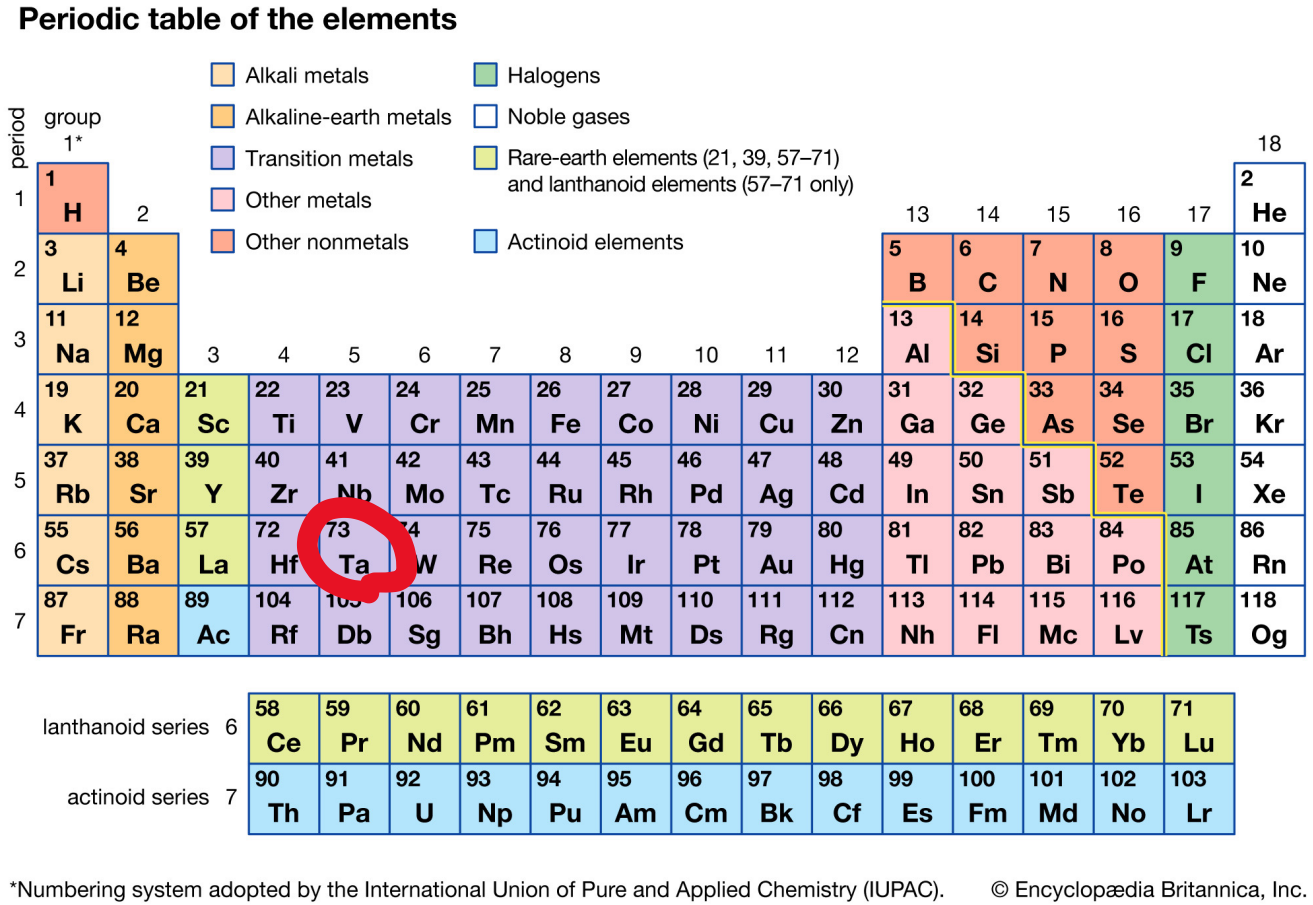
TaS2

TaS2 Metal or insulator?

- Ta electronic configuration

$$[\mathrm{Xe}]14\mathrm{f}^{14}5\mathrm{d}^{3}6S^{2}$$

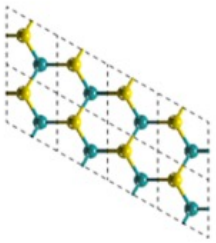
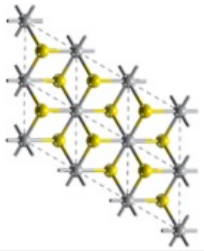
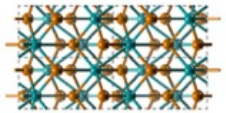
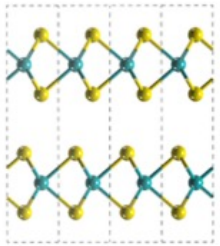
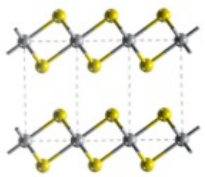
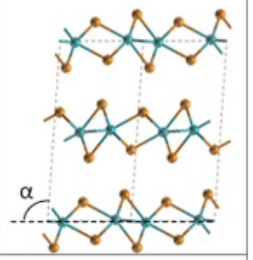


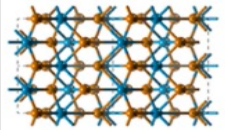
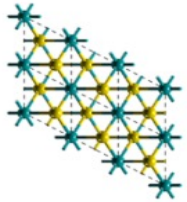
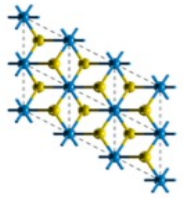
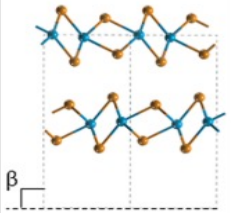
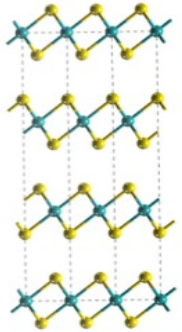
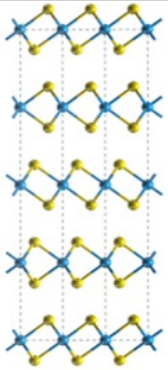
Physical properties

The Only insulator in Transtition metal dichalcogenides(TMD)

- Charge density wave
- Superconductivity(not cover)
- Metal-insulator transition
- Quantum spin liquid

TaS2 polytype

	2H	1T	1T′
Group & Structure	• $P6_3/mmc$ • Hexagonal (Trigonal prismatic)	• $P\bar{3}m1$ • Hexagonal (Octahedral)	• $P2_1/m$ • Monoclinic
Top View			
Side View			
Lattice Parameters	• a = b ≠ c • γ = 120	• a = b ≠ c • γ = 120	• α ≠ 90 °

	T_d	3R	4H
Group & Structure	• $Pmn2_1$ • Orthorhombic	• R3m • Rhombohedral	• $P6_3/mmc$ • Trigonal prismatic
Top View			
Side View			
Lattice Parameters	• a ≠ b ≠ c • β = 90	• a = b ≠ c • γ = 120	• a = b ≠ c • γ = 120

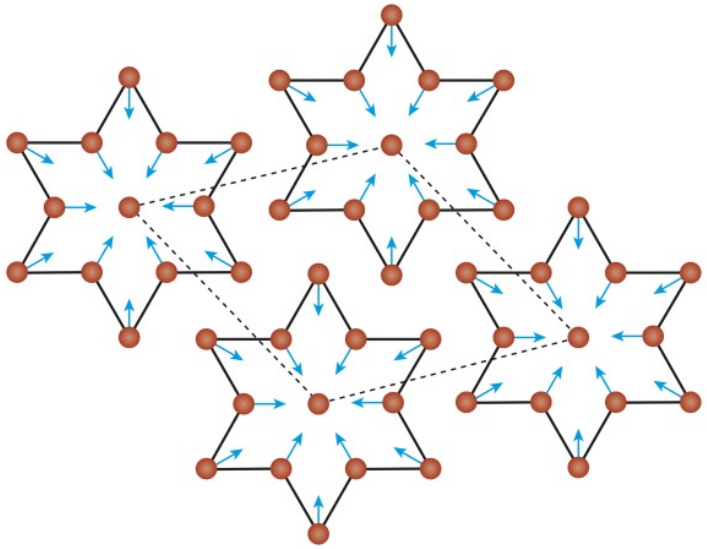
van der Waals Metallic Transition Metal Dichalcogenides Gang Hee Han, Dinh Loc Duong, Dong Hoon Keum, Seok Joon Yun, and Young Hee Lee *Chemical Reviews* **2018** *118* (13), 6297-6336

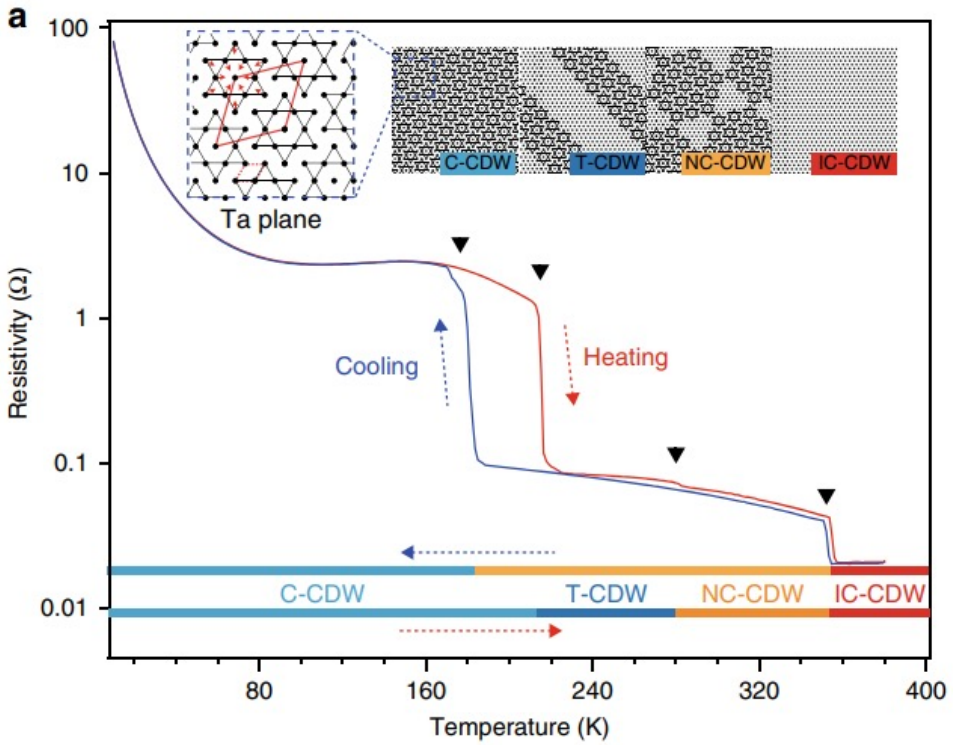
Physical properties

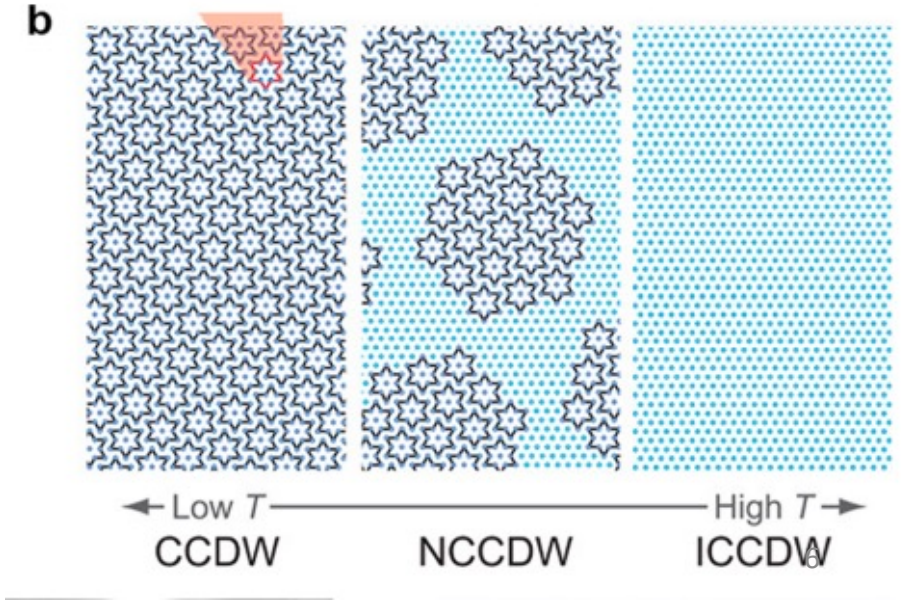
- Charge density wave
- Superconductivity(not cover)
- Metal-insulator transition
- Quantum spin liquid

