OpenMX developers meeting
Nov. 10th, 2023

Structure search, database, and applications for AB_2 type 2D materials

Institute for Solid State Physics,
University of Tokyo

Masahiro FUKUDA

Structure search, database, and applications for AB_2 type 2D materials

- Structure search for AB_2 monolayer
  - structure map

*M. Fukuda, et. al., Mater. Adv., **2**, 4392-4413 (2021).*

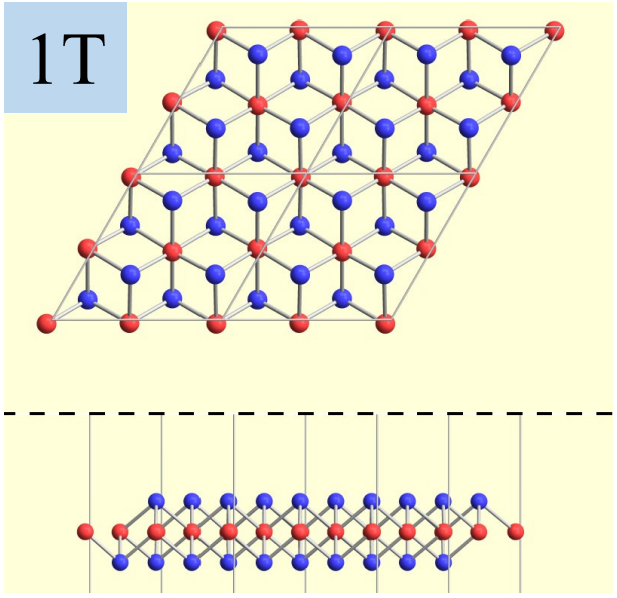
- Database
  - interactive website
  - data repository
- Applications
  - memory structure
  - penta monolayer (η-Au_2S, θ-Au_2S)

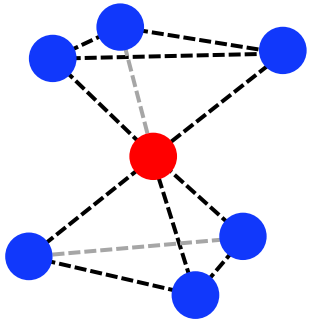
M. Fukuda, et. al., arXiv:2305.08111 [cond-mat.mtrl-sci]

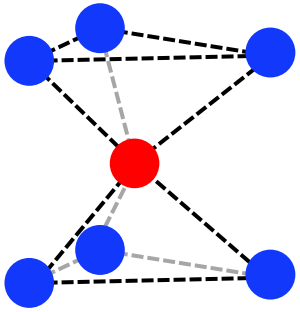
Structure search for AB_2 monolayer

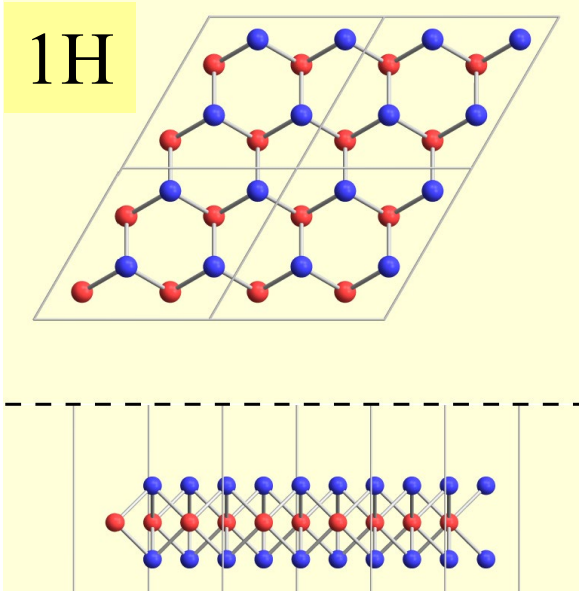
- Research purpose
  - Structure exploration for AB_2 type monolayers by high-throughput density functional theory (DFT) calculations

- Background
  - Various kinds of AB_2 type monolayers such as transition metal dichalcogenides (e.g. MoS_2) and MXenes (e.g. Ti_2C) have synthesized experimentally and have attracted attentions due to the diversity of the chemical and physical properties.
  - The combination of the elements is diverse even only for the AB_2 composition.
    → Sufficient room for exploring unknown AB_2 monolayers









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  - The combination of the elements is diverse even only for the AB_2 composition. → Sufficient room for exploring unknown AB_2 monolayers

- Approach
  - High-throughput calculations based on the DFT by using OpenMX were performed to create a structure map for AB_2 type monolayers.

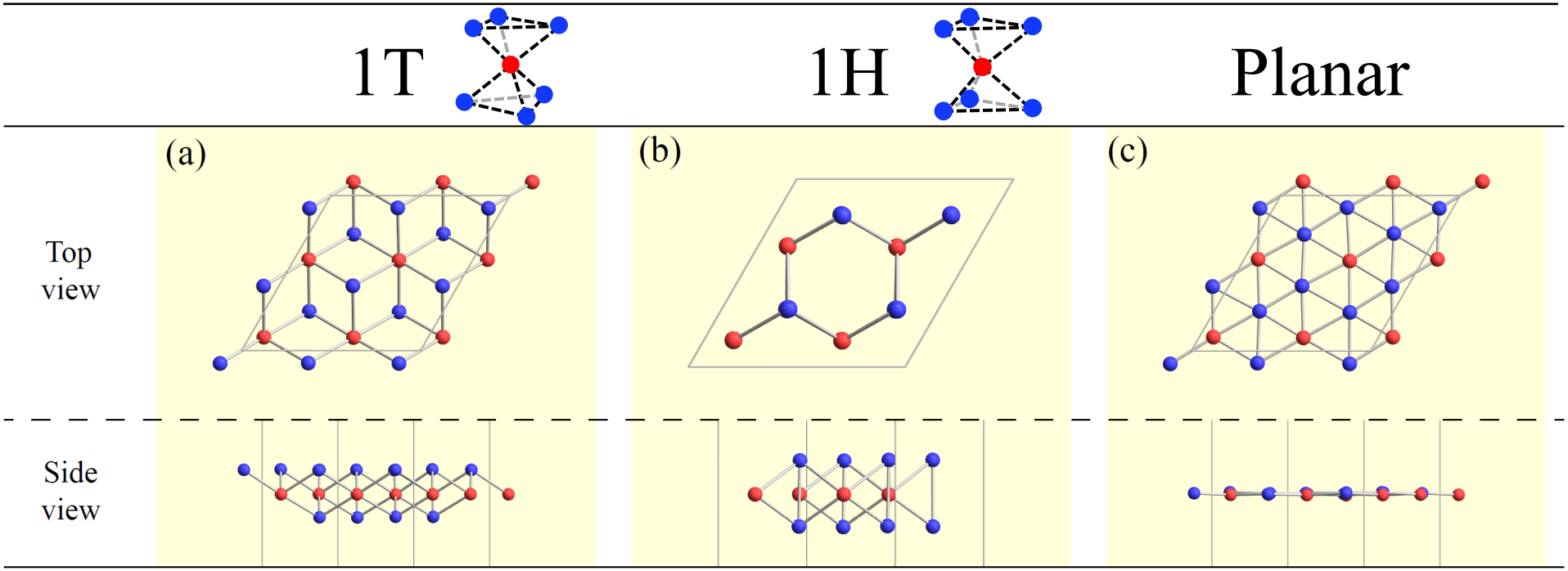
High-throughput calculation based on the DFT

- Software: OpenMX(http://www.openmx-square.org/)
- Functional: GGA-PBE
- Pseudo potential: Optimized Pseudo atomic orbitals
- k-point : 5×5×1
- Cutoff energy: 240 [Ry]
- Variable cell optimization and symmetry-unconstrained geometry optimization
- Selection of composition elements

I																	XVIII
H	II											XIII	XIV	XV	XVI	XVII	He
Li	Be											B	C	N	O	F	Ne
Na	Mg	III	IV	V	VI	VII	VIII	IX	X	XI	XII	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba		Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra		Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og

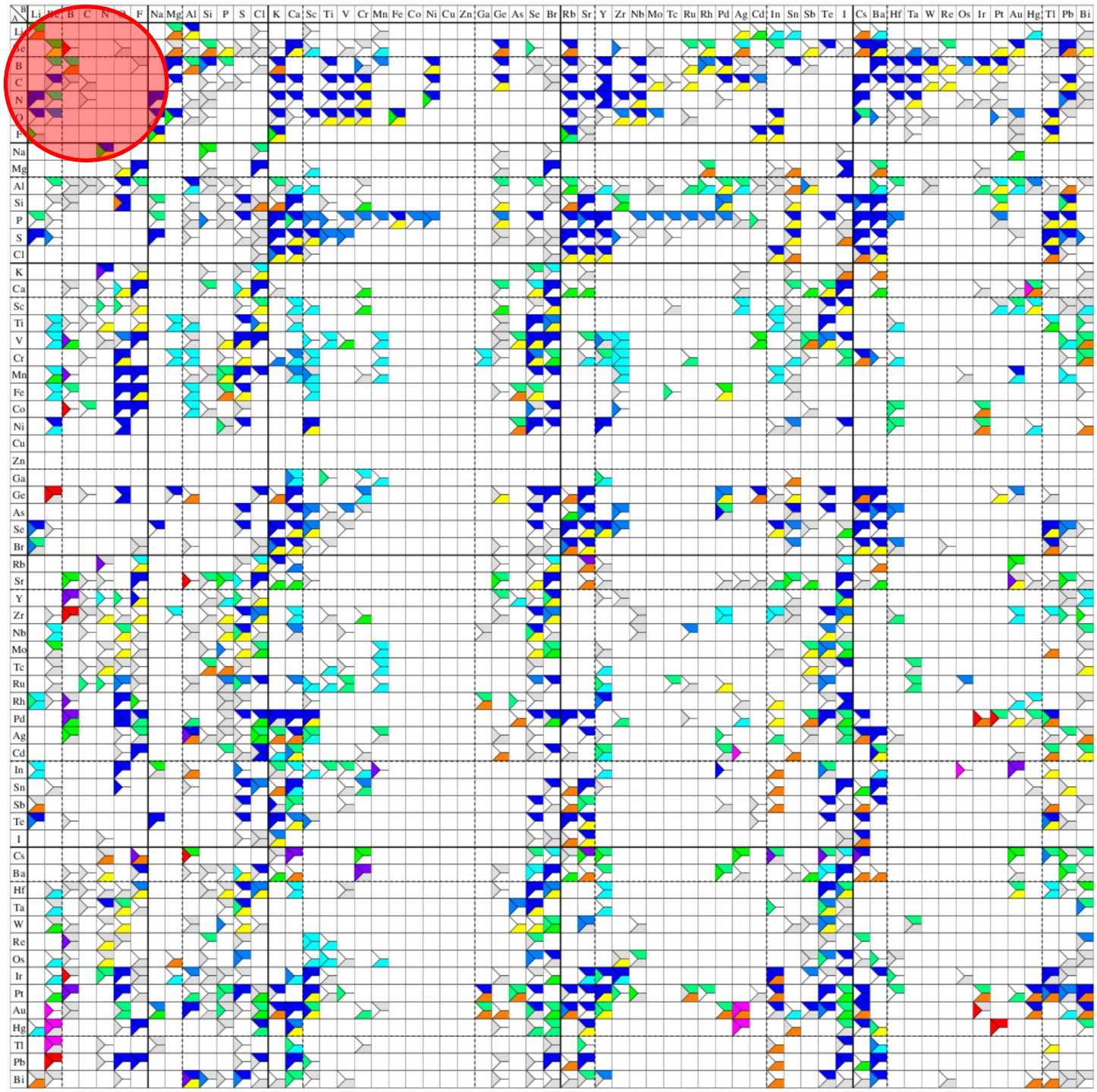
Possible AB_2 compounds: 62 elements × 62 elements = 3844 compounds

