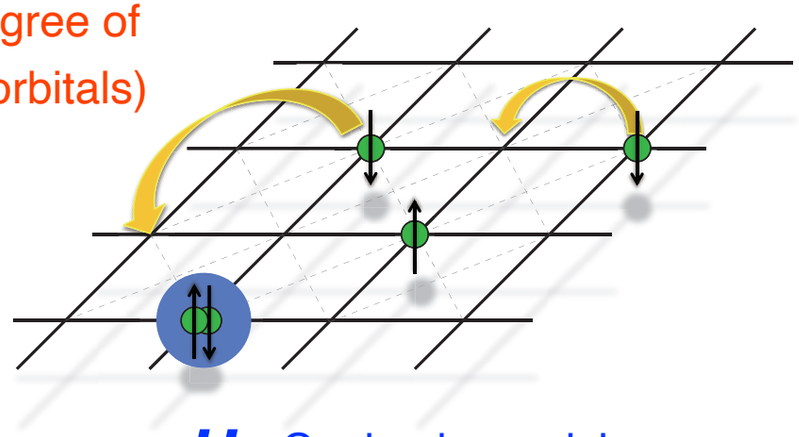
PBE+GGA (WIEN2k)




a small degree of freedom (orbitals)

**Effective model consisting of Wannier functions**

Wannier90



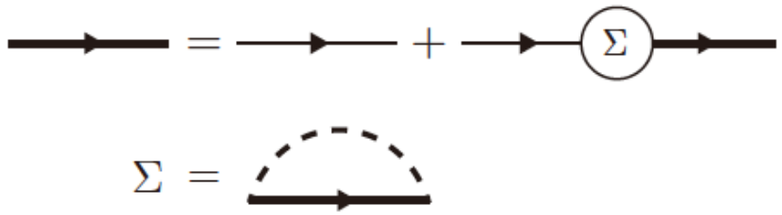
***+ U*** : Coulomb repulsion

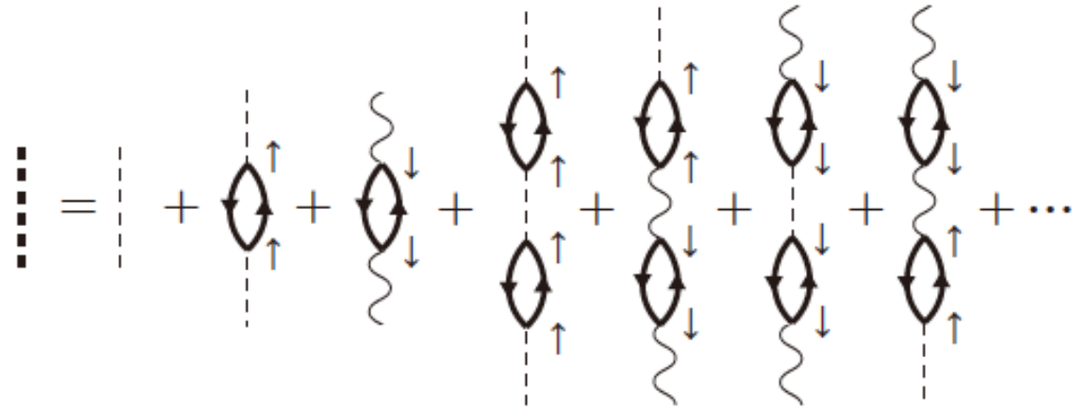
$$H = \sum_{i,j,\sigma} t_{ij} \hat{c}^{\dagger}_{i,\sigma} \hat{c}_{j,\sigma} + \sum_{i} U_i \hat{n}_{i,\uparrow} \hat{n}_{i,\downarrow}$$

**Hubbard model**

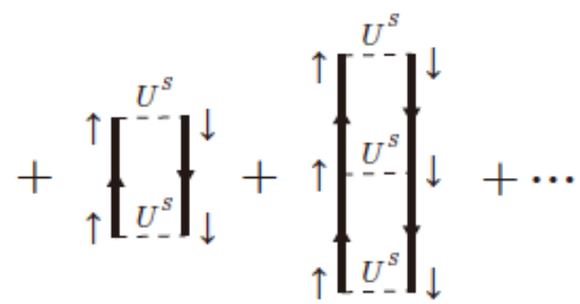
**By using the effective model, we can consider strong electron correlation**

# Method: FLEX + linearized Eliashberg eq.




**Fluctuation exchange (FLEX) approx.**:
determine self-energy (energy correction by U)
by considering ring & ladder diagram

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**Linearized Eliashberg eq.**：

λ = 1 means superconducting (SC) transition

In real calculation, we fix the temperature and see λ as a measure of how superconductivity is favored in this system

$$\lambda\Delta_{ll'}(k) = -\frac{T}{N}\sum_q \Gamma^s_{lm_1m_4l'}(k-q)G_{m_1m_2}(q)G_{m_4m_3}(-q)\Delta_{m_2m_3}(q)$$