1T-Charge density Wave(CDW)

- Commensurate
  - $\sqrt{13} \times \sqrt{13}$ supercell
  - Star of David (DoD)
- Nearly commensurate (below 350K)
- Incommensurate(below 180K)

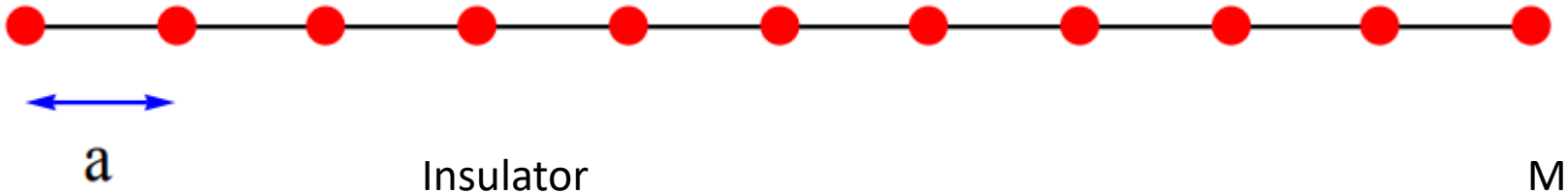




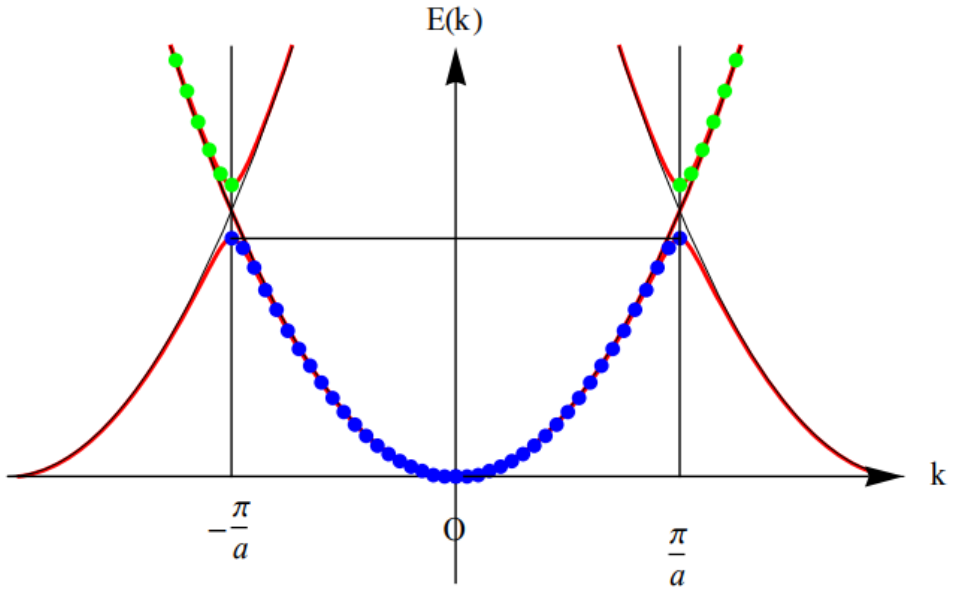


Wang, Y.D., Yao, W.L., Xin, Z.M. *et al.* Band insulator to Mott insulator transition in 1*T*-TaS_2. *Nat Commun* **11,** 4215 (2020). https://doi.org/10.1038/s41467-020-18040-4

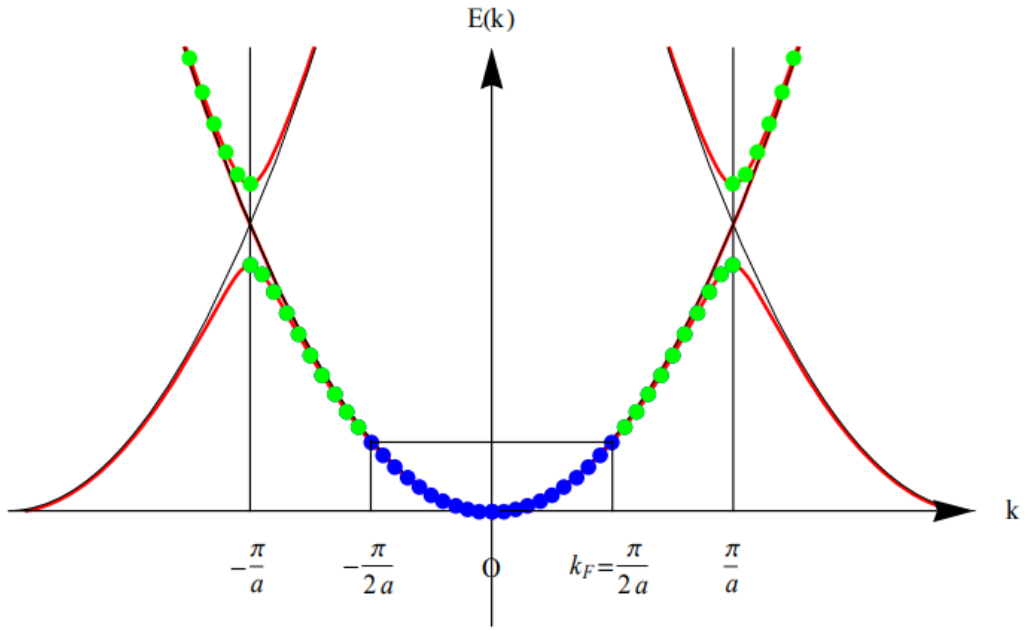
Charge density Wave (CDW)- Peierls picture



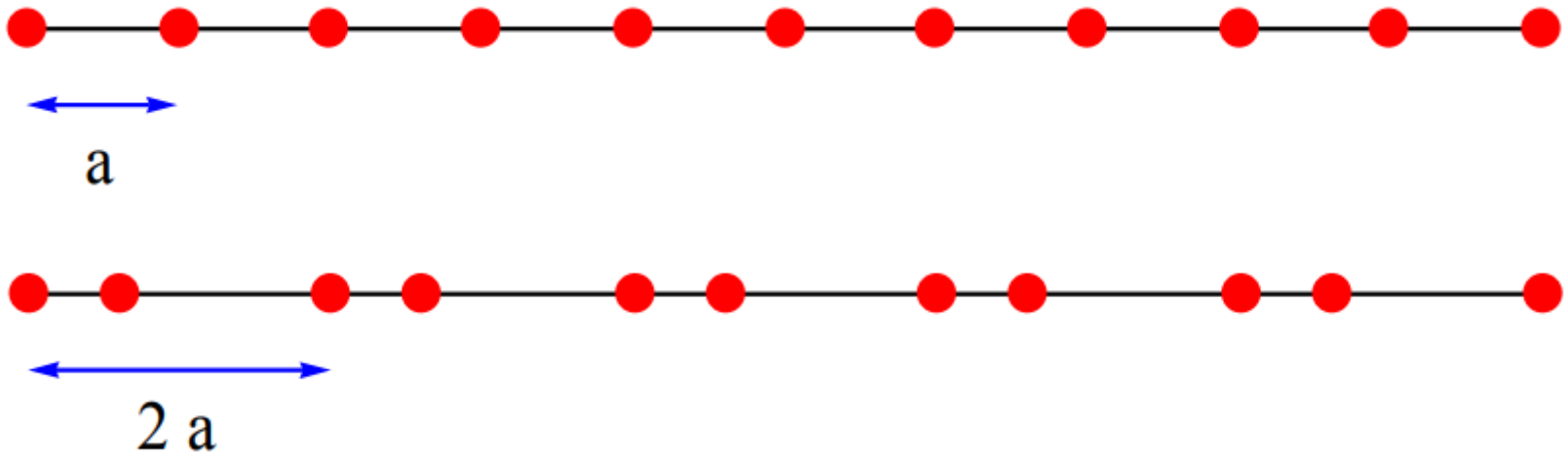
Insulator

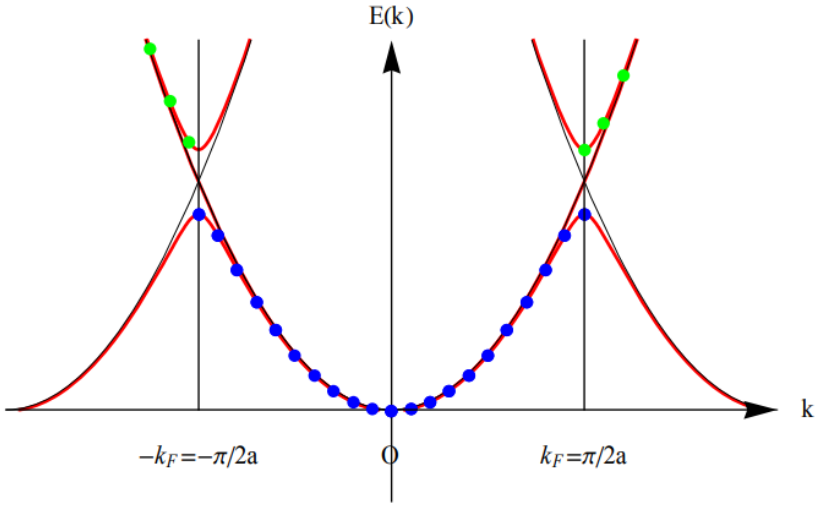


Metal



1D Peierls distortion





The system changes from metal to insulator (Peierls instability)

$$\Delta E = \Delta E_{electronic} + \Delta E_{lattice} .$$

Lecture Note on Charge density wave Masatsugu Sei Suzuki and Itsuko S. Suzuki Department of Physics, SUNY at Binghamton

CDW Peierls distortion (continue)

In 1D case, Peierls states that the system is always unstable, metal becomes insulator

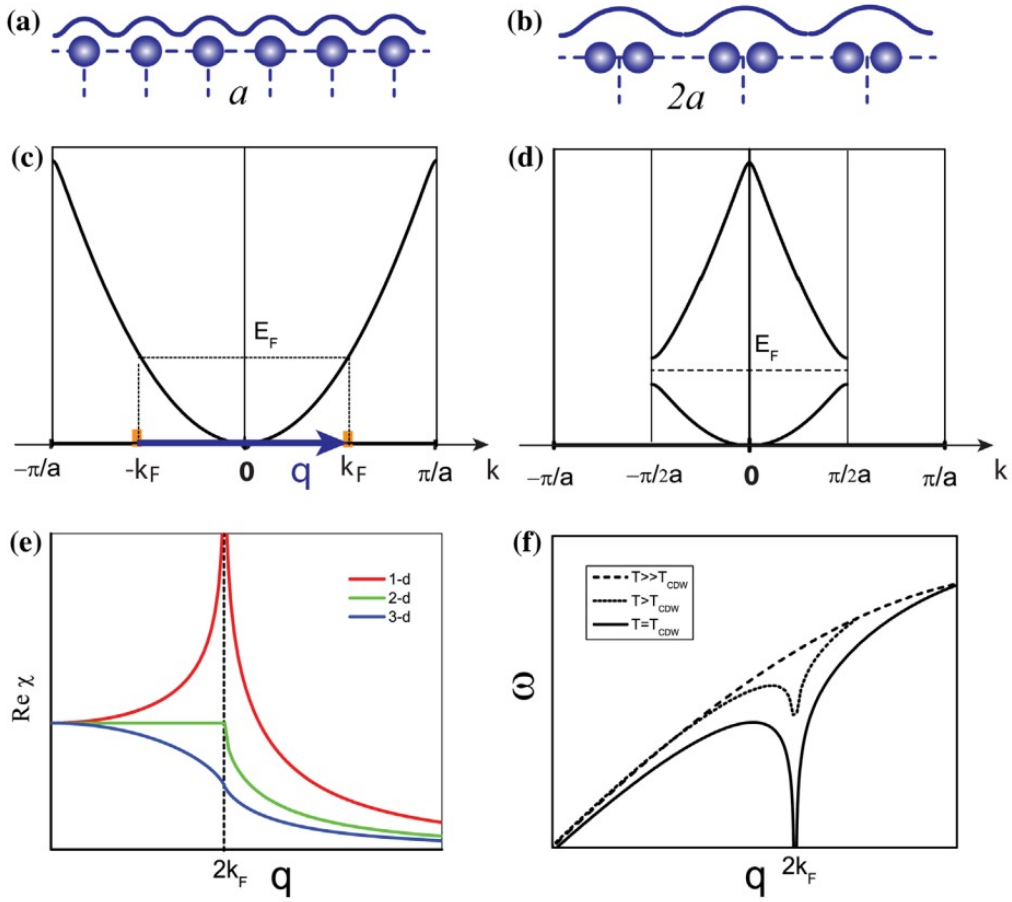
Lindhard response- the response due to external perturbation