Initial structures



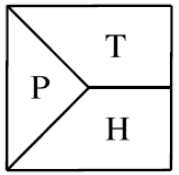
- We prepared the initial structures including fluctuation with respect to the ideal structures for atomic coordinates. The initial lattice vectors for variable cell optimizations were set to large enough to allow large structural change from the initial structure and to avoid trapping of local minima as far as possible.
- If the structure change drastically from the initial structure, we terminate the calculation.

$$3844 \text{ (compounds)} \times 3 = 11532$$

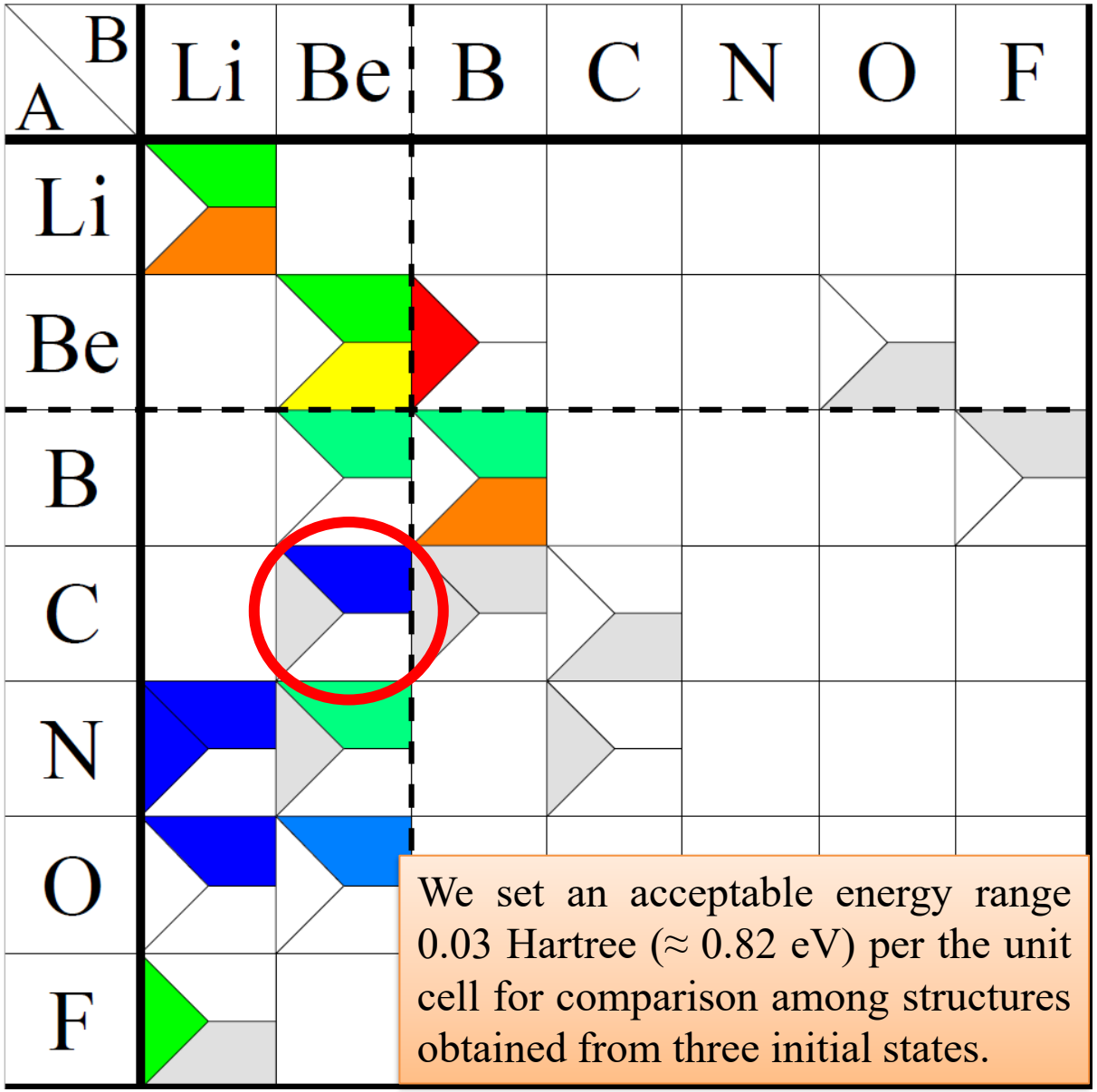


Structure map

Space-group classification



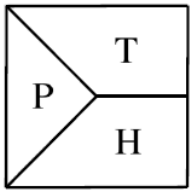
- $P\bar{3}m1$
- $P2_1/m$
- $P4mmm$
- $C2/m$
- $P\bar{6}m2$
- $Amm2$
- $Cmmm$
- memory
- planar
- distorted planar
- others (stable)



We set an acceptable energy range 0.03 Hartree (≈ 0.82 eV) per the unit cell for comparison among structures obtained from three initial states.

This structure map includes information of initial structures and space-groups of obtained structures for all the combination of AB_2 compounds.

Space-group classification



- $P\bar{3}m1$ → 1T
- $P2_1/m$
- $P4mmm$
- $C2/m$
- $P\bar{6}m2$ → 1H
- $Amm2$
- $Cmmm$
- memory
- planar
- distorted planar
- others (stable)

Comparison between experiment and calculation (transition metal dichalcogenides)

Experimental data by high-resolution STEM imaging[2]

B \ A	Ti	Zr	Hf	V	Nb	Ta	Mo	W	Re	Fe	Pd	Pt
S	1T	1T	1T[(e)]	1T	1H	1H	1H	1H	1T″	—	—	1T[(h)]
Se	1T[(a)]	1T[(c)]	1T[(f)]	1T	1H	1H[(g)]	1H	1H	1T″	1H	—	1T
Te	1T[(b)]	1T[(d)]	—	—	1T	—	1T′ 1H	1T′	—	—	—	—

[2] J. Zhou *et al.*, Nature **556**, 355 (2018)

Results of high-throughput DFT calculations

B \ A	Ti	Zr	Hf	V	Nb	Ta	Mo	W	Re	Fe	Pd	Pt
S	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{6}m2$	$P\bar{6}m2$	$P\bar{1}$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$	$P\bar{3}m1$
Se	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$ $P\bar{6}m2$ $C2/m$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{6}m2$	$P\bar{6}m2$	$P\bar{1}$ $C2/m$	$C2/m$ $P\bar{6}m2$ Cm	$P\bar{3}m1$	$P\bar{3}m1$
Te	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	$P2_1/m$ $P\bar{6}m2$	$P2_1/m$ $P\bar{6}m2$	$P2_1/m$ $P\bar{6}m2$ $C2/m$	$P2_1/m$ $P\bar{6}m2$	$P2_1/m$ $P\bar{6}m2$	$P\bar{1}$	—	$P\bar{3}m1$	$P\bar{3}m1$

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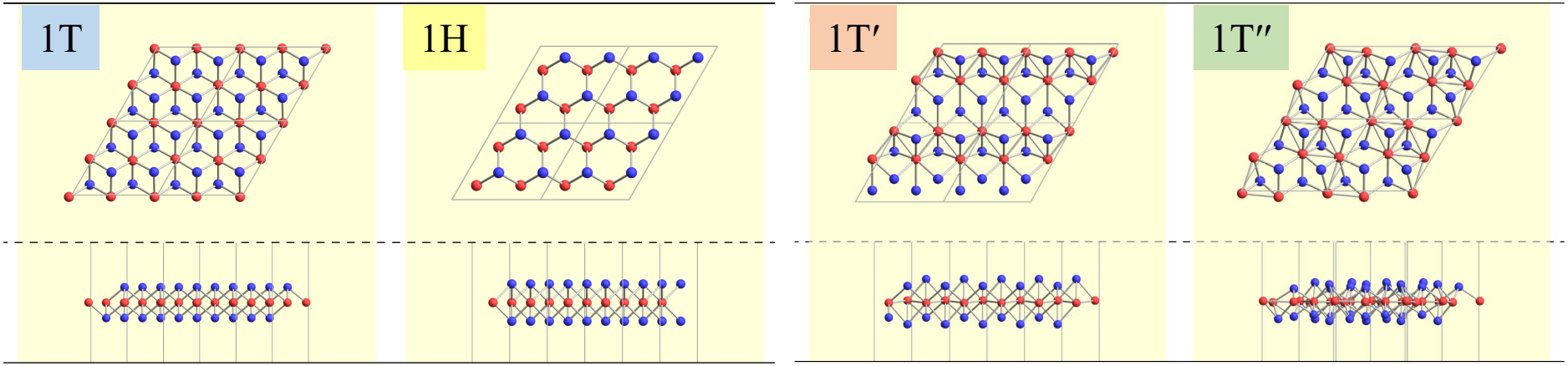
Experimental data by high-resolution STEM imaging[2]