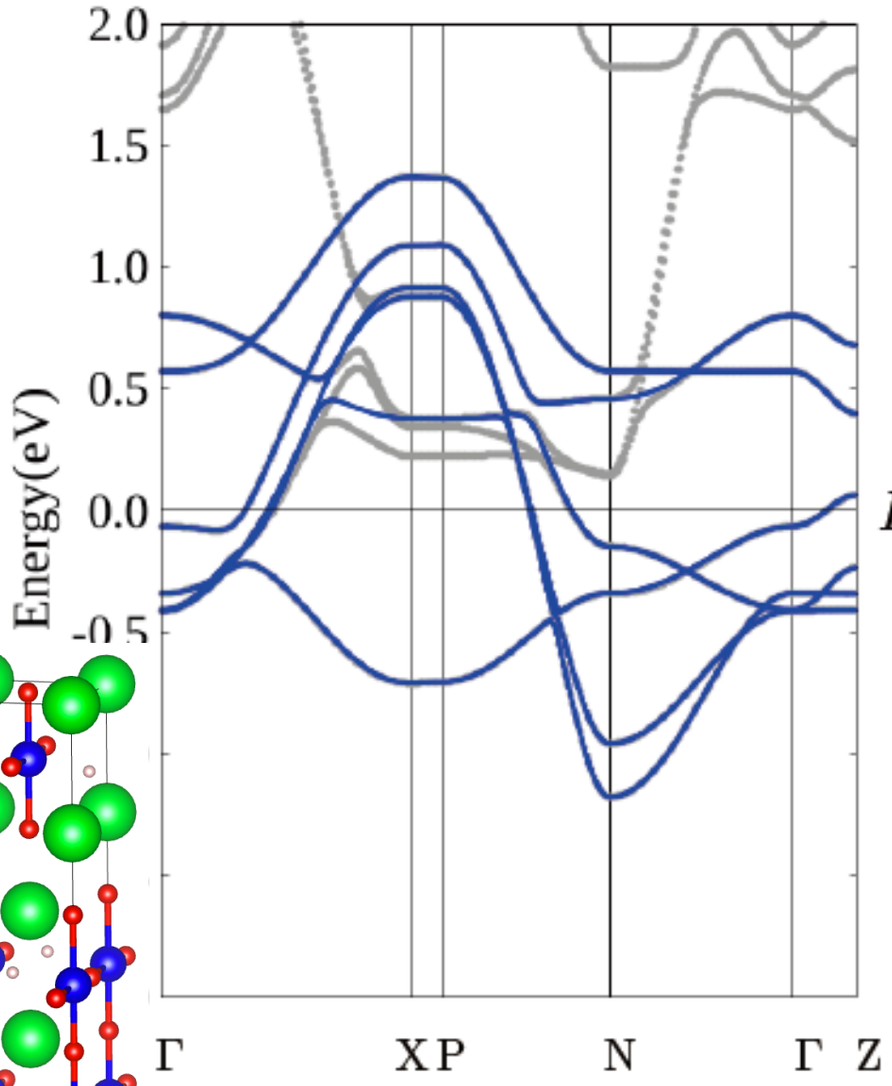
$\Delta_{ll'}(k)$: gap 関数

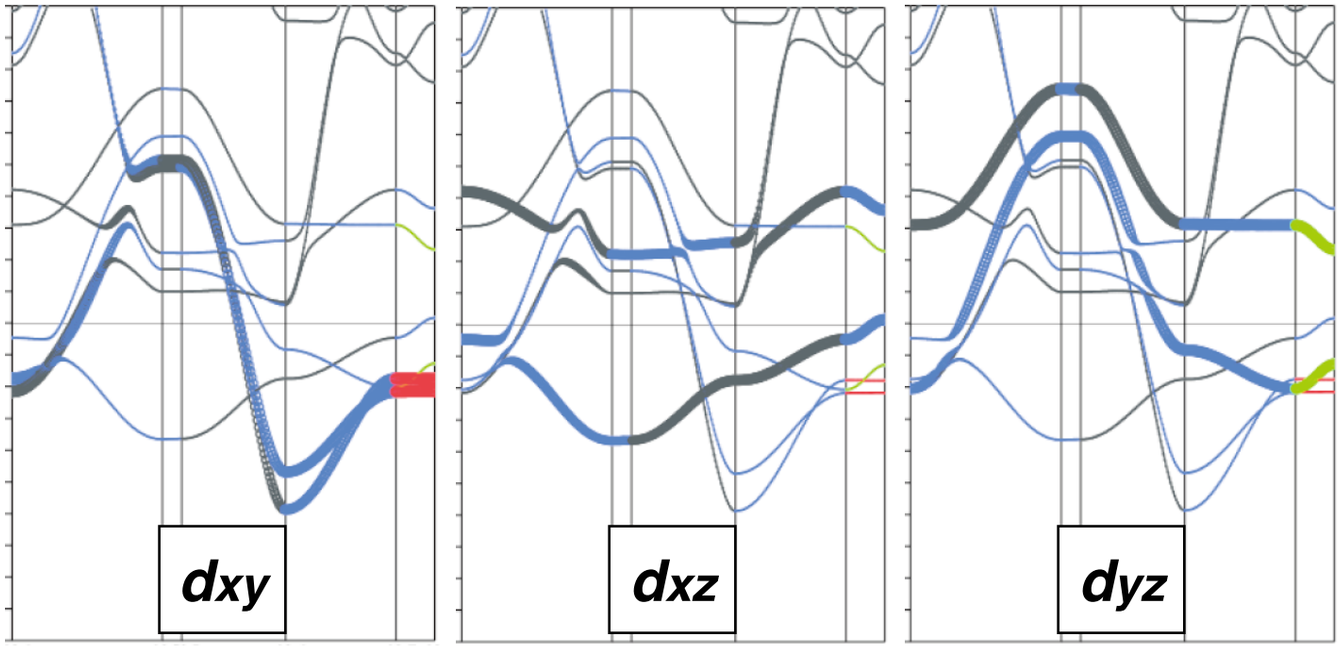
$\Gamma^s(k) = U + \frac{3}{2}U\chi^{sp}(k)U - \frac{1}{2}\chi^{ch}(k)U$: 有効相互作用

