Max Planck Institute
for Solid State Research

FINDING AND CHARACTERIZING NEW TOPOLOGICAL MATERIALS

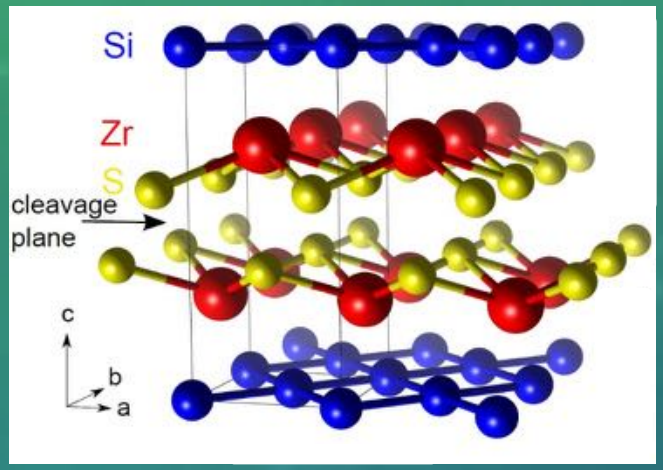
LESLIE MAREIKE SCHOOP

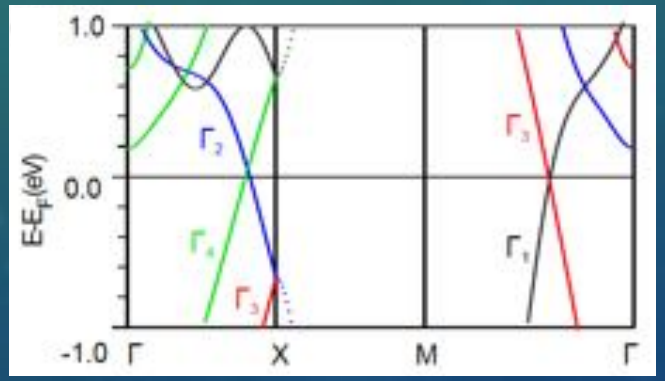
TOPOLOGICAL MATTER SCHOOL 2017

DONOSTIA-SAN SEBASTIAN

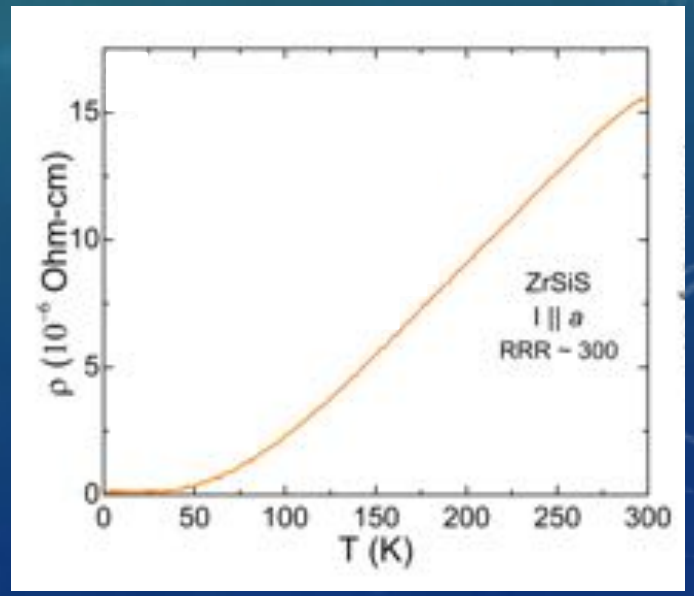
08/24/17

Crystal chemistry and structure





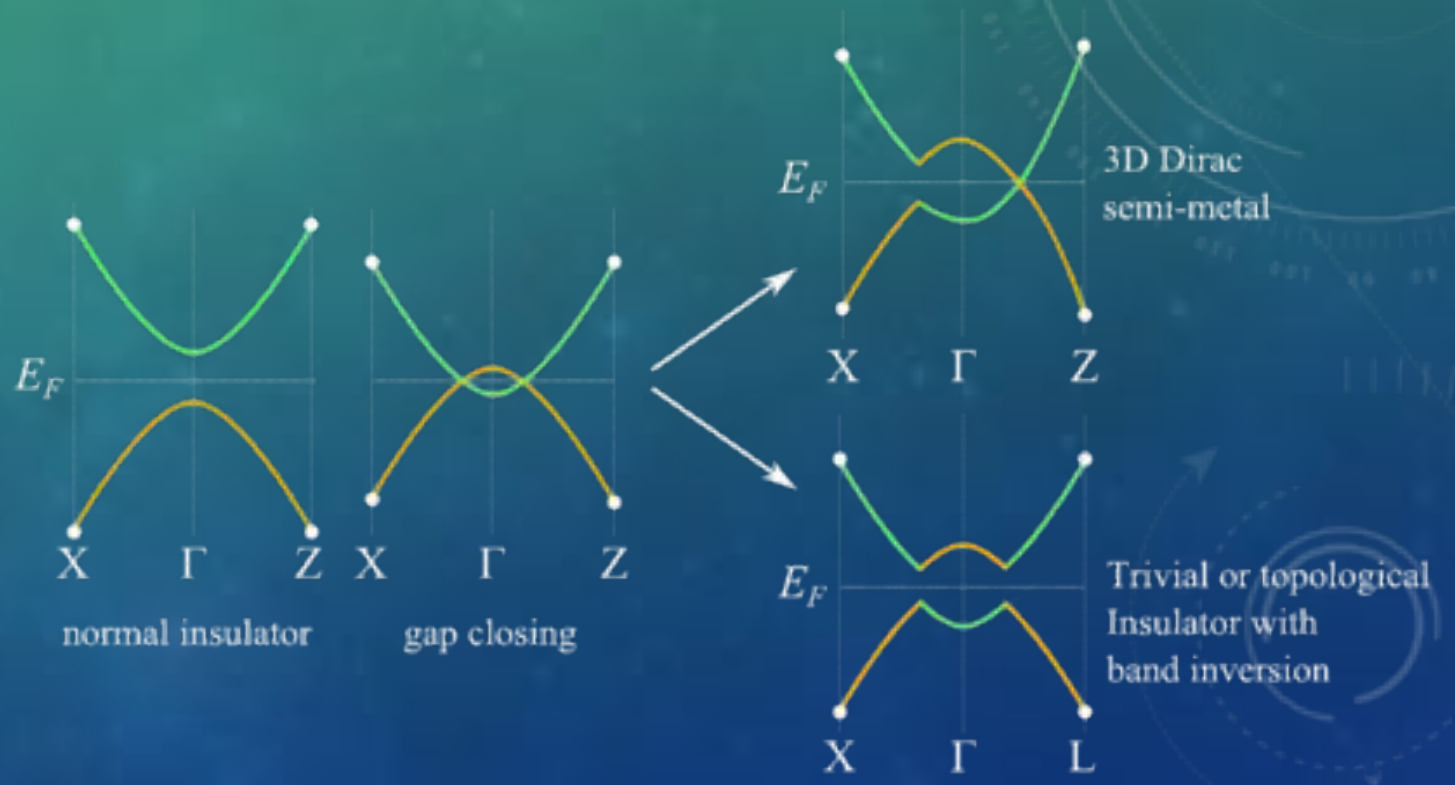
Electronic structure



Properties

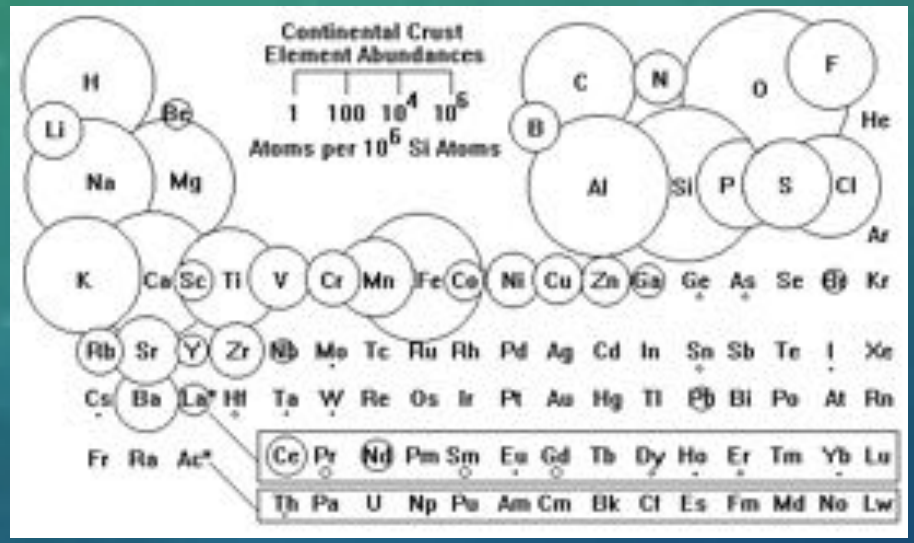
RECAP: WHAT TO WE NEED TO FIND A 3D DSM

- Charge Balance
- High symmetry
- “good” ratio between electronegativity and spin orbit coupling



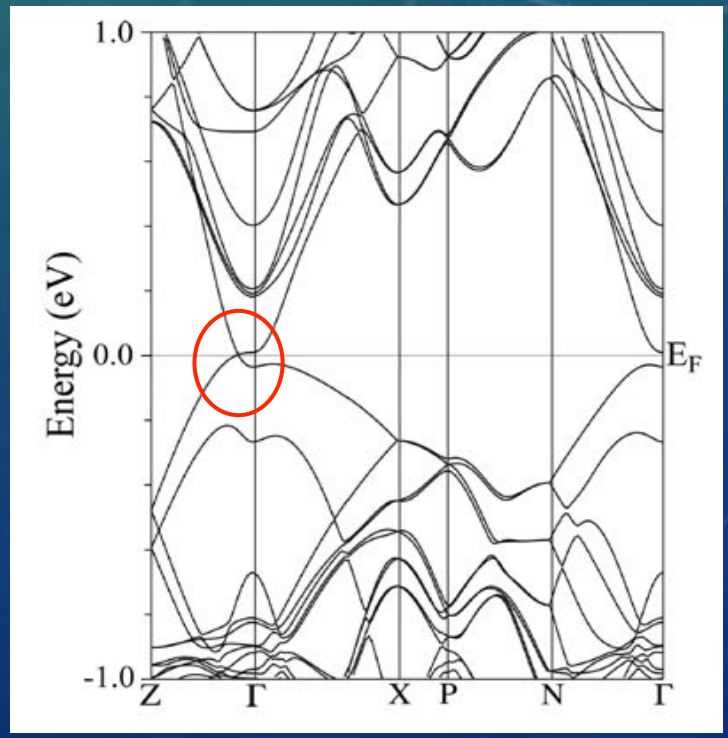
A CHEMIST'S PROBLEMS WITH KNOWN 3D DIRAC AND WEYL SEMIMETALS

- Toxic (arsenides)
- Air sensitive (Na_3Bi)
  - WTe_2 and $ZrTe_5$, both not stable in air when thin
- Very small range of linear bands

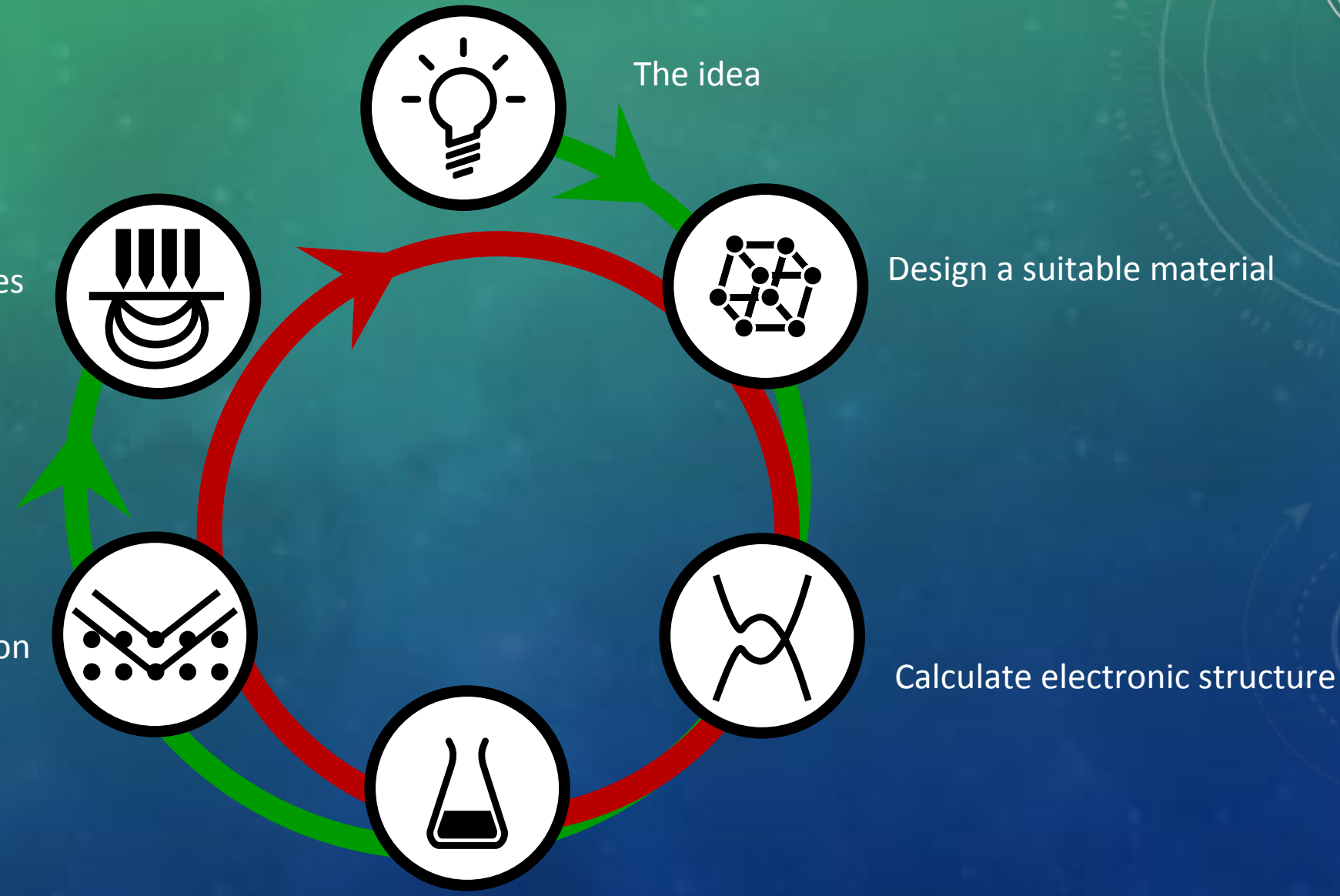


- None are made of only earth abundant elements

Cd_3As_2



HOW TO DEVELOP NEW MATERIALS

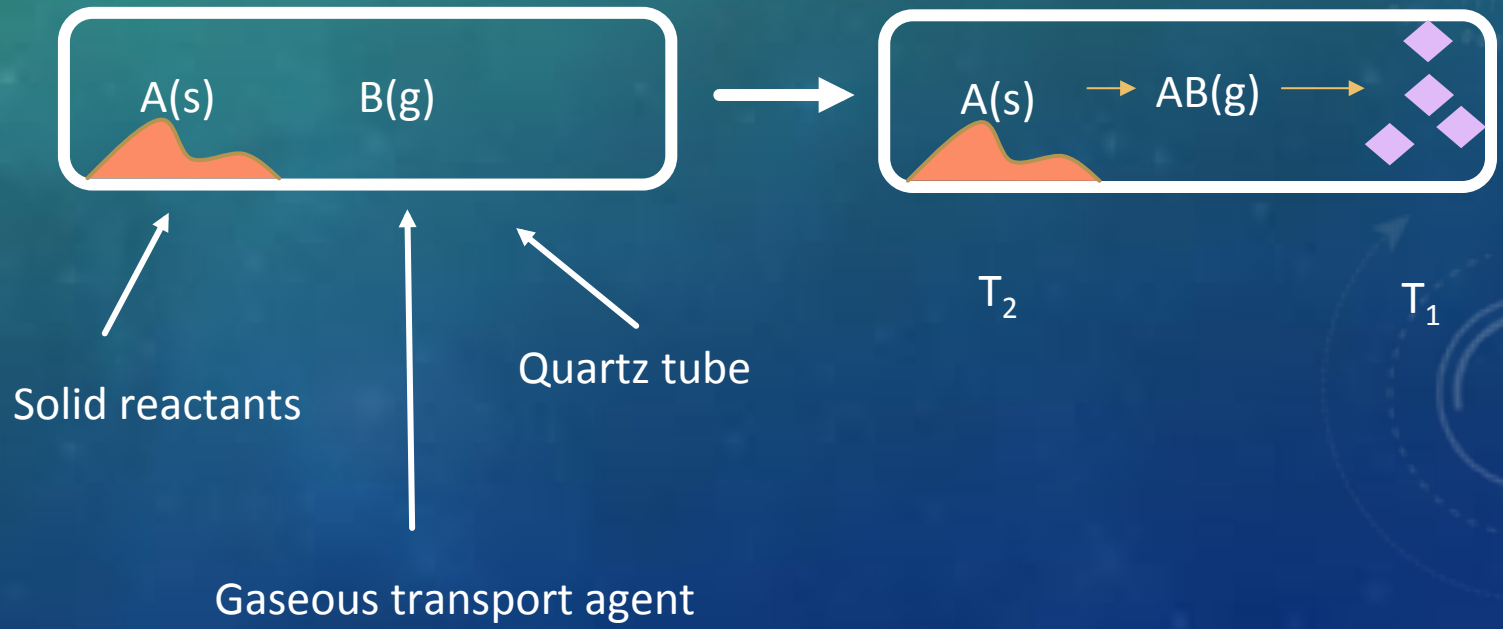


SYNTHESIS METHODS:

- Most common crystal growth methods:
- Vapor transport (e.g. TaAs, ZrSiS)
- Flux growth (e.g. Cd_3As_2, Na_3Bi, WTe_2)
- Bridgman growth (e.g. Bi_2Se_3, Bi_2Te_3, BTS)
- Floating zone (e.g. MnSi)

VAPOR TRANSPORT:

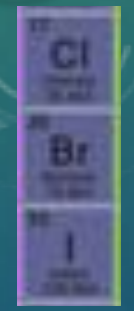
- Works usually well for materials containing S, Se , P or As
- Dependent on the ability to form volatile intermediate products that go to the gas phase
- Famous examples:
  - TaAs, NbP etc
  - ZrSiS



POSSIBLE TRANSPORT AGENTS

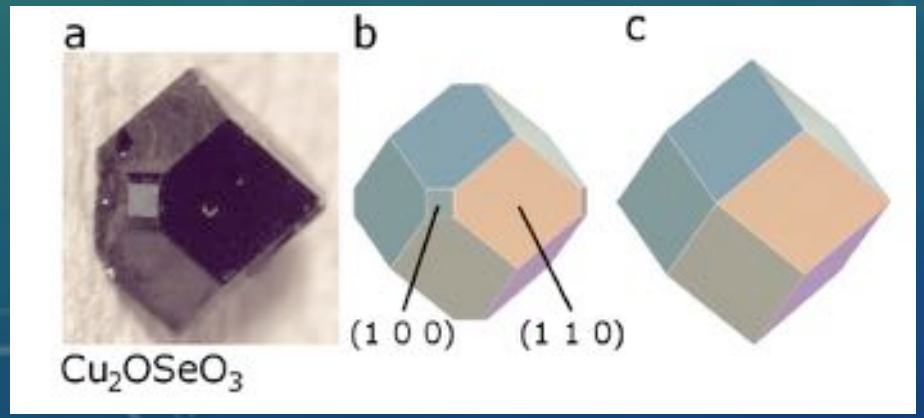
- I_2: easy to handle, works well for Zr, Hf, Nb and Ta compounds
- Br_2, a little harder to handle but sometimes better result
- Cl_2 nasty! But sometimes necessary (e.g. $RuCl_3$)
- $SeCl_4$ or $TeCl_4$: Good substitute for Cl_2
- NH_4Cl (HCl is active transport agent) works well for SnS_2 or oxysulfides

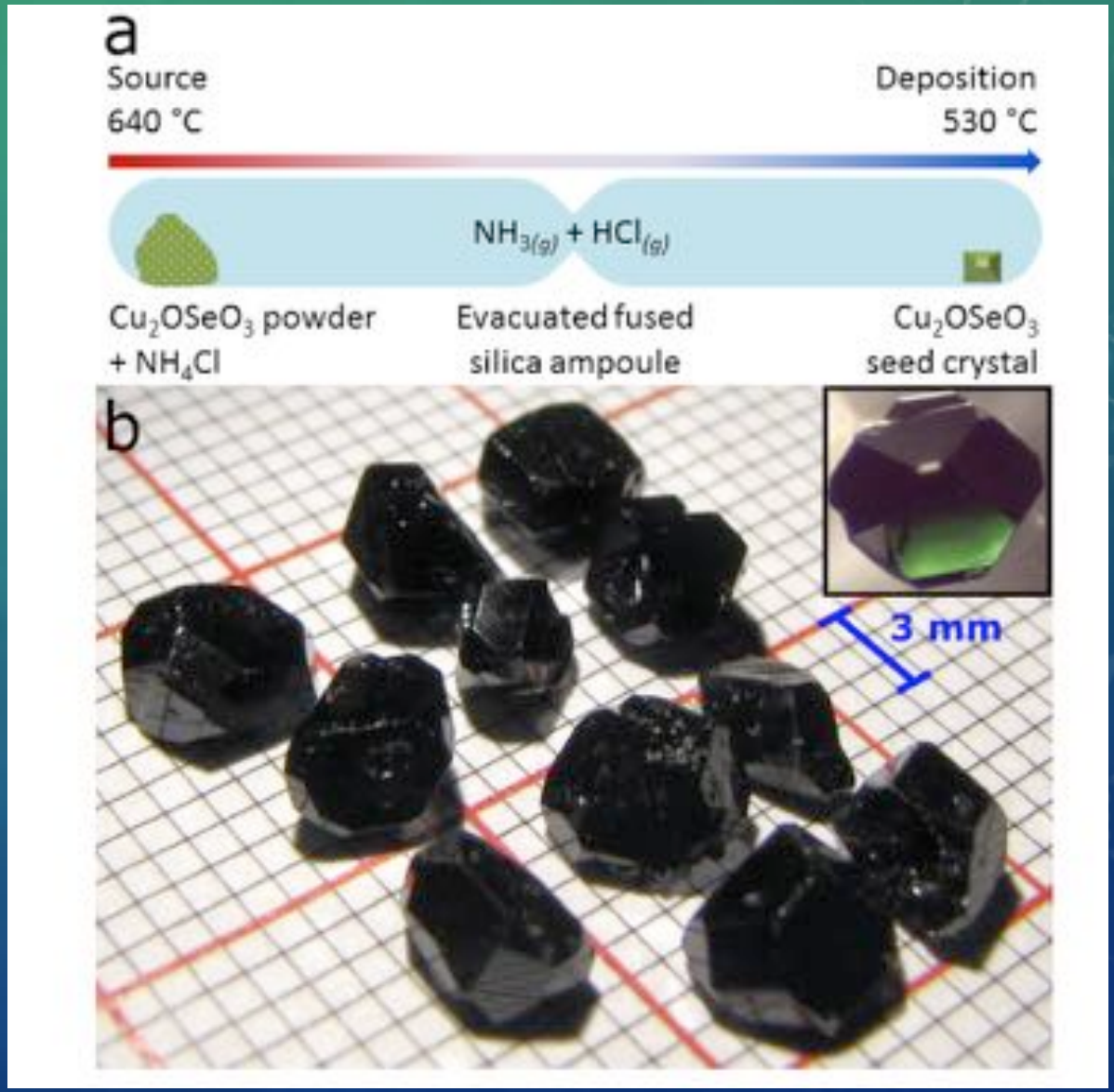
$SeCl_4 \rightarrow Se(g) + 2\ Cl_2(g)$
$NH_4Cl \rightarrow NH_3(g) + HCl$



SEED GROWTH

- Vapor transport can lead to extremely large single crystals
- Often extremely pure
- Seed growth can yield even larger crystals

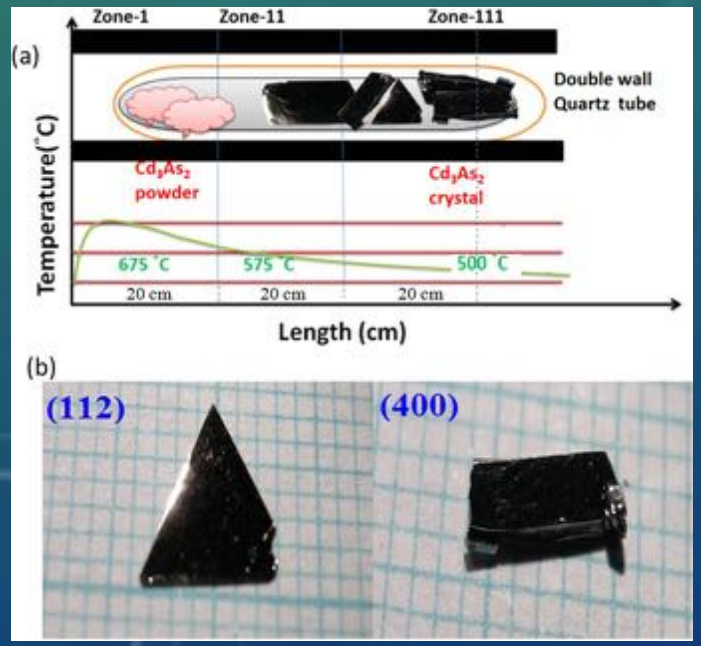




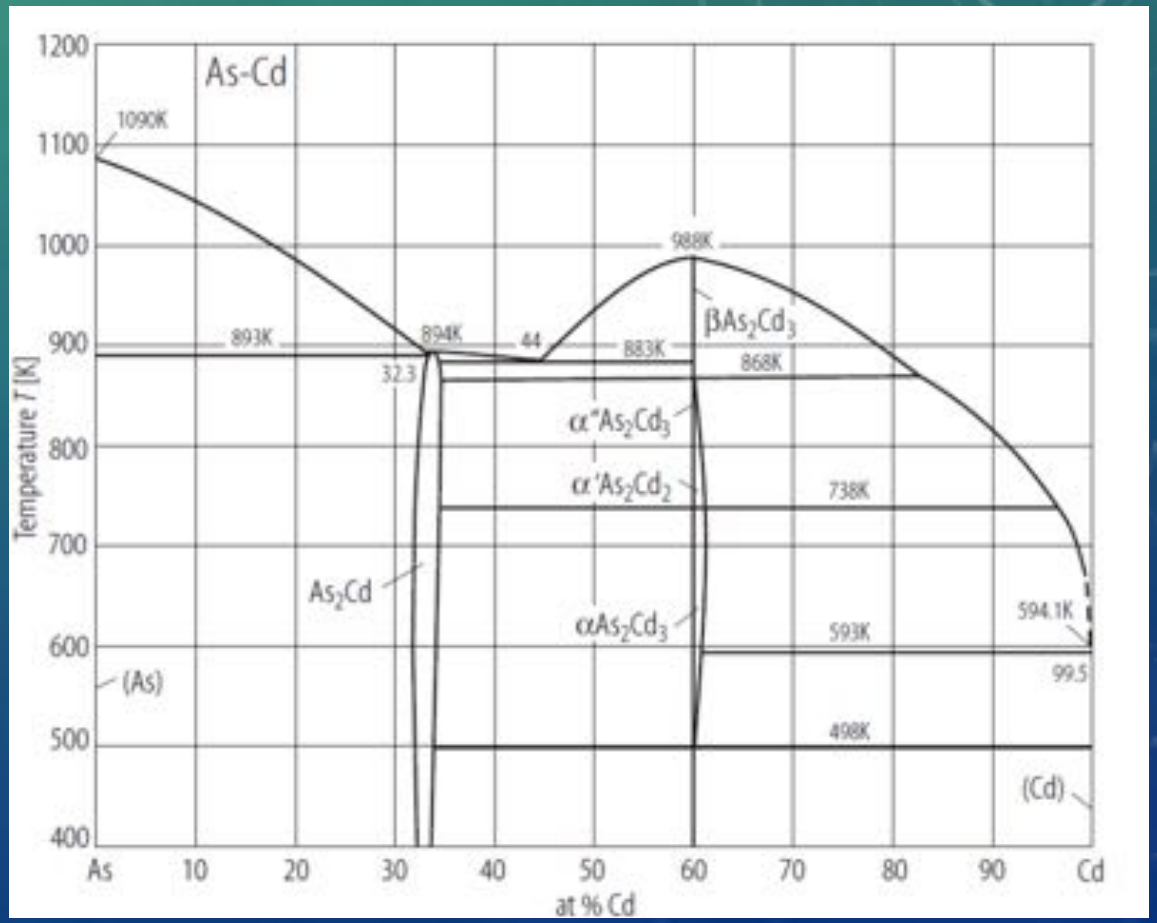
Panella, Trump, Marcus, McQueen, arXiv:1706.02411.