B \ A	Ti	Zr	Hf	V	Nb	Ta	Mo	W	Re	Fe	Pd	Pt
S	1T	1T	1T[(e)]	1T	1H	1H	1H	1H	1T″	—	—	1T[(h)]
Se	1T[(a)]	1T[(c)]	1T[(f)]	1T	1H	1H[(g)]	1H	1H	1T″	1H	—	1T
Te	1T[(b)]	1T[(d)]	—	—	1T	—	1T′ / 1H	1T′	—	—	—	—

[2] J. Zhou *et al.*, Nature **556**, 355 (2018)



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Experimental data by high-resolution STEM imaging[2]

B \ A	Ti	Zr	Hf	V	Nb	Ta	Mo	W	Re	Fe	Pd	Pt
S	1T	1T	1T[(e)]	1T	1H	1H	1H	1H	1T″	—	—	1T[(h)]
Se	1T[(a)]	1T[(c)]	1T[(f)]	1T	1H	1H[(g)]	1H	1H	1T″	1H	—	1T
Te	1T[(b)]	1T[(d)]	—	—	1T	—	1T′ 1H	1T′	—	—	—	—

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Results of high-throughput DFT calculations

B \ A	Ti	Zr	Hf	V	Nb	Ta	Mo	W	Re	Fe	Pd	Pt
S	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{6}m2$	$P\bar{6}m2$	$P\bar{1}$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$	$P\bar{3}m1$
Se	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{3}m1$ $P\bar{6}m2$ $C2/m$	$P\bar{3}m1$ $P\bar{6}m2$	$P\bar{6}m2$	$P\bar{6}m2$	$P\bar{1}$ $C2/m$	$C2/m$ $P\bar{6}m2$ Cm	$P\bar{3}m1$	$P\bar{3}m1$
Te	$P\bar{3}m1$	$P\bar{3}m1$	$P\bar{3}m1$	$P2_1/m$ $P\bar{6}m2$	$P2_1/m$ $P\bar{6}m2$	$P2_1/m$ $P\bar{6}m2$ $C2/m$	$P2_1/m$ $P\bar{6}m2$	$P2_1/m$ $P\bar{6}m2$	$P\bar{1}$	—	$P\bar{3}m1$	$P\bar{3}m1$

Families of AB_2 type 2D materials

1T/1H

- transition metal dioxides/dichalcogenides → TM-XVI
- transition metal dihalides → TM-XVII
- alkaline-earth-metal dihalides → II-XVII
- MXenes (transition metal carbides/nitrides) → XIV-TM, XV-TM
- dialkali-metal monochalcogenides, monohalides → XVI-I, XVII-I
- dialkaline-earth-metal monochalcogenides, monohalides → XVI-II, XVII-II

A \ B	I	II	TM	XII	XIII	XIV	XV	XVI	XVII
I	2		1		2		3		5
II	2	5	5			2	4	8	16
TM	11	11	22	3	11		19	63	47
XII	1	8					1		5
XIII	2	2	21		3	3	1	2	1
XIV	5	17	20	1		11		8	9
XV	10	10	16		4	7		11	
XVI	20	13	18		12	3		5	
XVII	17	14	2	2	8				

The number of 1T/1H type AB_2 monolayers for each combination of groups in the periodic table are summarized on the basis of our structure map.
→This table can be a guide to search unknown 1T/1H structures and families.

I							XVIII
H	II	XIII	XIV	XV	XVI	XVII	He
Li	Be	B	C	N	O	F	Ne
Na	Mg	Al	Si	P	S	Cl	Ar

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*M. Fukuda, et. al., Mater. Adv., **2**, 4392-4413 (2021).*

- Database
  - interactive website
  - data repository
- Applications
  - memory structure
  - penta monolayer (η-Au_2S, θ-Au_2S)

arXiv:2305.08111 [cond-mat.mtrl-sci]

Structure map of AB_2 type 2D materials

by high-throughput DFT calculations

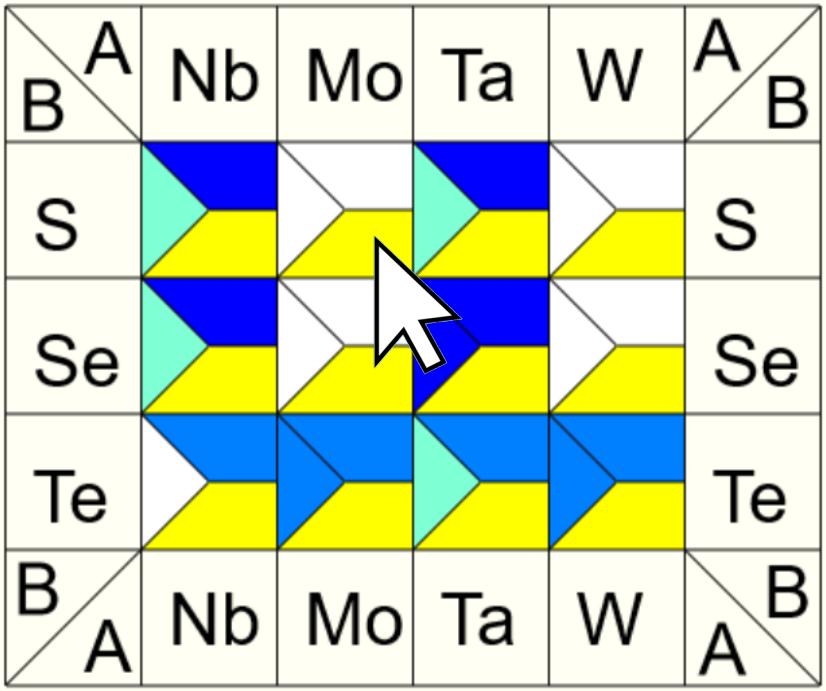
Masahiro Fukuda, Jingning Zhang, Yung-Ting Lee, and Taisuke Ozaki

The website provides an interactive structure map of AB_2 type 2D materials constructed by high-throughput DFT calculations using OpenMX. You can jump a page containing detailed information by clicking a colored region. The structure map will be restructured by specifying atomic symbols separated by a comma in forms of 'Atoms A' and 'Atoms B'. It is also possible to list all 2D compounds specified by either a space group or a characteristic structure in a form of 'Classification'. In addition to the structure map, one can see a spin map by specifying 'spin' in a form of 'Map', where compounds with larger total magnetic moments are colored by a vivid red. All the details of the maps can be found in arXiv: 1904.06047 [cond-mat.mtrl-sci]. A quick reference about the interactive structure and spin maps is available at here.

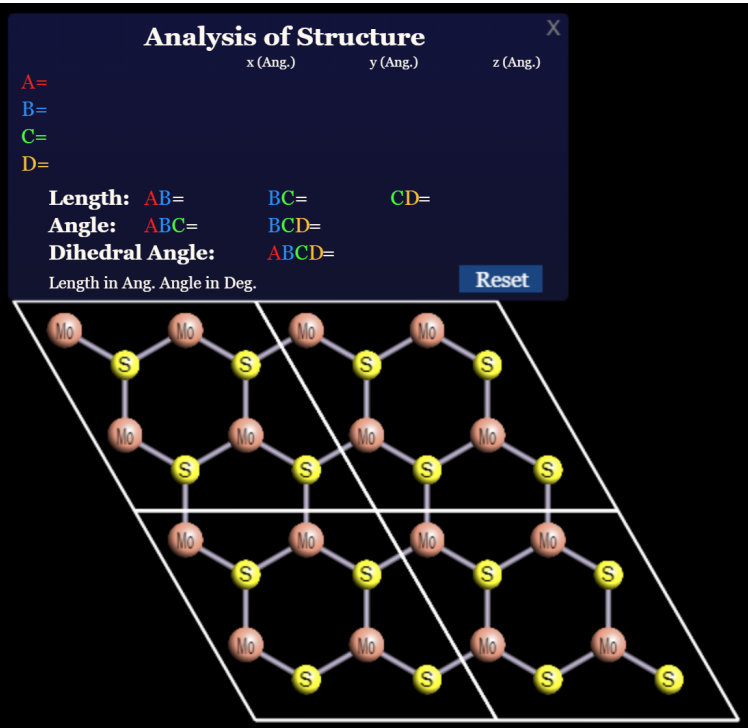
Atoms A Nb, Ta, Mo, W Atoms B S, Se,Te

Map structure Reverse A ⇔ B Classification -

P-3m1 P2_1/m P4/mmm C2/m P-6m2 Amm2 Cmmm memory planar



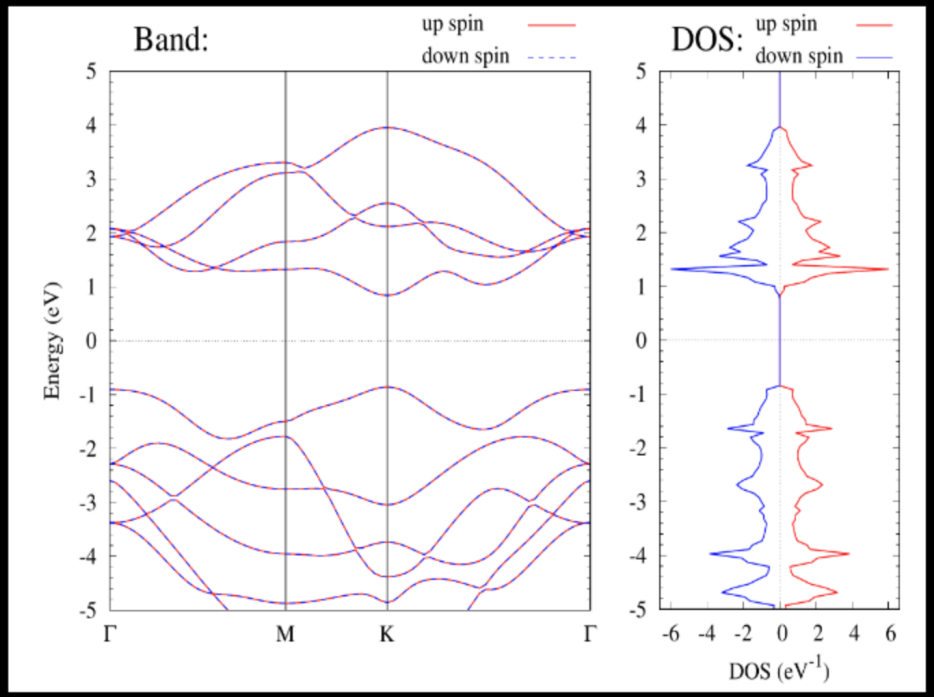
Interactive website



Compound: Mo1S2
Initial Structure: 1H
Space Group (Final): P-6m2
Lattice Parameters (a,b,gamma): 6.39, 6.39, 60.0
Energy (Hartree/12 atoms): -364.70281
Magnetic moment (muB/12 atoms): 0.0

Geo. Opt.
Mo1S2_H.cif
Mo1S2_H.md

Band and DOS calcs.: Mo1S2_H.cif Mo1S2_H.dat Mo1S2_H.pdf (Band+DOS)



Reset Supercell 2 × 2 × 1 Atoms rendering Bonds rendering Bond Color palepurple Number Symbol BGC black Atom Size 1.0 Bond Thickness 1.0 Bond Factor 1.0 Cells
Axes Perspective Structure Dynamics Net Charge off Spin off Force Velocity Rot on x 0 Rot on y 0 Rot on z 0 Save select
Structure Map Viewer Rotate: click+drag Zoom: scroll Translate: ctrl+click+drag Note: click the middle button for Safari

Our AB_2 structure map and database are available on the interactive website, www.openmx-square.org/2d-ab2/.