$\chi^{sp} = \chi^0/(1-U\chi^0),\quad \chi^{ch} = \chi^0/(1+U\chi^0)$: スピン/電荷感受率

$\chi^0_{m_1m_2m_3m_4}(q) = -\frac{T}{N}\sum_k G_{m_3m_1}(k+q)G_{m_2m_4}(k)$: 既約感受率

# Band structure: $Sr_3V_2O_5H_2$

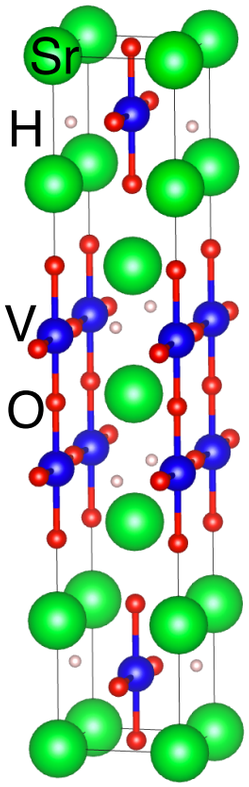


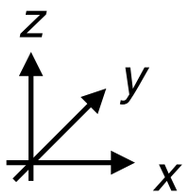

No bilayer splitting

**Both *dxz* and *dyz* form two-leg ladders**

*** bonding and anti-bonding bands are characteristic in a two-leg ladder**

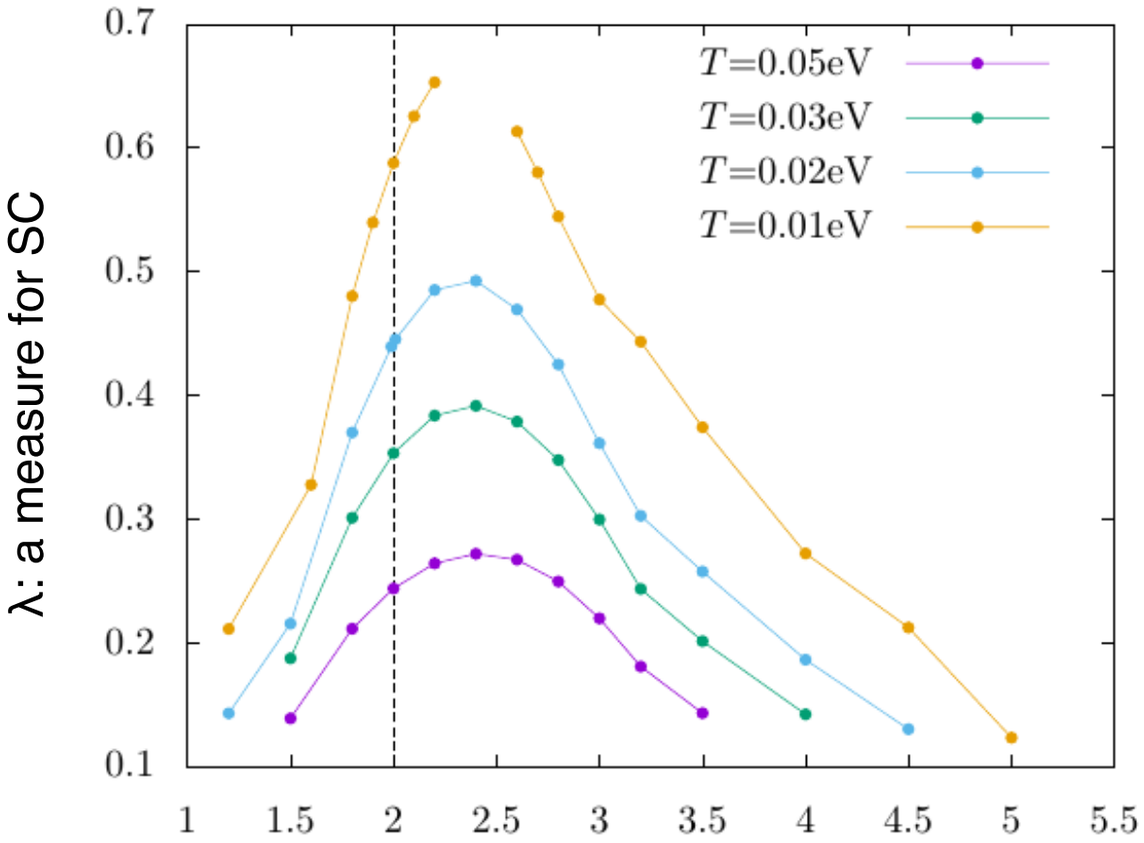



H is aligned along the x direction




X = (π, π, 0), P = (π, π, π), N = (π, 0, π), Z = (0, 0, π) in cartesian

# FLEX + Eliashberg: $Sr_3V_2O_5H_2$



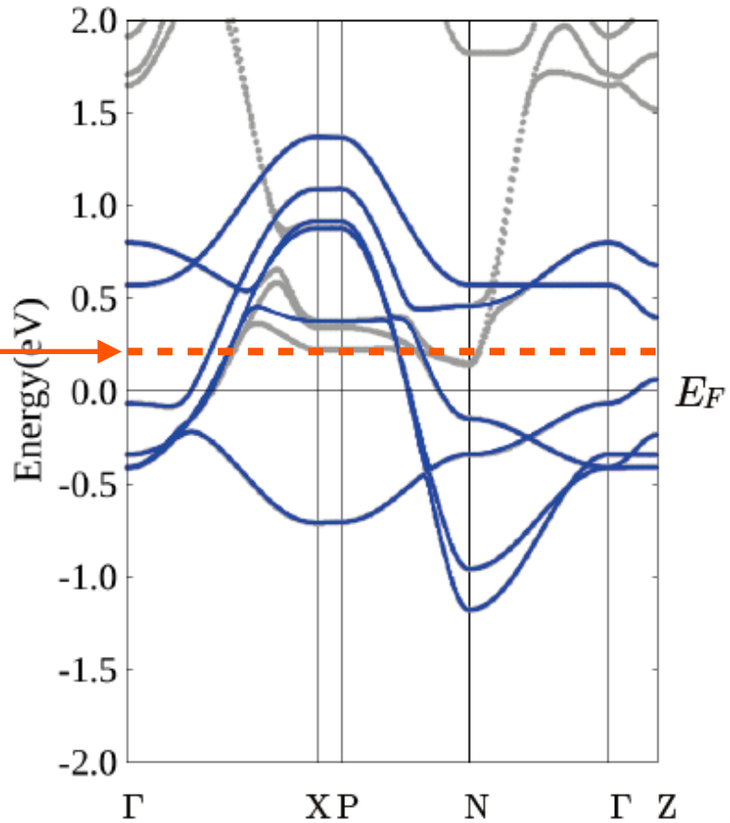

number of d electrons per vanadium (2 = non-doped)