Frohich Hamiltonian

$$\mathcal{H} = \sum_{\vec{k}} \varepsilon(\vec{k}) a^{+}_{\vec{k}} a_{\vec{k}} + \sum_{\vec{k}} \hbar\omega(\vec{q}) b^{+}_{\vec{q}} b_{\vec{q}} + \sum_{\vec{k},\vec{q}} g(\vec{q}) a^{+}_{\vec{k}+\vec{q}} a_{\vec{k}} (b^{+}_{-\vec{q}} + b_{\vec{q}}),$$

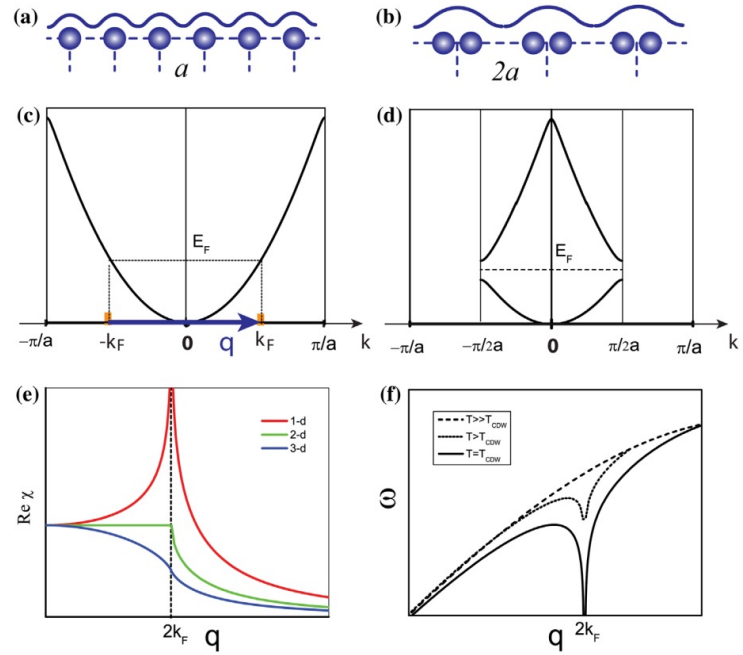
$$\tilde{\omega}(\vec{q})^2 = \omega(\vec{q})^2 + 2\omega(\vec{q})\left|g(\vec{q})\right|^2 \mathrm{Re}\left[\chi(\vec{q},\omega)\right],$$

Kohn anomaly



Xuetao Zhu, Jiandong Guo, Jiandi Zhang & E. W. Plummer (2017) Misconceptions associated with the origin of charge density waves, Advances in Physics: X, 2:3, 622-640, DOI: 10.1080/23746149.2017.1343098

Type 1	Quasi 1D Peierls picture
Type 2	Electron-phonon coupling but no fermi surface nesting
Type 3	No electron-phonon coupling no fermi surface nesting



	Peierls' model (1D atomic chain)	TTF-TCNQ (Quasi-1D material)	$NbSe_2$ (Quasi-2D material)	Sn/Ge or Pb/Ge (2D films on surface)	Cuprates
Fermi Surface Nesting	√	√ [27]	X [30–32]	√ [37,38]	√ [64,69,70]
Sharp Peak in Lindhard Function	√	√ [23]	X [30–32]	√ [38]	√ [32]
Kohn Anomaly	√	√ [25]	√ [20]	√ [39,40]	X [32]
Structural Transition	√	√ [24]	√ [15–19]	√ [37,38]	√ [67,68]
Metal–insulator Transition	√	√ [22]	X [34]	√ [37]	X [69]

Xuetao Zhu, Jiandong Guo, Jiandi Zhang & E. W. Plummer (2017) Misconceptions associated with the origin of charge density waves, Advances in Physics: X, 2:3, 622-640, DOI: 10.1080/23746149.2017.1343098

Really Brief on Density Functional Theory

$$H_{\text{tot}} = \sum_j \frac{\mathbf{P}_j^2}{2M_j} + \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_{i<i'} \frac{Z_j Z_{j'} e^2}{|\mathbf{R}_j - \mathbf{R}_{j'}|} + \sum_{i<i'} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_{i'}|} + \sum_{i,j} \frac{-Z_j e^2}{|\mathbf{R}_j - \mathbf{r}_i|}.$$

$$H = \sum_i \frac{\mathbf{p}_i^2}{2m} + \sum_i v(\mathbf{r}_i) + \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}$$

→ $$E_v[\rho] = \int v(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + T_s[\rho] + \frac{1}{2}e^2 \int \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{\text{xc}}[\rho].$$

$$T_s[\rho] = -\frac{\hbar^2}{2m} \sum_i^{\text{occ}} \int \varphi_i^*(\mathbf{r}) \nabla^2 \varphi_i(\mathbf{r})\, d\mathbf{r}$$

$$\left\{ \frac{p^2}{2m} + v(\mathbf{r}) + v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \right\} \varphi_i(\mathbf{r}) = \epsilon_i \varphi_i(\mathbf{r})$$

$$\rho(\mathbf{r}) = \sum_i^{\text{occ}} |\varphi_i(\mathbf{r})|^2,$$

$$v_{\text{H}}(\mathbf{r}) = e^2 \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}',$$

$$v_{\text{xc}}(\mathbf{r}) = \frac{\delta E_{\text{xc}}}{\delta \rho(\mathbf{r})}.$$

Chapeter 7 Fundamentals of Condensed Matter Physics, Cohen, Louie

Functional benchmark

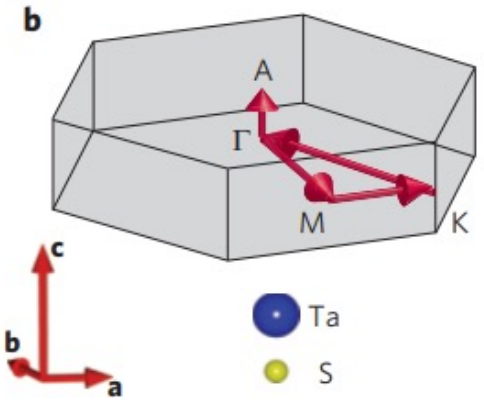
	1*T*	2*H*-AB	2*H*-AA′	3*R*
EXX+RPA				
a (Å)	3.362	3.316	3.310	3.310
c (Å)	5.90	12.25	12.05	18.30
Δ E (eV/f.u.)	0.084	0.010	0.00	0.010
optB86b-vdW				
a (Å)	3.352	3.317	3.320	3.317
c (Å)	5.90	12.30	12.00	18.30
Δ E (eV/f.u.)	0.063	0.016	0.00	0.008
Experiment				
a (Å)	3.3672(6)[a]	3.314[b]		3.32[c]
c (Å)	5.9020(9)[a]	12.097[b]		17.90[c]

Petr Lazar, Jana Martincová, and Michal Otyepka Phys. Rev. B **92**, 224104 – Published 8 December 2015

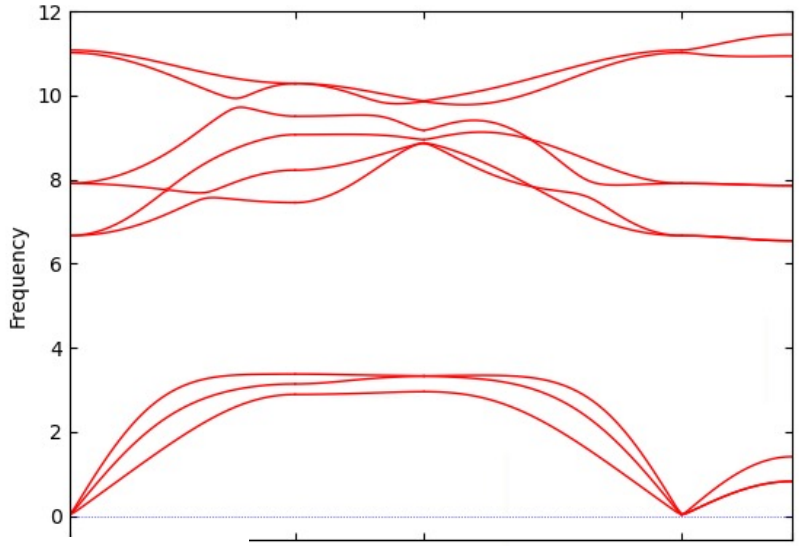
1T	a	c
pbe	3.377	6.947
opt86b	3.3484	5.932
Scan	3.365	6.118
rVV10 - 6.3	3.416	6.079
rVV10 - 15.7	3.416	6.079

2H	a	c
pbe	3.341	13.758
opt86b	3.317	12.0653
pbe-vdw	3.35	12.461
DF2-B86R	3.319	12.05
scan	3.325	12.751
Scan-af	3.326	12.786
rVV10 -6.3	3.369	12.467
rVV10-15.7	3.369	12.467

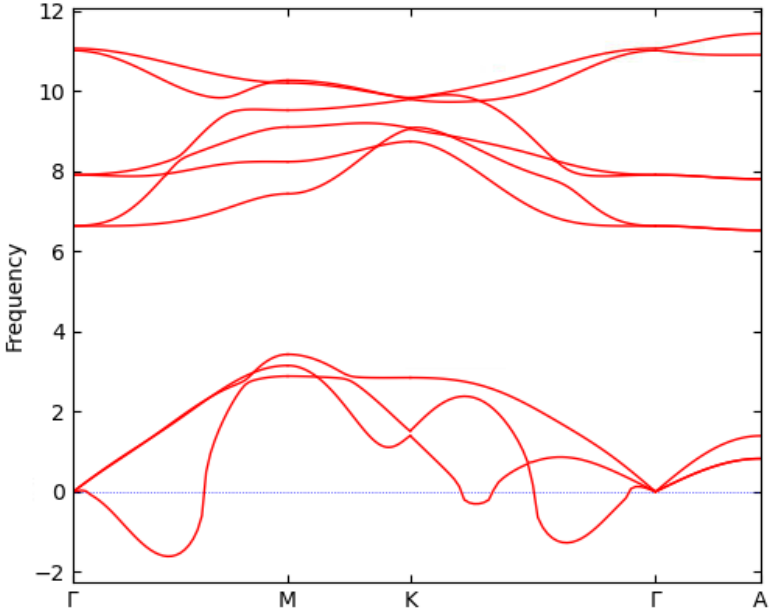
1T phonon



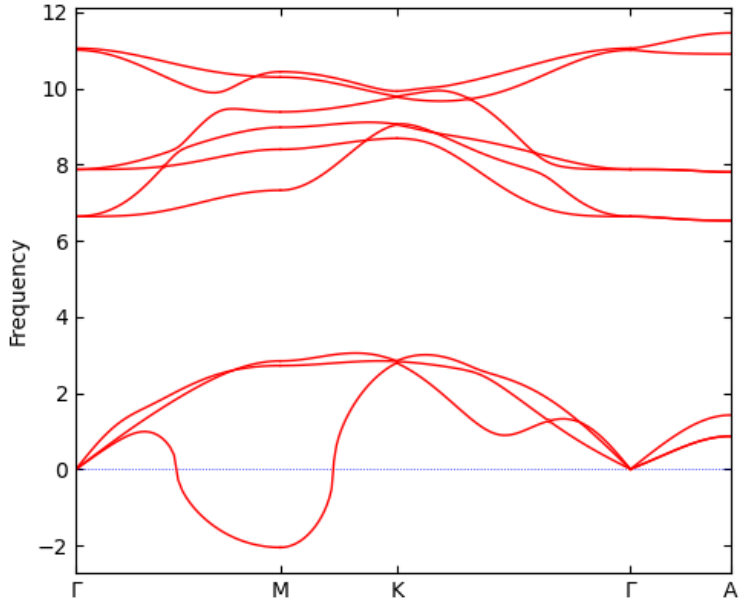
"2 2 2" density functional perutrbation theory
MP smearing 0.1



"4 4 2" finite diff
Gaussian smearing 0.1



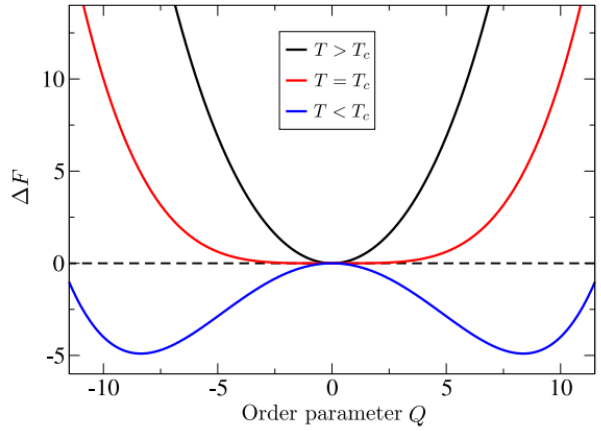
"3 3 2" finite diff
Gaussian smearing 0.1