LIMITATIONS OF VAPOR TRANSPORT:

- Cd_3As_2: competing phases!
- Grown with vapor transport: large crystals BUT RRR only about 8
- Grown from Flux: RRR > 4000
- Only flux grown crystals show ultra high mobility!

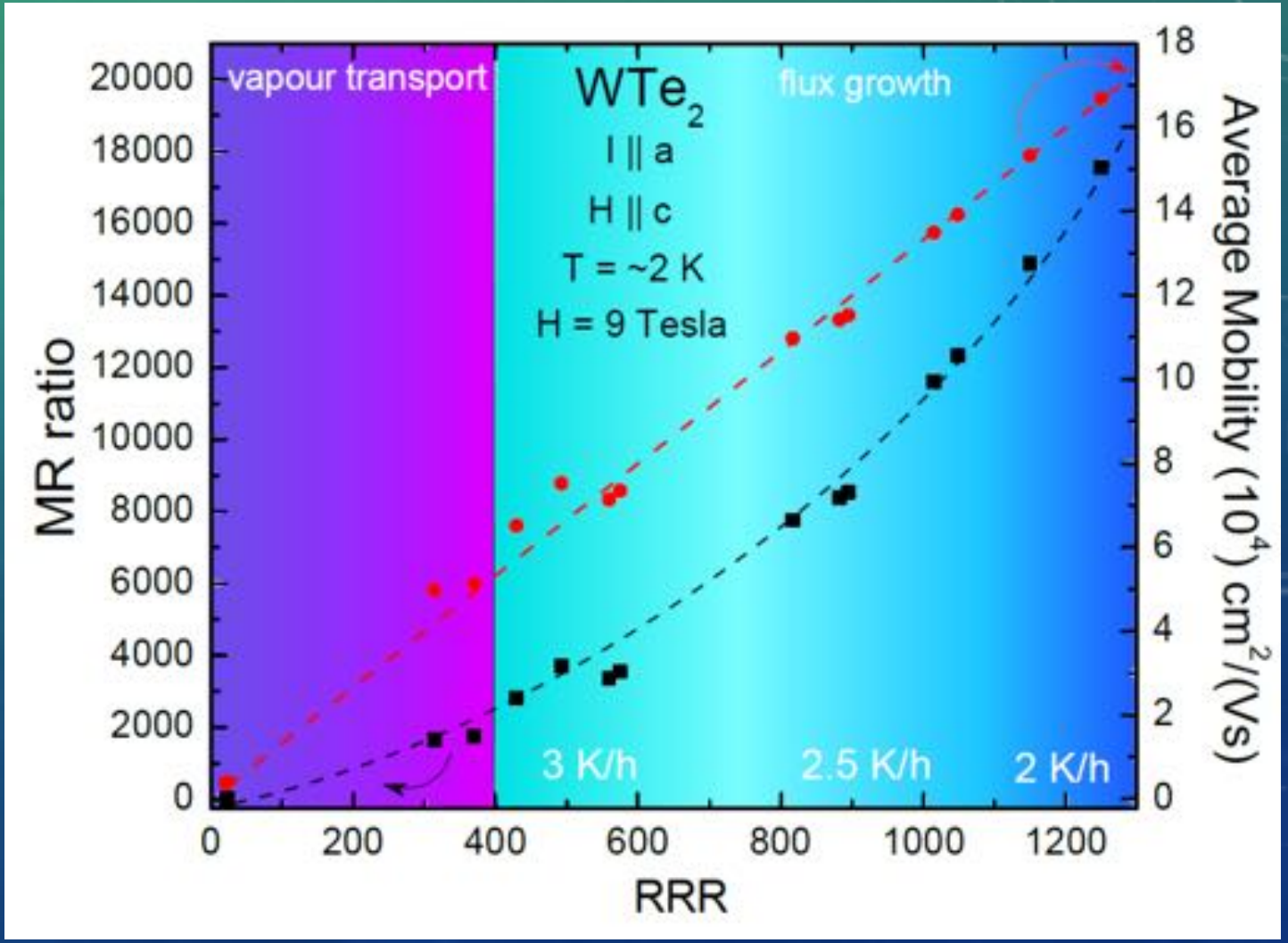


Scientific Reports **5**, Article number: 12966 (2015)



LIMITATIONS ON VAPOR TRANSPORT

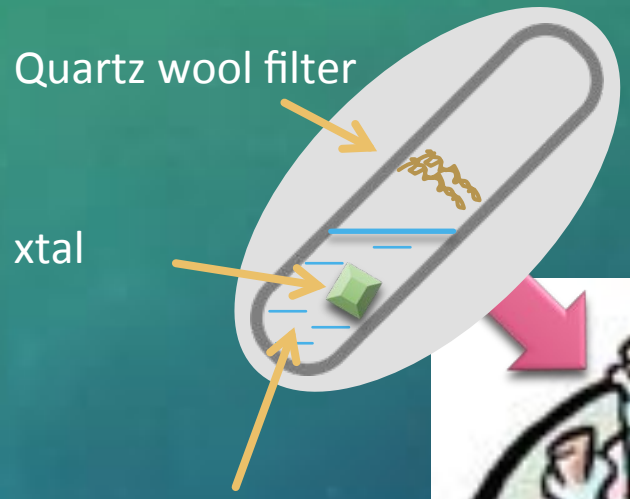
- WTe_2:
- Magnetoresistance MUCH higher if crystals are grown from Te flux
- Probably because Te vacancies form easily



Ali, Schoop, Xiong, Flynn, Gibson, Hirschberger, Ong, Cava. *EPL (Europhysics Letters)*, *110*(6), p.67002. (2015)

FLUX GROWTH

- Advantage: quench one phase, excess of volatile element possible
- Disadvantage: centrifuging at high T cause defects
- Famous examples:
  - Cd_3As_2, WTe_2, $ZrTe_5$ Fe-based supercondcutors, Na_3Bi

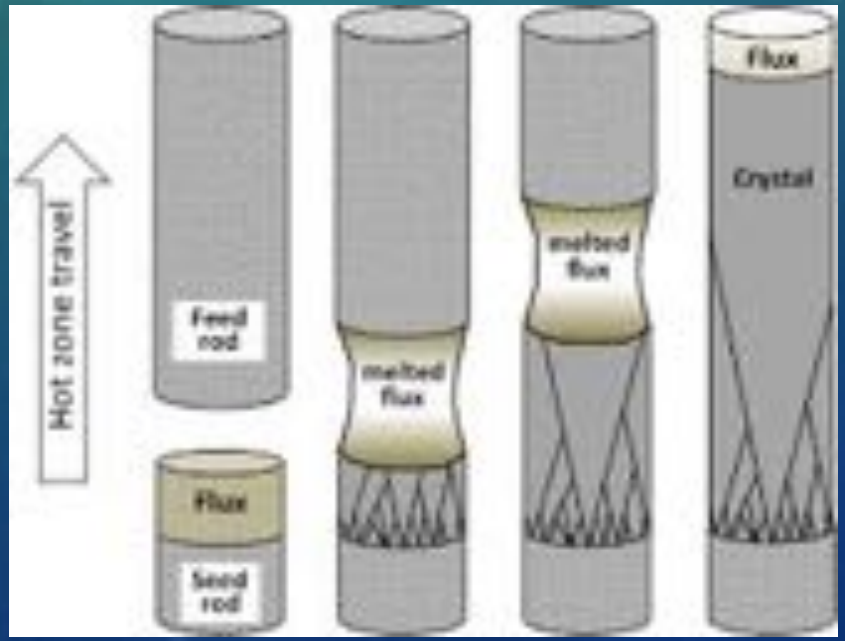


Flux Method

Centrifugation at high temperatures

POSSIBLE FLUXES

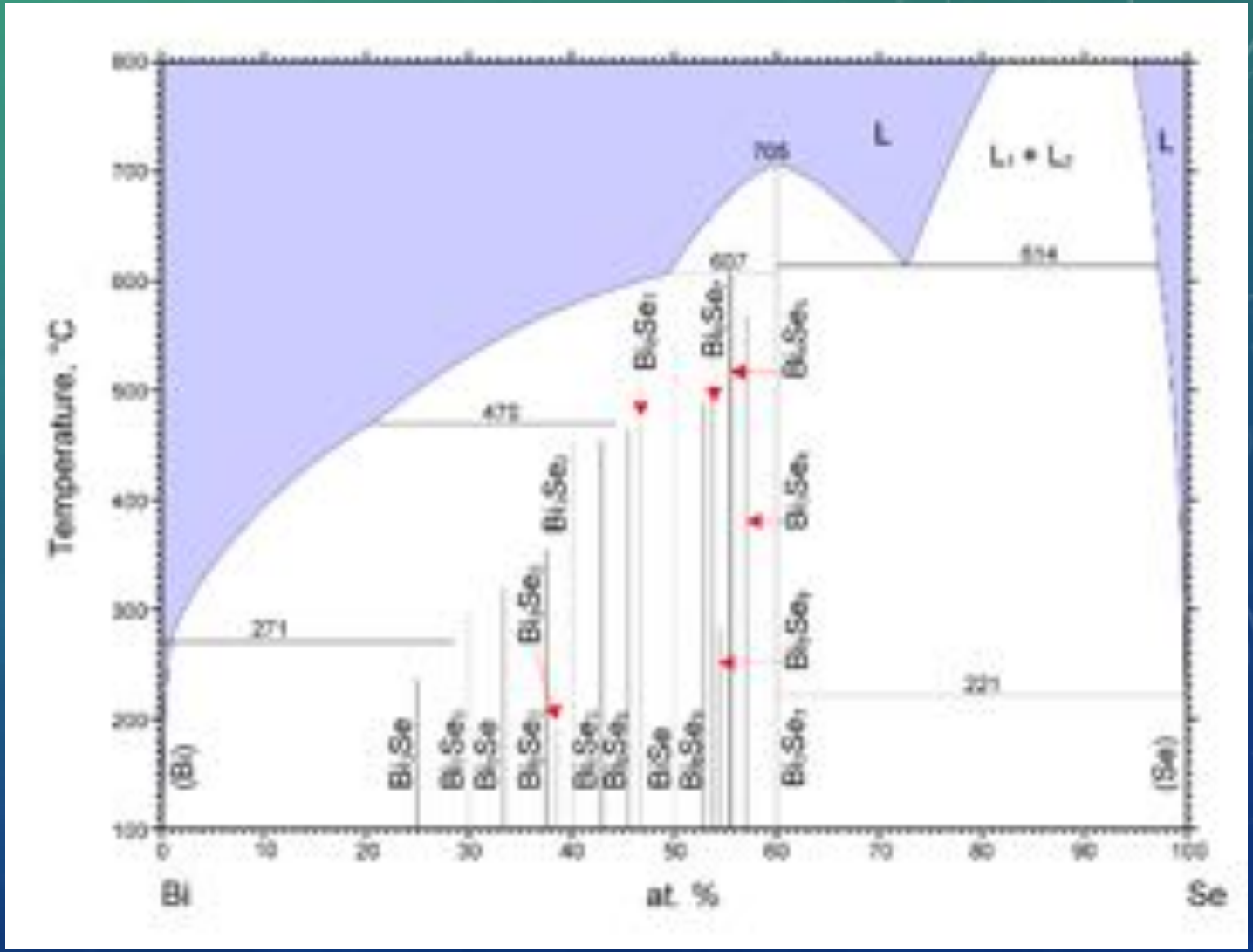
- Low melting point elements: In, Sn, Pb, Sb, Bi, Te
- Self flux or foreign flux possible
- Study phase diagrams!
- Salts and oxides



Salt and oxide fluxes

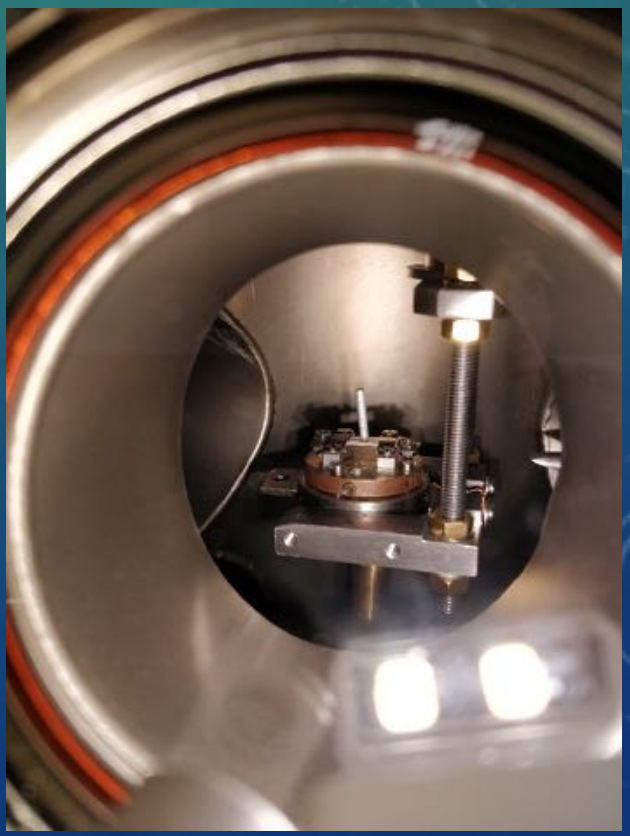
BRIDGMAN METHOD

- Very easy: just heat until everything melts and cool very slowly from one end to the other of the container
- Often the best solution but works only for special phases
- Famous examples: Bi_2Se_3 and other tetradymites



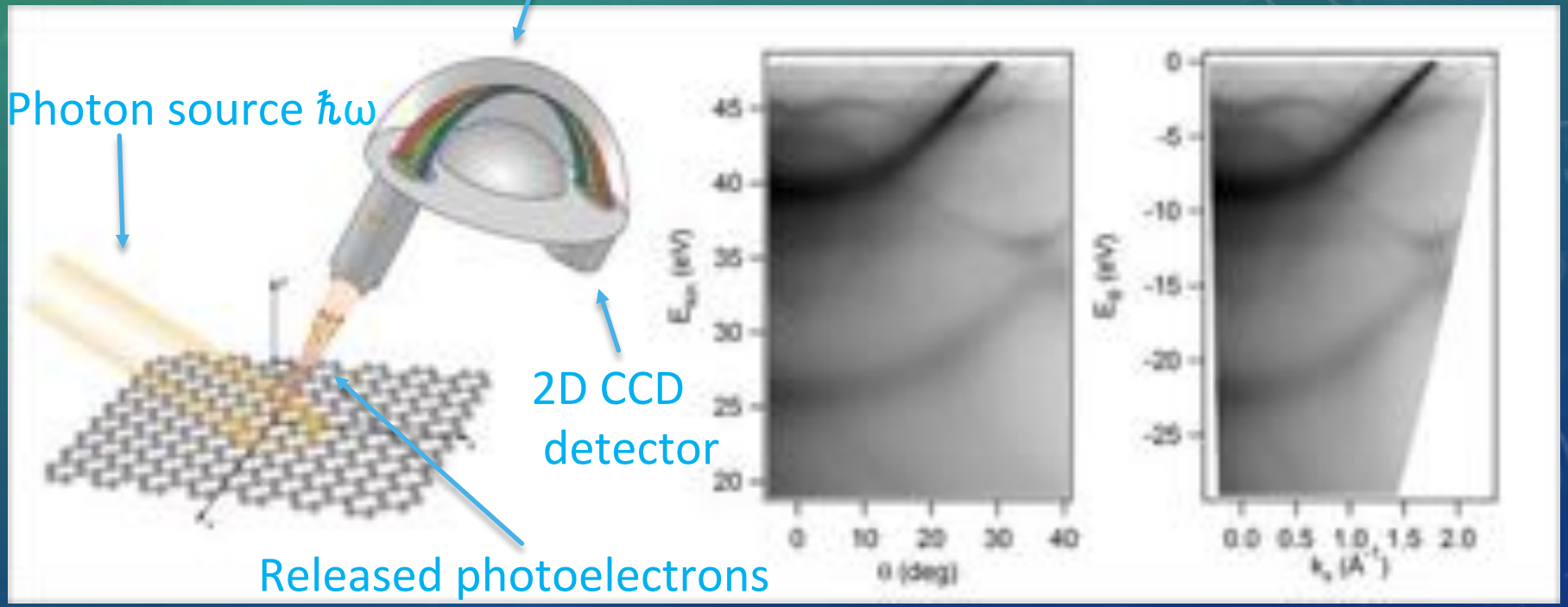
VERIFYING THE BAND STRUCTURE

- You successfully grew a large enough crystal! Yayy ☺
- Next Question: does it cleave???
- ARPES will be done in UHV and need a clean surface!!



HOW TO EXPERIMENTALLY VERIFY THE ELECTRONIC STRUCTURE

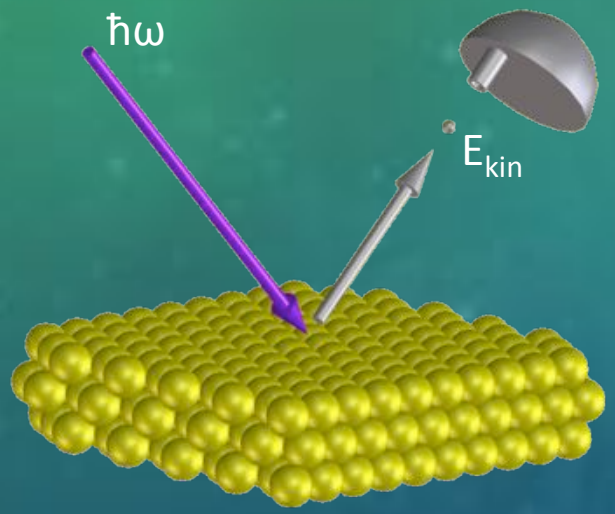
- Use Angle Resolved Photoelectron Spectroscopy to take an image of the band structure
- Surface sensitive!
- Large single crystals (min. 1 mm^2) that can be cleaved in UHV needed

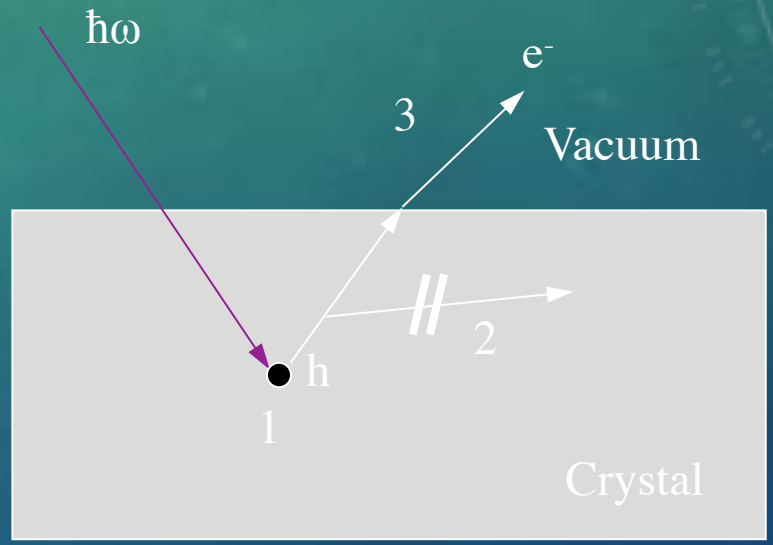


$$k\downarrow{||} = \sqrt{2m}/\hbar \sqrt{E\downarrow kin}\ \sin\theta$$

$E_B = \hbar\omega - \varphi - E_{kin}$

THE PHOTOELECTRIC EFFECT



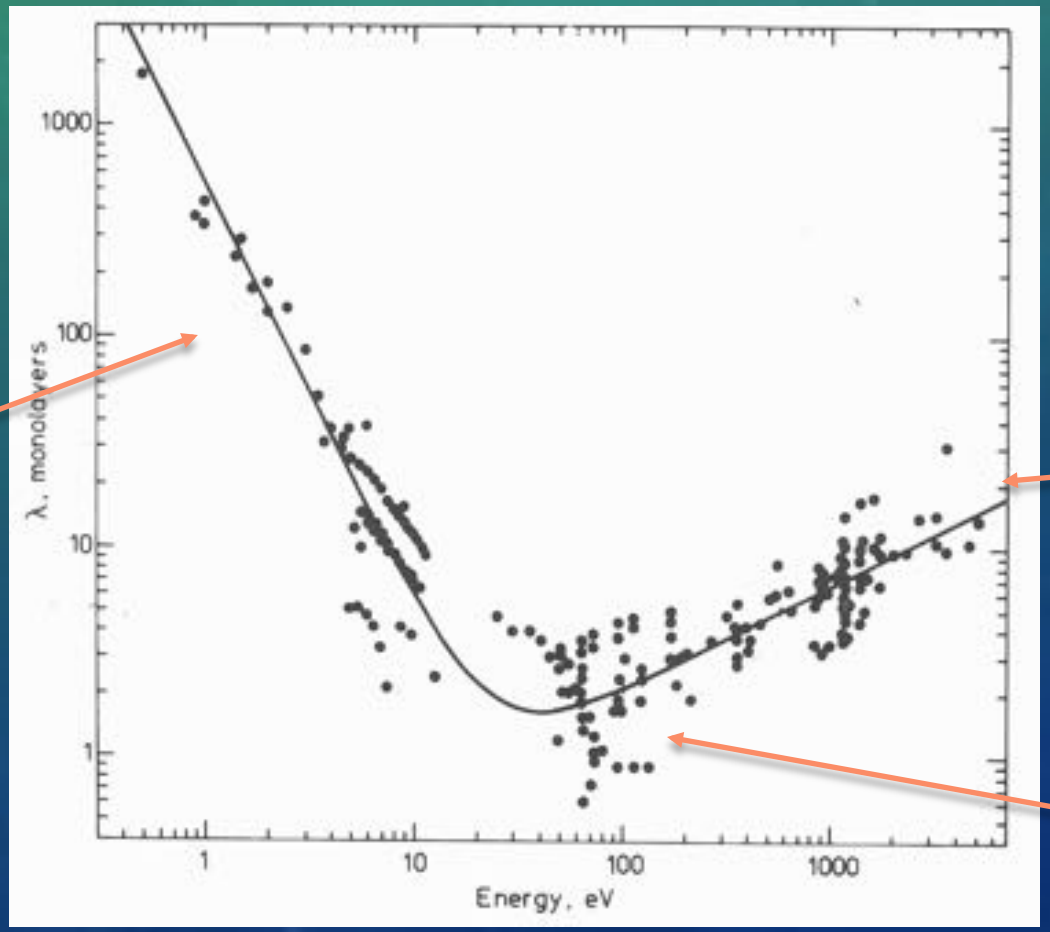


The three-step-model describes the photoelectric effect:

1. Excitation of the electron
2. Propagation to the surface (most limiting factor)
3. Transition into the vacuum

One-step-model is more “correct”, but less intuitive…

THE PHOTOELECTRIC EFFECT -THE „UNIVERSAL“ CURVE



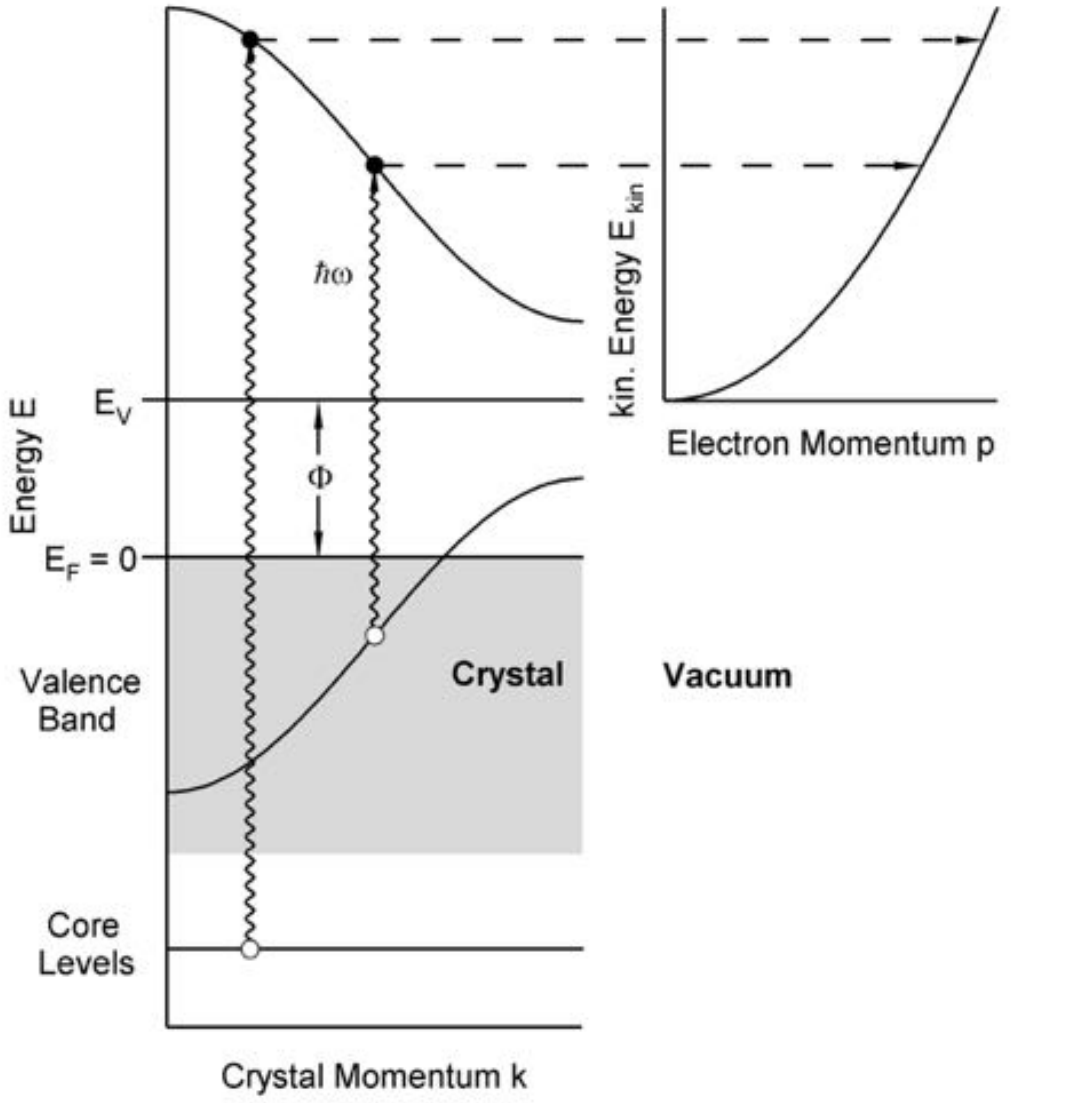
Too low energy to exceed work function

Limiting factor is that electrons can leave the crystals, not how deep photons can enter

Too small BZ and Small cross section (photons don’t really kick electrons out)

Optimal range for ARPES

ENERGY CONVERSION:



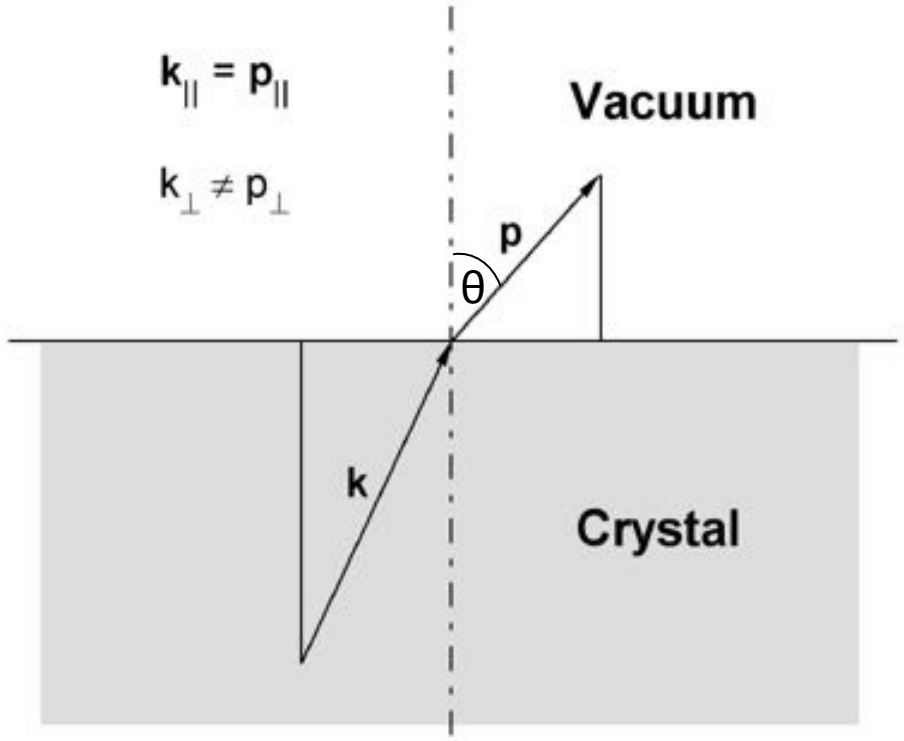
Measured kinetic Energy
Wanted: binding energy

$$E_i = \hbar\omega - \Phi - E_{kin}$$

with
E_{kin}: kinetic energy of the emitted electron
Φ: work function
E_i: initial state energy (negative binding energy)
ħω: photon energy

The photoelectron has a certain momentum and kinetic energy:
The energy reference for the binding energy is the Fermi level.