Small electron doping yields a high λ

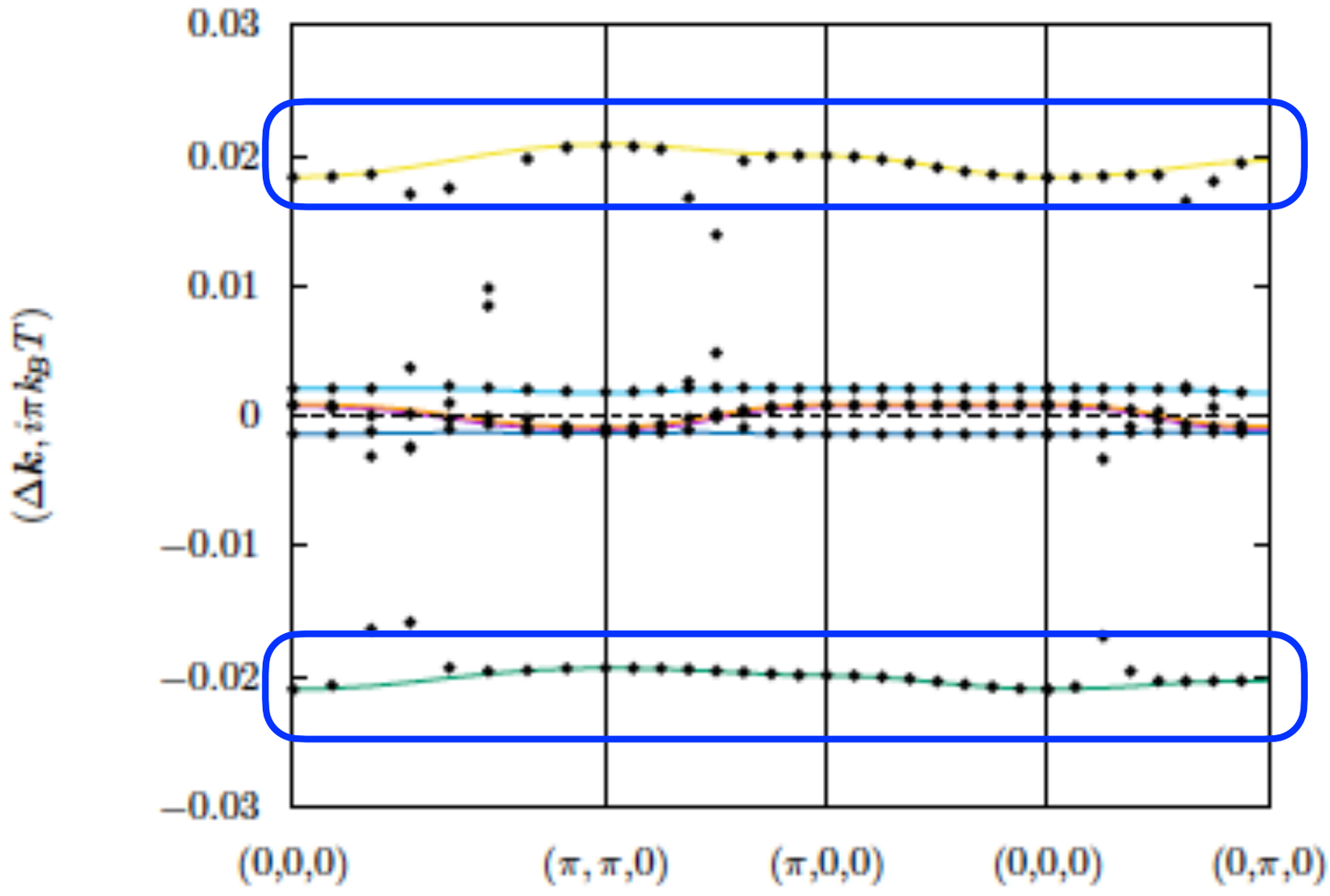
(comparable to some cuprates!)