ISSP Data Repository

- Data repository using Gitlab
- Download all the input files and results easily

→ Promoting data utilization

masahiro.fukuda › Structure map of AB2 type 2D materials by high-throughput DFT calculations

S

Structure map of AB2 type 2D materials by high-throughput DFT calculations

Project ID: 43

3 Commits | 1 Branch | 0 Tags | 347.7 MB Project Storage

master | structure-map-of-ab2-type-2d-materials-by-high-throughput-dft-calculations | Find file | Clone

README | Creative Commons Attribution 4.0 International

Name	Last commit	Last update
data	first commit	1 year ago
.gitattributes	first commit	1 year ago
LICENSE	Add LICENSE	5 months ago
Readme.md	update the URL of gitlab	1 year ago

Usage

- Install Database
  - Using git

```
git clone https://isspns-gitlab.issp.u-tokyo.ac.jp/masahiro.fukuda/structure-map-of-ab2-type-2d-materials-by-high-throughput-dft-cal
```

  - On browser

    Click the download button of this project.

https://datarepo.mdcl.issp.u-tokyo.ac.jp/repo/6

Structure search, database, and applications for AB_2 type 2D materials

- Structure search for AB_2 monolayer
  - structure map

*M. Fukuda, et. al., Mater. Adv., **2**, 4392-4413 (2021).*

- Database
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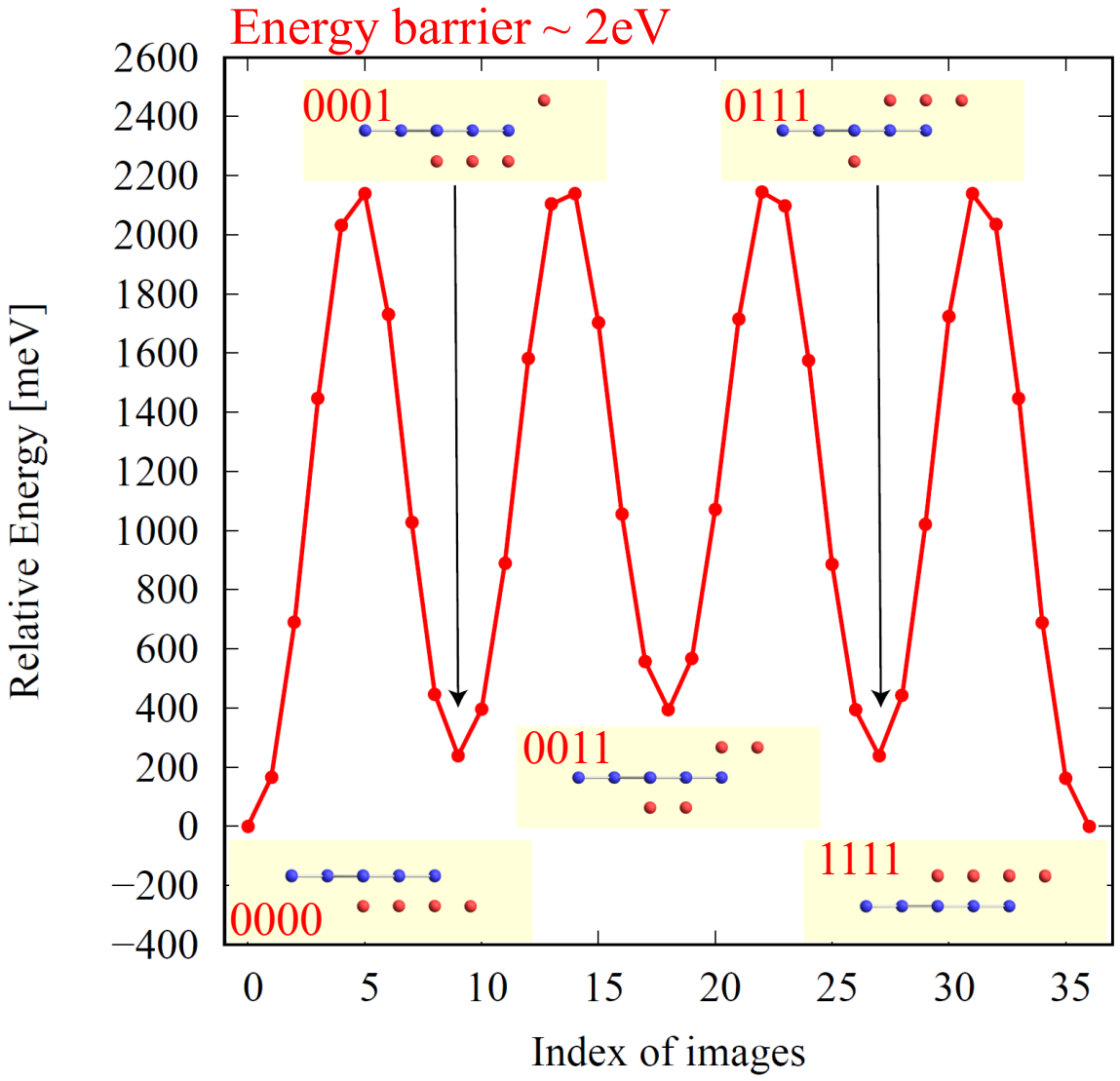
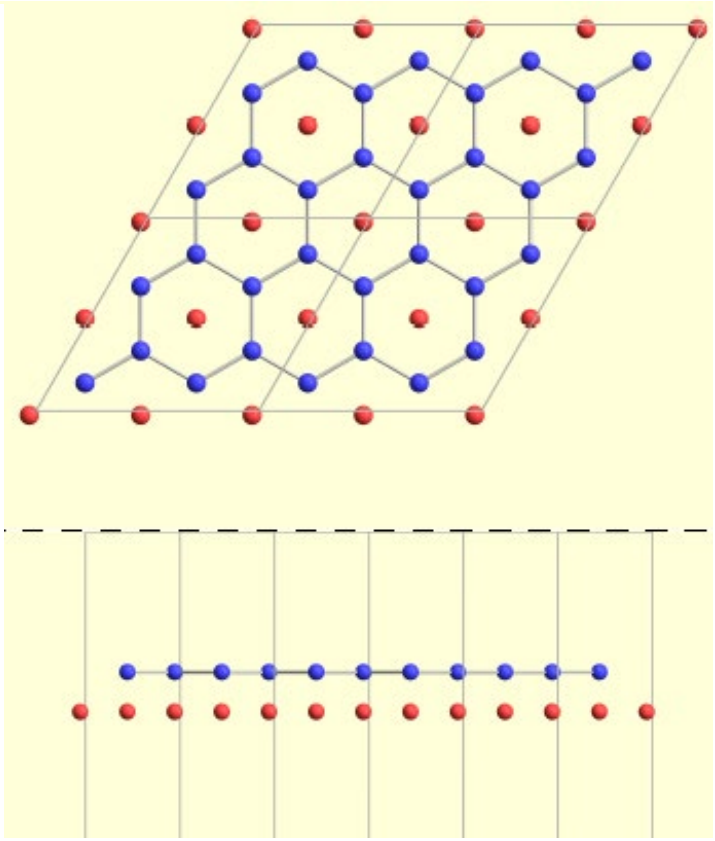
  - memory structure
  - penta monolayer (η-Au_2S, θ-Au_2S)

arXiv:2305.08111 [cond-mat.mtrl-sci]

NEB calculation for memory structure of $SrAl_2$





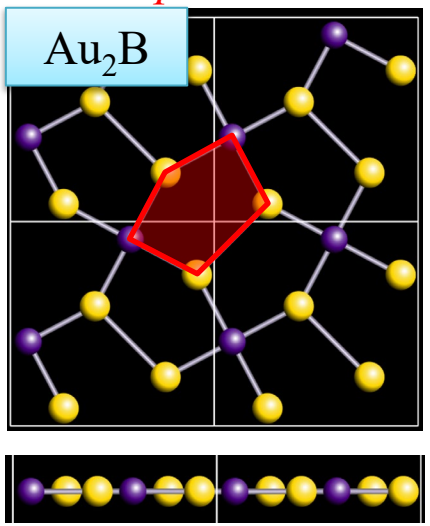
Since the positions (above or below) of red atoms can represent binary digits, we call the buckled structures “memory structure”.

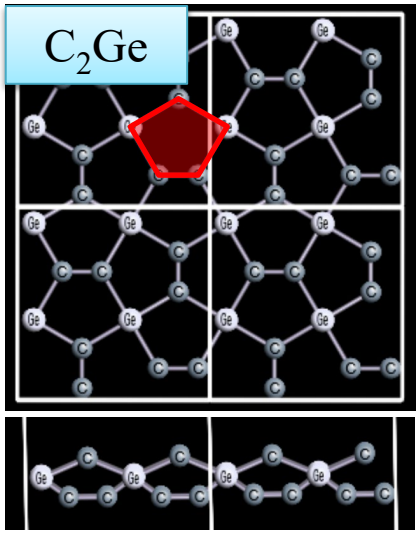
This structure can be a candidate for a data storage application with an extremely high areal density.