MOMENTUM CONVERSION:

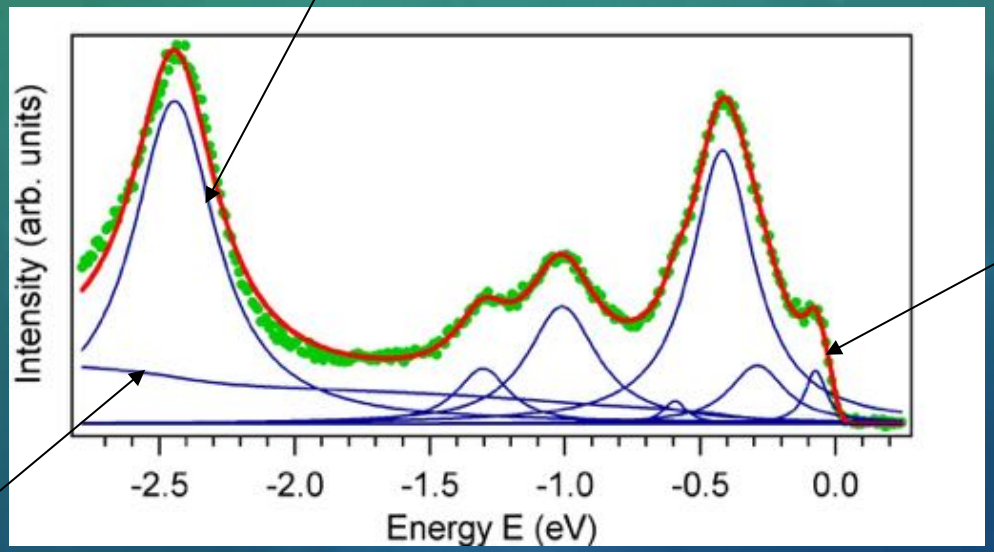


Adjust: exit angle θ
Wanted: momentum ($K_{||}$)

The photoelectron has a certain momentum and kinetic energy:
Only the momentum component parallel to the surface is conserved.

$$k\downarrow|| = \sqrt{2m}/\hbar \sqrt{E\downarrow kin} \sin\theta$$

ENERGY DISTRIBUTION CURVES (EDCS)



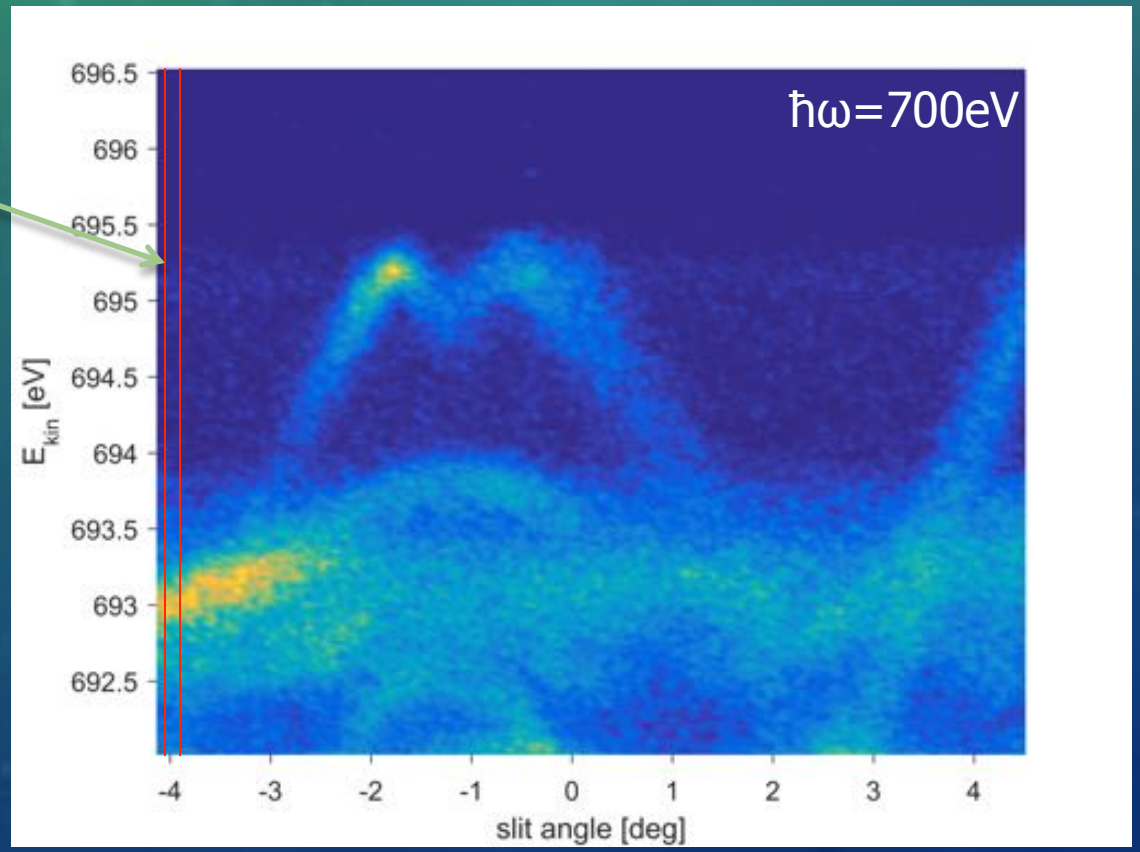
Normal emission is an important position as here the Γ-points are located.

Fit of an EDC:
- Lorentz curve
- Fermi-Dirac Function
- Shirley Background

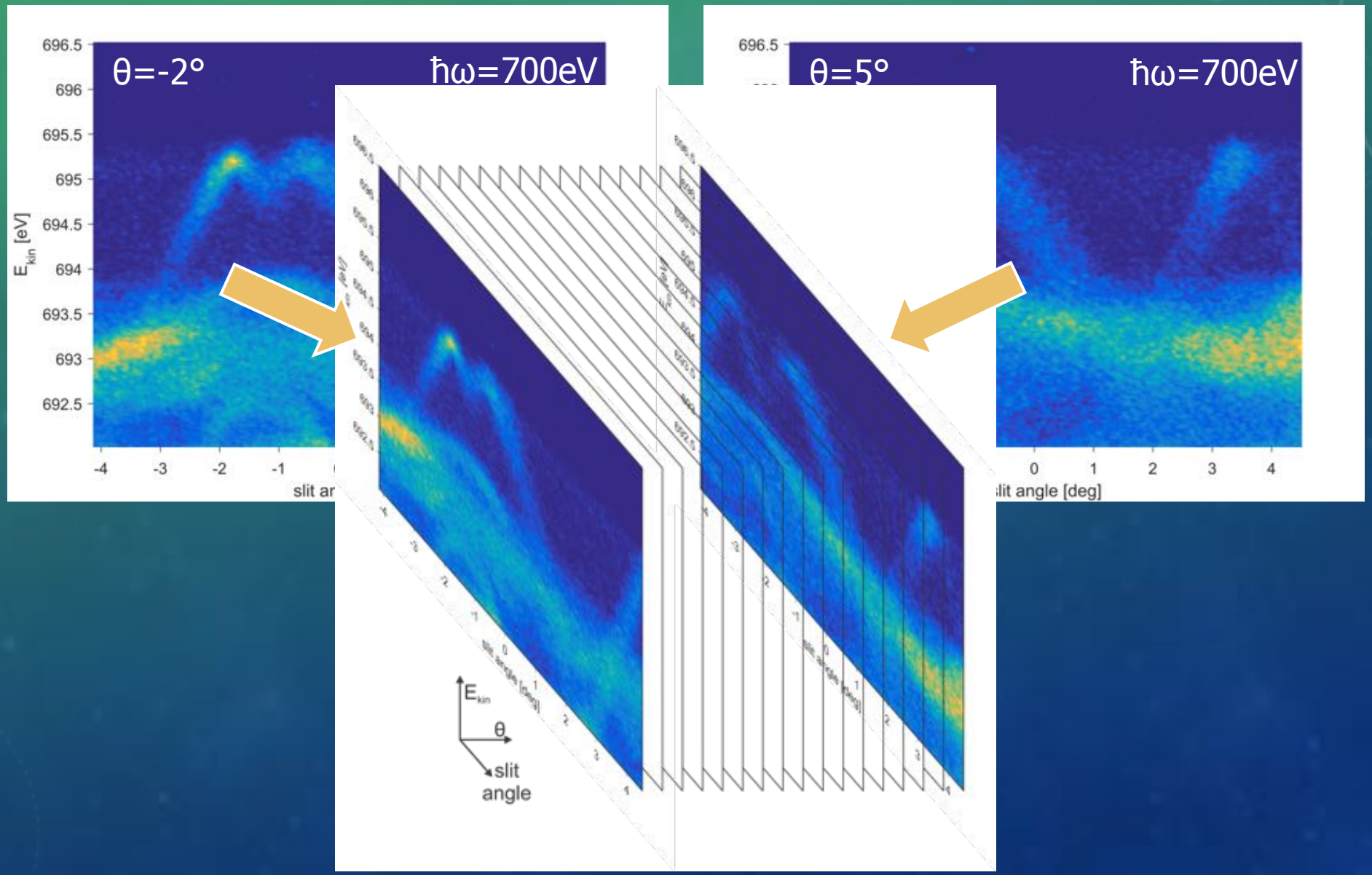
THE IMAGE WE GET OUT OF THE MACHINE

Analyzer usually contains a CCD camera nowadays, which allows to measure EDCs as a function of slit angle showing the band structure.

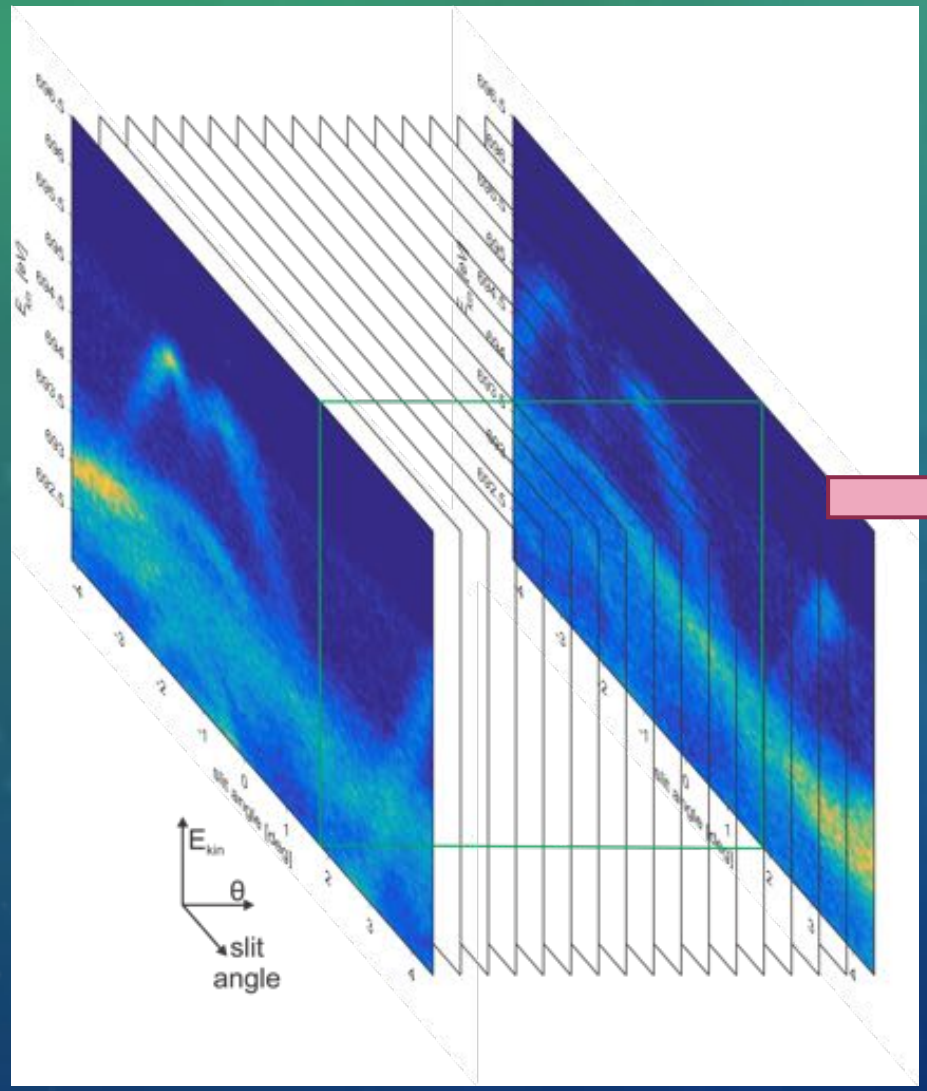
Individual EDCs



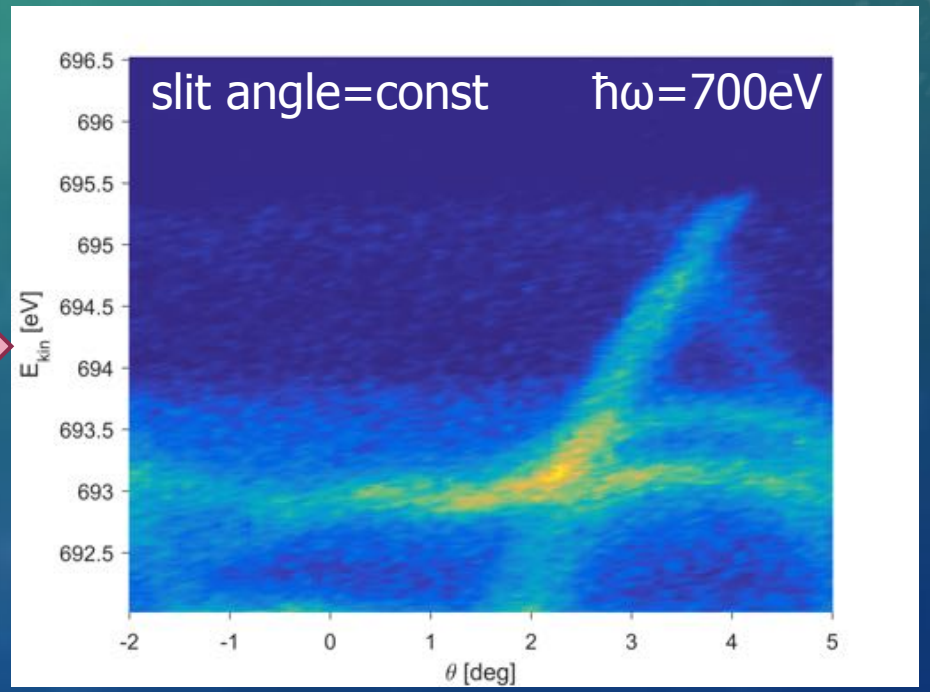
MEASURING THE FULL BZ



PLOTTING ALONG DIFFERENT DIRECTIONS

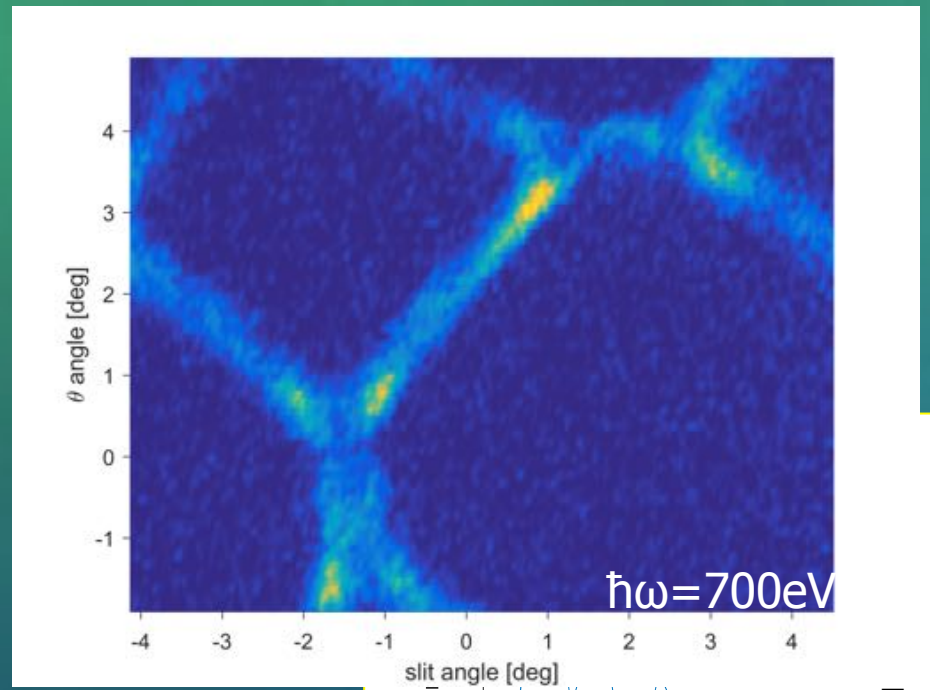


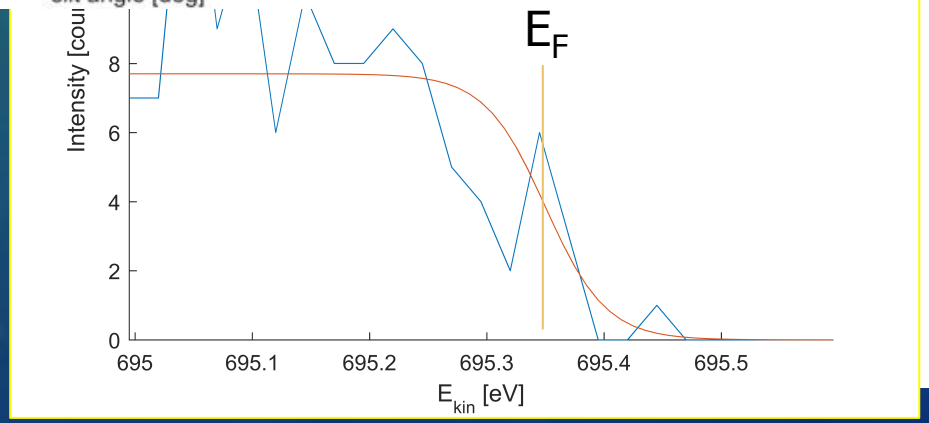
Cut along the slit angle

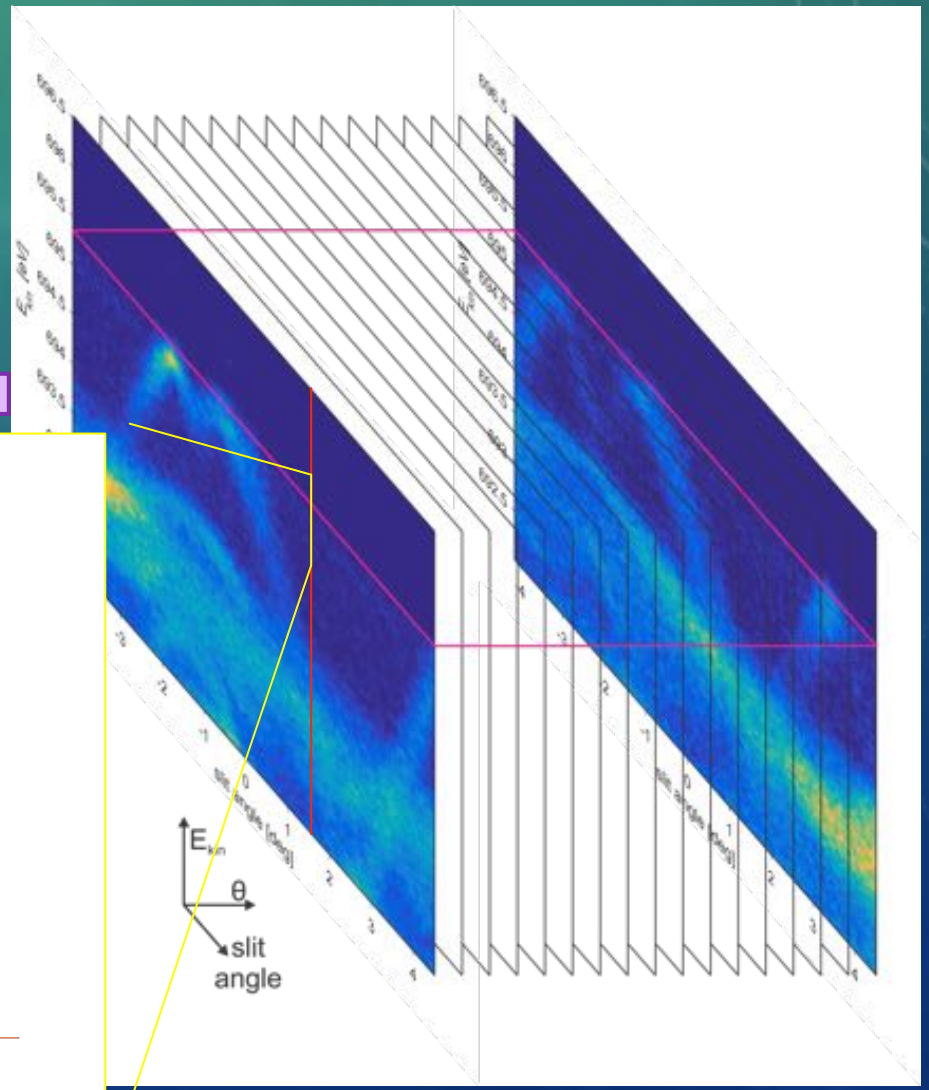


FERMI SURFACE PLOT

Constant energy plot - FS





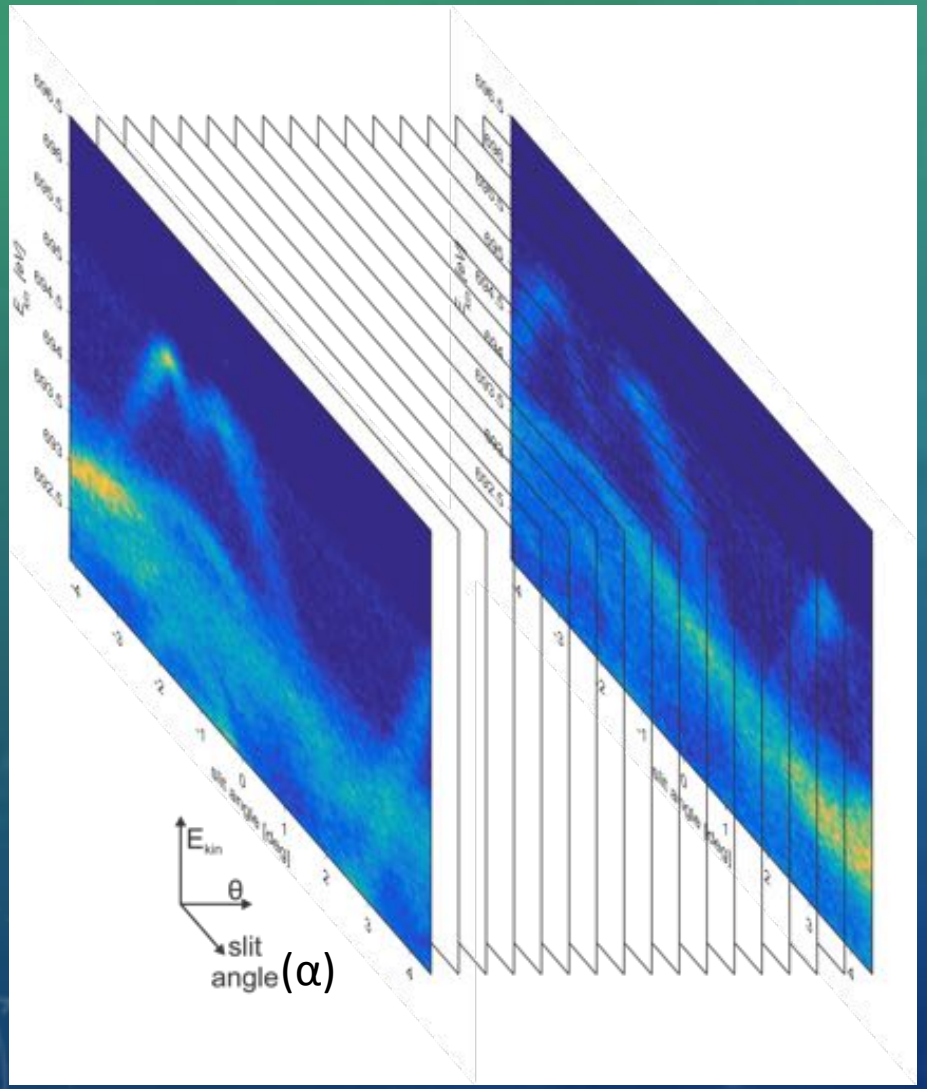


K SPACE CONVERSION

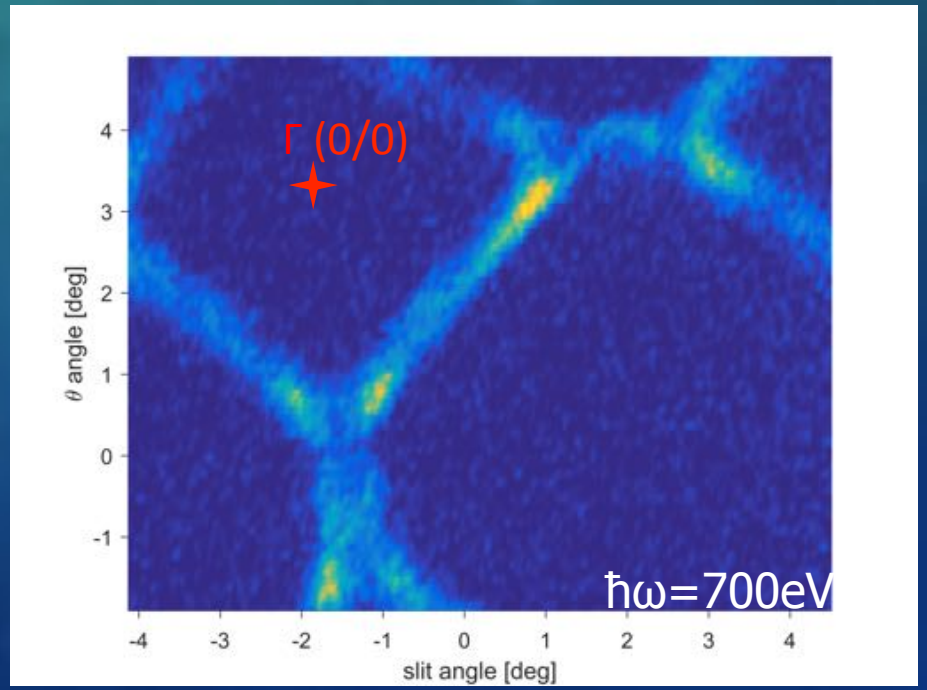
$$E_B = E_F - E_{kin}$$

$$k_x = \sqrt{2m}/\hbar \sqrt{E_{kin}} \sin\alpha \cos\theta$$

$$k_y = \sqrt{2m}/\hbar \sqrt{E_{kin}} \sin\theta$$



Constant energy plot - FS



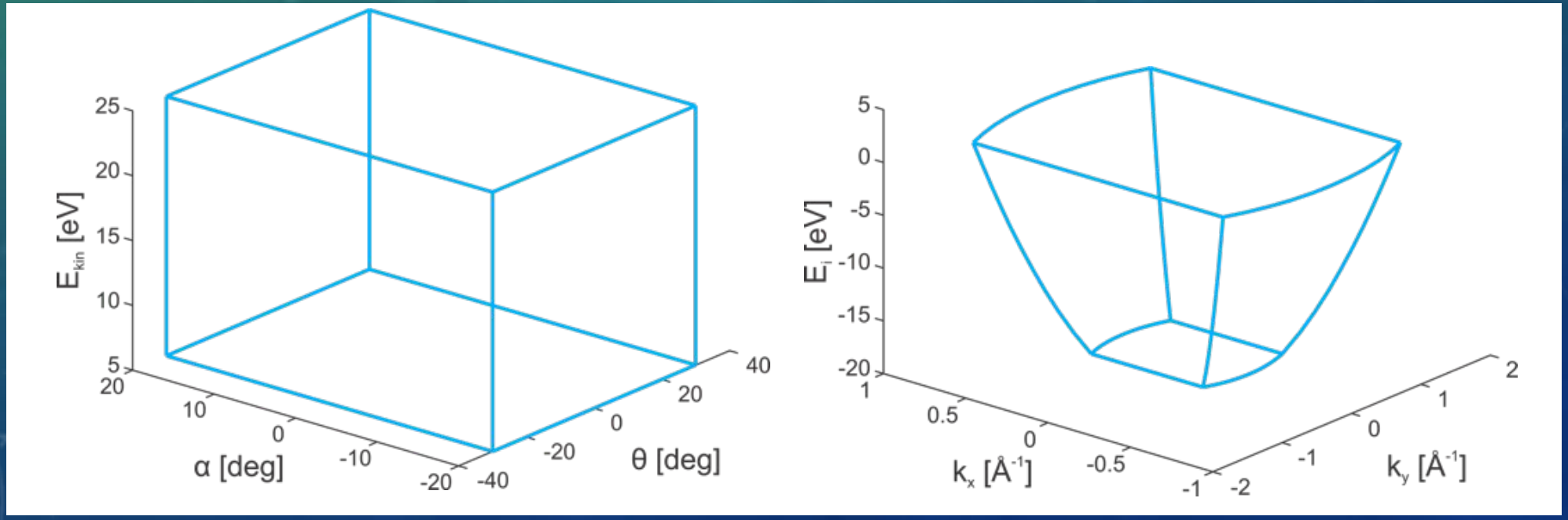
K SPACE CONVERSION

$$k_x = \sqrt{2m}/\hbar \sqrt{E_{kin}} \sin\alpha \cos\theta$$

$$k_y = \sqrt{2m}/\hbar \sqrt{E_{kin}} \sin\theta$$

≈ 0.512

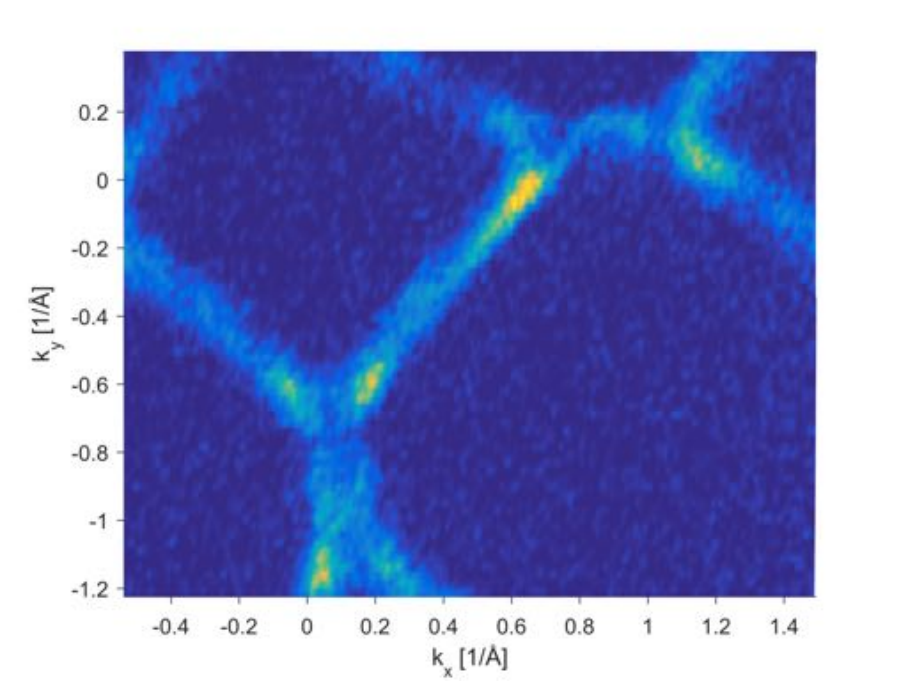
Important:
Constant angle slices are not constant $k_{||}$ slices
→ interpolation between data points necessary
Constant energy slices remain meaningful