U = 2.5 eV, J = J' = U/8, U' = U-2J

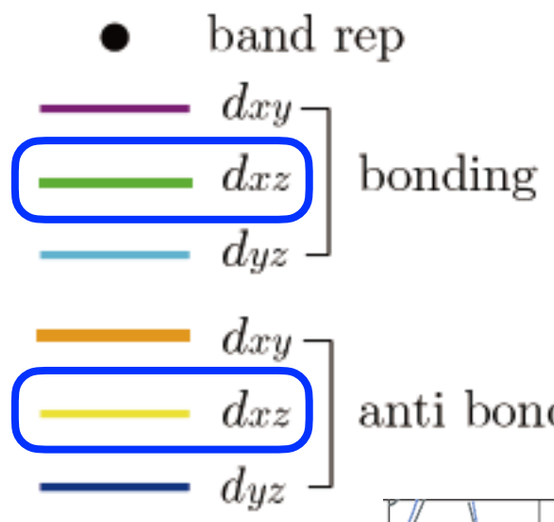
chemical potential for optimal doping

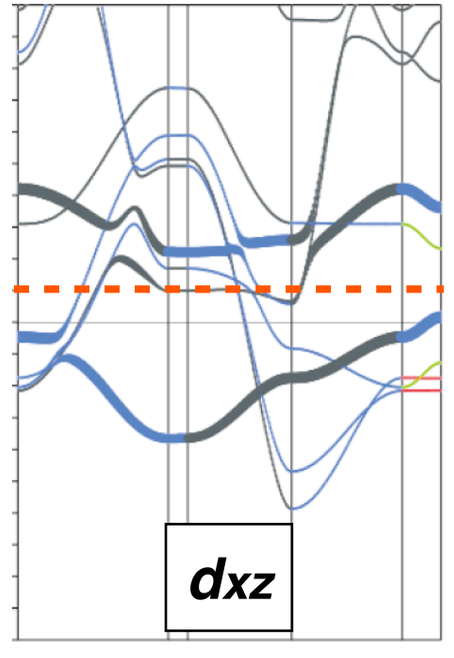


# gap function: $Sr_3V_2O_5H_2$



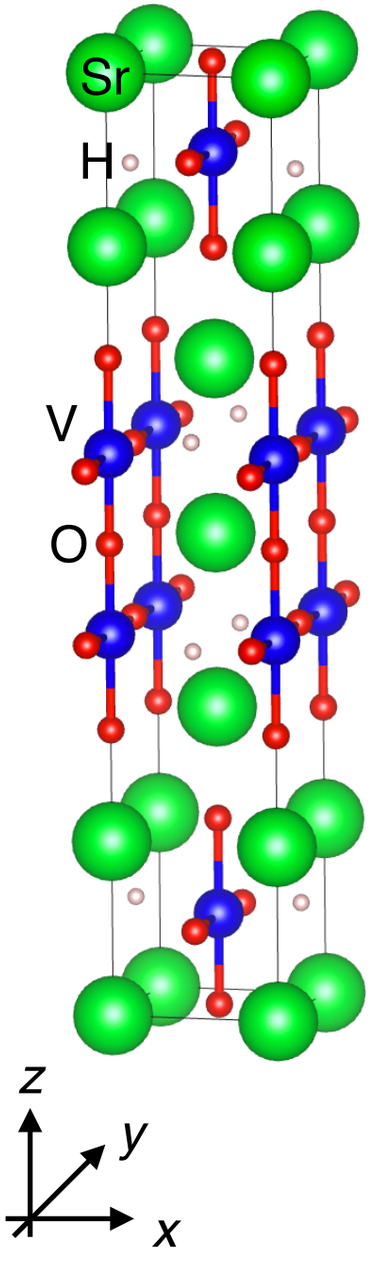

[T = 0.02 eV、 n = 2.4]