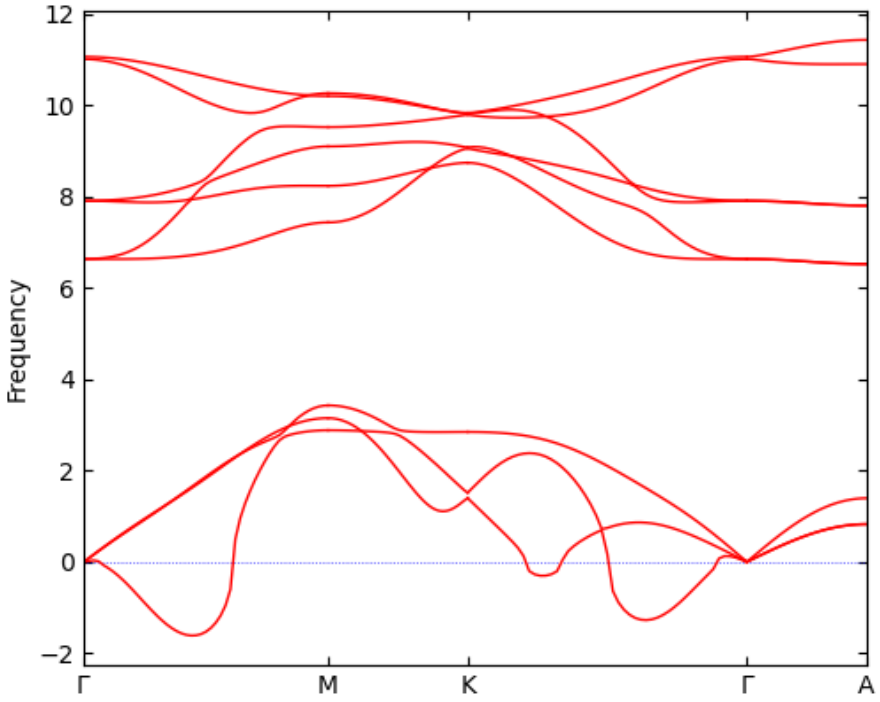
1T CDW is has 13 unitcells in plane

Imaginary phonon mode

- Calculation might done wrong
  - Phonon calc need extremely precise calculation (VASP EDIFF = 1 E-8)
  - Sensitive to supercell you construct
  - Cut-off energy k point density



- Some interesting physics happens
  - Negative curverture for Potential energy surface
  - Higher order Anharmonic effect need to be considered
    - Phonon-phonon coupling
  - System is dynamical instable
  - Ferroelectric (PbTiO3)
  - Superionic conduction (Li3N)
  - CDW



The Physical Significance of Imaginary Phonon Modes in Crystals Ioanna Pallikara, Prakriti Kayastha, Jonathan M. Skelton, Lucy D. Whalley arXiv:2203.01244

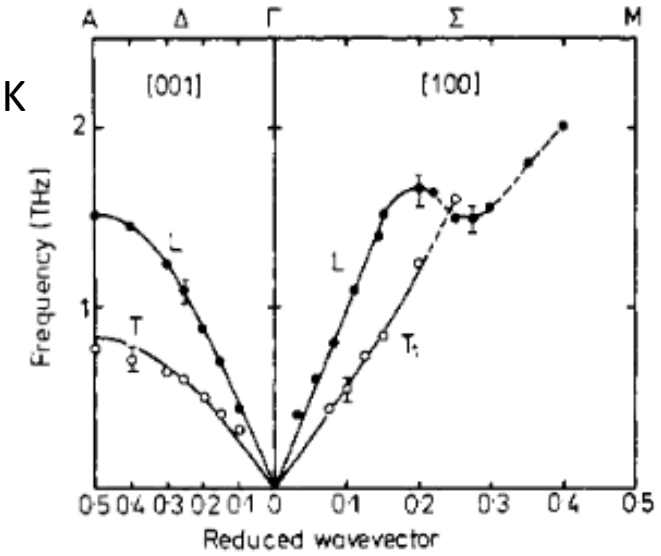
Jahn-Teller effectSecond-order structural phase transitions, free energy curvature, and temperature-dependent anharmonic phonons in the self-consistent harmonic approximation: Theory and stochastic implementation Raffaello Bianco, Ion Errea, Lorenzo Paulatto, Matteo Calandra, and Francesco Mauri Phys. Rev. B **96**, 014111 – Published 18 July 2017

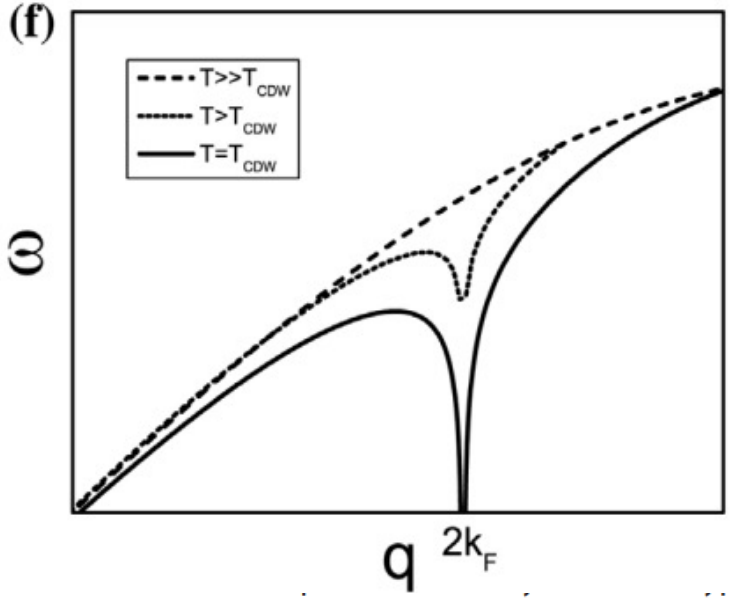
Phonon

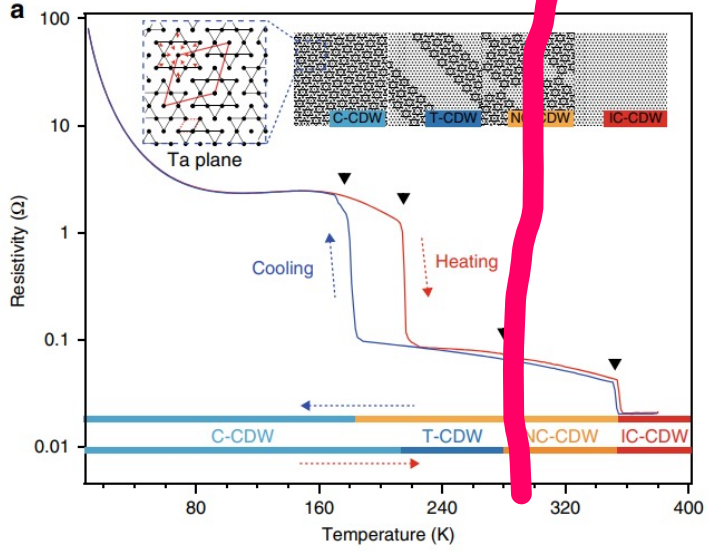
- Harmonic approximation
  - Frozen Phonon (Supercell approach)
  - Density functional perturbation Theory(DFPT)
- To consider anharmonic effect and temperature dependence
  - stochastic self-consistent harmonic approximation(SSCHA)
  - Mapping from AIMD
  - Self-consistent phonon(SCPH)

Experiment data for Kohn anomaly

290 K







TaS2
Quasi-2D

yes
?
yes
Yes and no

F. Clerc, C. Battaglia, M. Bovet, L. Despont, C. Monney, H. Cercellier, M. G. Garnier, P. Aebi, H. Berger, and L. ForróPhys. Rev. B 74, 155114 – Published 17 October 2006

K R A Ziebeck et al 1977 J. Phys. F: Met. Phys. 7 1139

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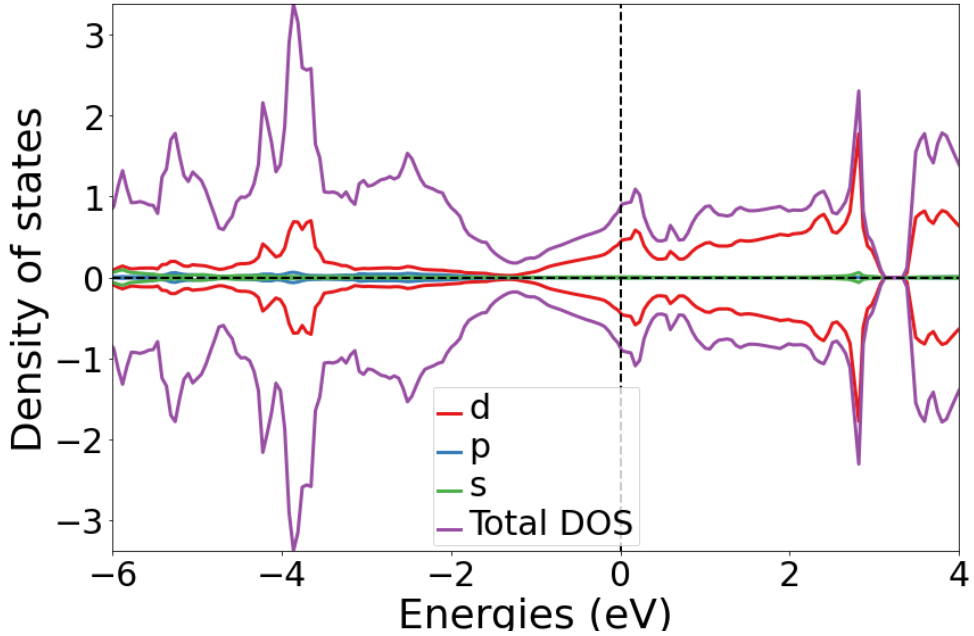
Sharp Peak in Lindhard Function	√	√ [23]	X [30–32]	√ [38]	√ [32]
Kohn Anomaly	√	√ [25]	√ [20]	√ [39,40]	X [32]
Structural Transition	√	√ [24]	√ [15–19]	√ [37,38]	√ [67,68]
Metal–insulator Transition	√	√ [22]	X [34]	√ [37]	X [69]

Physical properties

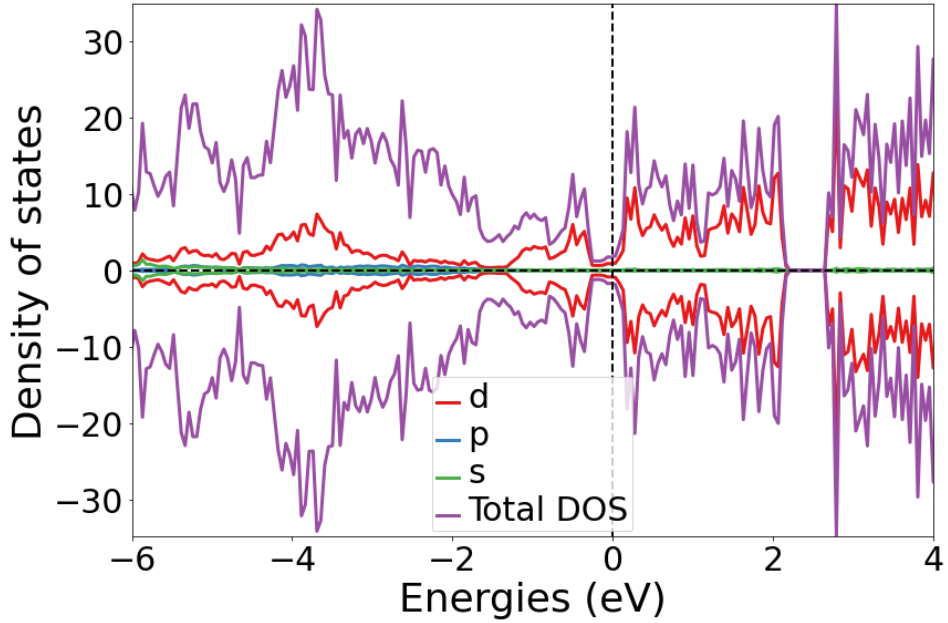
- Charge density wave
- Superconductivity(not cover)
- Metal-insulator transition
- Quantum spin liquid

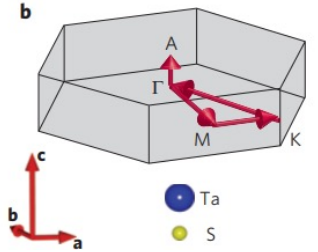
TaS2 considered to be mott insulator(maybe?)