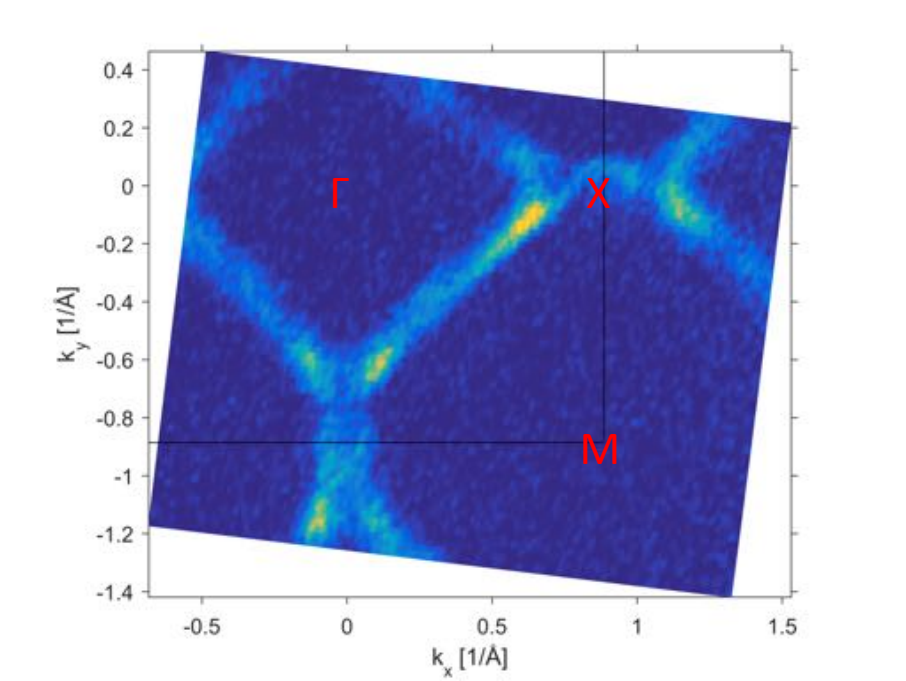


FINALIZING YOUR DATA ANALYSIS

Usually k_x and k_y are defined along high symmetry lines
→ rotate data cube after conversion

$$(k_x \; k_y) = \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix}$$





ARPES DATA ANALYSIS - SUMMARY

Steps:

1. Find α-offset, θ-offset (Γ should be at (0/0)) and E_F
   - find Γ through symmetry and sample geometry
   - determine E_F by fitting to Fermi-Dirac function
2. Use conversion equations

$$E_B = E_F - E_{kin}$$

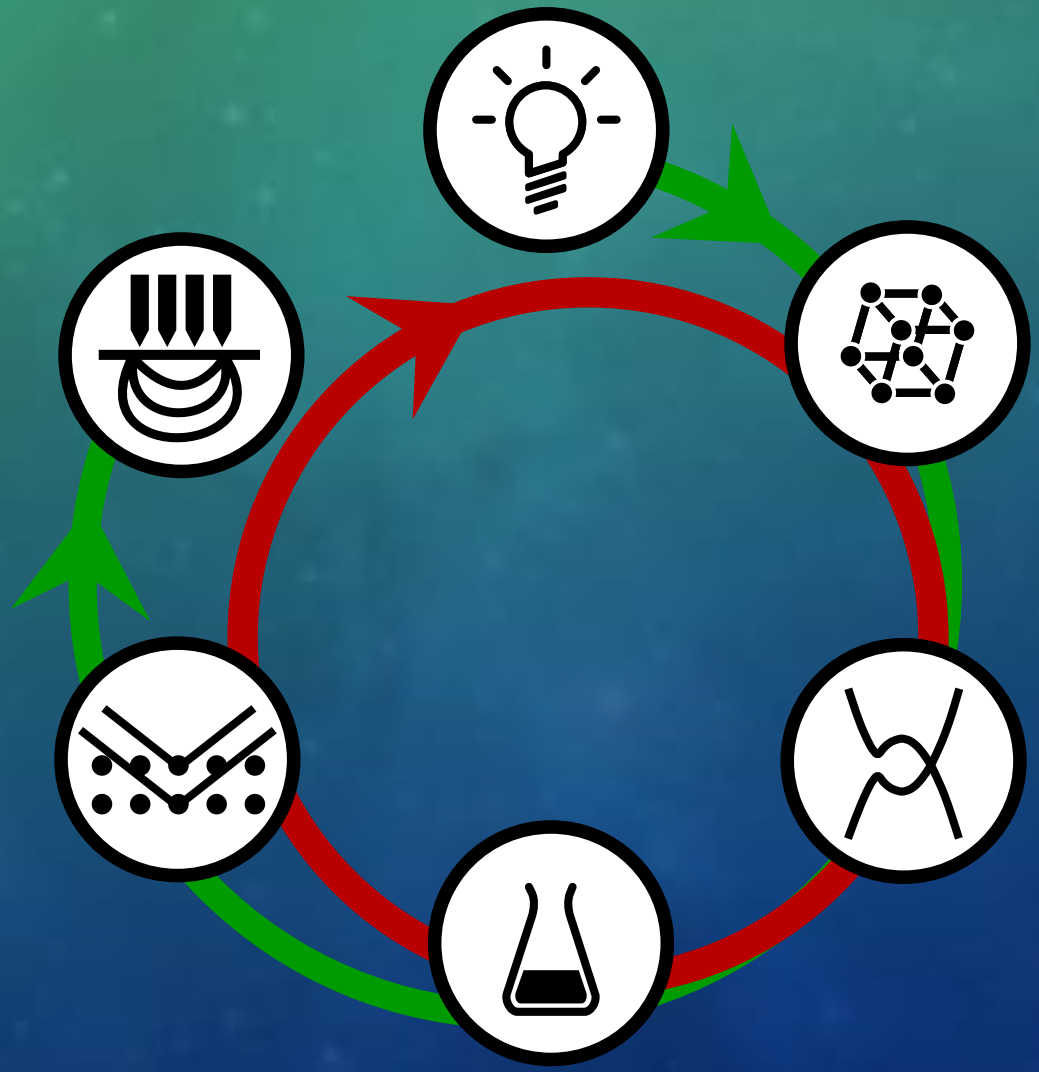
$$k_x = \sqrt{2m}/\hbar \sqrt{E_{kin}} \sin\alpha \cos\theta$$

$$k_y = \sqrt{2m}/\hbar \sqrt{E_{kin}} \sin\theta$$

3. Rotate data cube to align high symmetry lines along k_x or k_y

$$(k_x' \; k_y') = \begin{pmatrix} \cos\varphi & -\sin\varphi \\ \sin\varphi & \cos\varphi \end{pmatrix} (k_x \; k_y)$$

SOME EXAMPLES OF THE “FULL LOOP”



WHERE TO LOOK?

- Roald Hoffmann and Wolfgang Tremel: Phase transitions in square net compounds

Square Nets of Main Group Elements in Solid-State Materials

Wolfgang Tremel[1] and Roald Hoffmann*

Contribution from the Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853. *Received May 29, 1986*

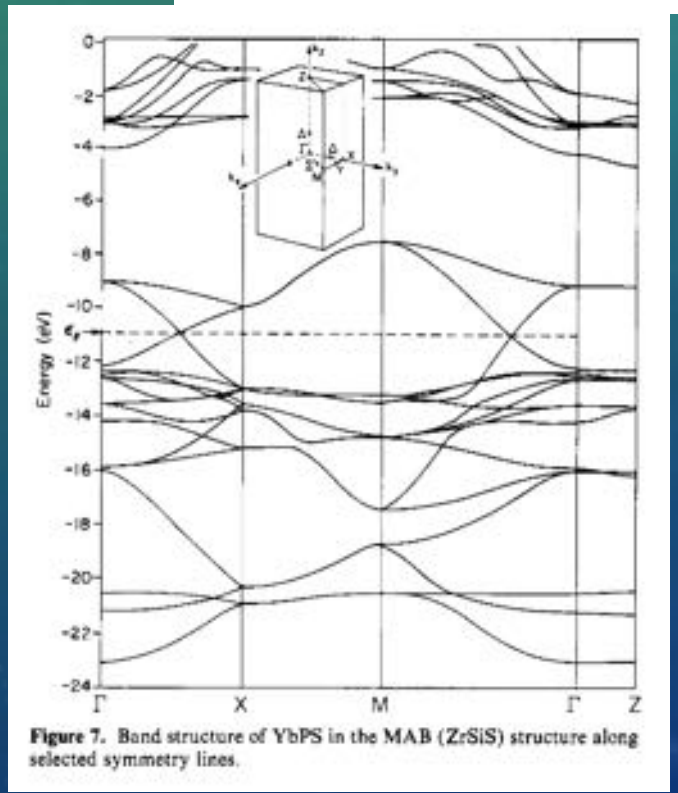
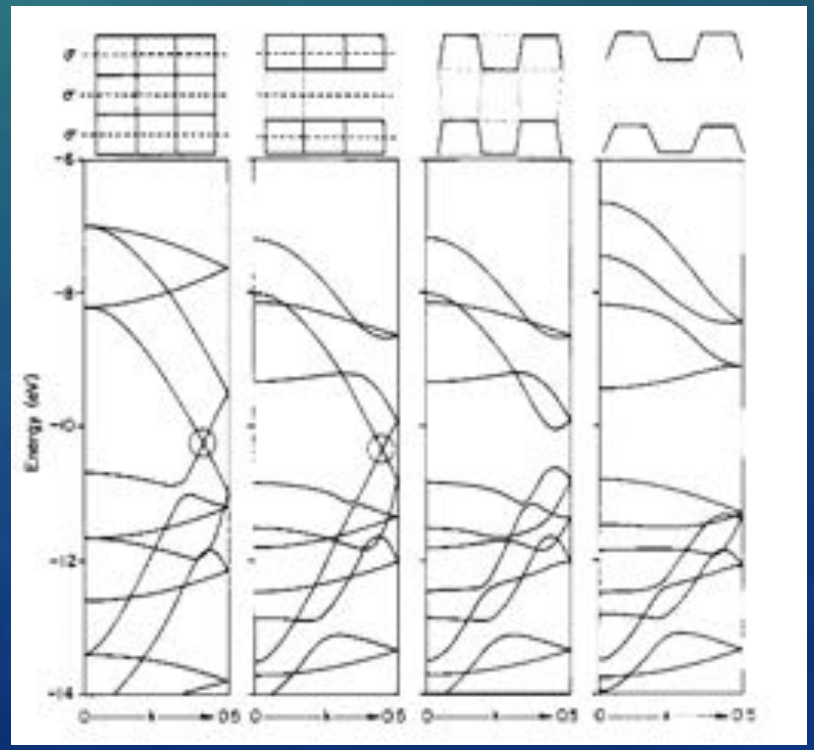
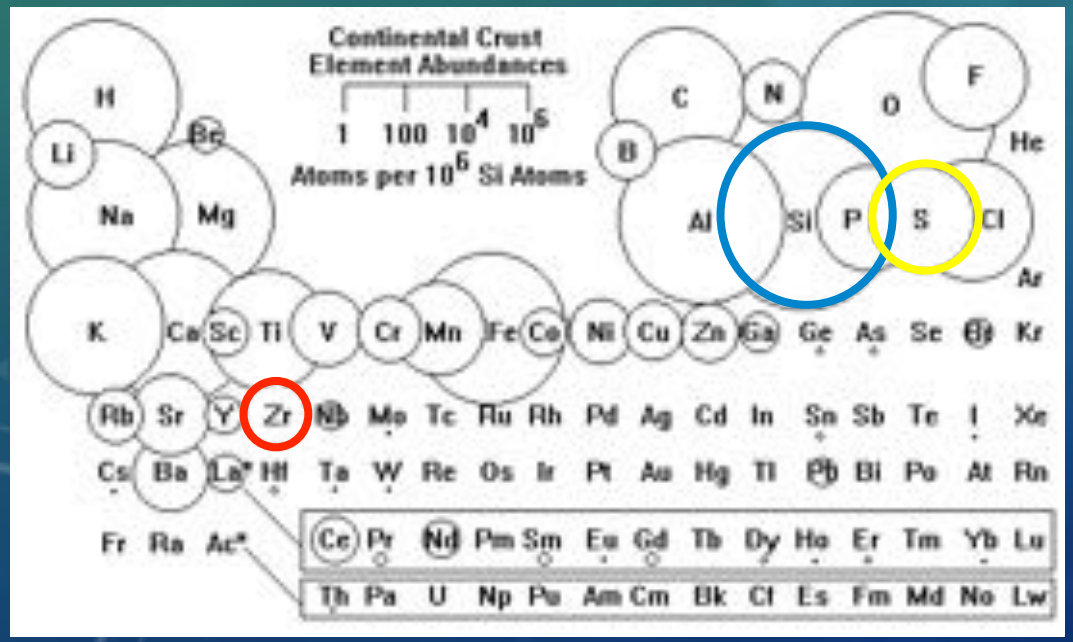


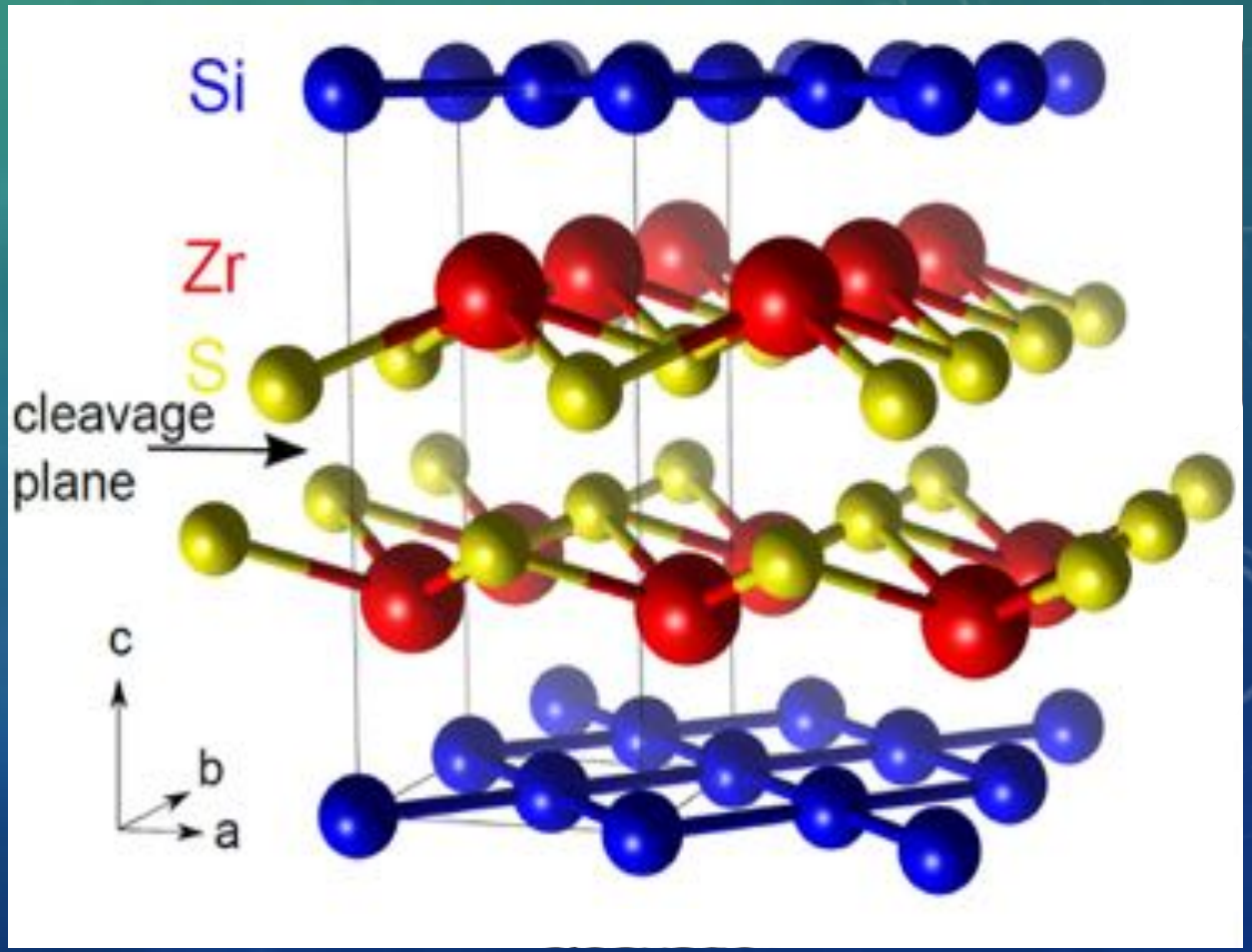
Figure 7. Band structure of YbPS in the MAB (ZrSiS) structure along selected symmetry lines.



ZrSiS WOULD FULFILL ALL MY REQUIREMENTS

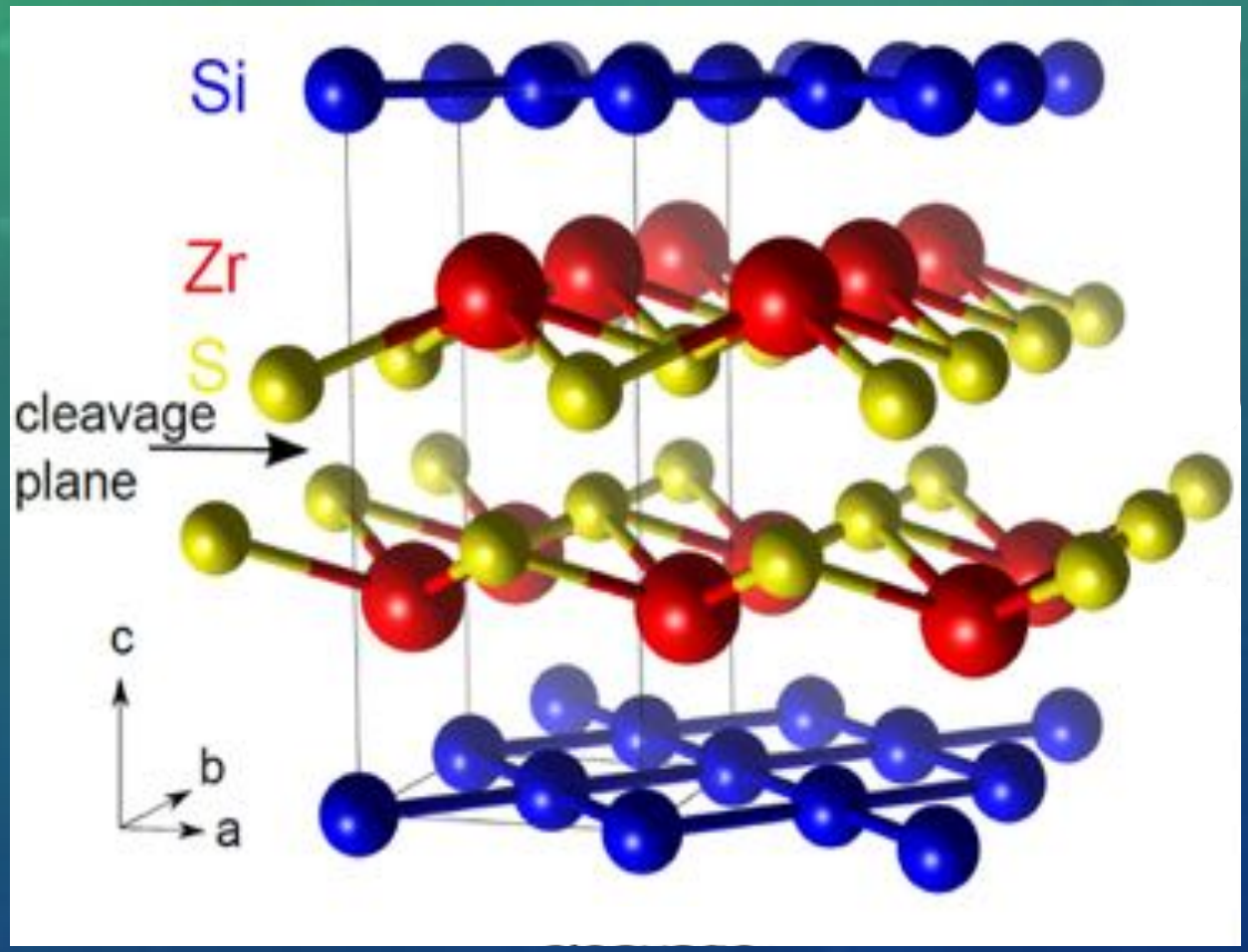
- Non toxic
- Only earth abundant elements
- Very stable in air and water
- Should be cleavable

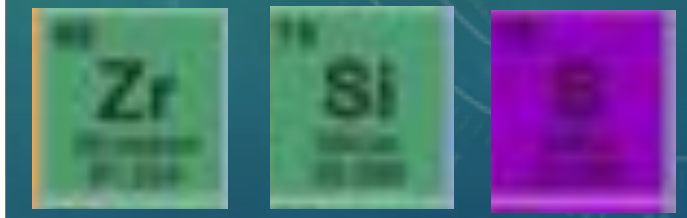




ZINTL PHASES: COUNT ELECTRONS TO FIND NUMBER OF BONDS

- Number of bonds in Polyanions:
- b(xx) = 8(or18) - VEC(x)





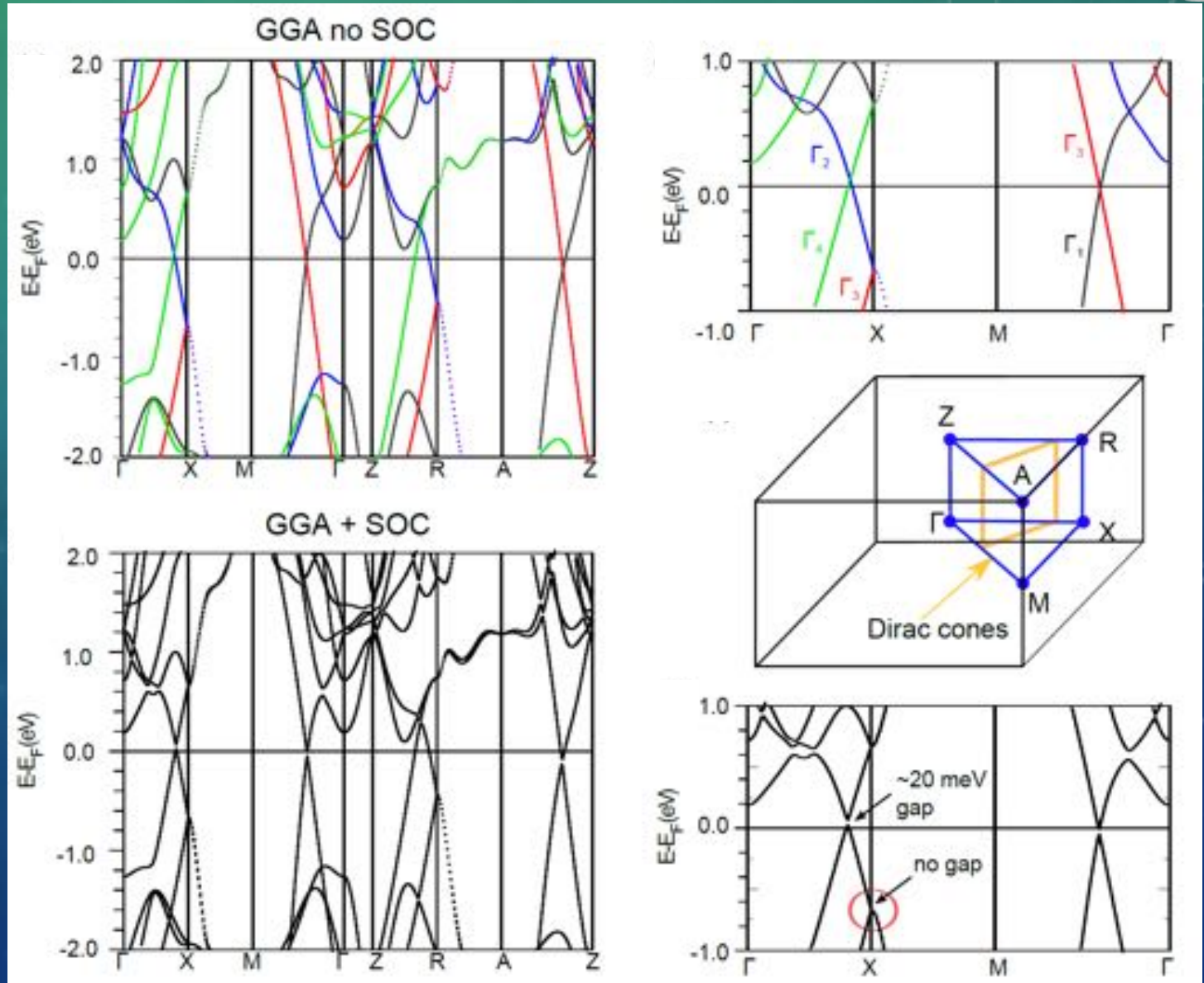
4+4+6 = 14

14 per Si

b(Si-Si)=18-14 =4

BULK BAND STRUCTURE OF ZrSiS

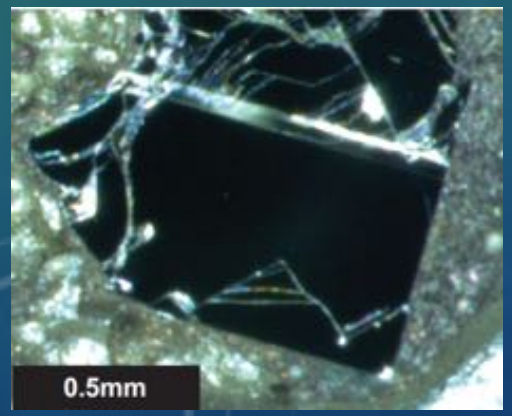
- Huge range of linear dispersion
- Many Dirac cones around the Fermi level
- Line node!
- Get gapped by SOC, but SOC is small