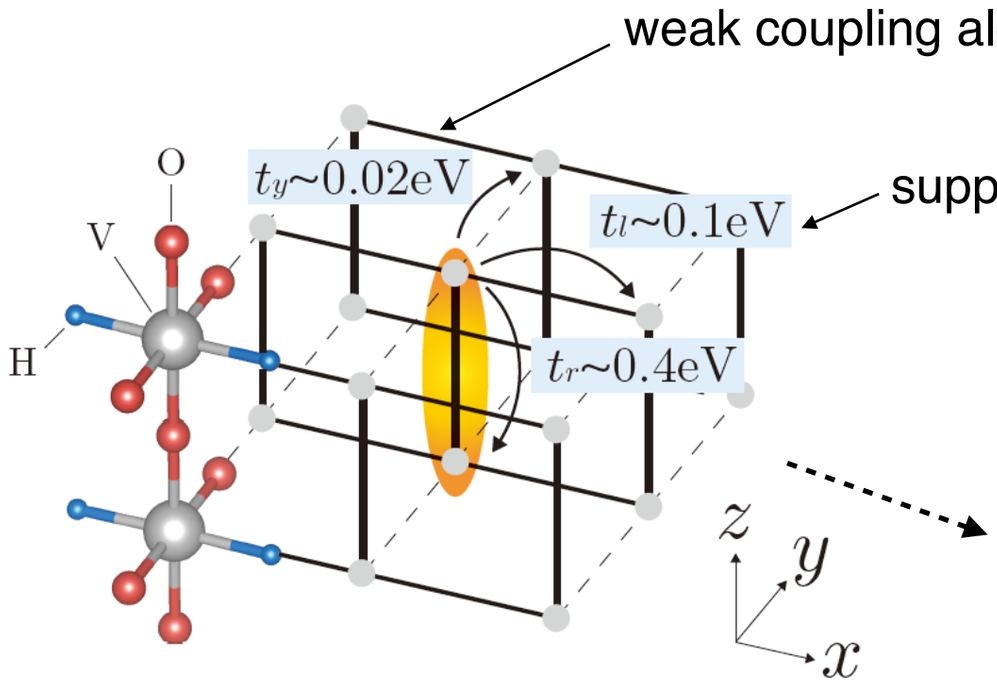


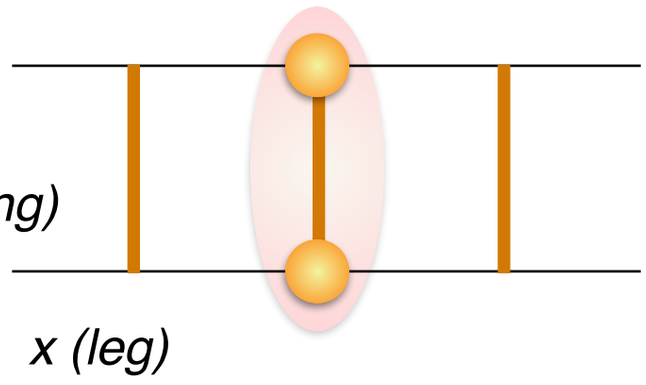




- ***dxz* is a key for this superconductivity**
- **Sign change between bilayer-split *dxz* bands**

# ladder-like electronic states in $Sr_3V_2O_5H_2$




H almost breaks a chemical bond along x (leg direction)