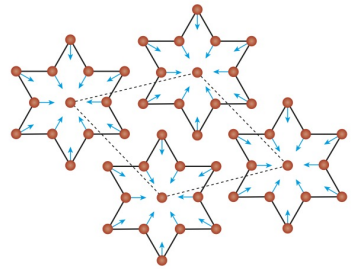
undistorded

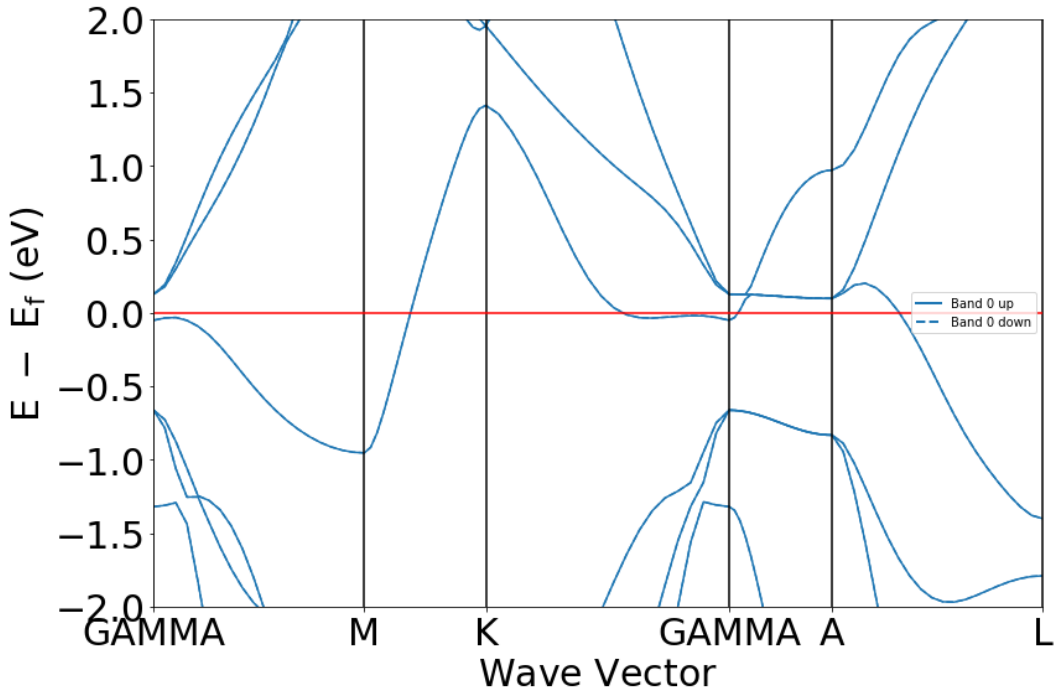


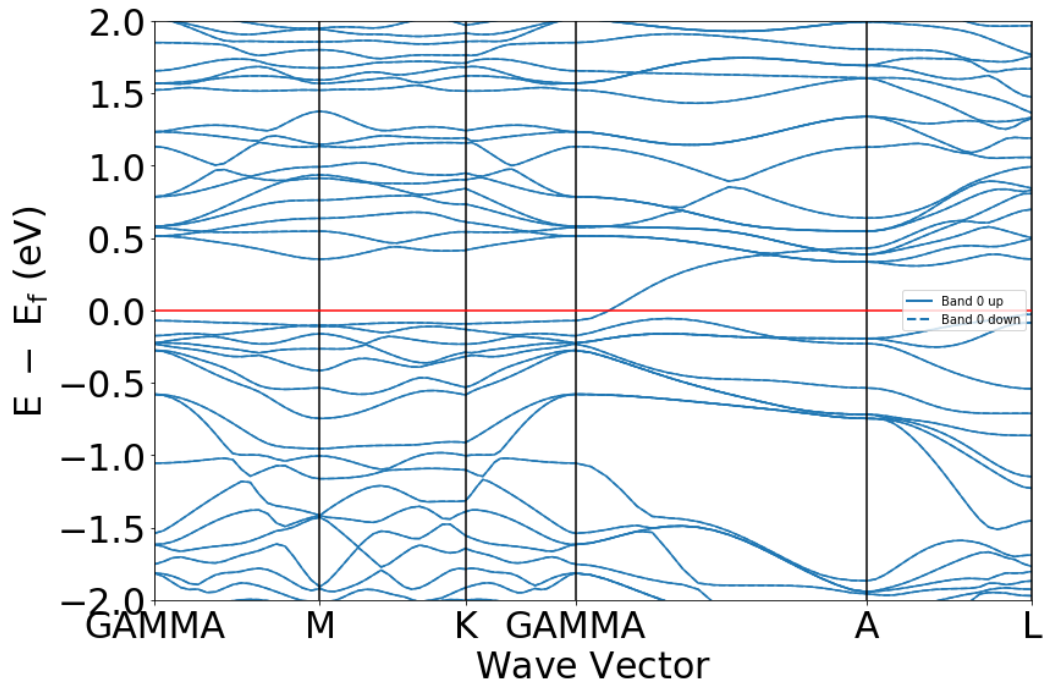
SOD







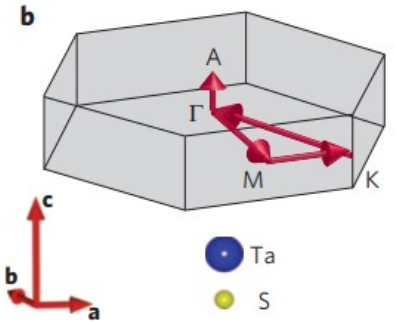




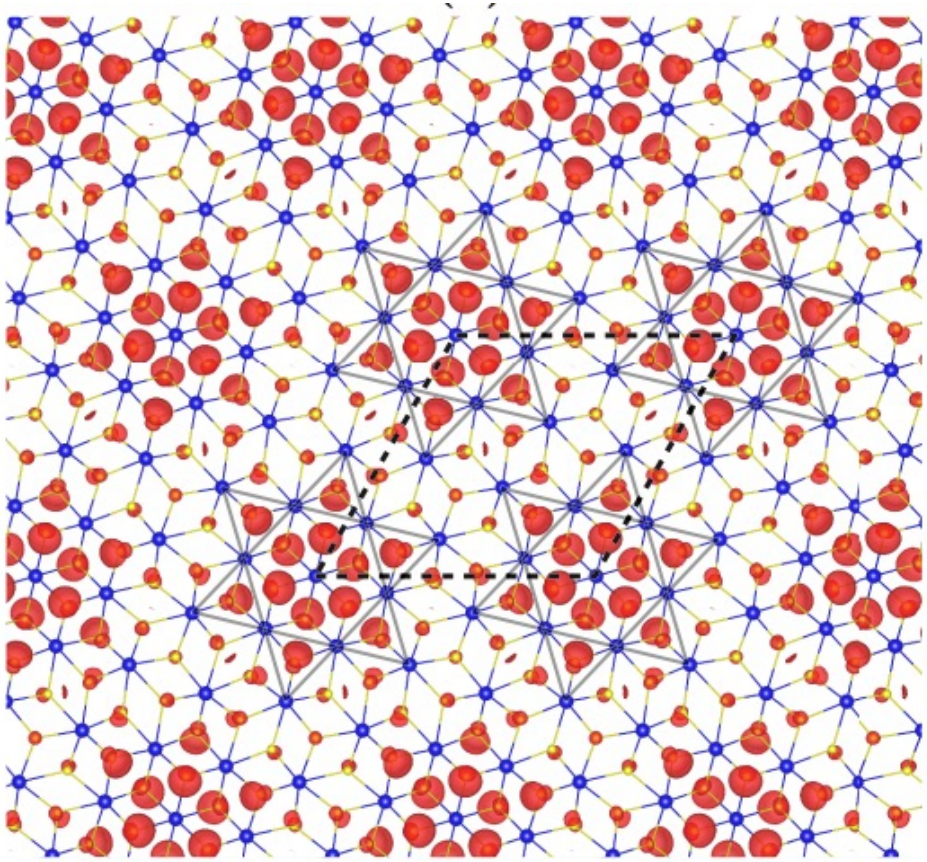
Computation report of gap opening

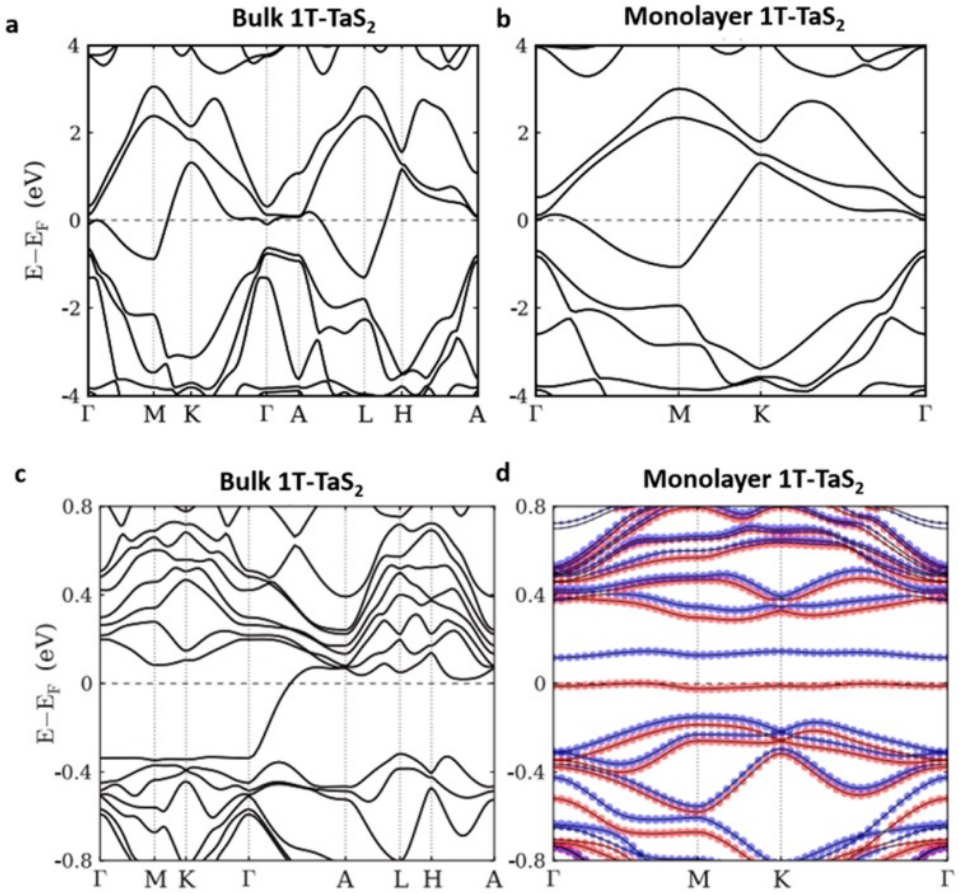
- Spin polarization in monolayer
- Using DFT+U in monolayer

Band gap by spin polarization



Charge density difference of undistorted and CDW





undistorted

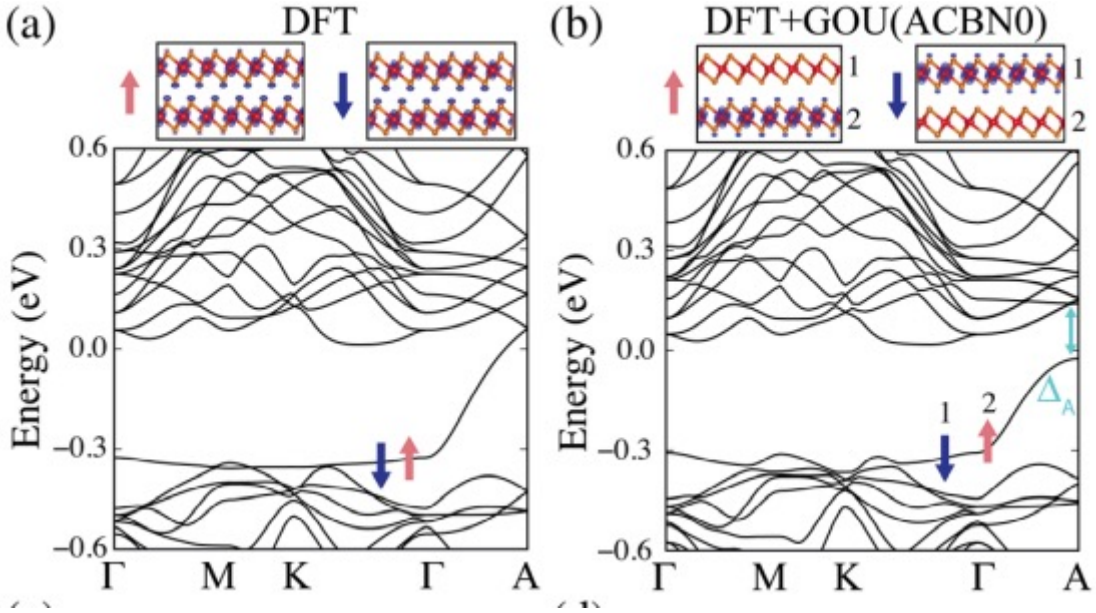
CDW

Spin polarization driven by a charge-density wave in monolayer 1T−TaS2Qingyun Zhang, Li-Yong Gan, Yingchun Cheng, and Udo SchwingenschlöglPhys. Rev. B 90, 081103(R) – Published 6 August 2014More