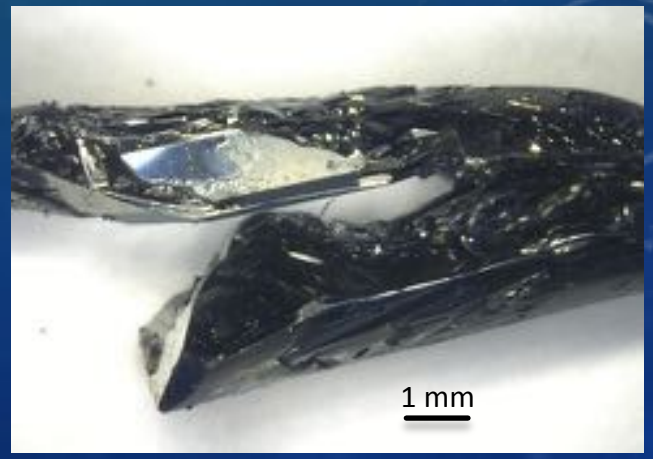
Schoop, Ali, Straßer, Topp, Duppel, Parkin, Lotsch, Ast, *Nat. Comm., 7, 11696 (2016)*

MAKING THE SAMPLE

- Large crystals grown with vapor transport
- Cleaves well



$$Zr + Si + S \xrightarrow{I_2} ZrSiS$$



CHARACTERIZING THE SAMPLE

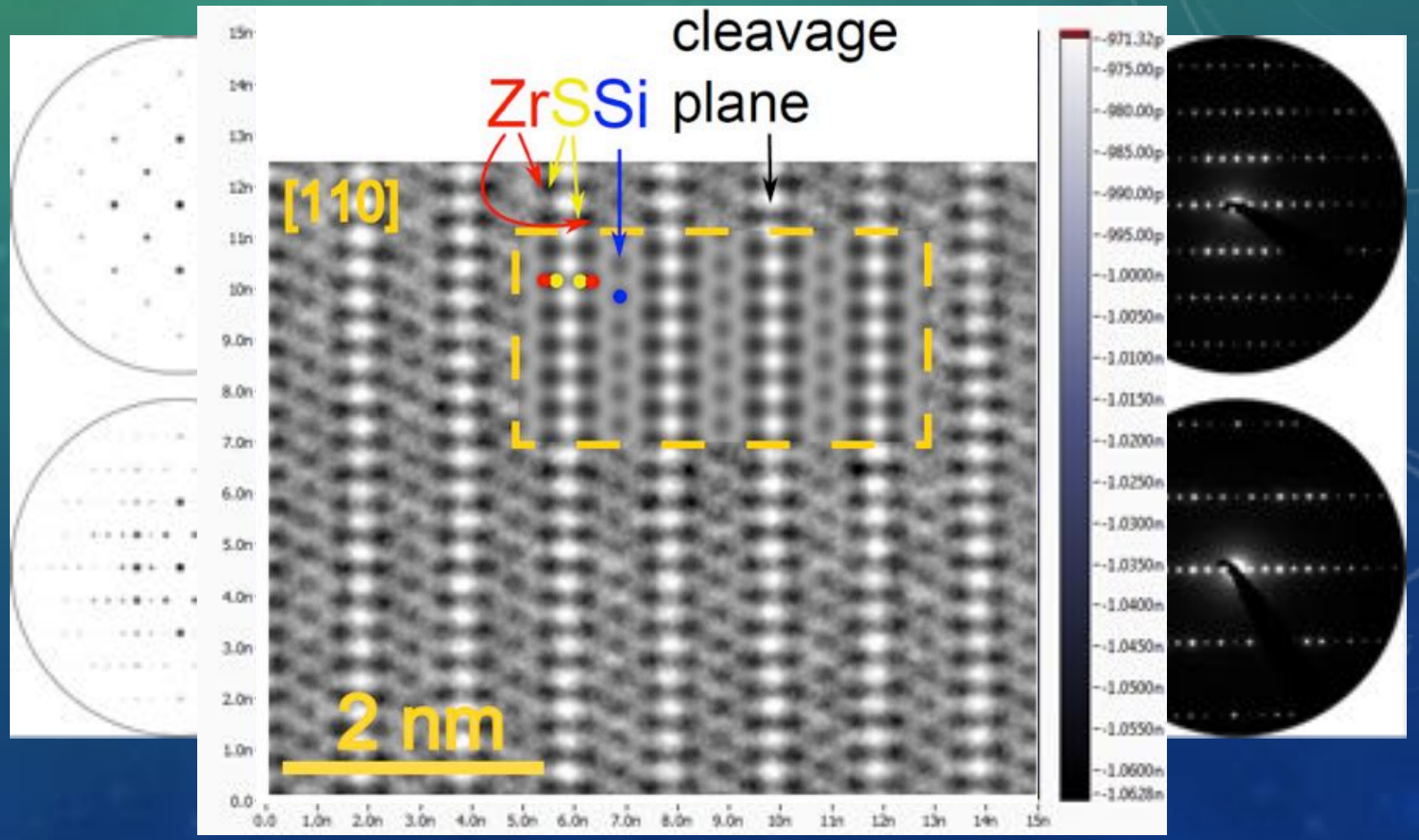
1) single crystal diffraction: R value of 2%

2) electron diffraction

3) High resolution TEM

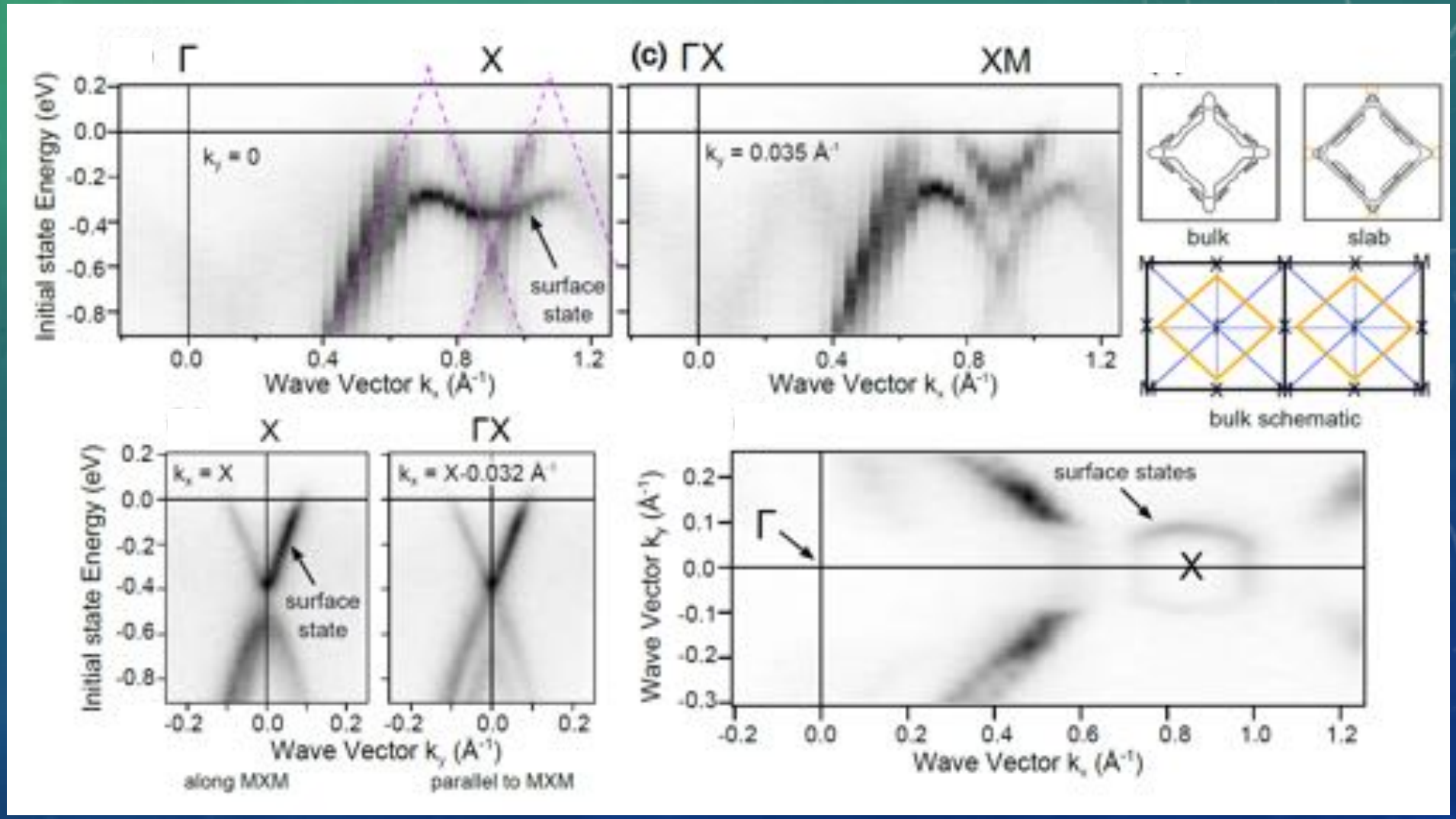
4) Chemical analysis

5) STM topography



ARPES MEASUREMENTS

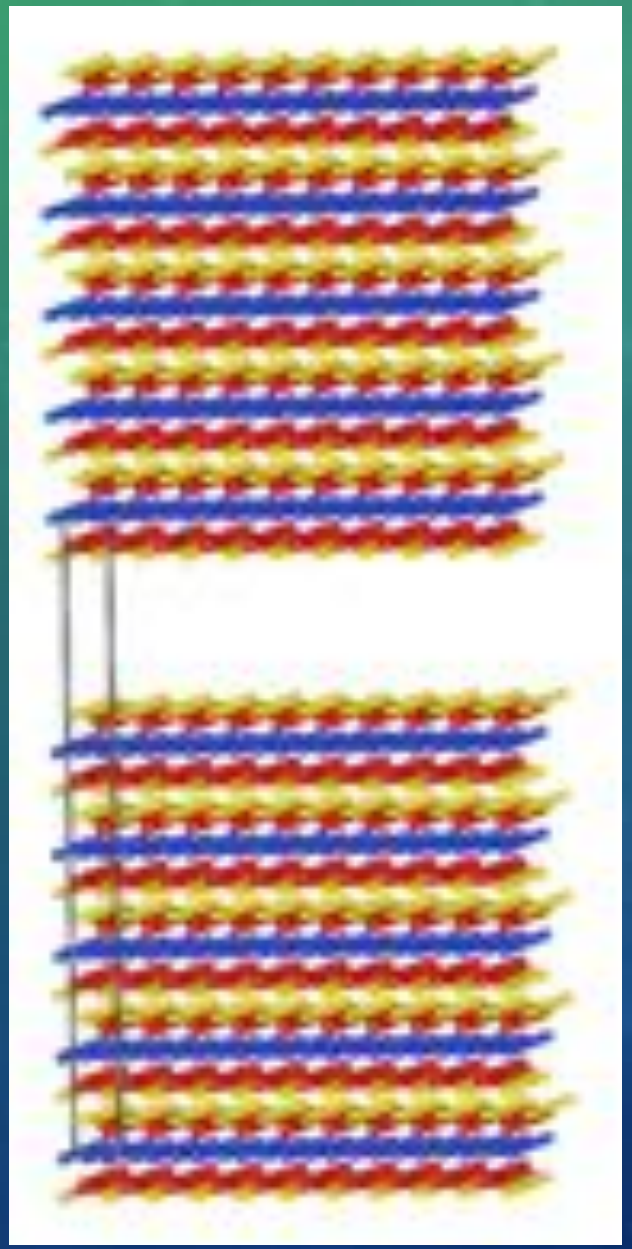
- Surface states appear
- Large liner dispersion visible

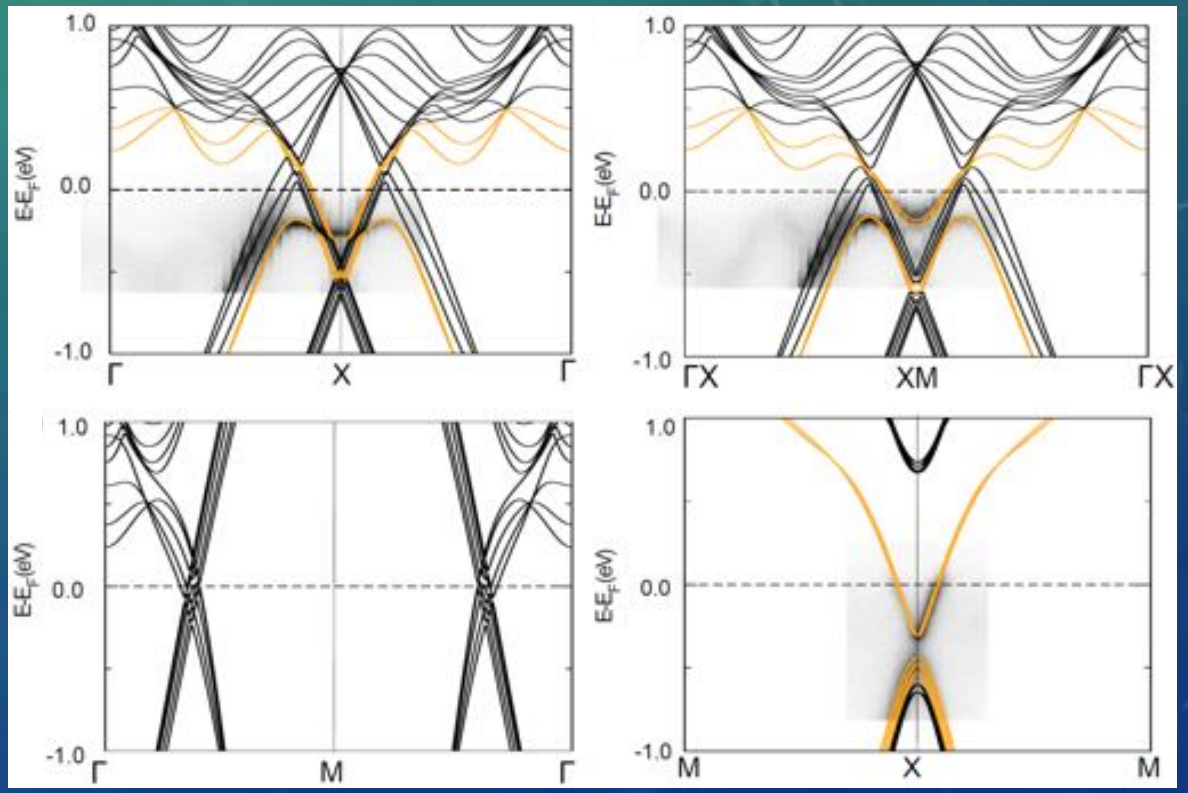


Schoop, Ali, Strasser, Topp, Duppel, Parkin, Lotsch, Ast, *Nat. Comm., 7, 11696 (2016)*

SURFACE STATES?

- Calculate a slab
- Perfect match between DFT and ARPES





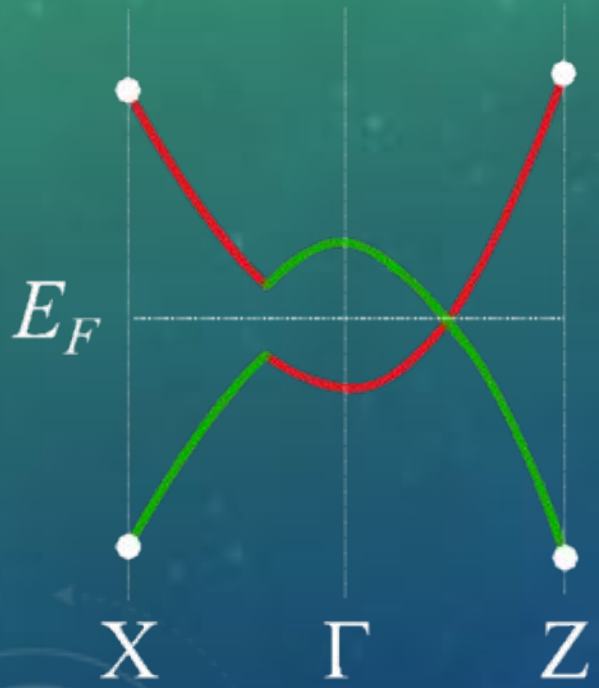
GOING BEYOND ZrSiS

- The family of MXZ compounds with the same structure than ZrSiS hosts many more Dirac materials
- Nearly 200 more compounds to investigate
  - High tunability, lots of room for improvement!

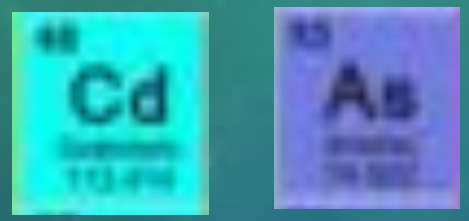
M	Z	X					
		O	S	Se	Te	As	Sb
Zr	Si	ZrSiO	ZrSiS	ZrSiSe	ZrSiTe		
	Ge		ZrGeS	ZrGeSe	ZrGeTe		
	Sn				ZrSnTe		
Hf	Si		HfSiS	HfSiSe	HfSiTe		
	Ge		HfGeS	HfGeSe	HfGeTe		
Nb	Si					NbSiAs	NbSiSb
	Ge					NbGeAs	NbGeSb
La	Sb				LaSbTe		
Ce					CeSbTe		
Pr					PrSbTe		
Nd					NdSbTe		
Sm					SmSbTe		
Gd					GdSbTe		

REALIZING NON-SYMMORPHIC SEMIMETALS

"conventional DSM"



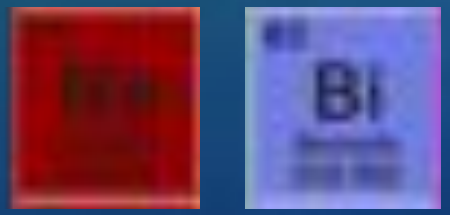
Cd_3As_2



3*2+2*5 = 16

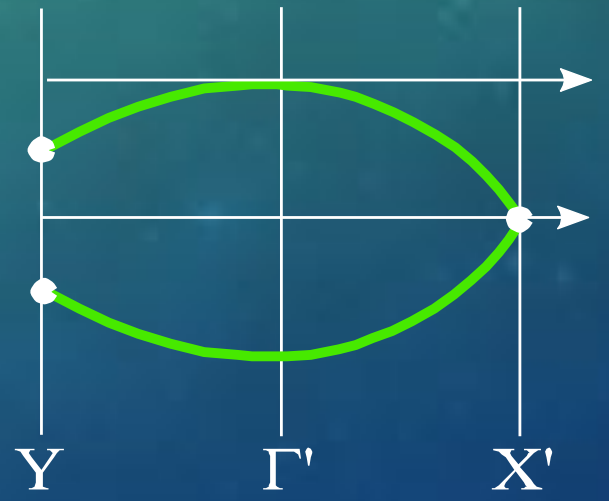
8 per As

Na_3Bi



3*1+5 = 8

"non-symmorphic DSM"



Trivial insulator (even e^-/site)

Non-trivial Dirac metal (odd e^-/site)

- Require odd electron count (per formula unit)
- Chemically unstable!

Gibson et al. Physical Review B 91 (20), 205128 (2015)

HOW TO TACKLE THIS CHALLENGE EXPERIMENTALLY?

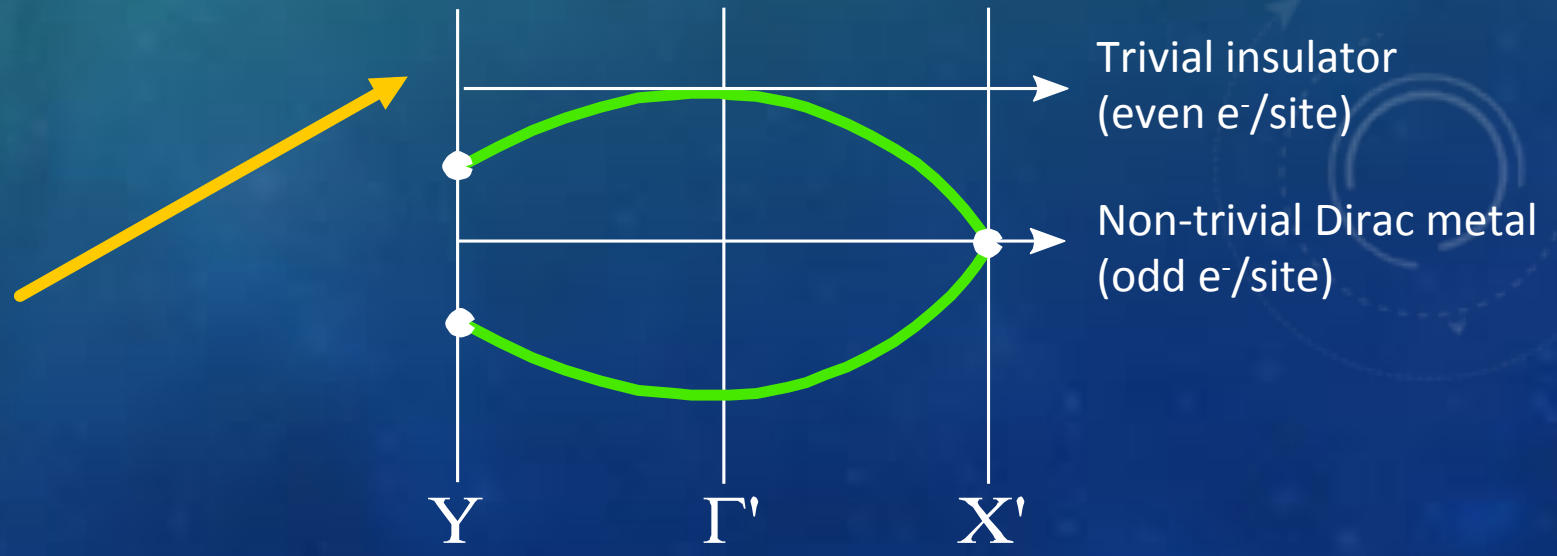
Two steps:

(a) Can we experimentally verify that band degeneracies forced by NS-Symmetry exist below the Fermi level?

(b) After finding a model compound, can we move this degeneracy to the Fermi level?

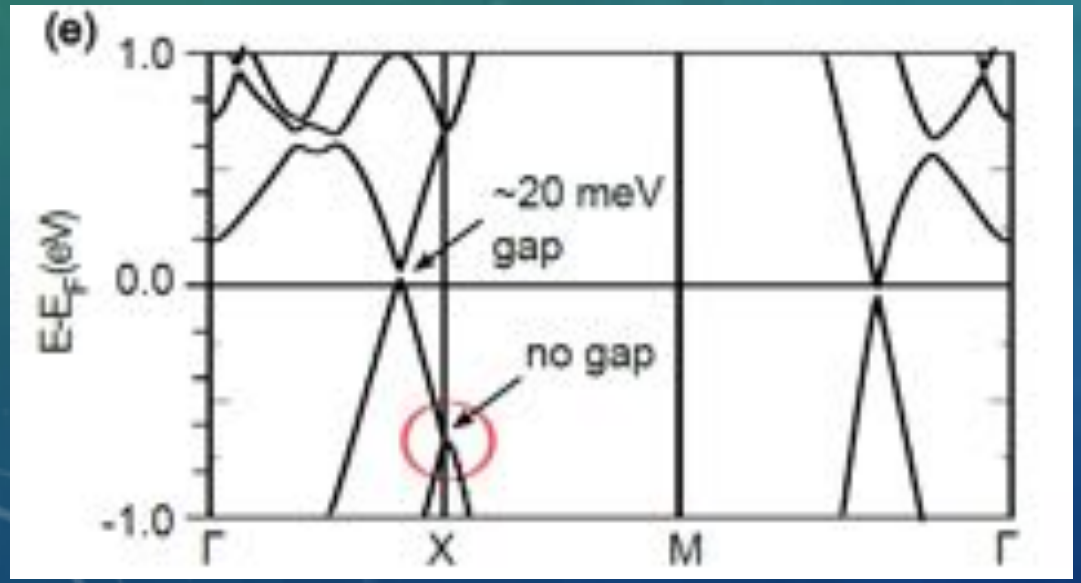
(a) Realize this case:

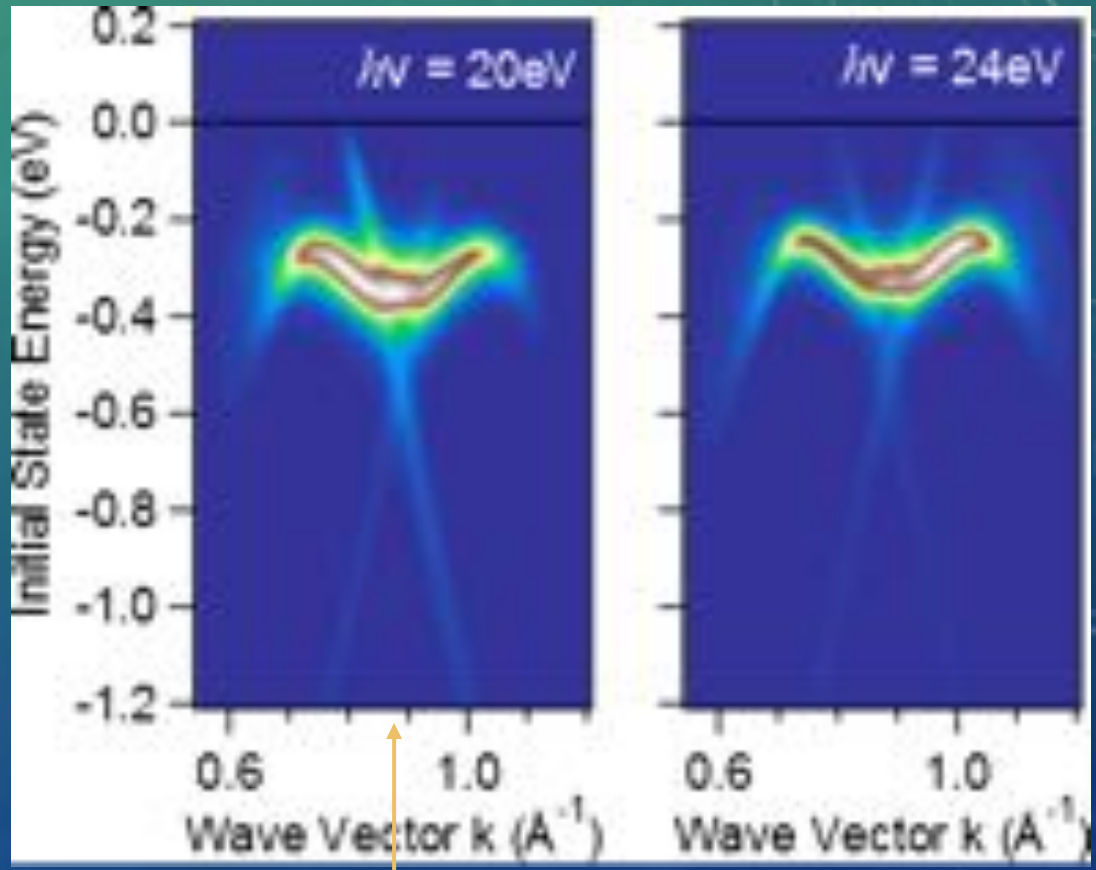
(b) Shift Fermi level



STEP A: ZrSiS

- Space group P4/nmm

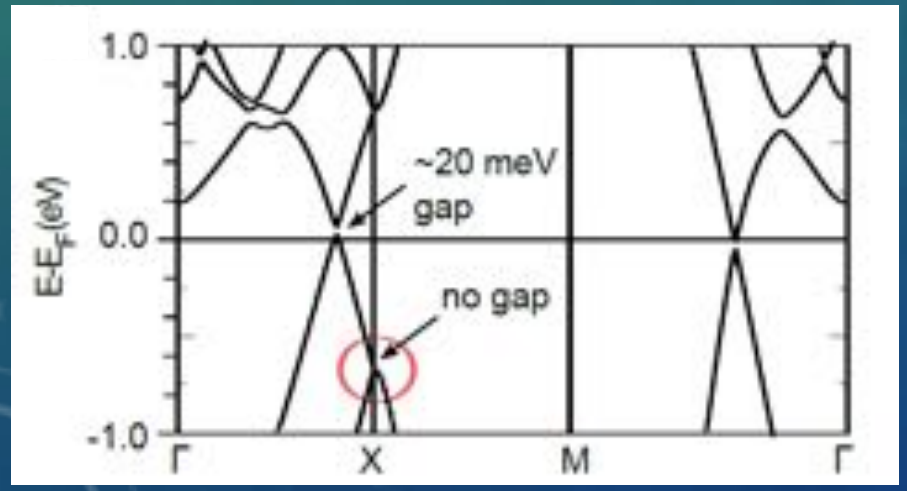




X point

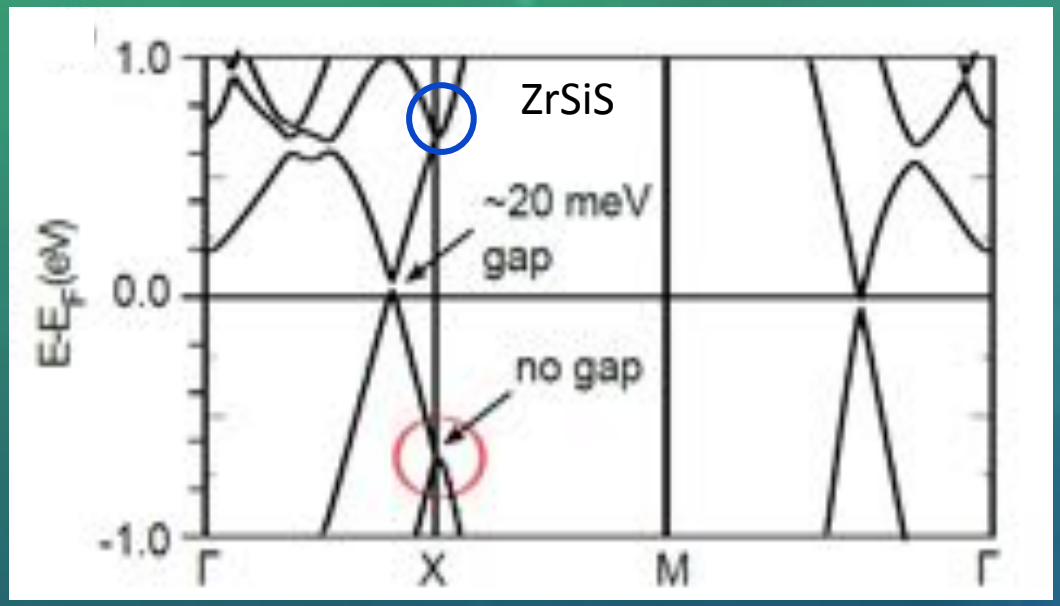
MOVE NON-SYMMORPHIC CROSSING TO THE FERMI LEVEL?