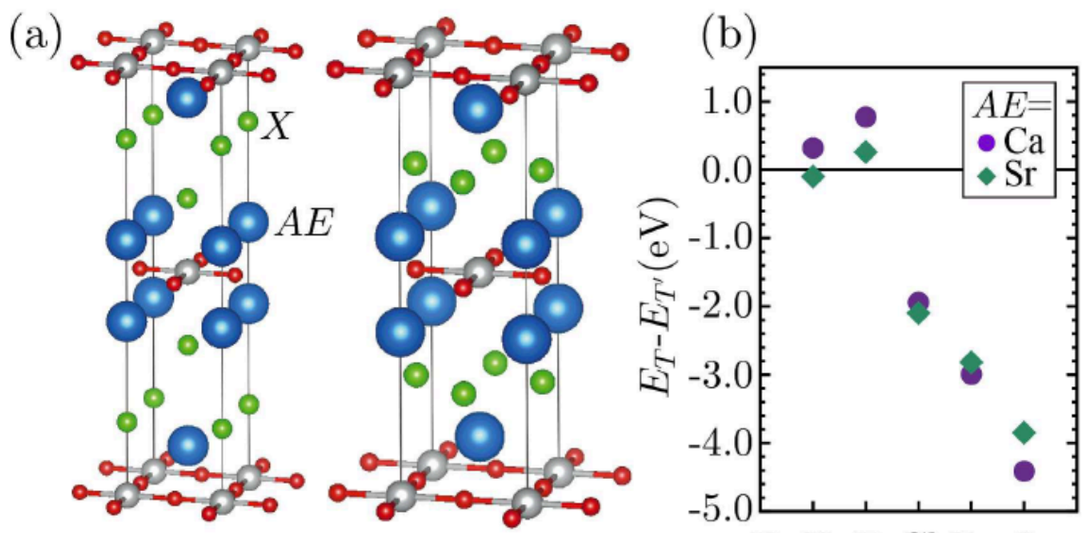
→ dxz forms a ladder with strong rung coupling

→ favorable for Cooper pairing

E. Dagotto *et al.*, *Phys. Rev. B* **45**, 5744 (1992).

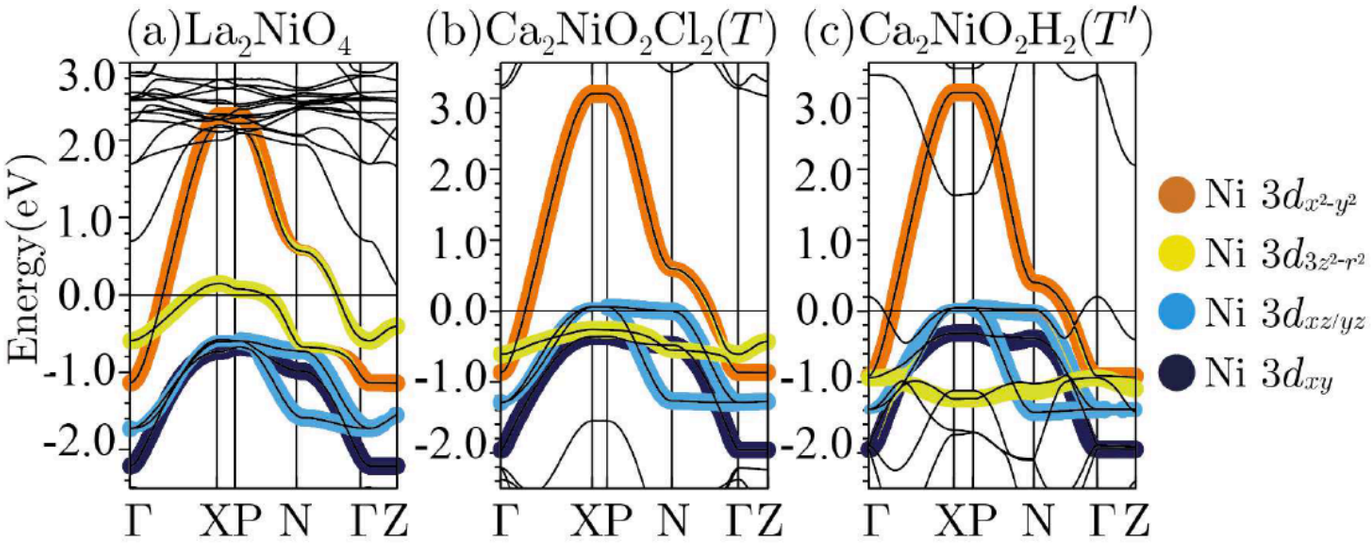
# Another candidate:

# $A_2NiO_2X_2$ ($A$ = Ca, Sr; $X$ = H, F, Cl, etc.)




N. Kitamine, **MO**, and K.Kuroki, arXiv:2007.01553 (2020).

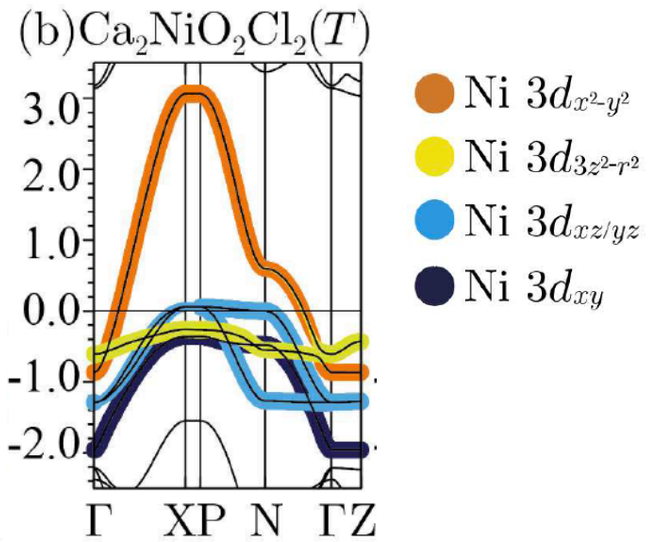
Monolayer systems with apical oxygen being replaced with other anions