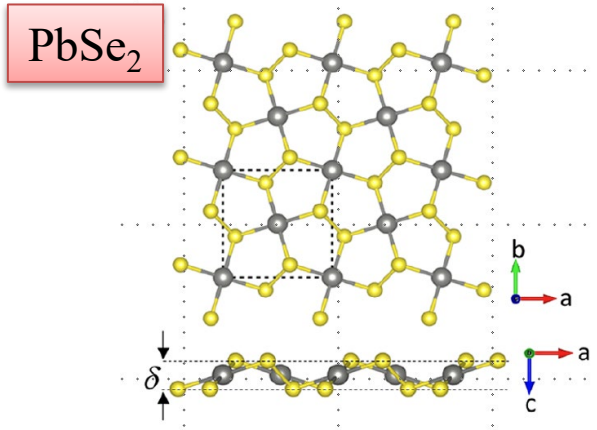
Penta-monolayers obtained in structure search for AB_2 type monolayers by high-throughput DFT calculations

planar

buckled

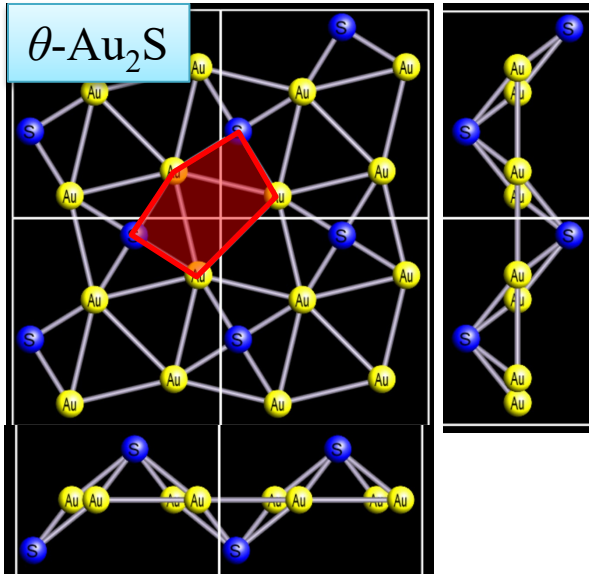


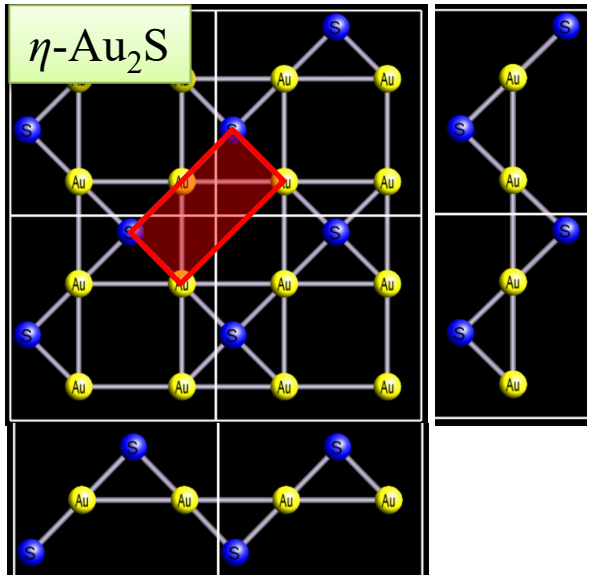




Experimentally synthesized monolayer

J. Am. Chem. Soc. 2017, 139, 14090−14097

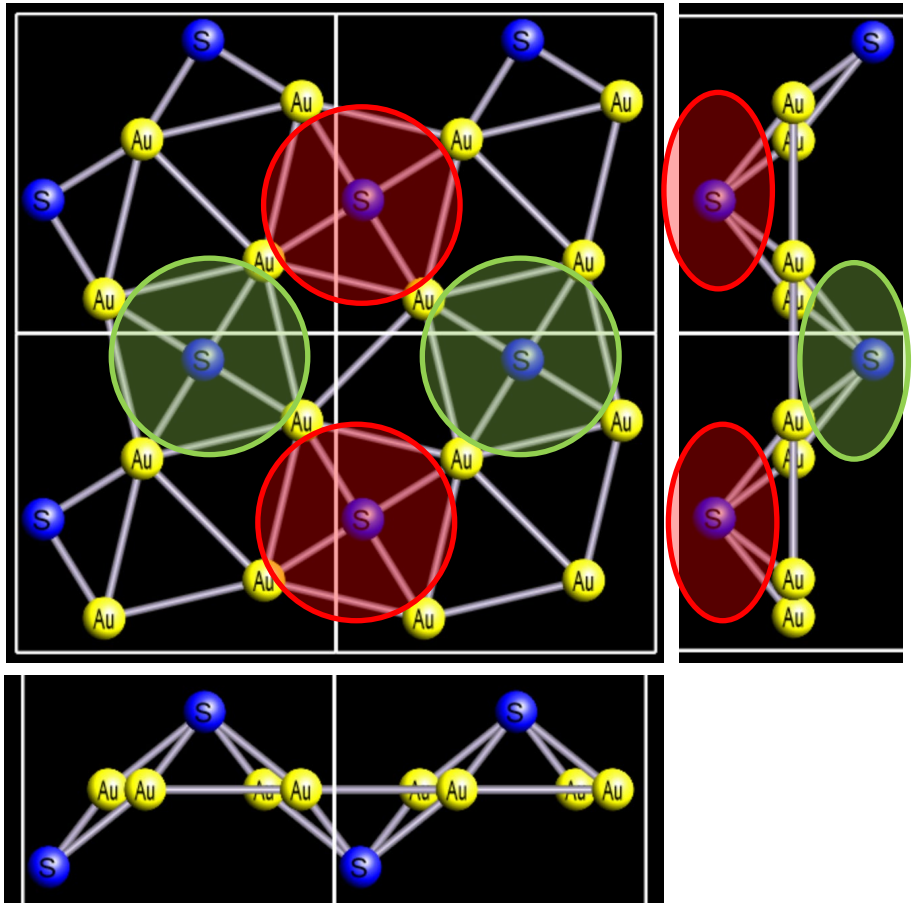




Q. Wu, et. al., The J. Phys. Chem. Lett. 10, 3773 (2019)

θ-Au_2S

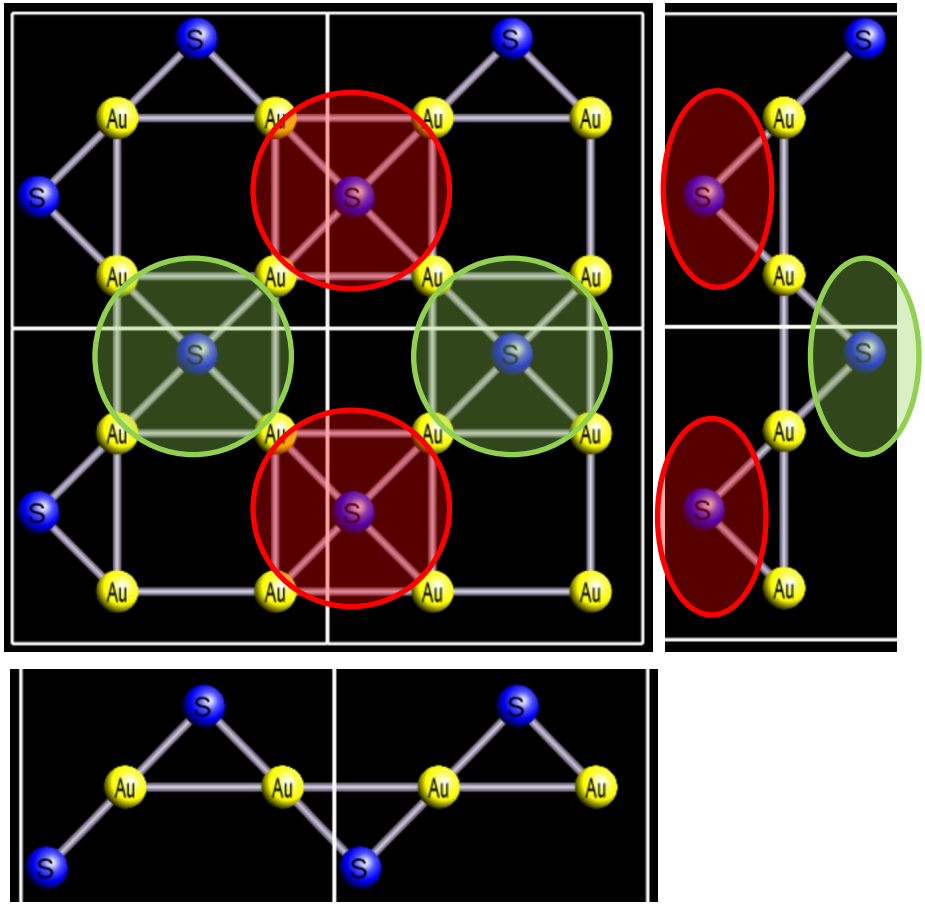
(Discovered by HTP calculations of AB_2 2D materials)



5.67[Å]

Total energy = -443.3368[Hatree/unit cell]
= -13.7901 [Hatree/ Å^2]