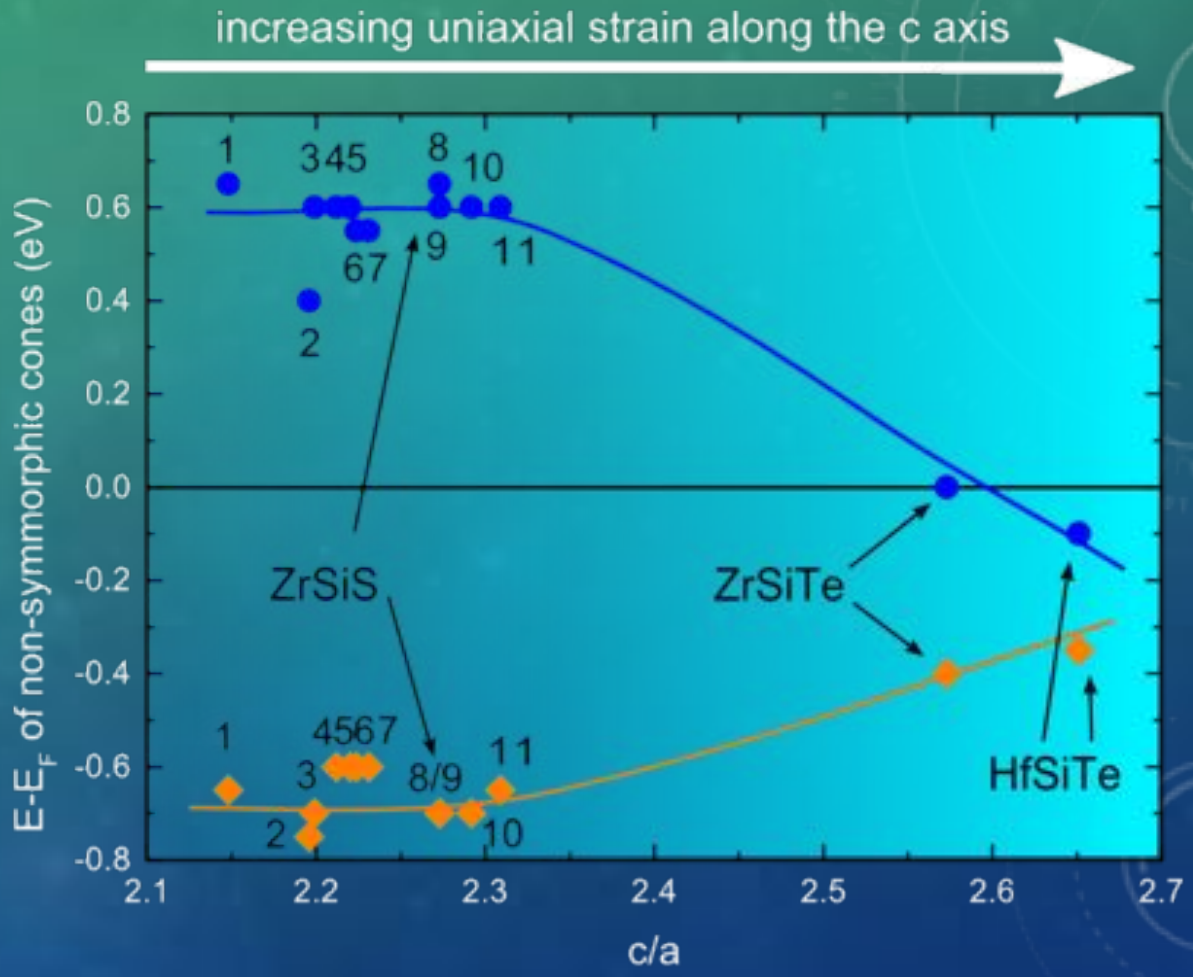
- Family of MZX compounds
- Isoelectronic



M	Z	X					
		O	S	Se	Te	As	Sb
Zr	Si	ZrSiO	ZrSiS	ZrSiSe	ZrSiTe		
	Ge		ZrGeS	ZrGeSe	ZrGeTe		
	Sn				ZrSnTe		
Hf	Si		HfSiS	HfSiSe	HfSiTe		
	Ge		HfGeS	HfGeSe	HfGeTe		
Nb	Si					NbSiAs	NbSiSb
	Ge					NbGeAs	NbGeSb
La	Sb				LaSbTe		
Ce					CeSbTe		
Pr					PrSbTe		
Nd					NdSbTe		
Sm					SmSbTe		
Gd					GdSbTe		

STEP B: ZrSiTe



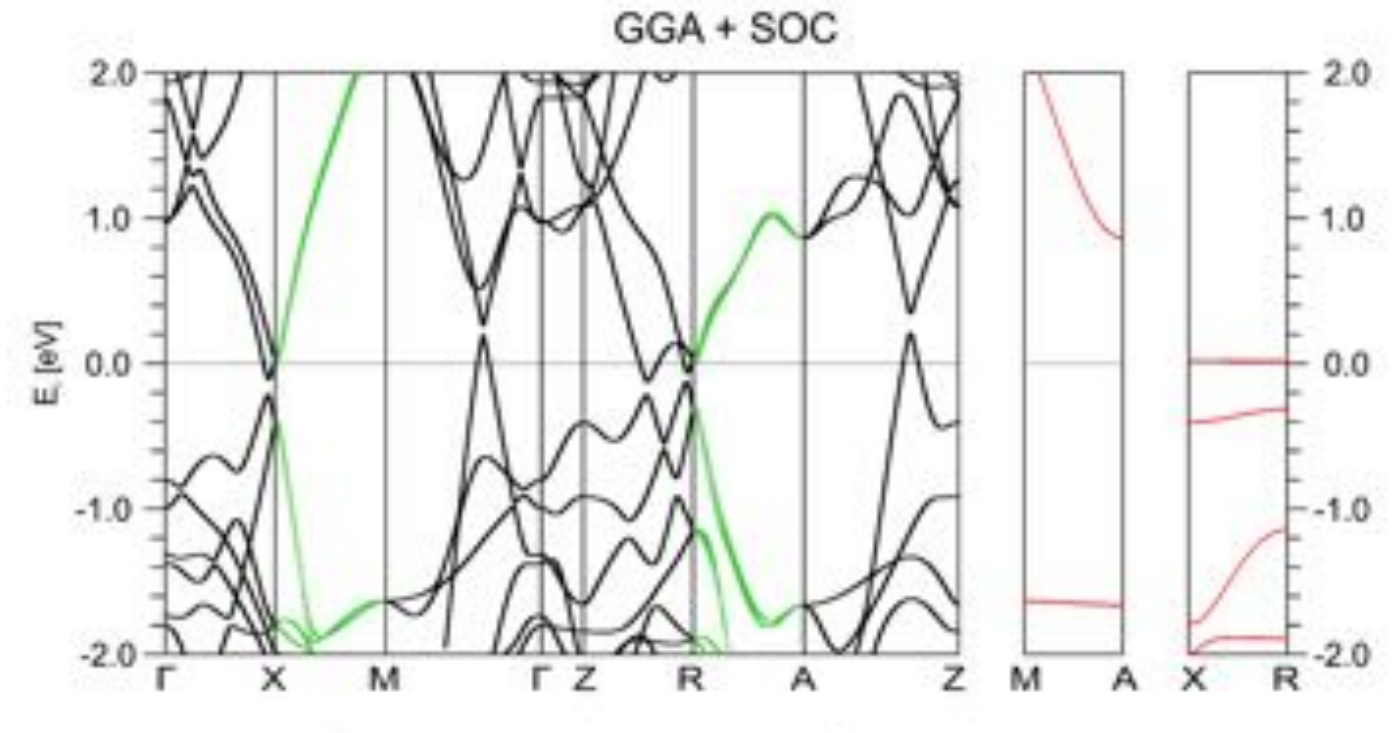


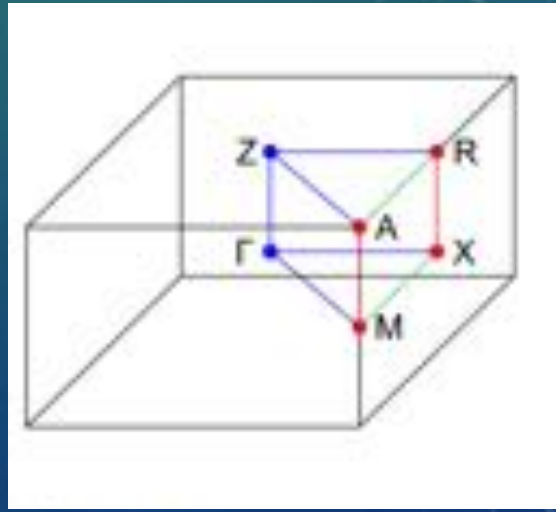
ZrSiTe:

- Non-symmorphic band degeneracy at the Fermi level

1: ZrSnTe 2: HfGeTe 3: HfGeS 4: ZrGeS 5: HfGeSe 6: ZrGeTe
7: ZrGeSe 8: ZrSiS 9: HfSiS 10: HfSiSe 11: ZrSiSe

BULK BAND STRUCTURE OF ZrSiTe

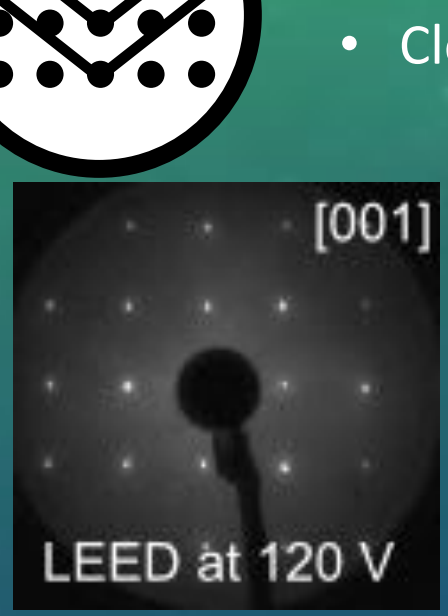


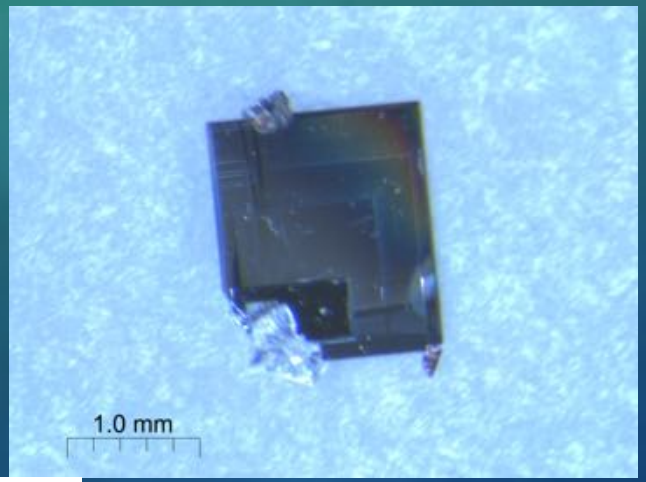


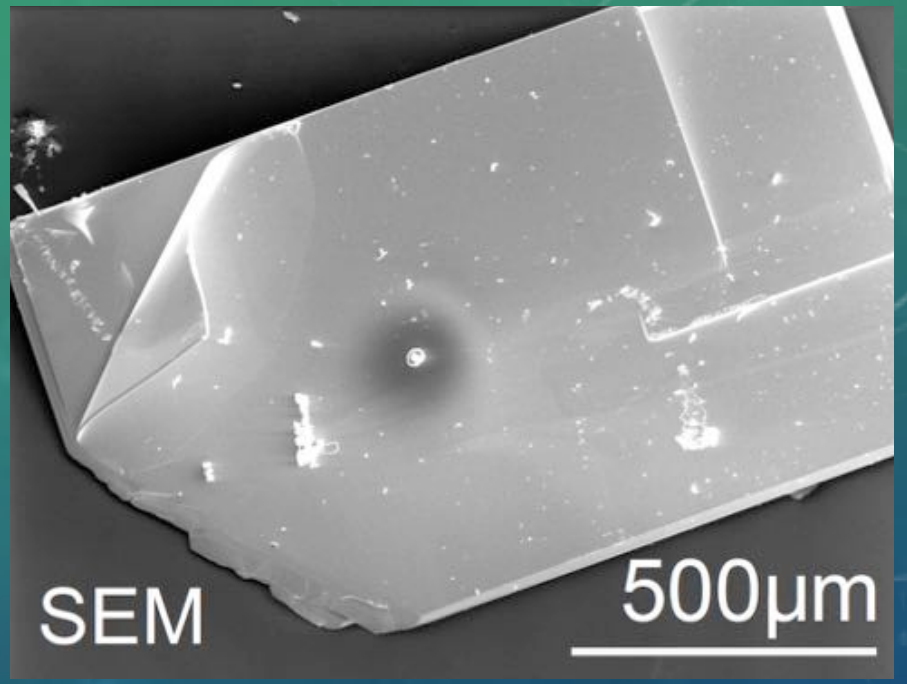
Topp, Lippmann, Varykhalov, Duppel, Lotsch, Ast, Schoop, *New J Phys.*, 18, 125014 (2016)

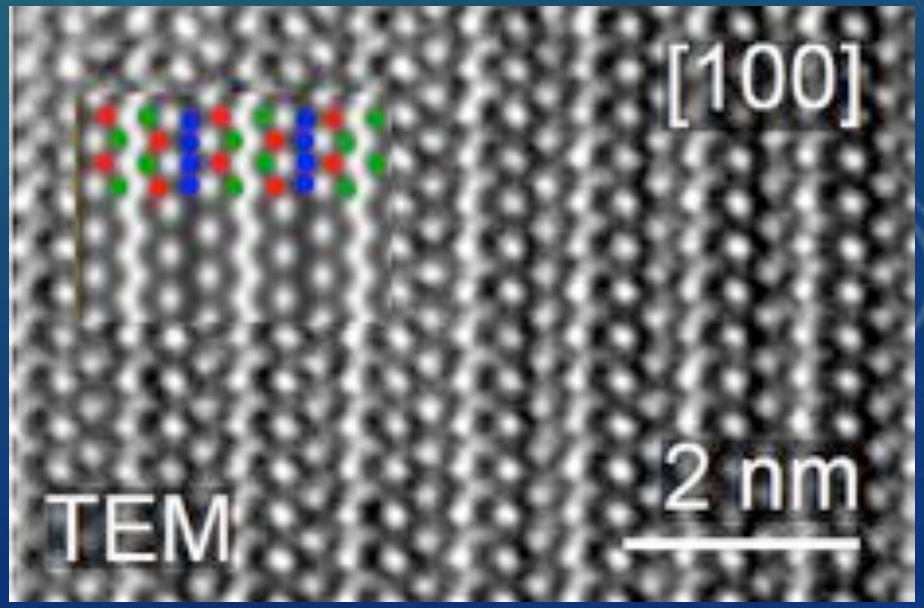
ZrSiTe CRYSTAL GROWTH

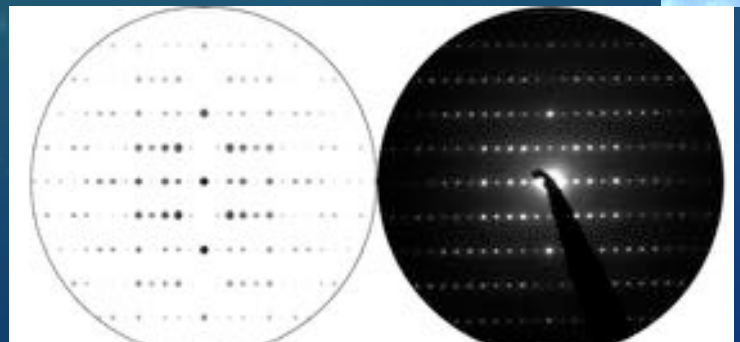
- High temperature phase! Quench samples
- Crystals are air sensitive
- Cleaves with scotch tape



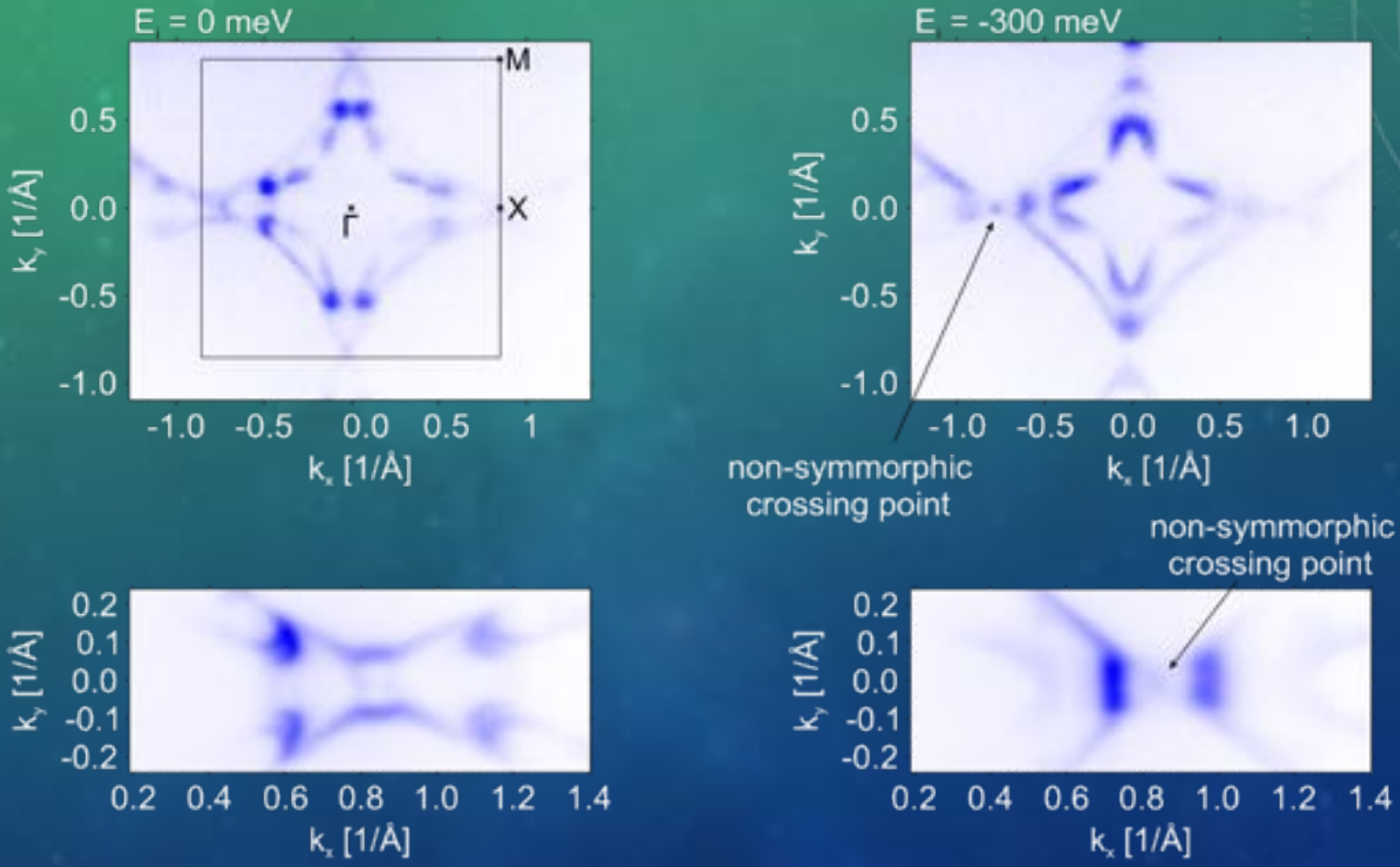






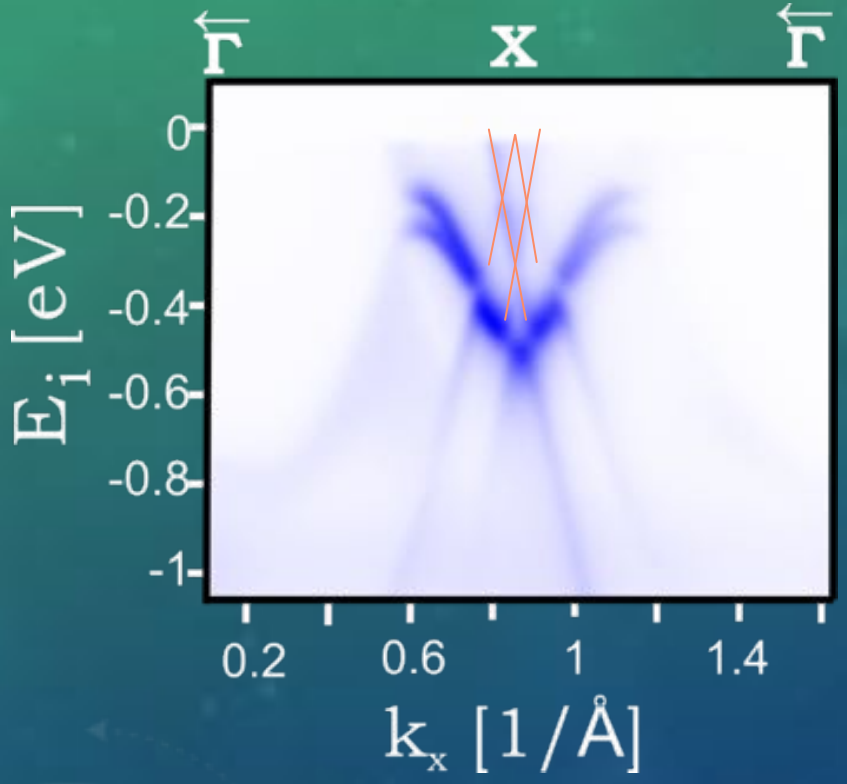


ARPES ON ZrSiTe

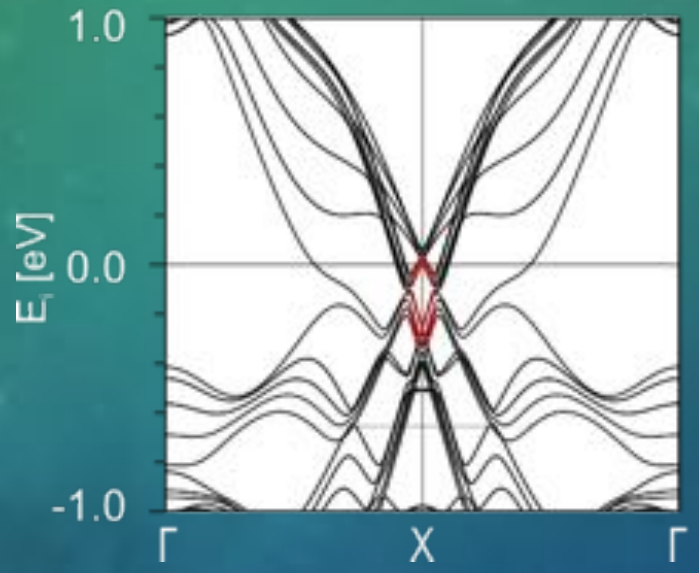


Topp, Lippmann, Varykhalov, Duppel, Lotsch, Ast, Schoop, *New J Phys.*, 18, 125014 (2016)

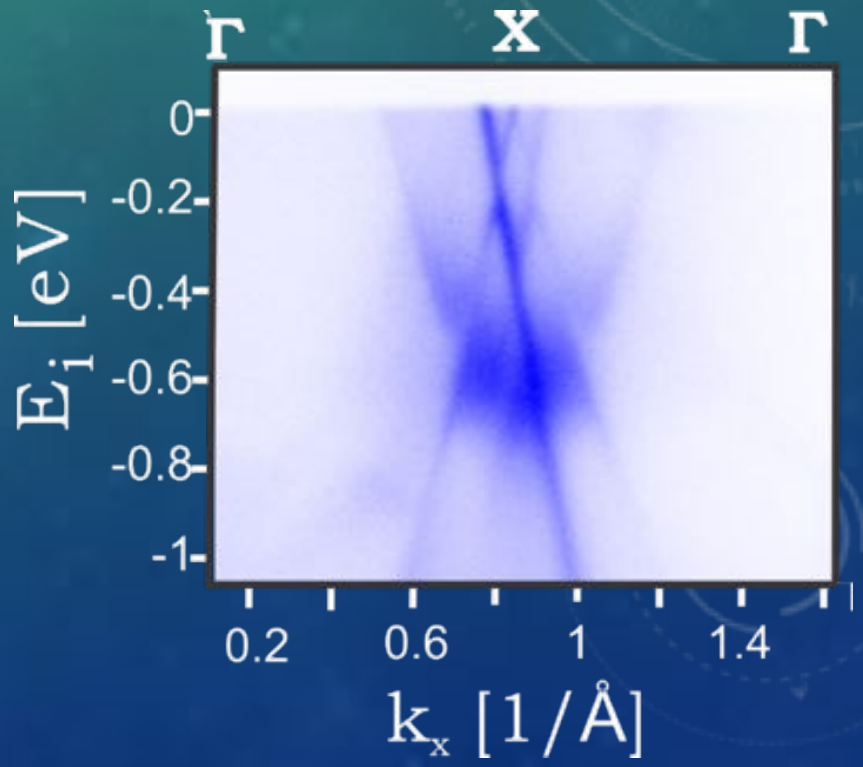
ARPES ON ZrSiTe



Slab calculation (GGA + SOC)

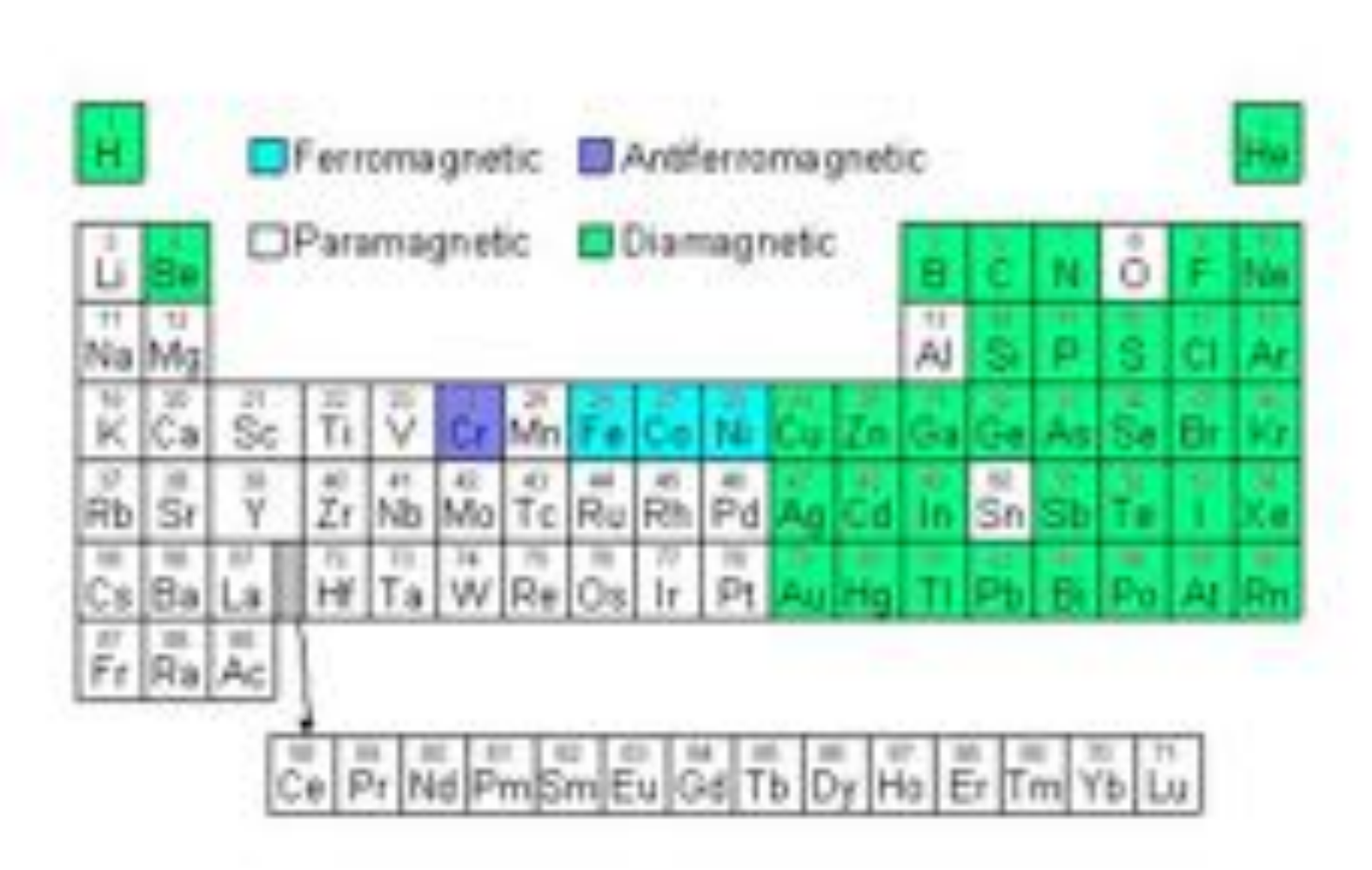


Potassium on surface



Topp, Lippmann, Varykhalov, Duppel, Lotsch, Ast, Schoop, *New J Phys.*, 18, 125014 (2016)

CAN WE USE CHEMISTRY IT MAKE WEYL SEMIMETALS?