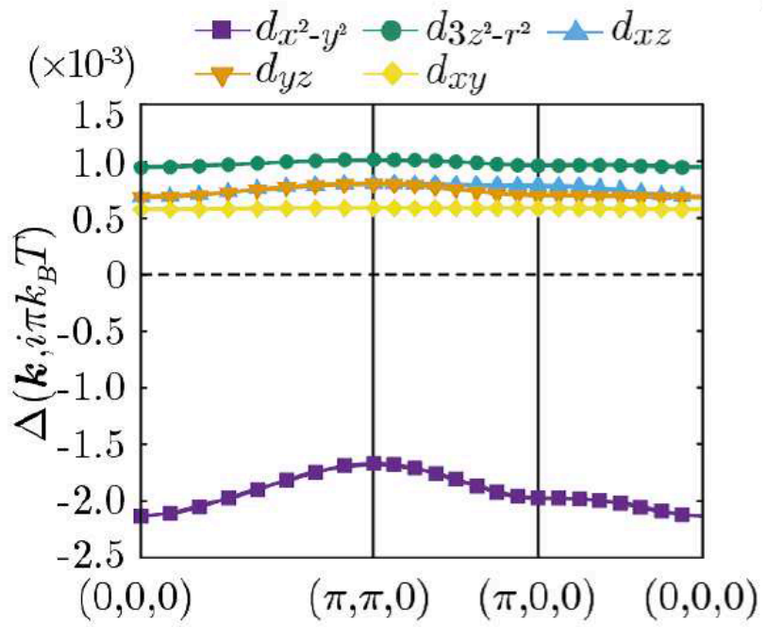



*d* orbitals other than $dx^2$-$y^2$ lie near the Fermi level and acts as "glue" for Cooper pair of $dx^2$-$y^2$

# Superconductivity

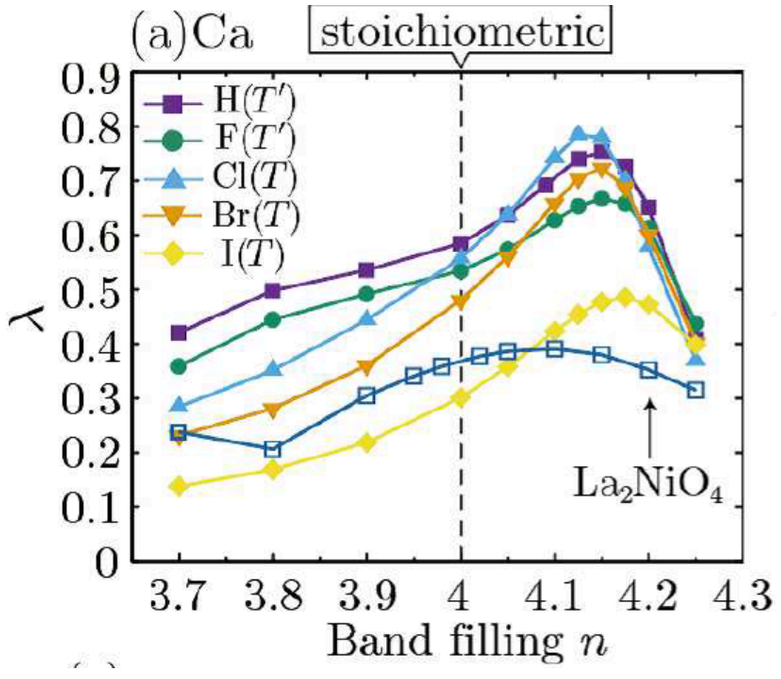
N. Kitamine, **MO**, and K.Kuroki, arXiv:2007.01553 (2020).




Sign change between $dx^2$-$y^2$ and other *d* orbitals

→ evidence of a role as “glue”




Electron doping seems necessary

# Summary of Part 2

$Sr_3V_2O_5H_2$ possibly hosts unconventional superconductivity by electron doping, where $d_{xz}$ orbitals form the two-leg ladder with a strong coupling along the rung direction

$A_2NiO_2X_2$ is another candidate where *d* orbitals other than $dx^2$-$y^2$ acts as a glue of Cooper pair of $dx^2$-$y^2$ orbital. Here the characteristic crystal field by anion substitution is a key to realize this situation.

* the crystal structure is assumed in this study, so theoretical determination of the anion positions are important future issues. From the experimental viewpoint, the carrier control is also an important issue.

N. Kitamine, **MO**, and K.Kuroki, "*Designing nickelate superconductors with $d^8$ configuration exploiting mixed-anion strategy*", arXiv:2007.01553 (2020).