DFT+U

U is determined by self-consistent way (ACBN0)

CDW



Conclusion:

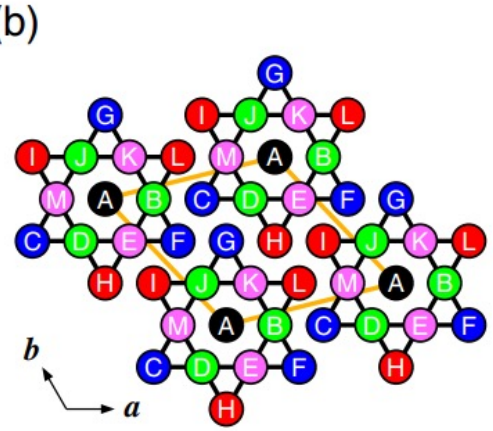
Spin polarization opens gap only for monolayer CDW not for bulk

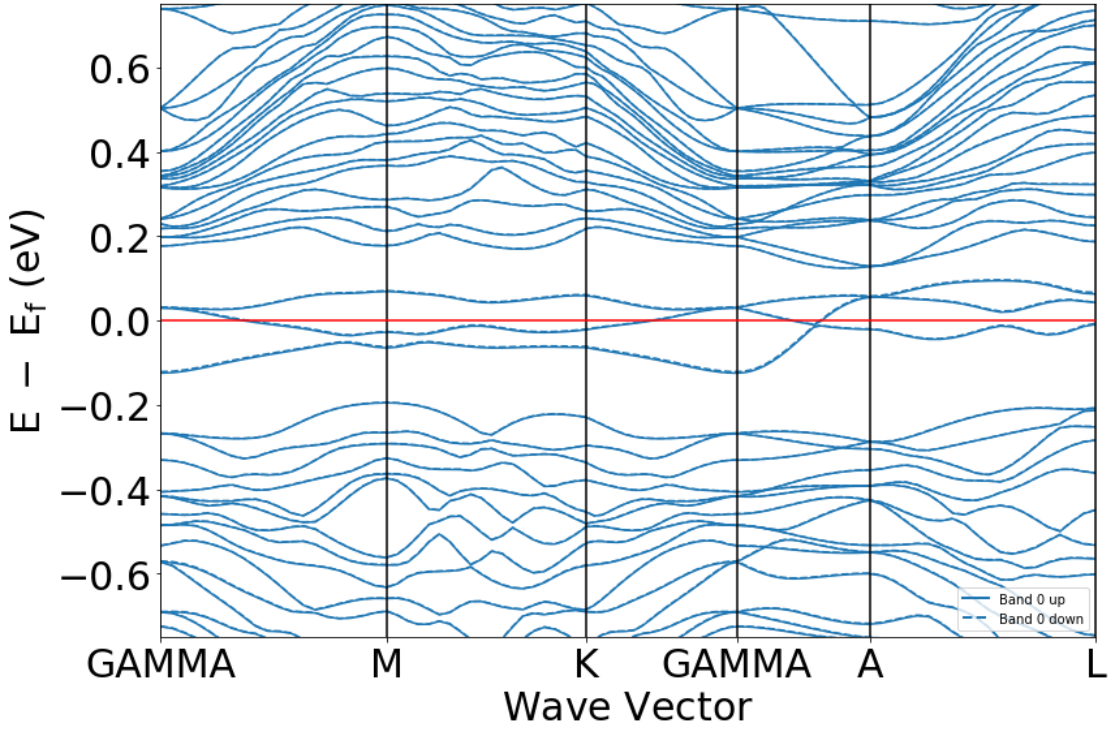
DFT+U with self-consistent U indicates mott insulator

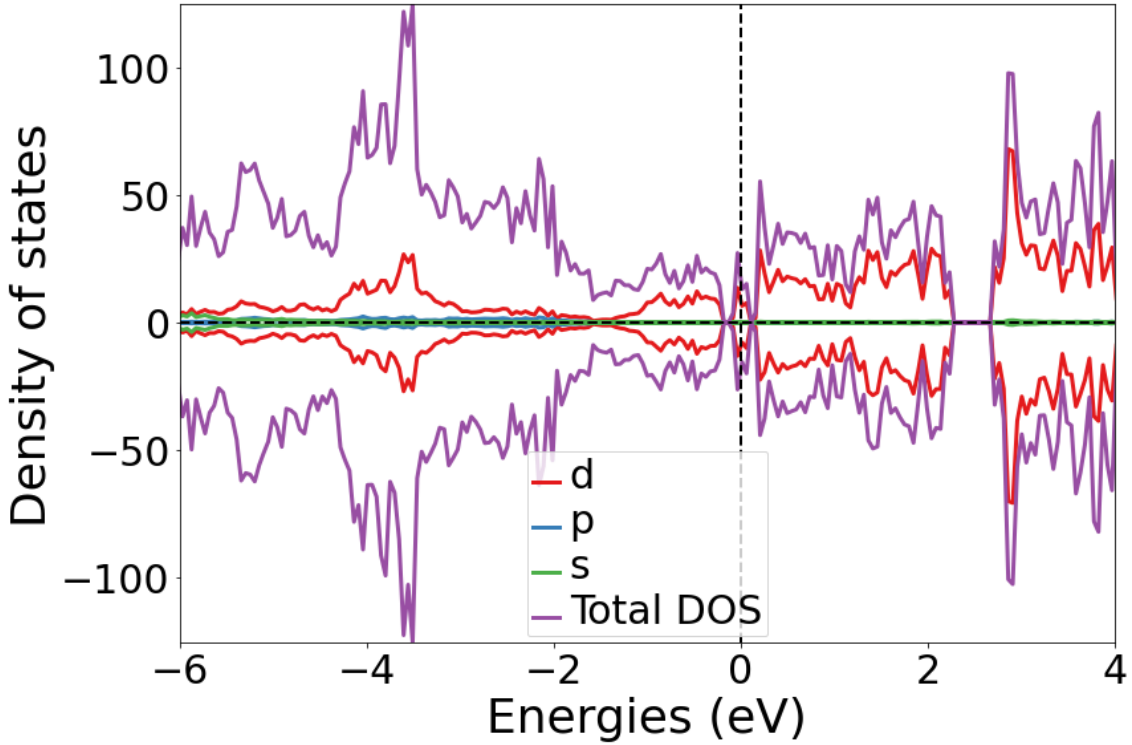
Identification of the Mott Insulating Charge Density Wave State in 1T−TaS2 Dongbin Shin, Nicolas Tancogne-Dejean, Jin Zhang, Mahmut Sait Okyay, Angel Rubio, and Noejung Park Phys. Rev. Lett. **126**, 196406 – Published 13 May 2021; Erratum Phys. Rev. Lett. **128**, 029902 (2022)

Some interesting band structure plot

AEB stacking





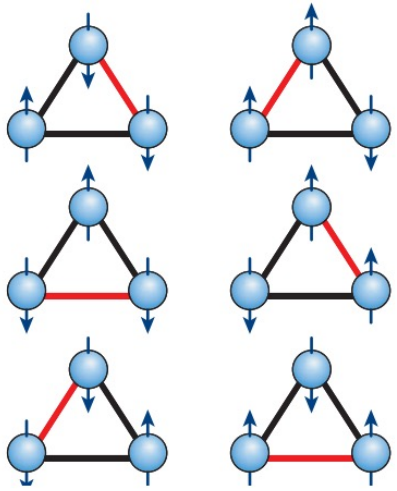


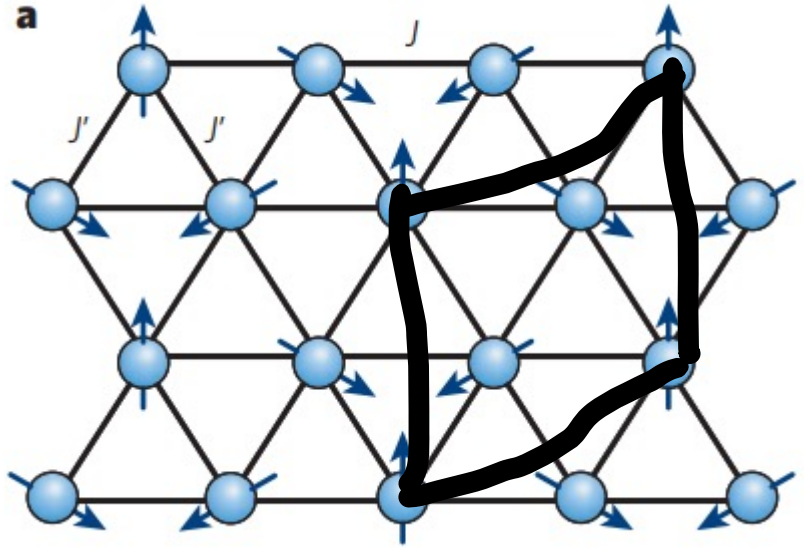
Physical properties

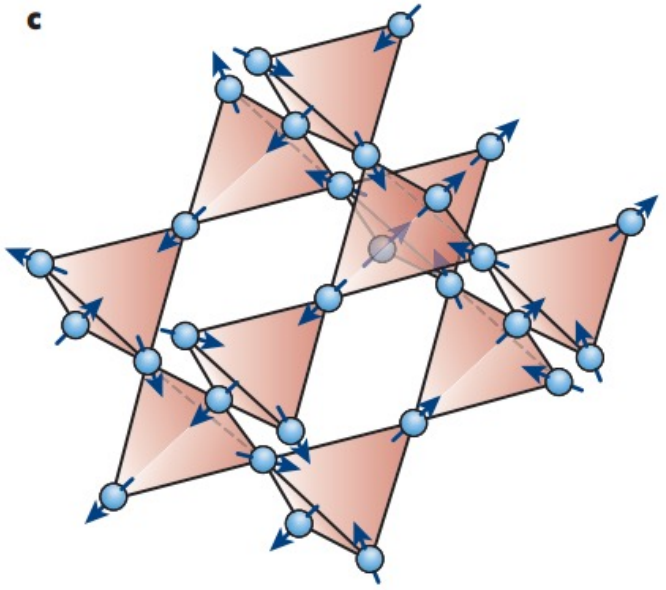
- Charge density wave
- Superconductivity(not cover)
- Metal-insulator transition
- Quantum spin liquid

Quantum Spin Liquid(QSL)

- Non-magnetic, spin = 0
- Classical spin liquid: spin feezed at low T
  - Spin Ice- we some how know the spin orientation
  - Triangular lattice antiferromagnet
- Quantum spin liquid:
  - Quantum fluctuation prevent magnetic order
  - Paramagnetic like ground state





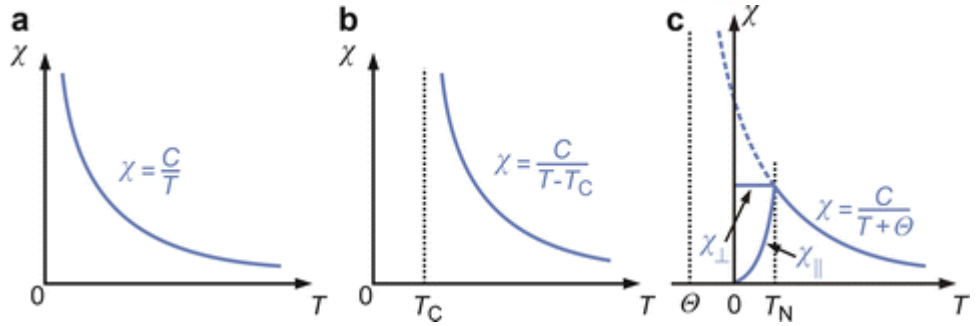


Balents, L. Spin liquids in frustrated magnets. *Nature* **464,** 199–208 (2010). https://doi.org/10.1038/nature08917