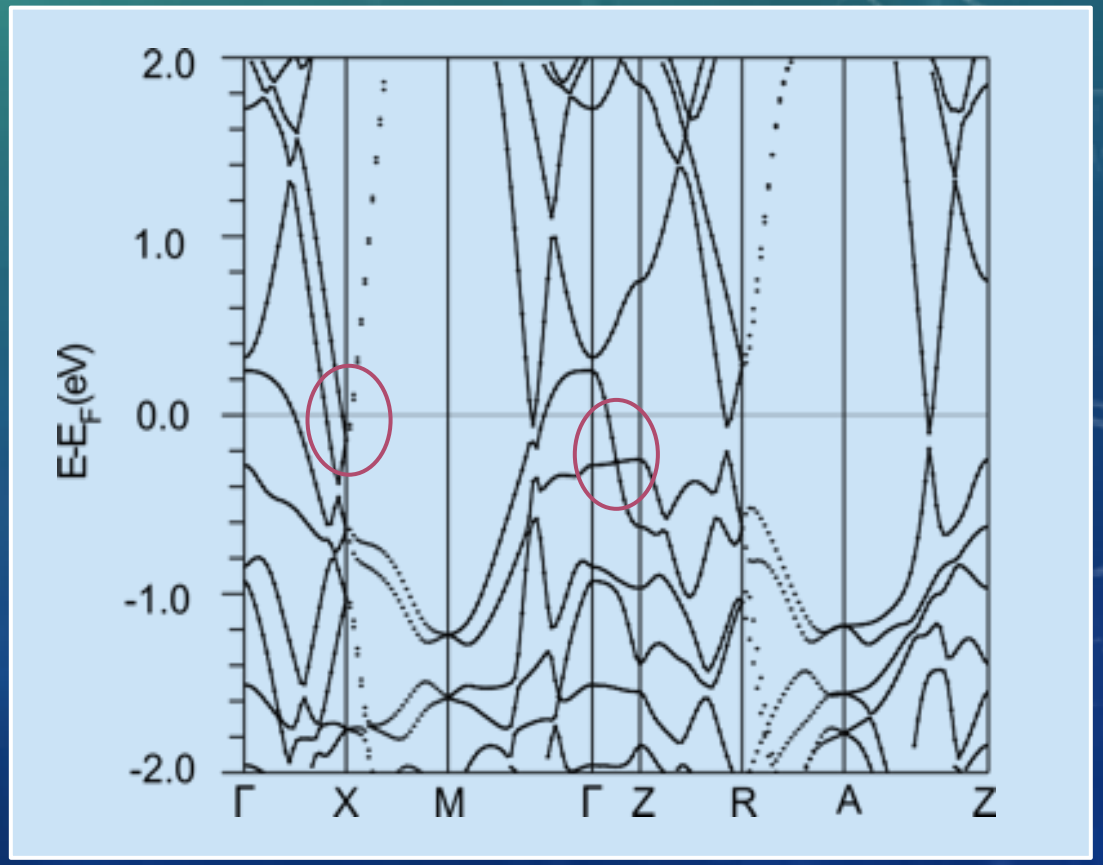


WHAT ABOUT THE RARE EARTH COMPOUNDS? LnSbTe

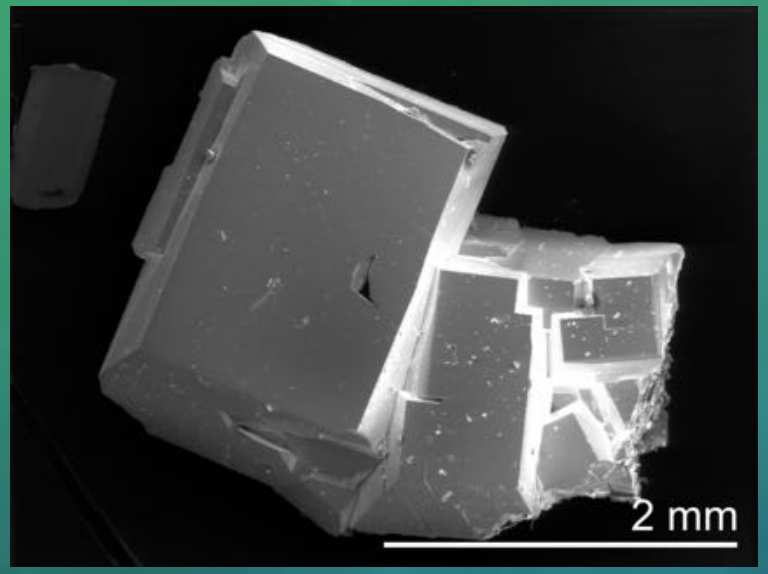
Do the LnSbTe phases order magnetically?

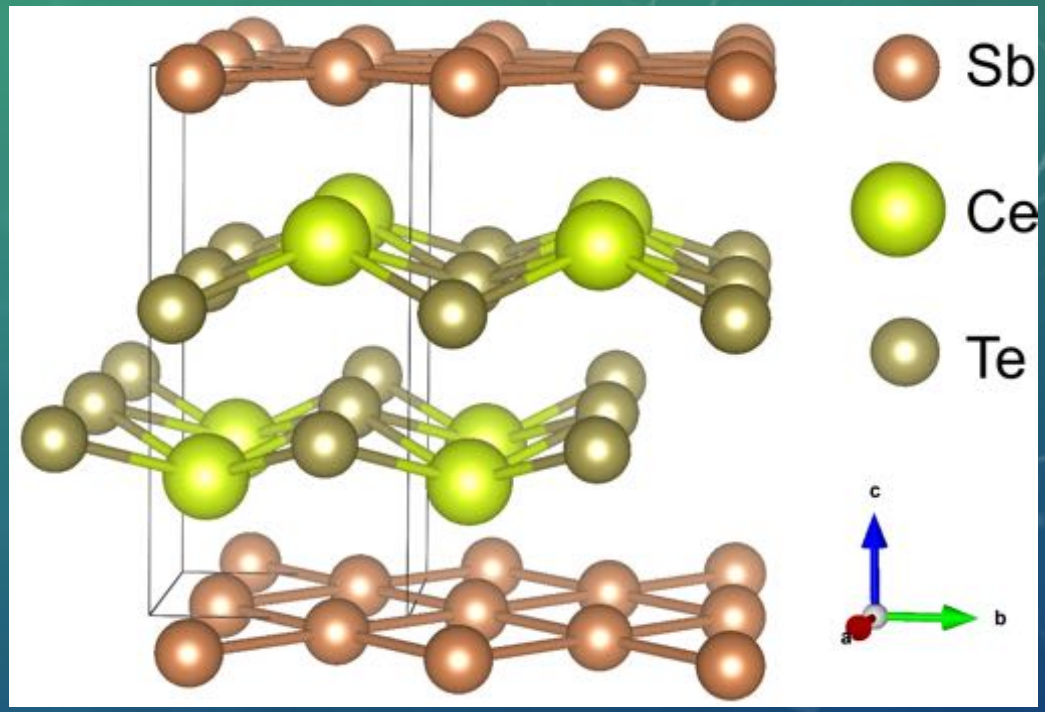
M	Z	X					
		O	S	Se	Te	As	Sb
Zr	Si	ZrSiO	ZrSiS	ZrSiSe	ZrSiTe		
	Ge		ZrGeS	ZrGeSe	ZrGeTe		
	Sn				ZrSnTe		
Hf	Si		HfSiS	HfSiSe	HfSiTe		
	Ge		HfGeS	HfGeSe	HfGeTe		
Nb	Si					NbSiAs	NbSiSb
	Ge					NbGeAs	NbGeSb
La	Sb				LaSbTe		
Ce					CeSbTe		
Pr					PrSbTe		
Nd					NdSbTe		
Sm					SmSbTe		
Gd					GdSbTe		

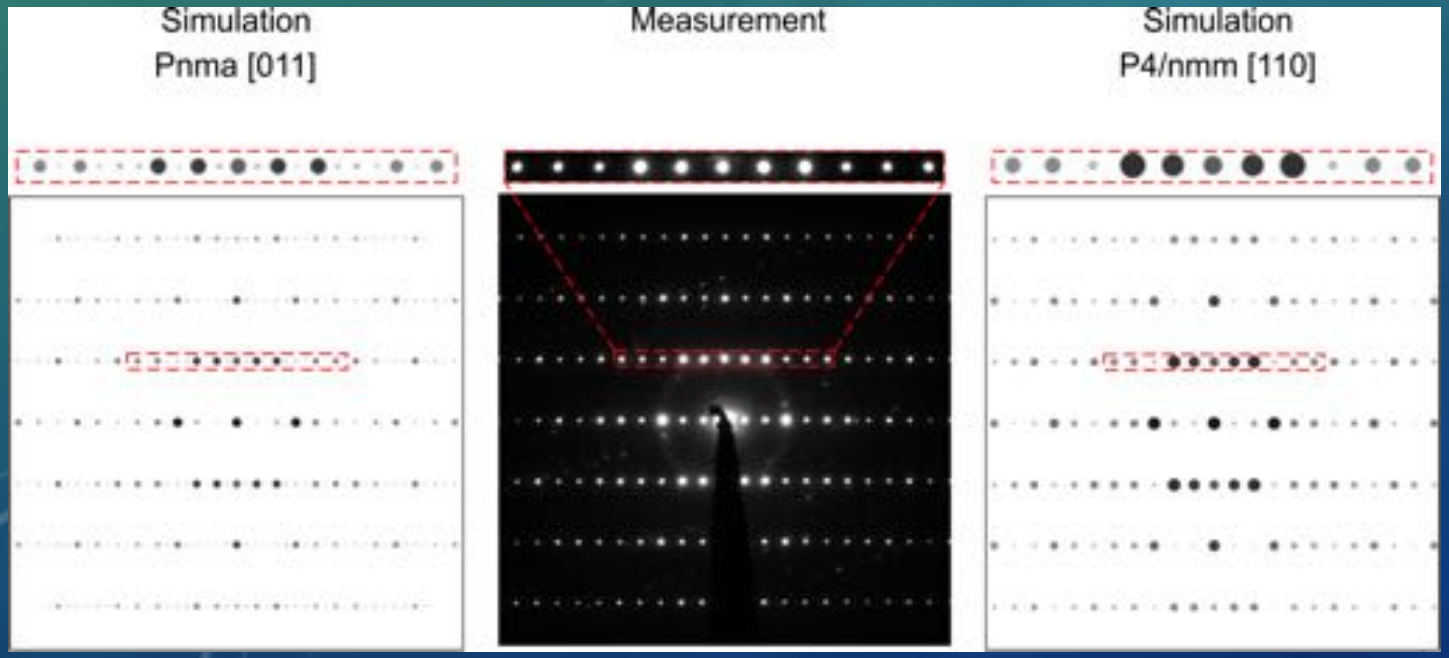
LaSbTe



CRYSTAL GROWTH OF CeSbTe

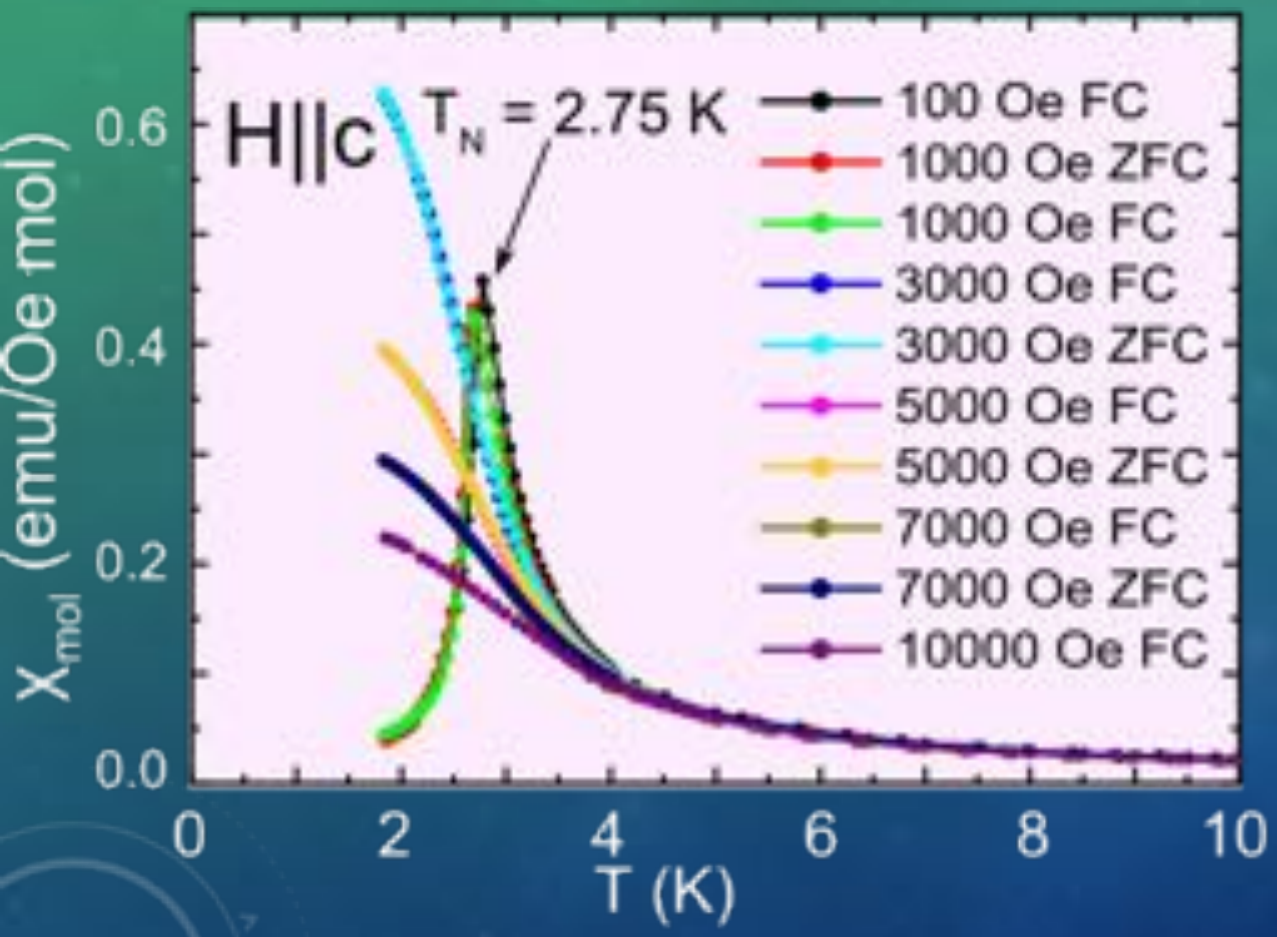


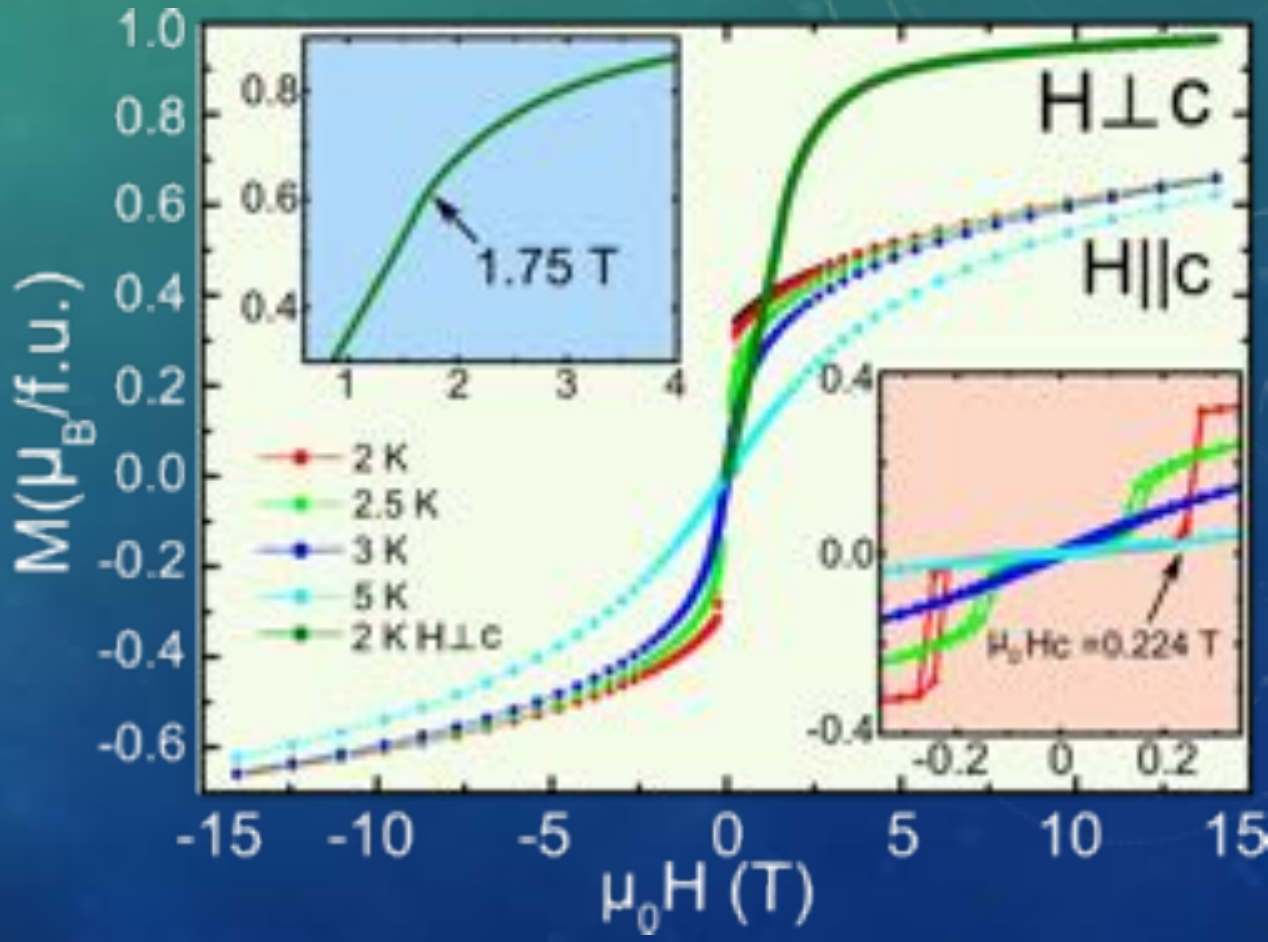




Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017) arXiv:1707.03408

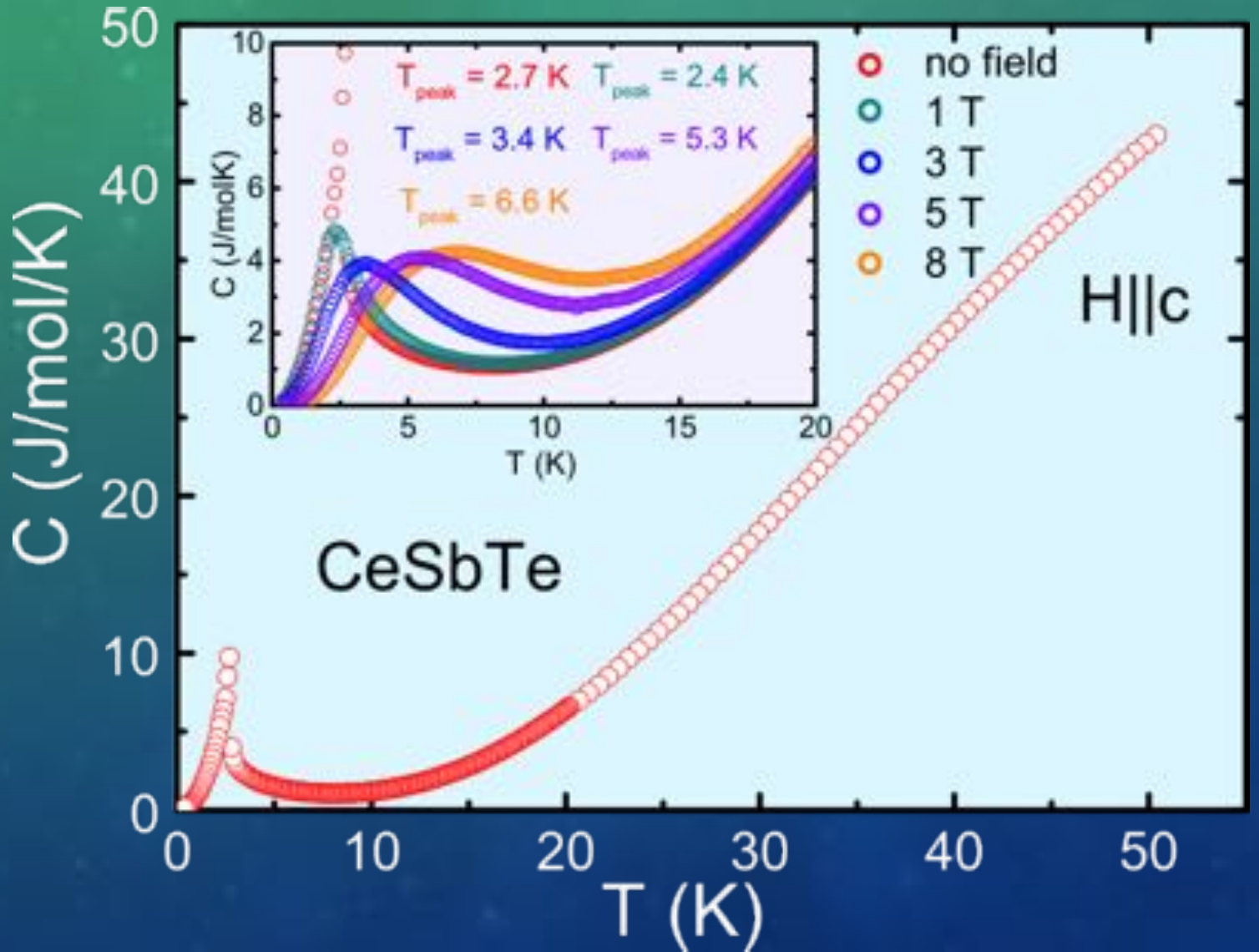
MAGNETIC PROPERTIES OF CeSbTe





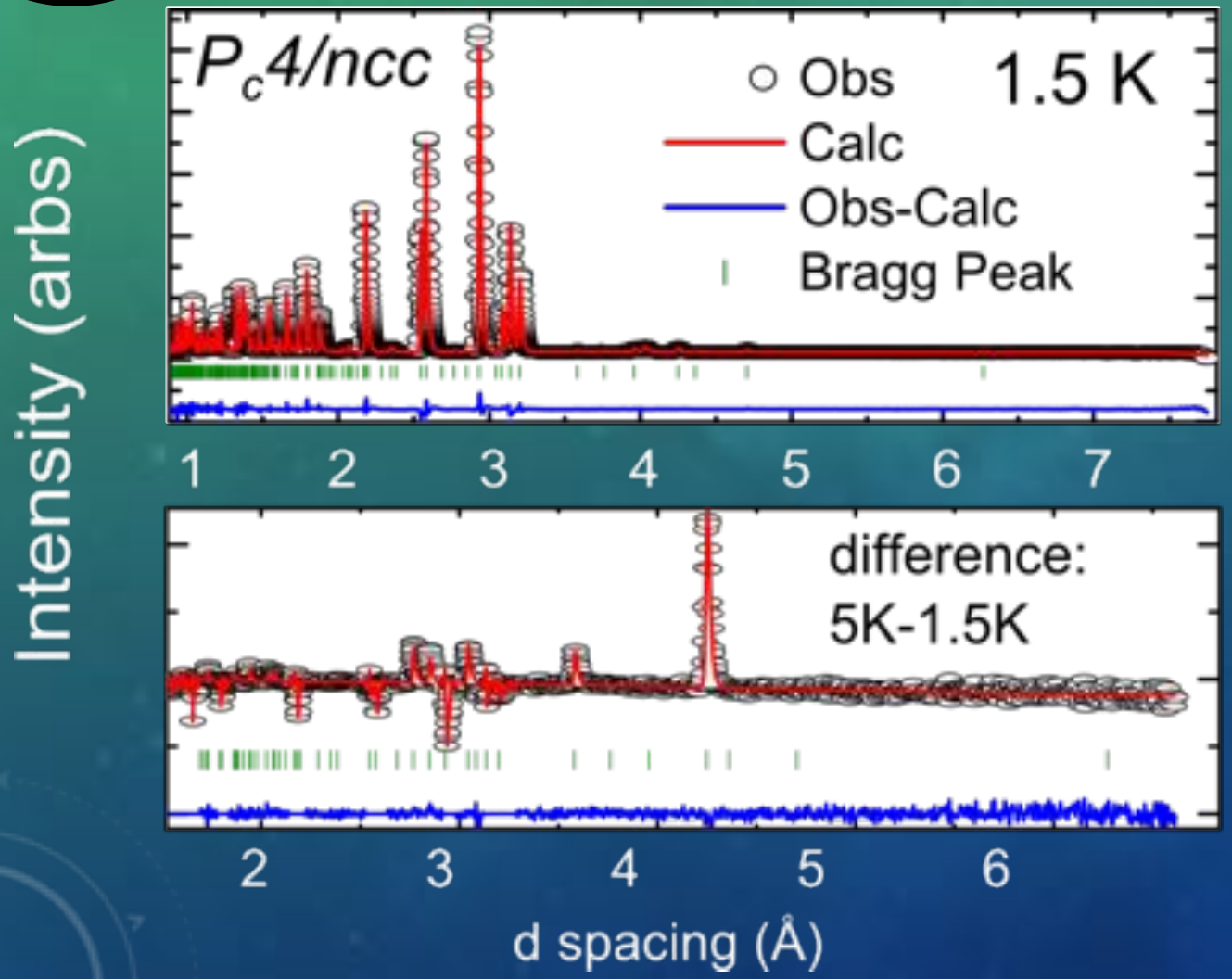
Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017) arXiv:1707.03408