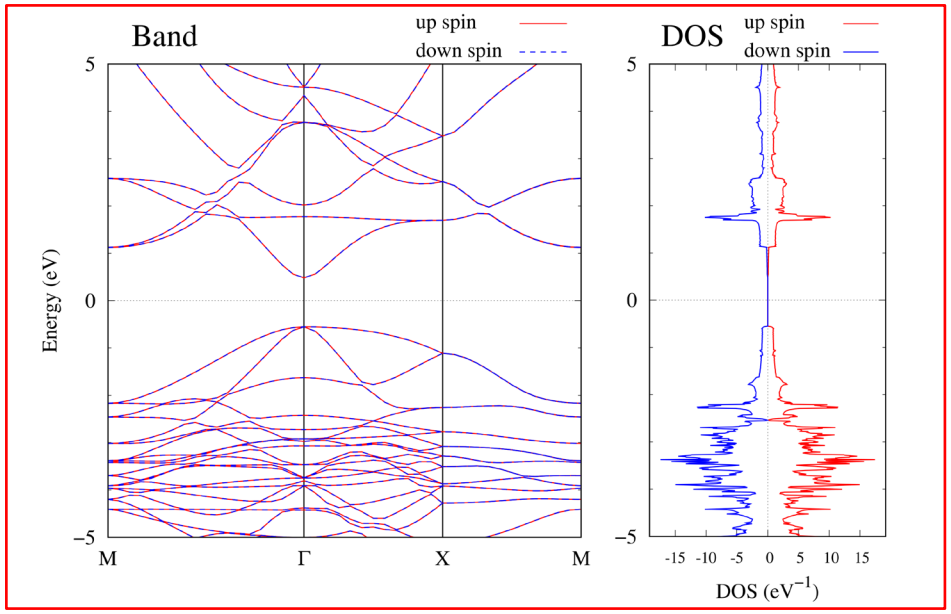
η-Au_2S

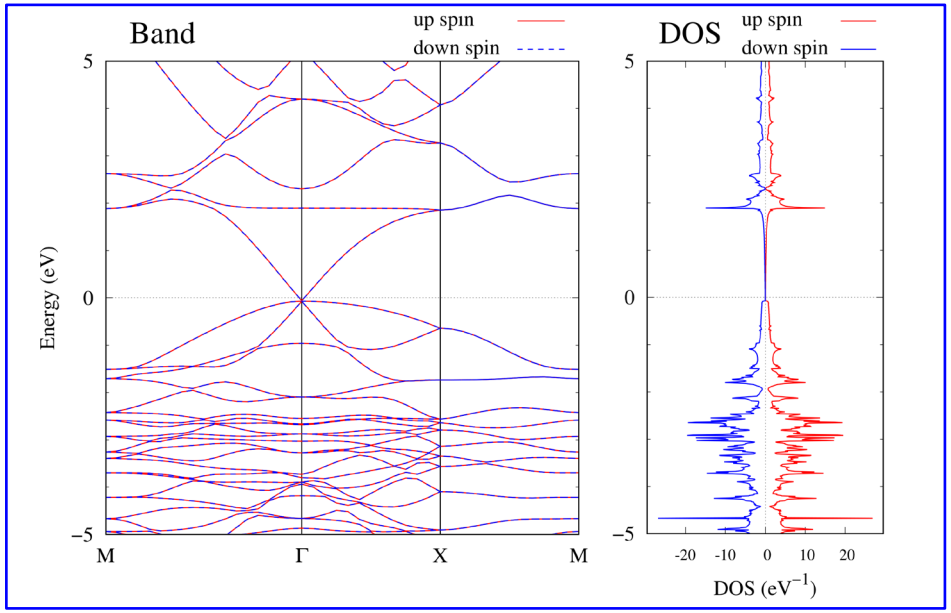


5.84[Å]

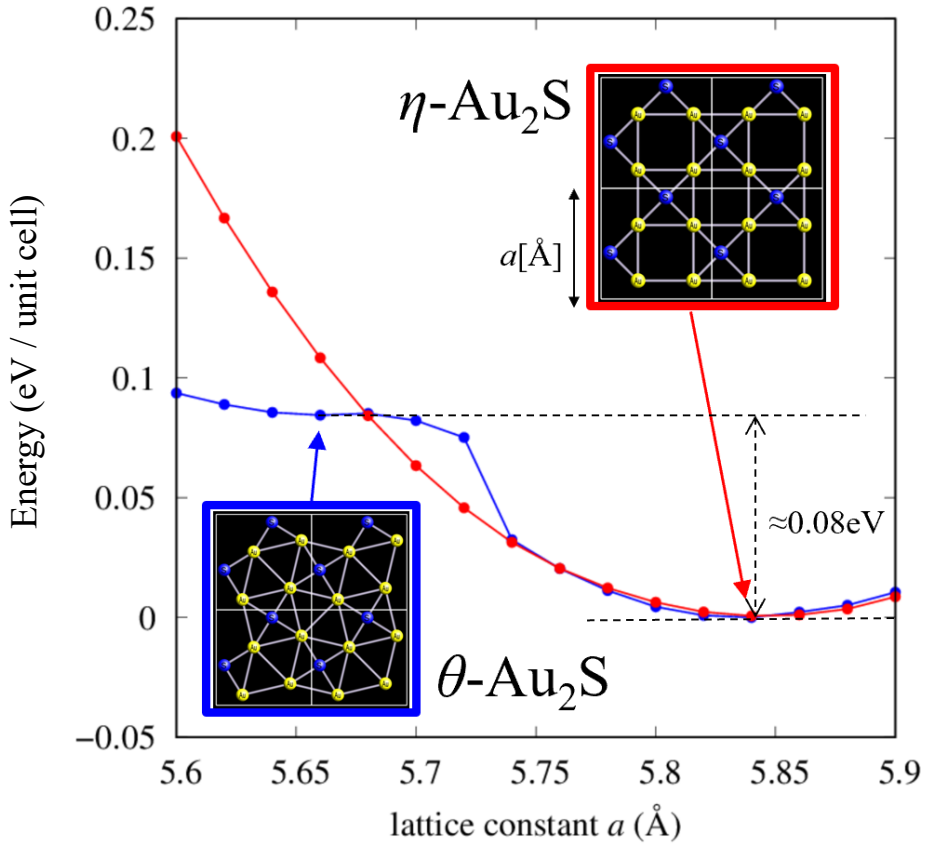
Total energy = -443.3399 [Hatree/unit cell]
= -12.9990 [Hatree/ Å^2]

Analysis of geometric structures and physical properties of Au_2S monolayer under strain based on DFT



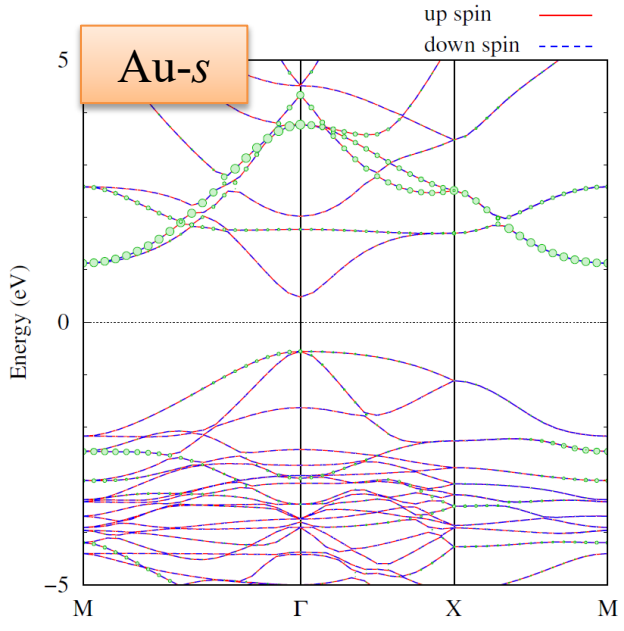


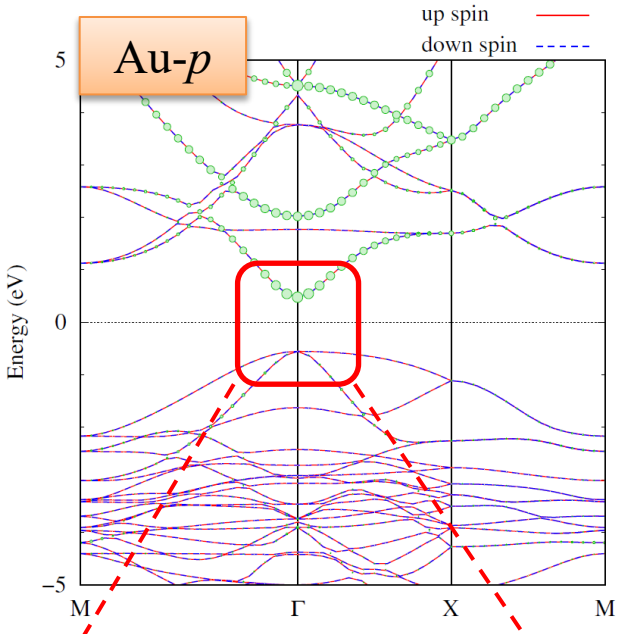
DFT: GGA-PBE
Program code: OpenMX
(http://www.openmx-square.org/)

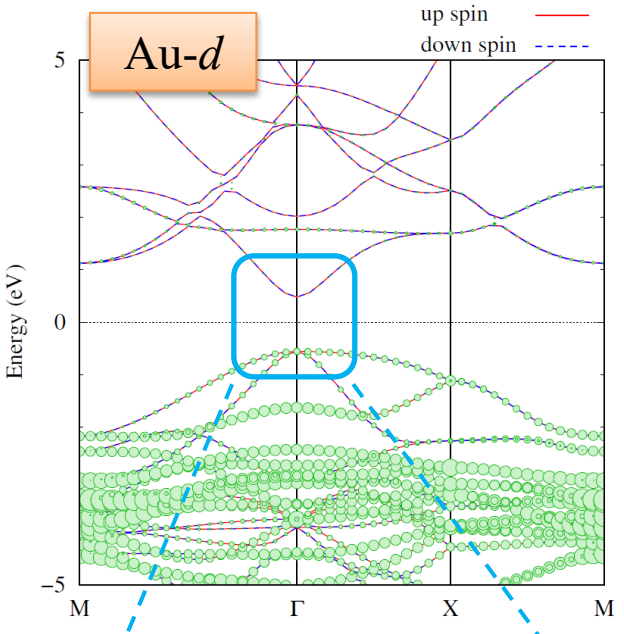


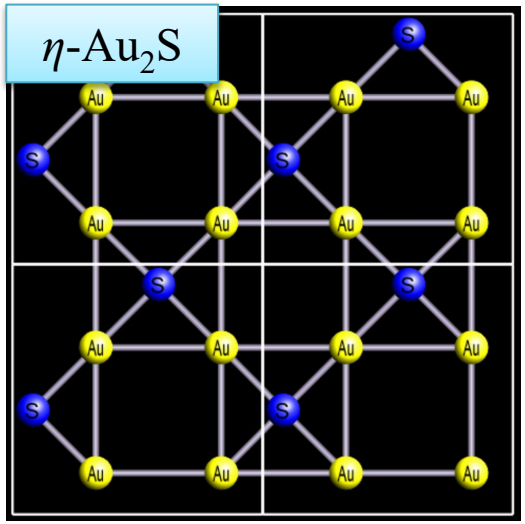
Compressive biaxial strain causes the phase transition from η-Au_2S to θ-Au_2S. The band structure and bandgap of Au_2S are changed drastically under strain because of the phase transition.