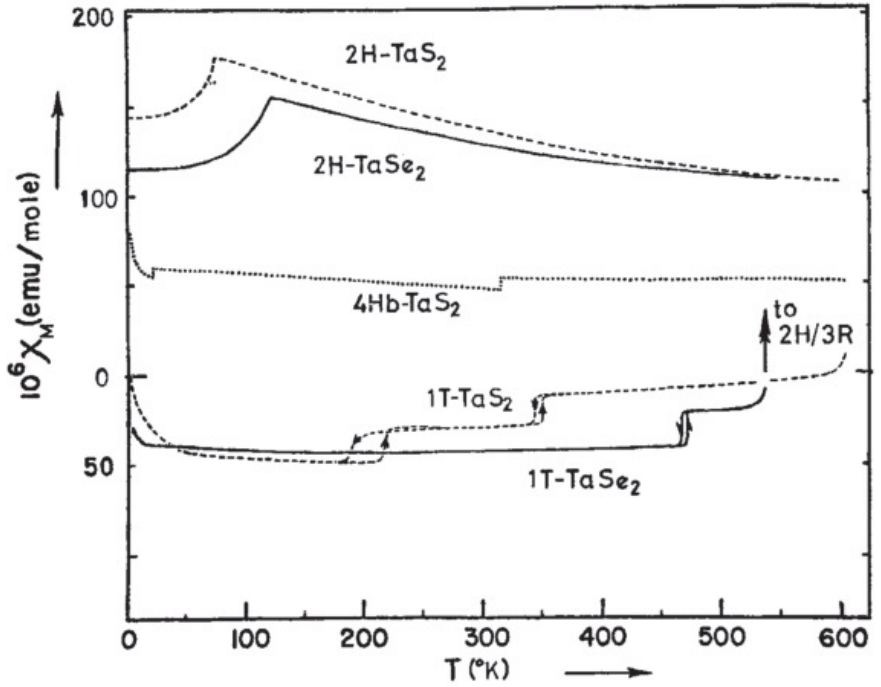
Quantum Spin Liquid(QSL)

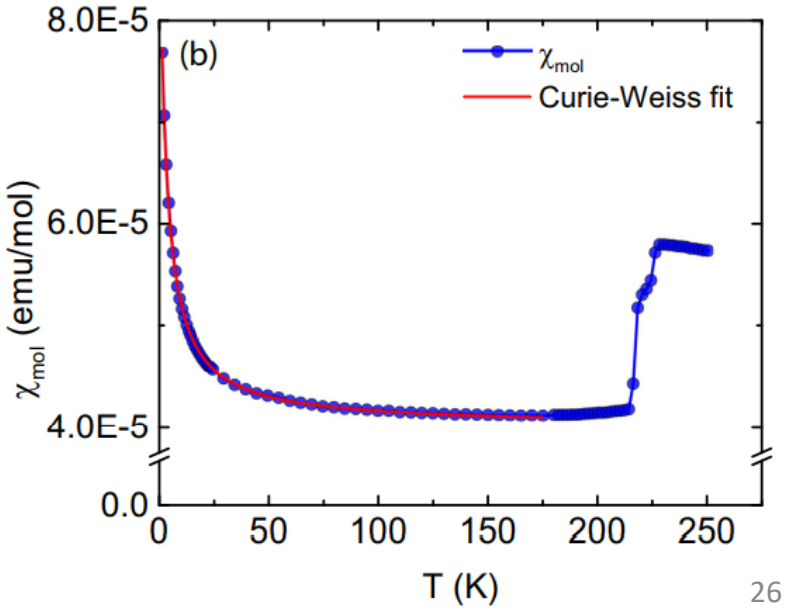
- Lets say TaS2 in a mott insulator
  - The spins will form local moments, antiferromagnetic ground state
  - Or a QSL state which has paramagnetic behavior , following Curie Weiss Law

$$\chi = \frac{C}{T - \theta_{CW}} + \chi_0.$$



Law, K. T. & Lee, P. A. 1*T*-TaS_2 as a quantum spin liquid. *Proc. Natl. Acad. Sci. USA* **114**, 6996–7000 (2017).



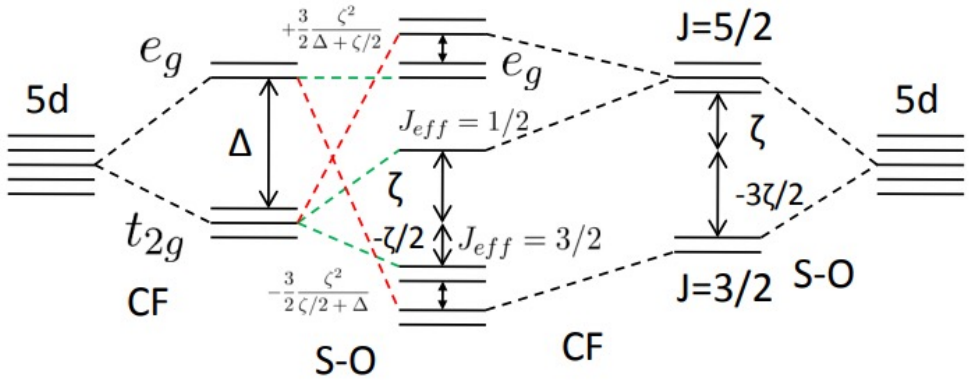


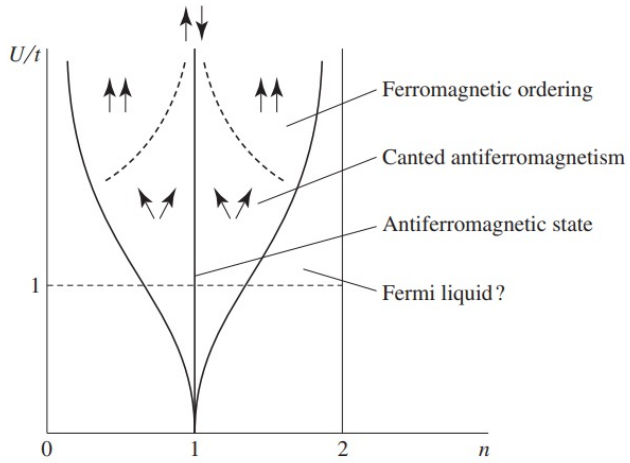
Gapless excitations in the ground state of 1T−TaS2 A. Ribak, I. Silber, C. Baines, K. Chashka, Z. Salman, Y. Dagan, and A. Kanigel Phys. Rev. B **96**, 195131 – Published 15 November 2017

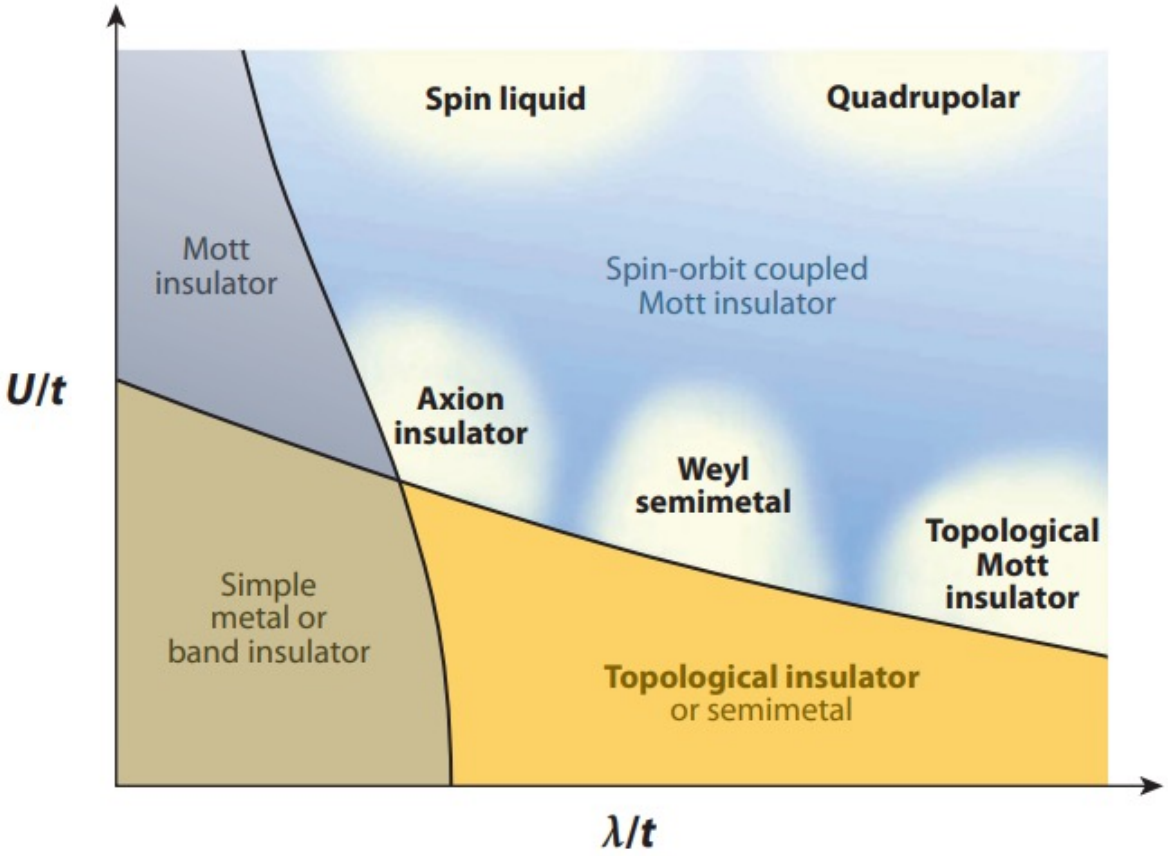
General discussion

$$H = \sum_{i,j;\alpha\beta} t_{ij,\alpha\beta}\, c^{\dagger}_{i\alpha} c_{j\beta} + \text{h.c.} + \lambda \sum_{i} \boldsymbol{L}_i \cdot \boldsymbol{S}_i + U \sum_{i,\alpha} n_{i\alpha}(n_{i\alpha} - 1),$$

Heavy element- spin orbit coupling







Khomskii, D. (2014). *Transition Metal Compounds*. Cambridge: Cambridge University Press. doi:10.1017/CBO9781139096782

Correlated Quantum Phenomena in the Strong Spin-Orbit Regime William Witczak-Krempa, Gang Chen, Yong Baek Kim, Leon Balents Annual Review of Condensed Matter Physics 2014 5:1, 57-82

Mixing of t2g–eg orbitals in 4d and 5d transition metal oxides Georgios L. Stamokostas and Gregory A. Fiete Phys. Rev. B **97**, 085150 – Published 26 February 2018

General discussion continued

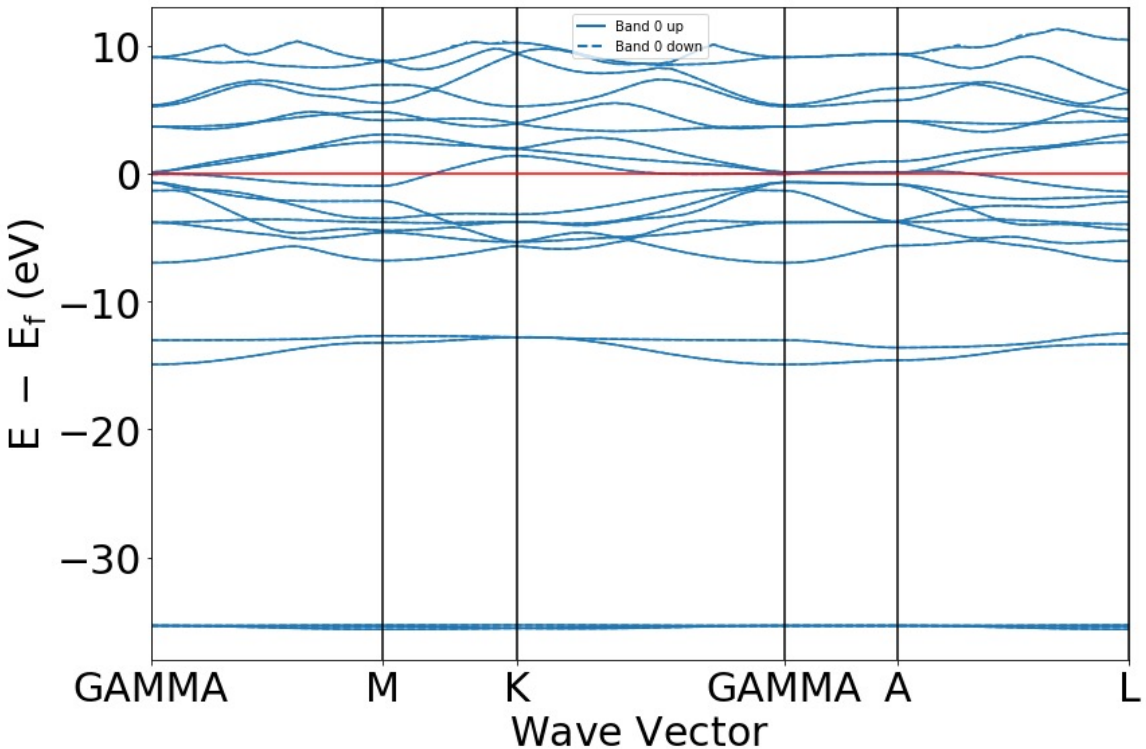
- Heavy element- spin orbit coupling
- Failure of VASP, scalar relativistic for valence electrons pseudopotential