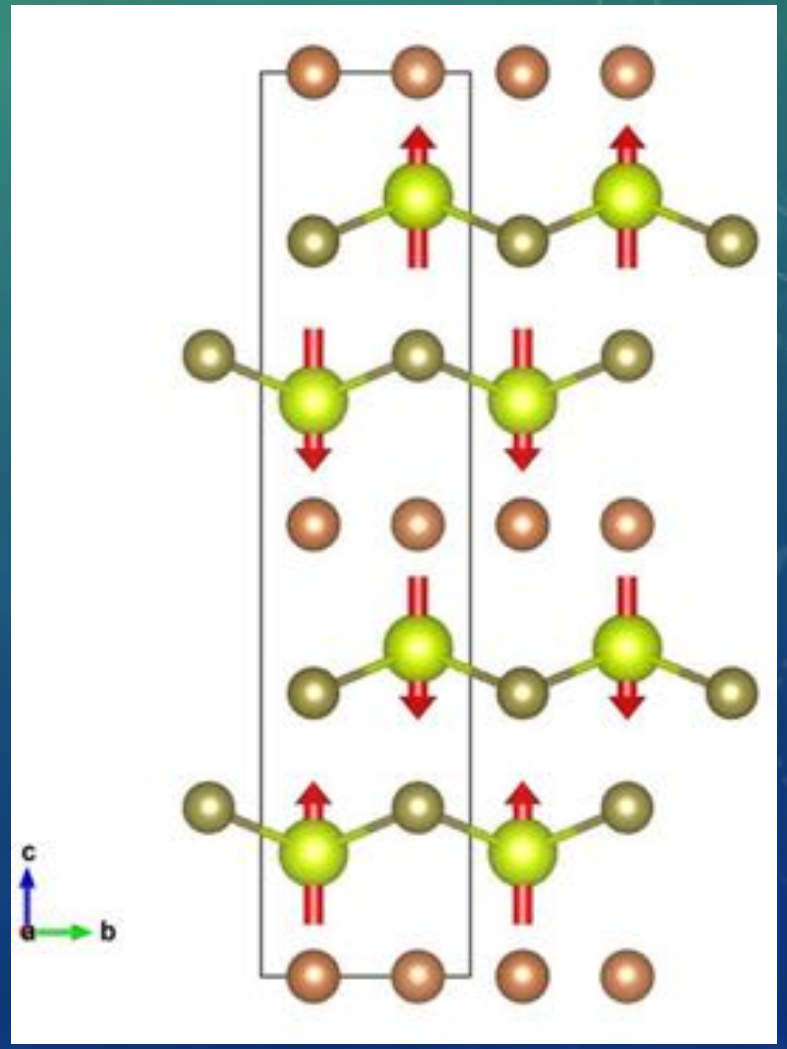
MAGNETIC PROPERTIES OF CeSbTe



Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017) arXiv:1707.03408

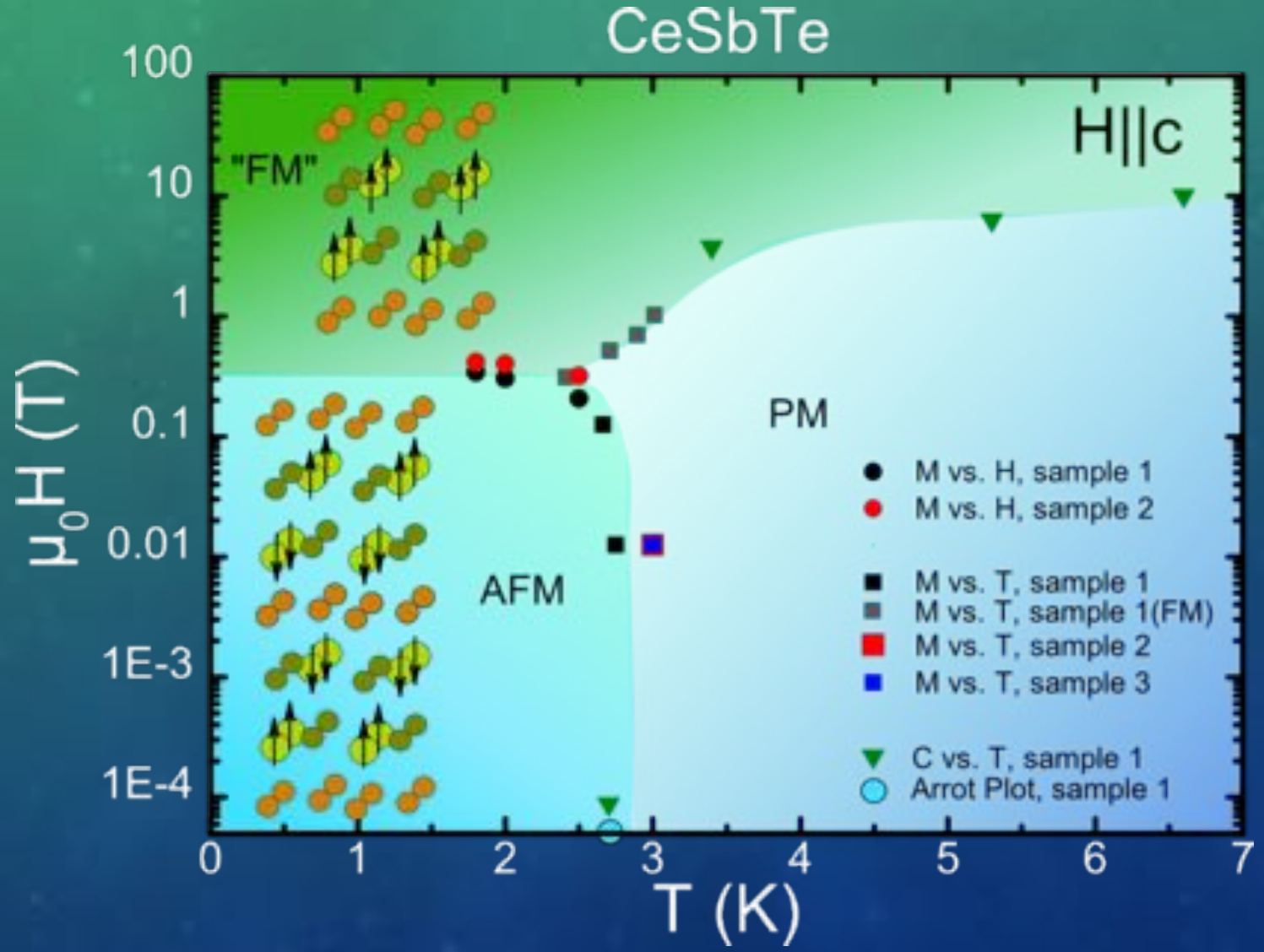
ANTIFERROMAGNETIC STRUCTURE OF CeSbTe





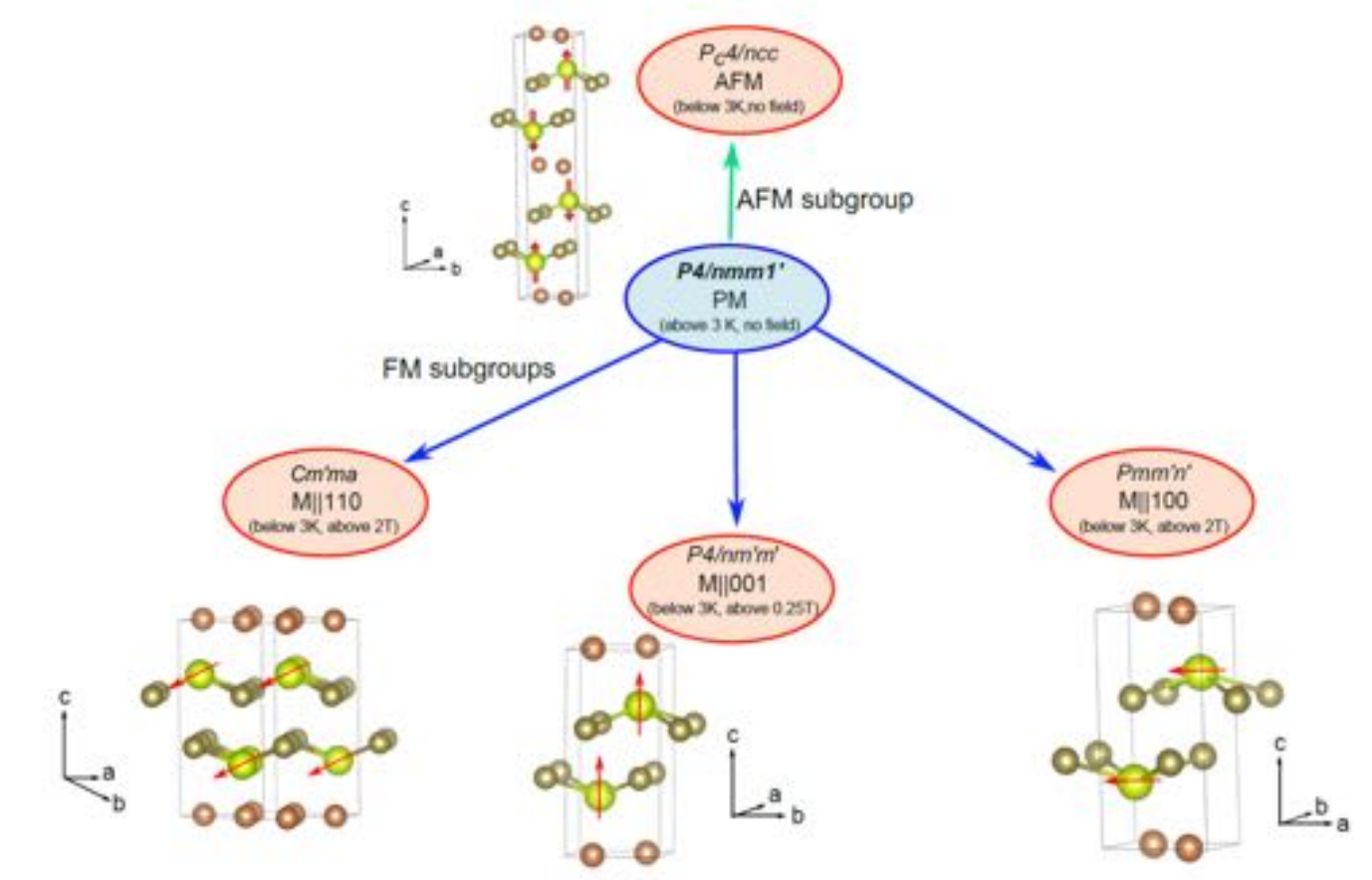
Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017)

MAGNETIC PHASE DIAGRAM OF CeSbTe



Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017) arXiv: 1707.03408

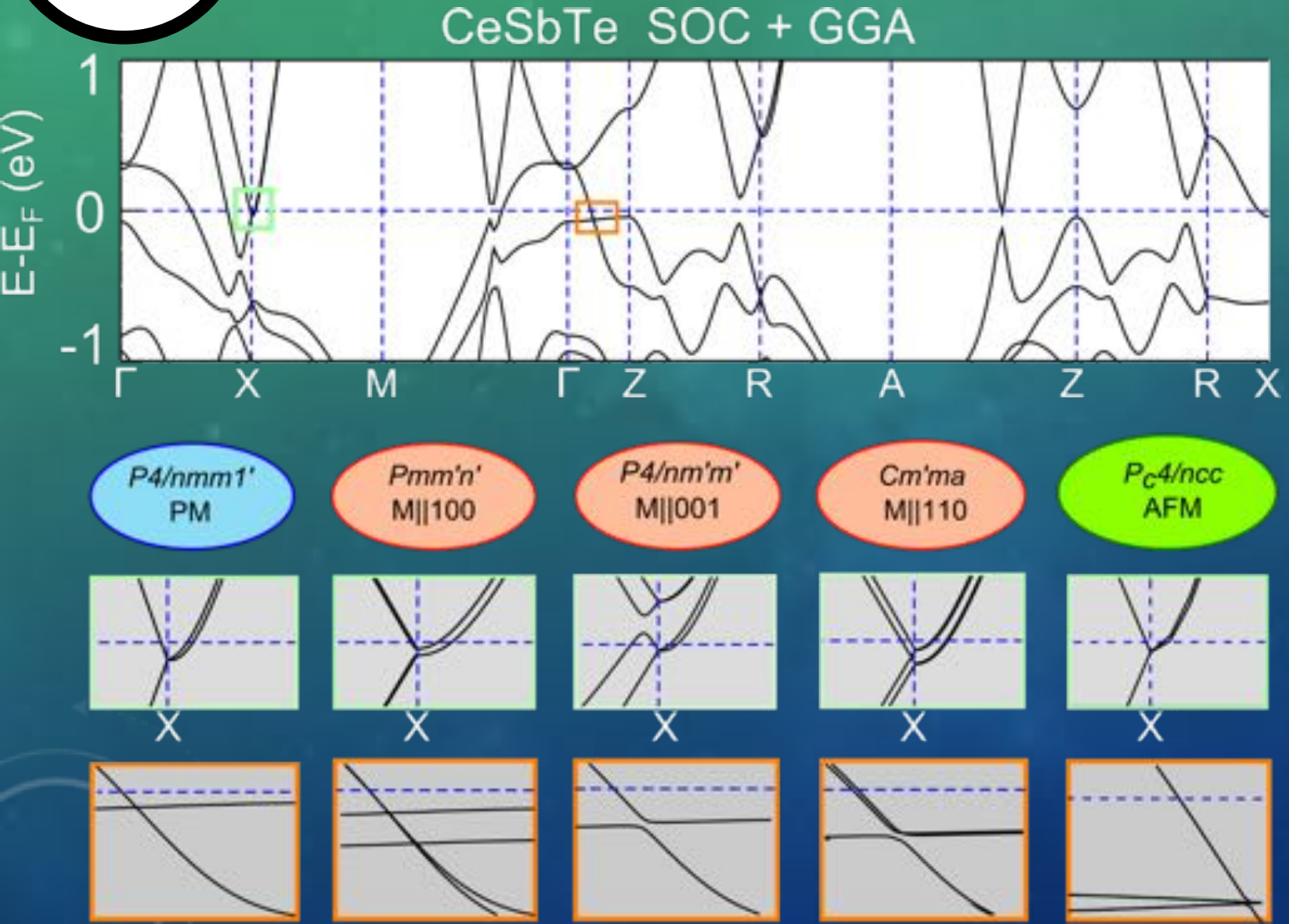
GROUP THEORY ANALYSIS

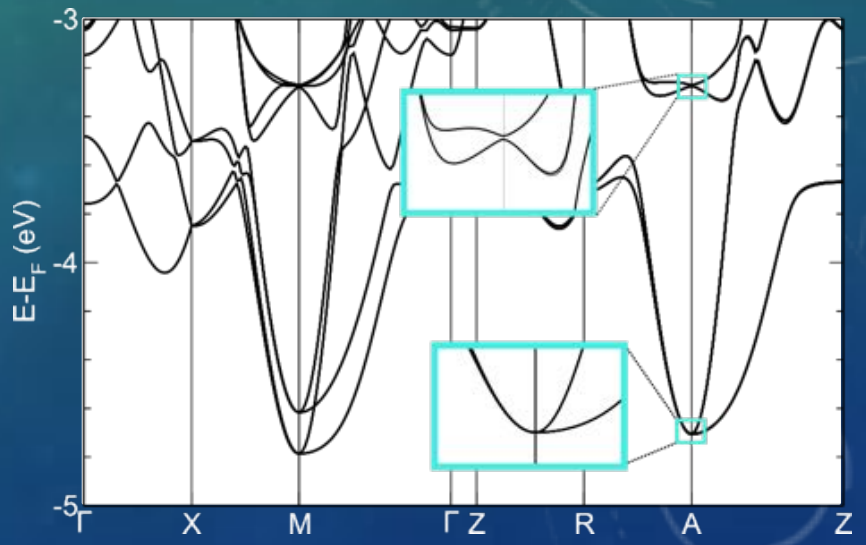


TRIMs :	A	R	X	M	Γ	Z
PM $(P4/nmm)$	2-4	2-4	2-4	2-4	2	2
AFM (P_c4/ncc)	4-8	2-4	2-4	2-4	2	2-4
FM $(Pmm'n')$	2	2	2	2	1-2	1-2
FM $(P4/nm'm')$	2-4	2	2	2-4	1-2	1-2
FM $(Cm'ma)$	1-2	2	1-2	1-2	1-2	1-2

Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017) arXiv:1707.03408

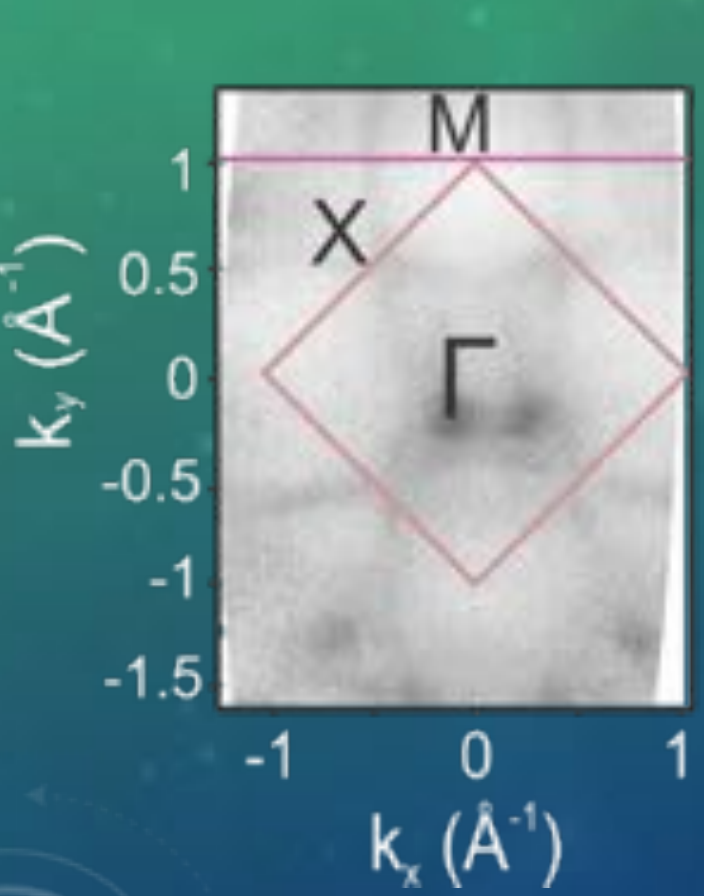
CeSbTe – A MODEL SYSTEM TO UNDERSTAND MAGNETIC NON-SYMMORPHIC MATERIALS?

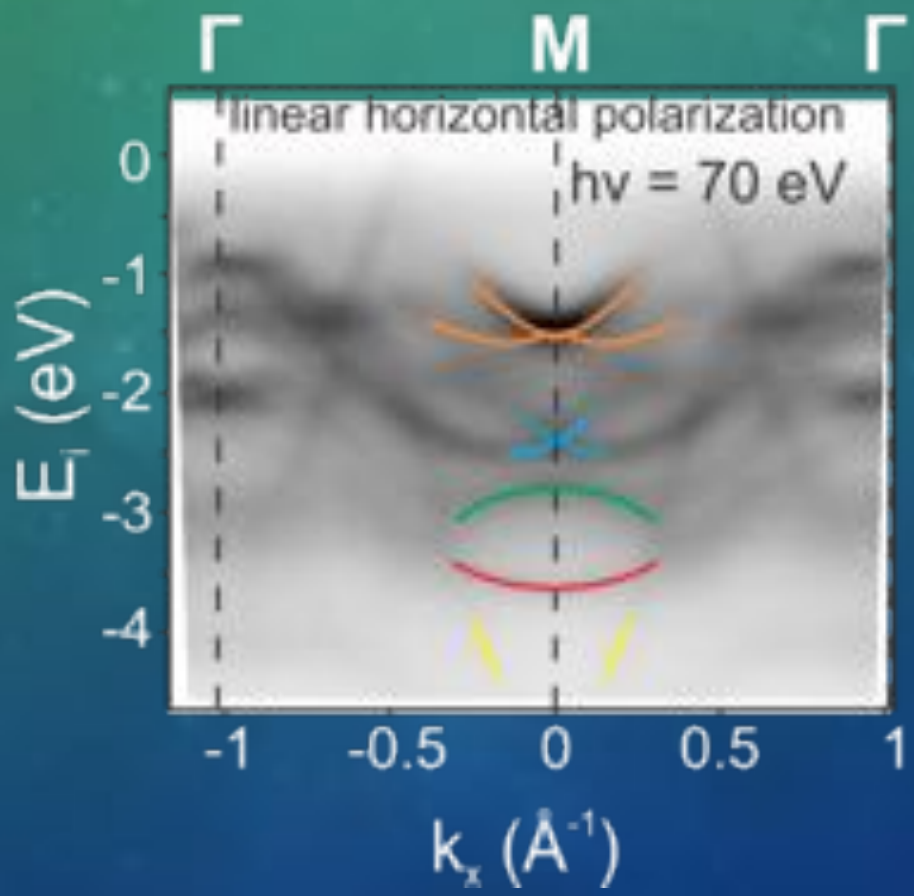


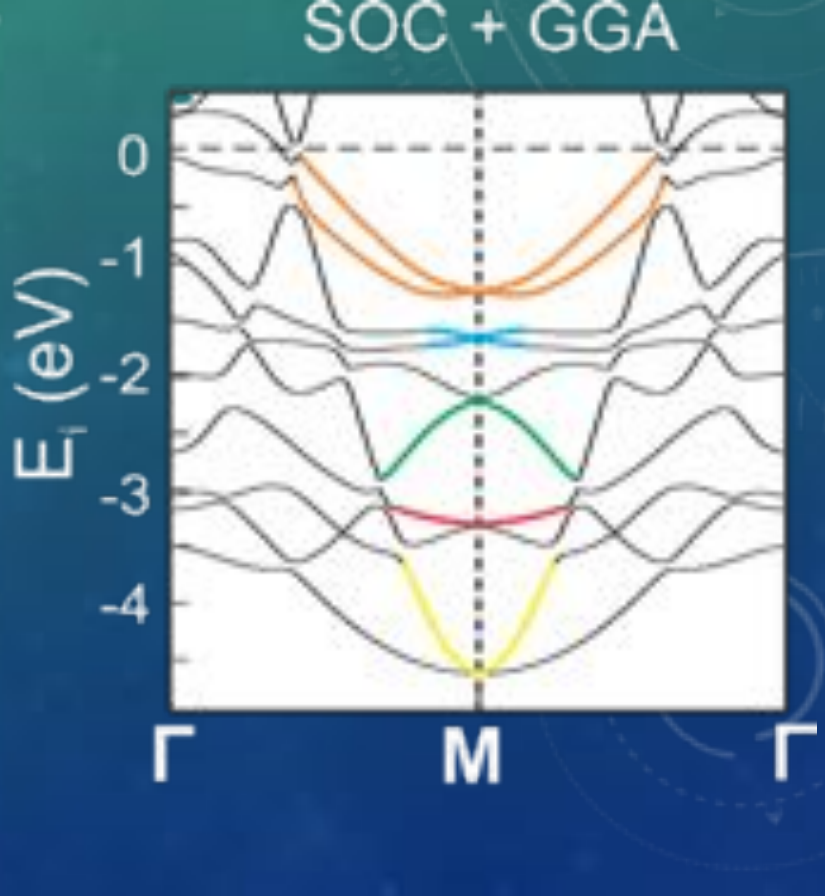


Schoop, Topp, Lippmann, Orlandi, Muechler, Vergniory, Sun, Rost, Duppel, Krivenkov, Sheoran, Manuel, Varykhalov, Yan, Kremer, Ast, Lotsch *submitted* (2017) arXiv:1707.03408

APRES CONFIRMS BAND STRUCTURE OF PARAMAGNETIC PHASE

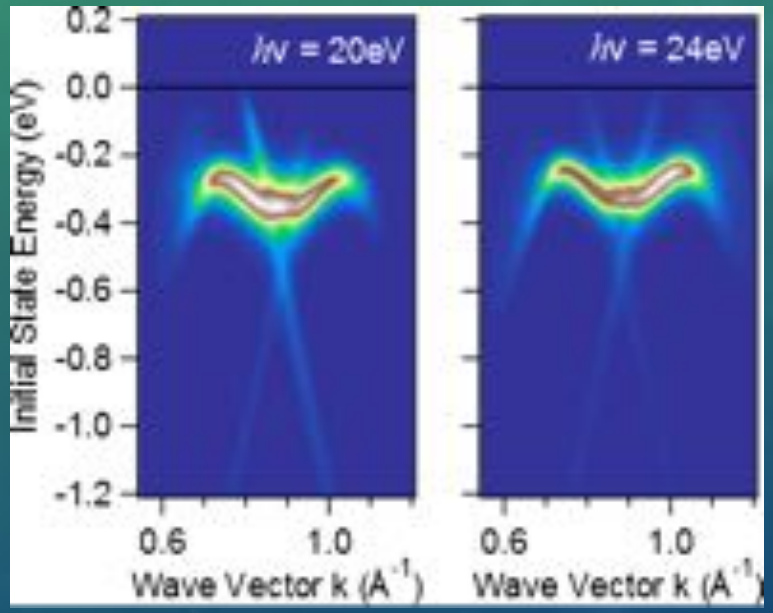


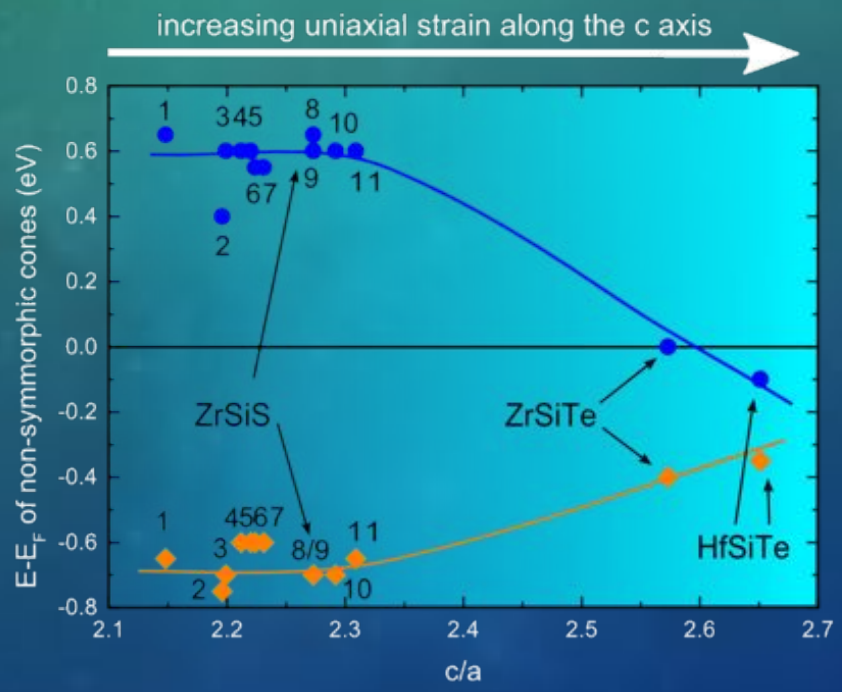


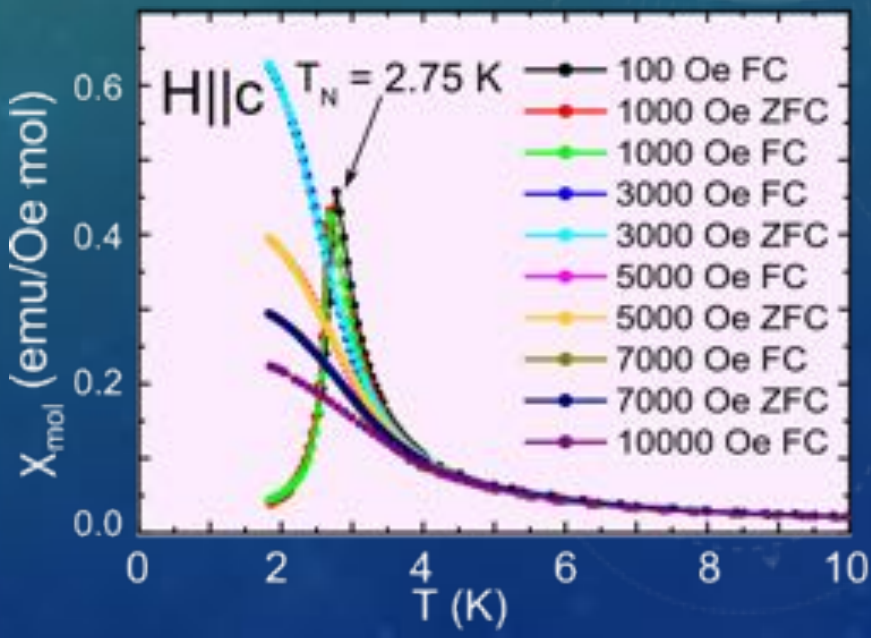


SUMMARY

- Square nets are a very rich playground for Dirac/Weyl physics!







Liner bands

Tune the electronic strucutre

Make it magnetic

THANK YOU!

- Bettina Lotsch
- Viola Duppel
- Christian Ast
- Carola Strasser
- Andreas Topp
- Judith Lippmann
- Andreas Rost
- Judith Lippmann
- Qingyu He
- Lihui Zhu
- Raquel Queiroz
- Andrey Varykhalov (Bessy)
- Steffen Wiedmann (HMFL)
- Nigel Hussey (HMFL)
- Lukas Muechler (Princeton)
- Maia Vergniory (DIPC)