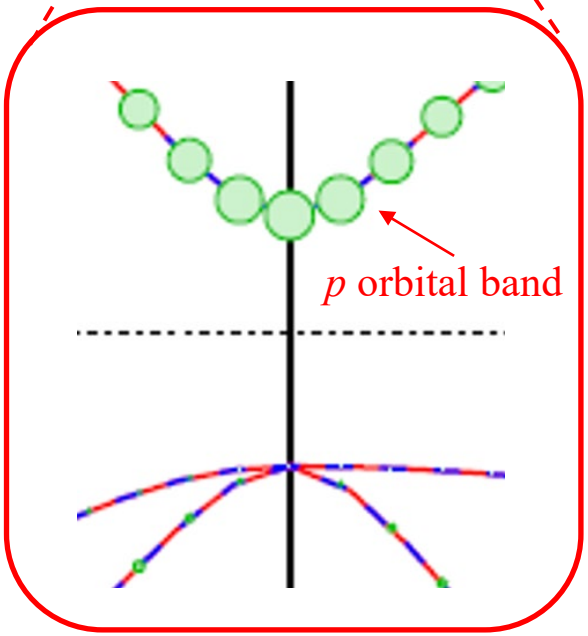
Band decomposition into each contribution of pseudo-atomic orbital

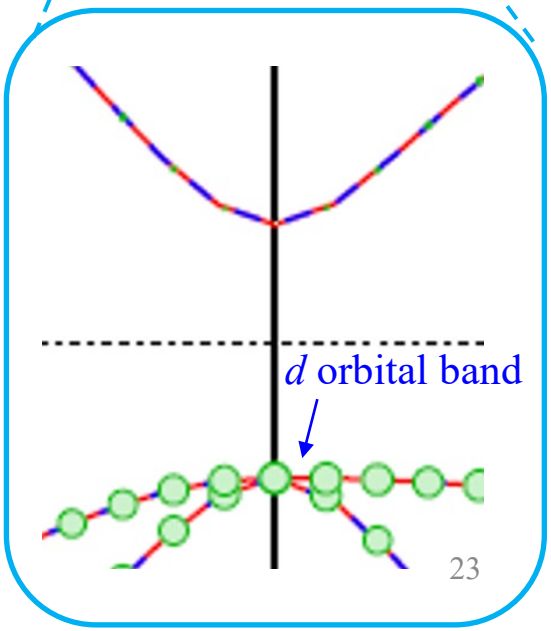




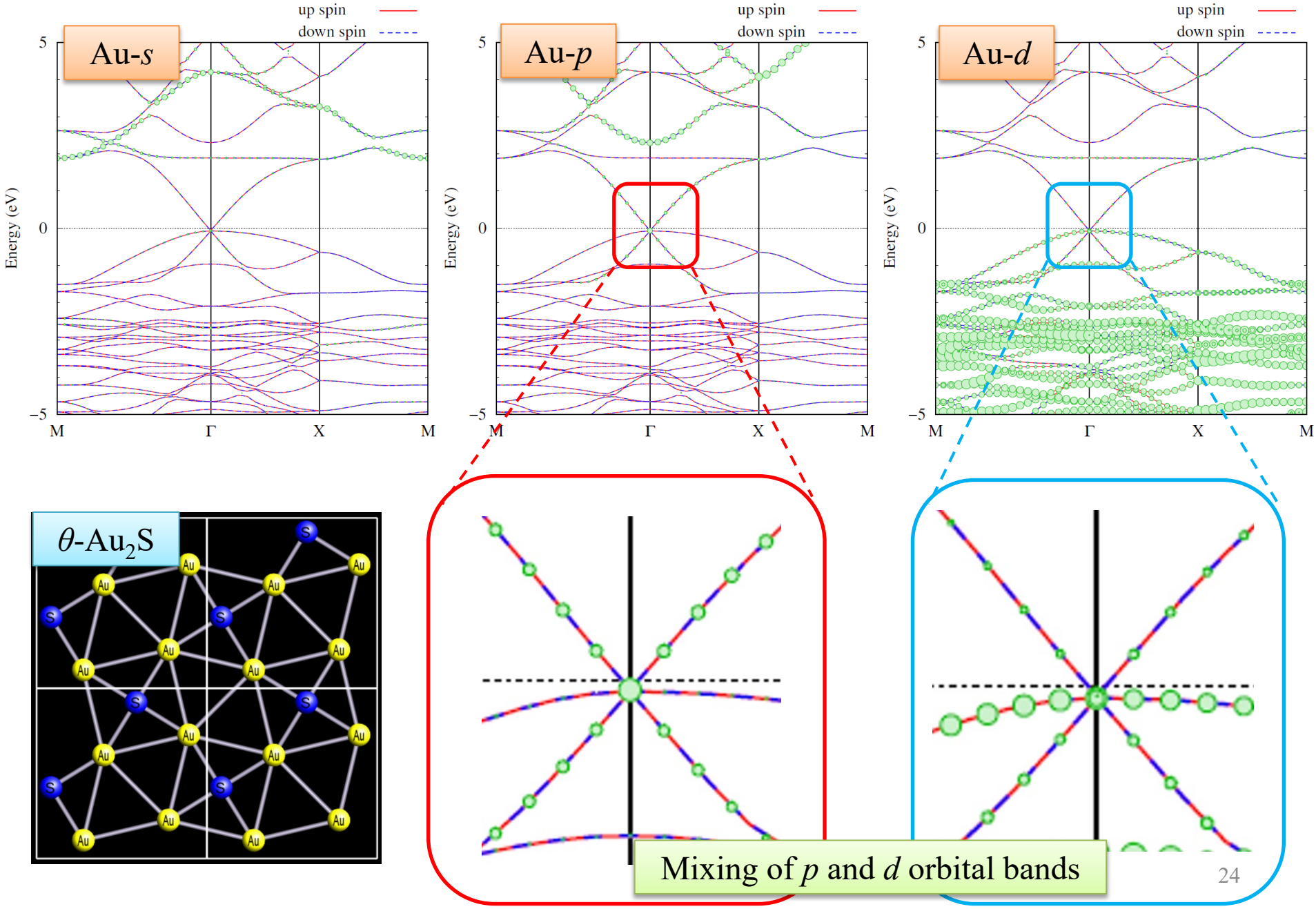




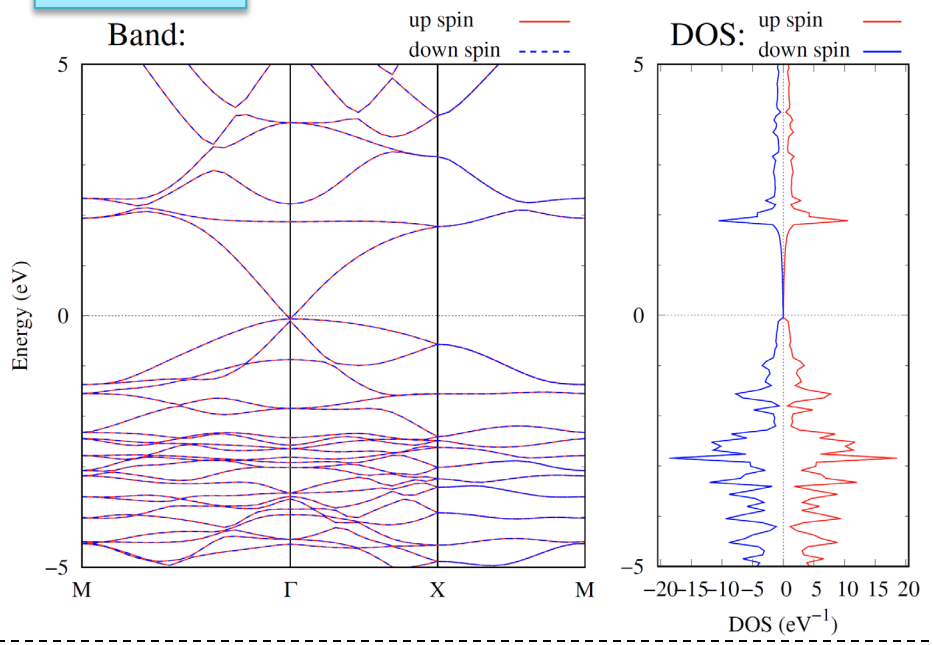




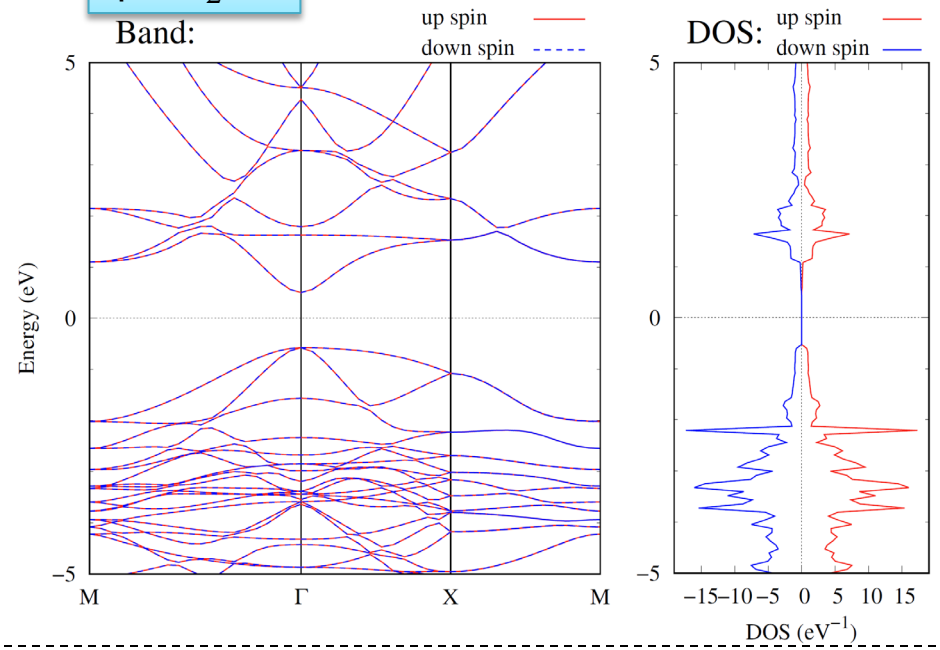
Band decomposition into each contribution of pseudo-atomic orbital