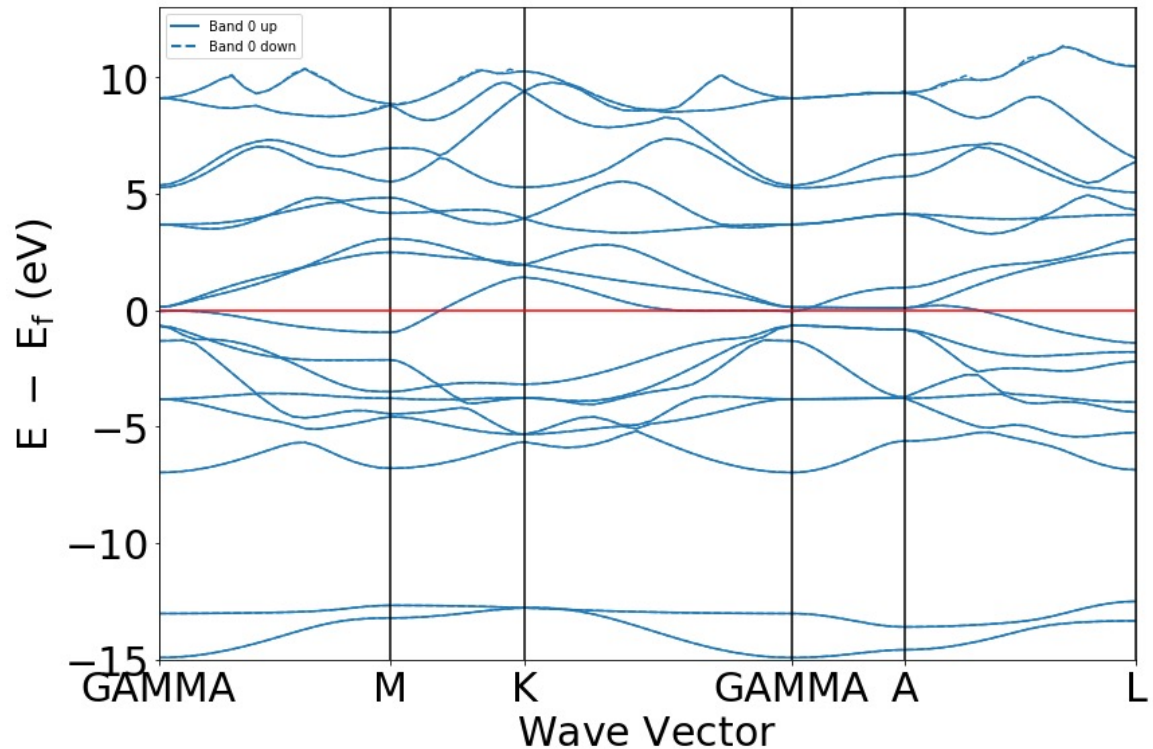
$$E_n = -\frac{e^2}{8\pi\varepsilon_0 a_0 n^2} \qquad \mathcal{H}_{\text{Darwin}} = \frac{\hbar^2}{8m_e^2c^2} 4\pi \left(\frac{Ze^2}{4\pi\varepsilon_0}\right) \delta^3(\vec{r})$$

$$\mathcal{H}_{\text{SO}} = \left(\frac{Ze^2}{4\pi\varepsilon_0}\right)\left(\frac{g_s - 1}{2m_e^2c^2}\right)\frac{\vec{L}\cdot\vec{S}}{r^3}$$

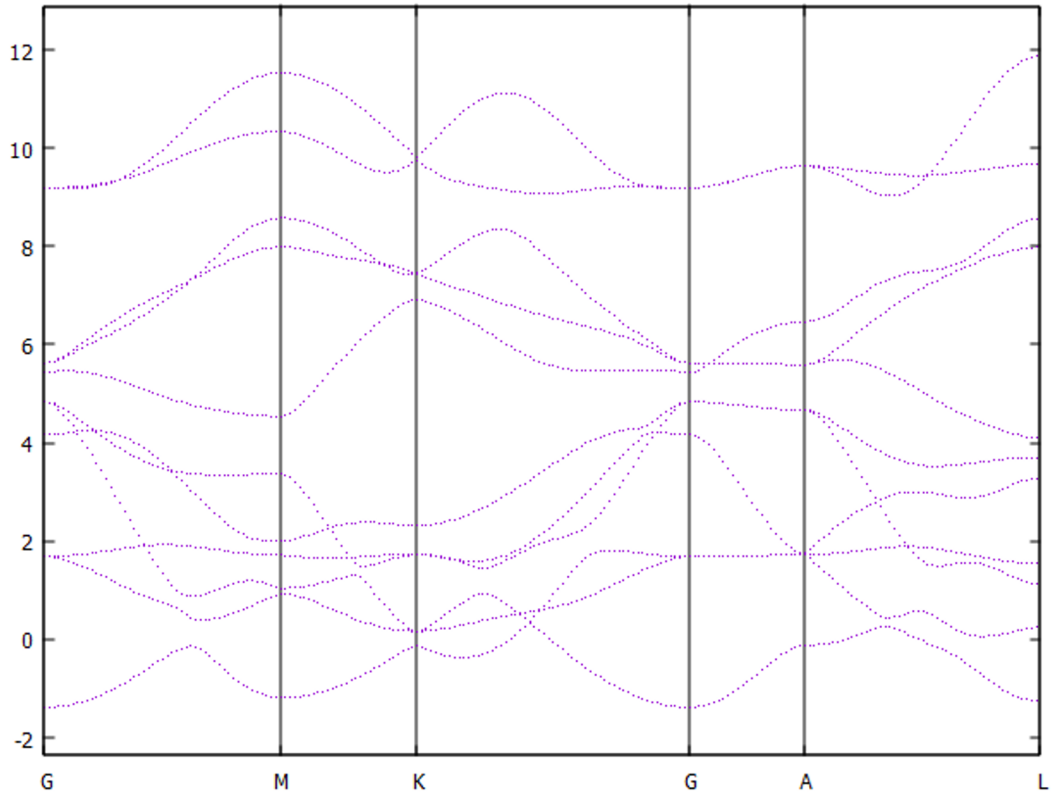
- Failure of exchange-correlation, not treat it with many-body problem

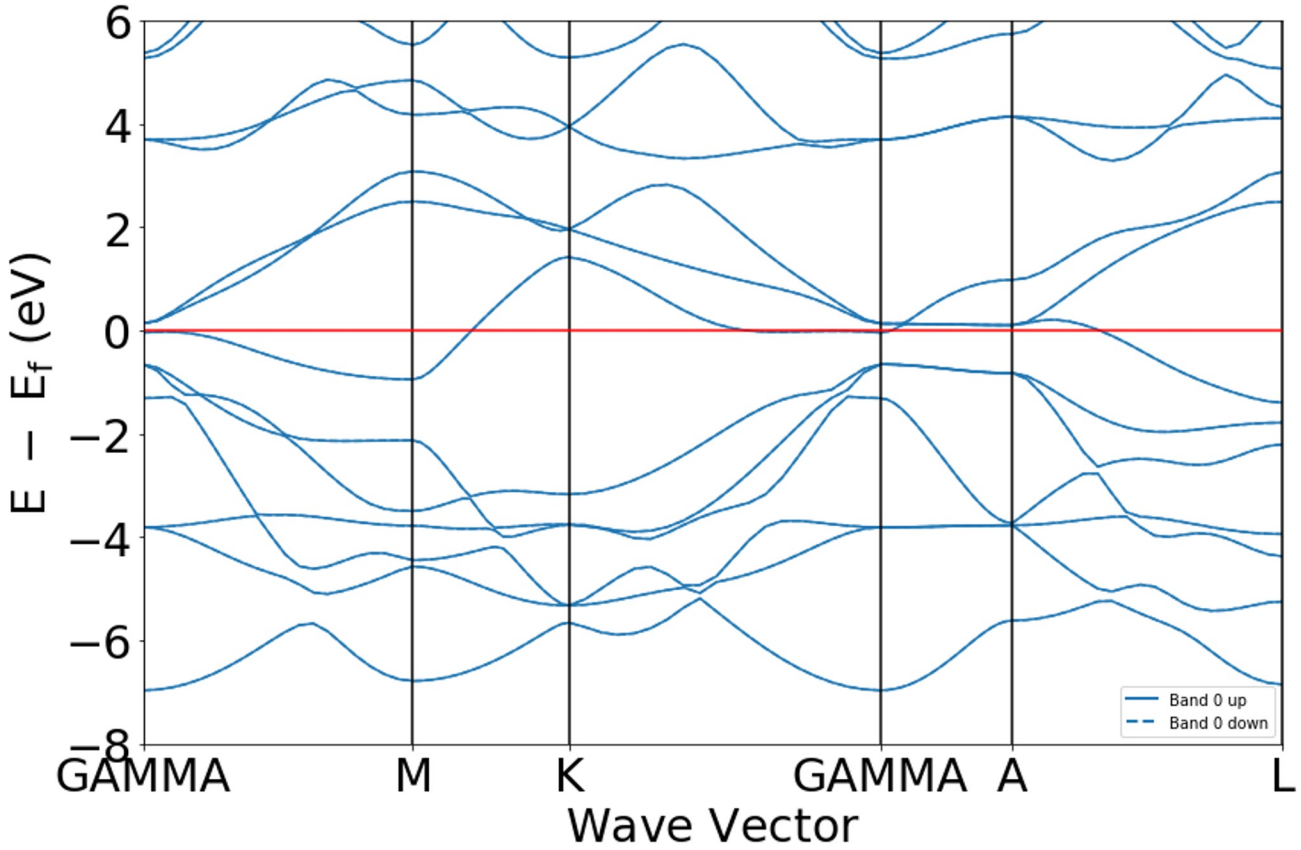
- Questions

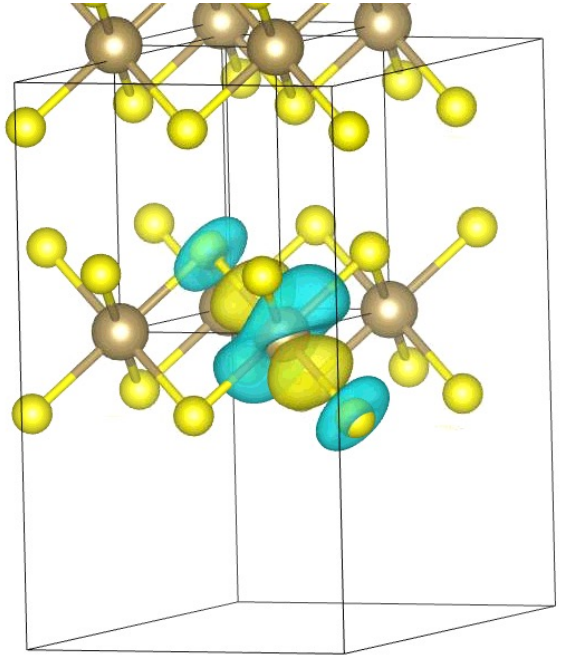

Band 0 up
Band 0 down
10
0
−10
−20
−30
E − E$_f$ (eV)
GAMMA
M
K
GAMMA
A
L
Wave Vector

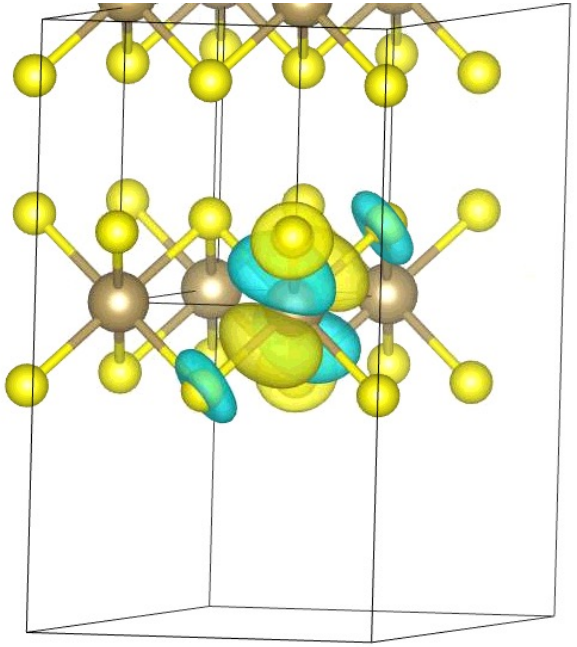

Band 0 up
Band 0 down
10
5
0
−5
−10
−15
E − E$_f$ (eV)
GAMMA
M
K
GAMMA
A
L
Wave Vector

Wannier interpolation with ‘Ta’:d , ’S’:p









Wannier orbital