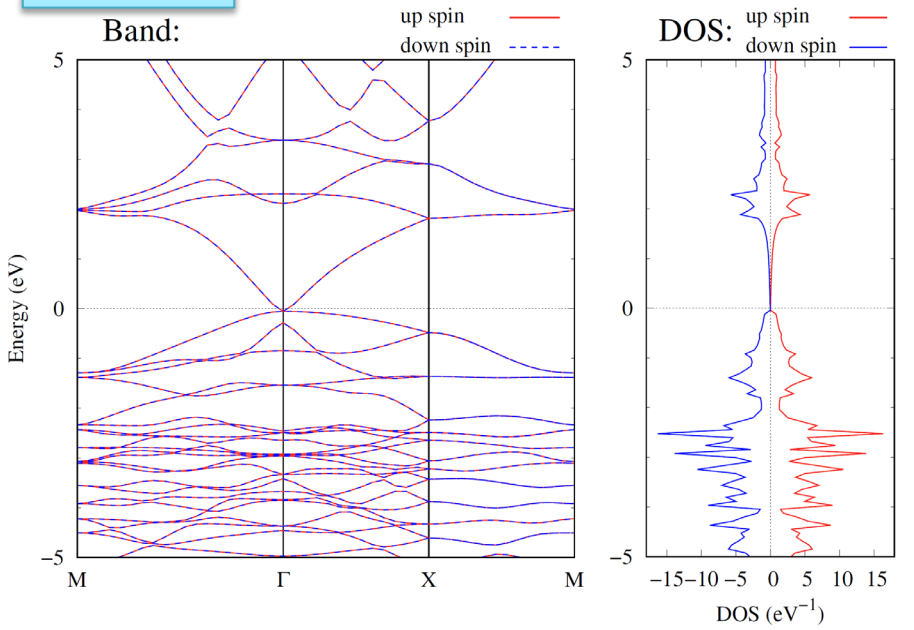
θ-Au_2Se



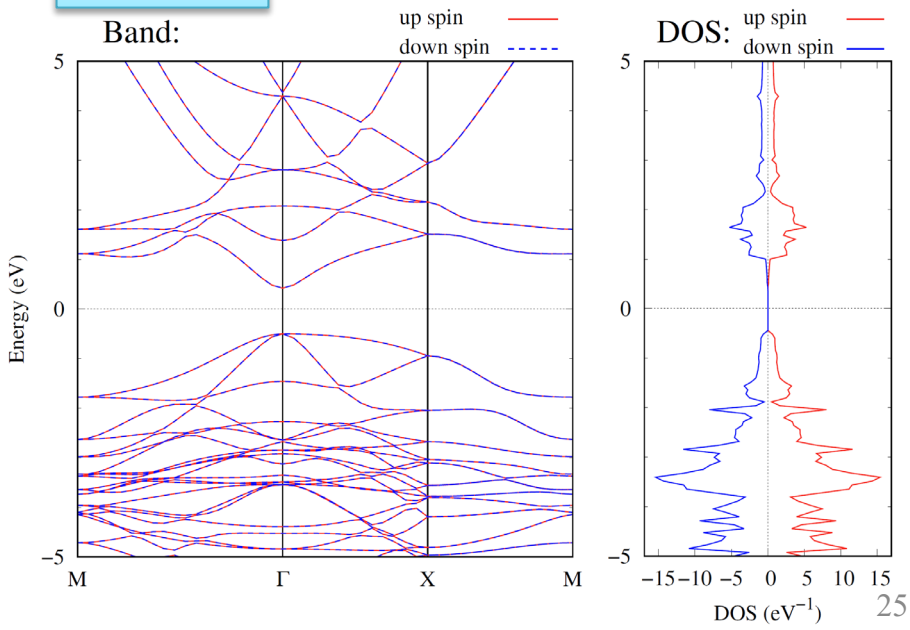
η-Au_2Se



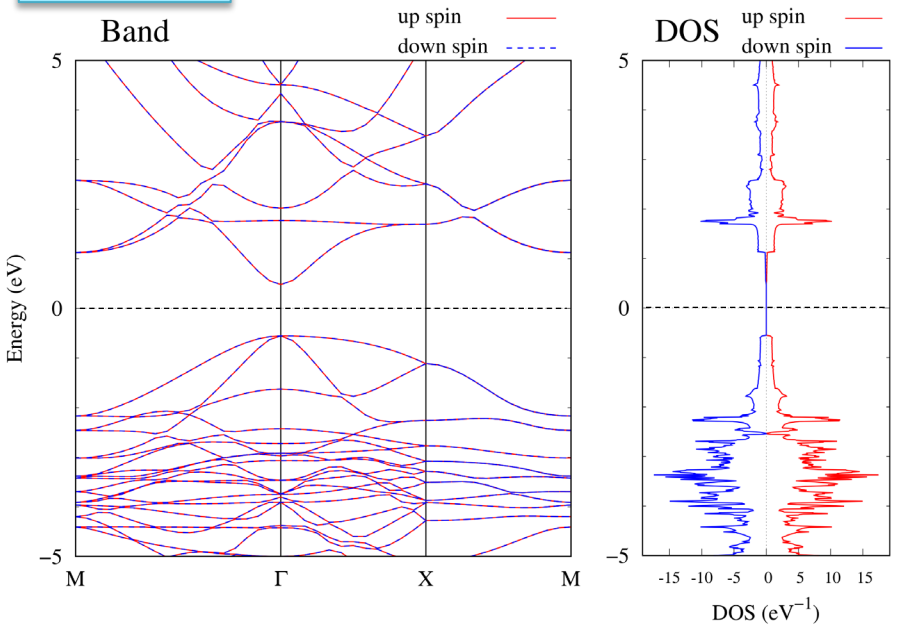
θ-Au_2Te



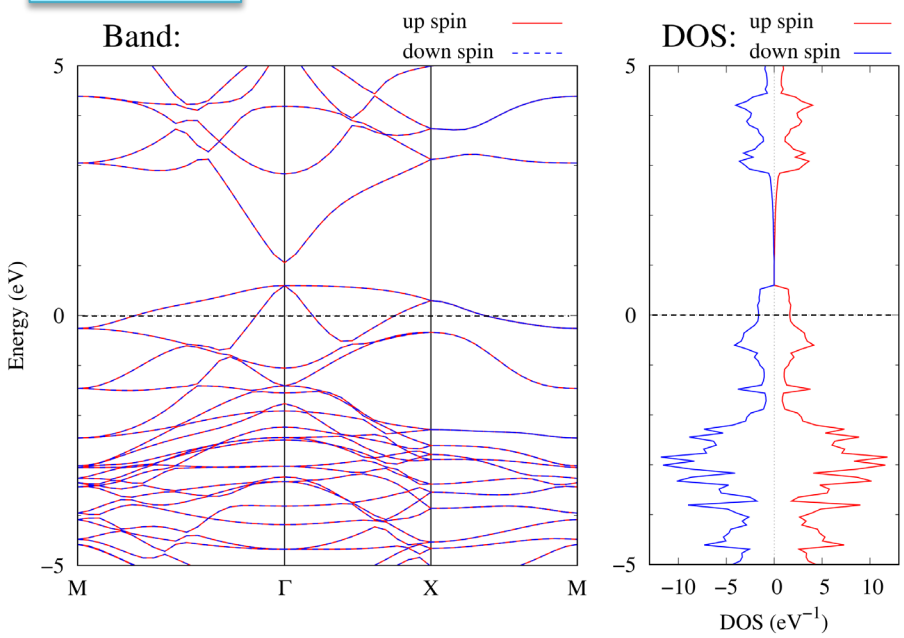
η-Au_2Te



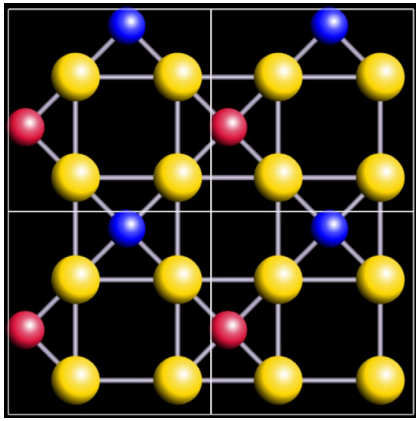
η-Au_2S

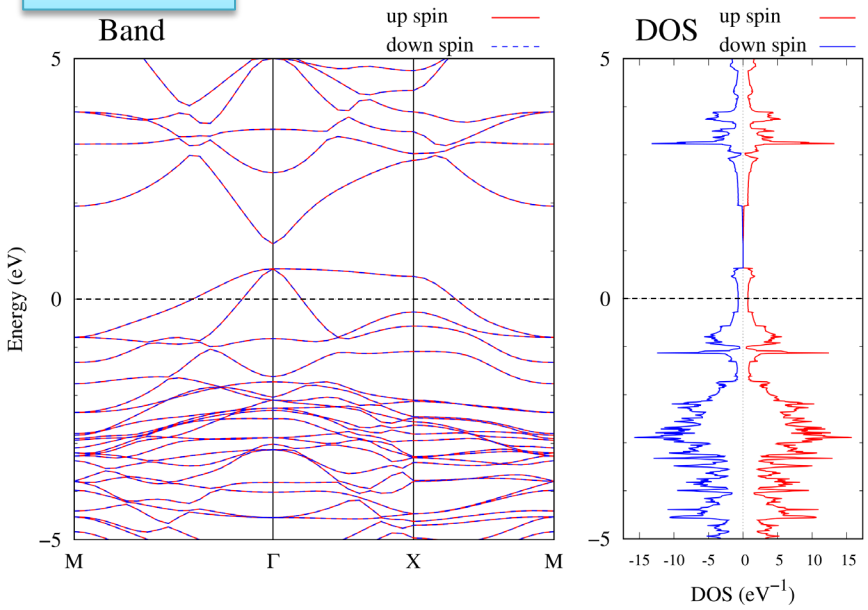


η-Au_2P



η-Au_4PS





The mixing of atomic species changes the Fermi level and the band structure.

Summary

- High-throughput calculations based on DFT by using OpenMX have been performed to create a structure map for AB_2 type monolayers.
- The structure map of AB_2 type 2D materials will give new viewpoints and directions to search unknown 2D materials.

- Our structure map is available in the interactive website and ISSP Data Repository (Gitlab).

- NEB calculation for $SrAl_2$ indicated that it may be possible to control some of memory structures as binary digits storage applications.
- The band structures and bandgaps of Au_2S, Au_2Se and Au_2Te, are changed drastically under strain because of the phase transition ($\theta \leftrightarrow \eta$).
- The family of Au_2X type monolayer may have a potential to acquire a diversity of physical quantities by replacing the X element or absorbing additional atoms without breaking the basic Au lattice network.